The Interaction between Nitric Acid and Unsaturated Compounds.

Thesis presented for the Degree of Doctor of Science of the University of London.

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The principal products of the interaction of fuming nitric acid with acetylene or ethylene are carbon dioxide and trinitromethane. As well, in the interaction with ethylene, and intermediate to the formation of trinitromethane, is formed the addition compound, -nitroethyl alcohol.

The course of reaction is fundamentally the same for both compounds, and takes place under varying conditions of temperature, concentration of acid and the presence or absence of metallic salts, though a marked effect - the simplification of the reaction and the reduction of by-products- is obtained by the addition of mercuric nitrate.

Measurement of the quantities of carbon dioxide and of trinitromethane formed shows that at a maximum only fifty per cent of the carbon of the hydrocarbon molecule is nitrated while fifty per cent is oxidised, and this is accompanied to a varying extent by a second reaction involving direct oxidation to carbon dioxide.

The tetranitromethane which can be isolated by further nitration always represents considerably more than that which can be estimated as nitroform in the reaction mixture. Hence there are present in the product substances other than trinitromethane, but possibly inter-

-mediate to its formation, which are capable on further nitration of yielding tetranitromethane.

Evidence is adduced that the reaction is in all cases one of simple addition to the unsaturated bond of the component parts of the nitric acid molecule, analogous to the addition to unsaturated compounds of the component parts of oxides of nitrogen. Hence, the nitric acid, through the medium of addition, is able to exercise its function both as a nitrating and as an oxidising agent, one carbon of the hydrocarbon molecule becoming nitrated, the other becoming oxidised, finally to carbon dioxide.

The influence of mercuric nitrate is largely to increase the rate of absorption and hence of ibteraction. The mechanism of its effect is complex, but is largely to prevent the alternate reaction of simple exidation, and hence to increase prpportionally the the addition reaction producing the nitro alcohol.

A similar activating influence of the mercury salt is noticed in the nitration of aramatic compounds, and from this a theory of the mechanism of aromatic nitration is developed.

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INTRODUCTION.

The interaction between nitric acid and an unsaturated linkage has never received detailed investigation. Various qualitative examinations have from time to time been made, and suggestions have been put forward as to the probable course of the reaction, some postulating complete oxidation, some the formation of nitrogen-containing substances. But the nature of such substances was in most cases a matter of some doubt. One investigor only, Cohn (B. 24. 3865. 1891), examining the action of moist oxides of nitrogen on benzaldiphenylmaleide, came to the conclusion that the actual agent was nitric acid, and that interaction occurred involving addition of the component parts of the acid, (OH) and (NO_2), to the double bond, a course of reaction fundamentally in harmony with that followed by oxides of nitrogen in the absence of water, when saturation of the bond by the component parts of the oxides takes place. In the presence of concentrated sulphuric acid this reaction had been definitely shown to occur, (Wieland and Sakellarios. B. 53. 201. 1920; Anschutz and Hilbert. B. 54. 1854. 1921.), and ethylene and diphenyl ethylene, in the presence of a "mixed acid", add the radicles (OH) and (NO_2) to the double bond forming a nitroalcohol.

For war purposes, in 1917, I examined under the direction of Professor Orton, (Bangor), the action of fuming nitric acid on acetylene, and we succeeded in preparing in good yield tetranitromethane. The reactions leading to the formation of this substance, and, antecedent to it, trinitromethane, were not, for obvious reasons, further investigated at that time. But the actual nitration of one of the carbon atoms of acetylene showed by this work, and the positively catalytic effect on the formation of tetranitromethane of mercuric nitrate, have led me to make a thorough examination of the question, and to study under varying conditions the reactions of nitric acid with acetylene and ethylene respectively.

Owing to the highly reactive nature of any possible nitro or hydroxy addition compounds between nitric acid and these unsaturated hydrocarbons, it was obvious from the outset that the existance of certain intermediate steps in the series of reactions could at best be represented hypothetically, and could be supported mainly by analogy. A very careful and detailed analysis of the existing literature has therefore beed made, including more particularly the well-known and established reactions between oxides of nitrogen and unsaturated compounds. Suggestive evidence for the close analogy of reaction had already been found in the work of Cohn and of Wieland and Sakellarios, (ibid). Further, it seemed desirable, especially in the light of the discovered effect of the metallic salt, mercuric nitrate, to examine at some lenght the conditions of degradation of nitric acid by metals and metallic salts, and, where known, by organic compounds, and with a view to establishing the optimum conditions for (a) the hydroxyl dissociation of the acid and (b) the addition of this radicle plus the radicle (NO_2) to the double bond, this has been done.

Considerable light has been thrown upon the series of reactions initiated by the action of nitric acid on acetylene and ethylene, and on other unsaturated compounds as revealed by the literature, by an interpretation of these reactions in terms of modern conceptions of valency, and, as far as we can postulate them, of reactive conditions within the molecule. While it is not possible at present to do more than put forward a hypothetical explanation of chemical interaction between organic compounds based on electronic conceptions arising out of our modern knowledge of the structure of the atom, so much suggestive light is thrown upon hitherto unexplained reactions by such application, that it affords a valuable working hypothesis, supported by some measure of probability, and it is as such that it is applied in the present investigation.

Following a short discussion of the present position of this theory as originally put forward by Lowry, Lapworth &c, the whole mechansim of the reaction, including the possible influence of mercury, has been considered in terms of electronic structure. The application of this to the influence of mercury salts has opened up the whole question of catalysis from this point of view, and a suggested theory of the mechanism of catalysis is put forward.

The evidence which arises from this investigation that mercury salts can actually promote the nitration of carbon through the medium of addition at an unsaturated linkage of the component parts of the nitric acid molecule, led to the question whether such influence could not be extended to nitration in aromatic systems, and for this purpose a detailed examination of the course of the reactions occuring in a nitrating mixture in a large number of aromatic nitrations has been carried out, and from the influence of mercury revealed by such an examination, considerable support has been obtained for the mechanism of substitution by preliminary addition to the aromatic nucleus.

The present work, therefore, resolves itself into ~~two~~ three main lines of research: an examination of (a) the mechanism of the interaction between nitric acid and the unsaturated linking in acetylene and ethylene, (b) the effect on such reaction of metallic salts and (c) the influence of mercuric nitrate on aromatic nitrations. From experimental data and from a discussion of the conditions affecting the degradation of nitric acid, and of the known mechanism of reaction between oxides of nitrogen and unsaturated linkages, a course of reaction has been put forward, and the evidence for the existence of such a reaction mechanism in the nitration of romatic compounds is criticised.

The Degradation of Nitric Acid.

Consideration of the possible stages of reduction which may exist between the highly oxidised nitrogen atom in nitrogen pentoxide and the completely reduced nitrogen in ammonia illustrates very clearly the unique susceptibility of nitric acid to degradation and reduction The existance of seven stable reduction products, represented by N_2O_5; NO_2; N_2O_3; NO; N_2O; NOH; NH_2OH; N_2; NH_3; offers numerous possibilities of interaction between nitric acid and any element or compound which is itself capable of oxidation; and the nature of the reduction product is influenced by the character of thr agent effecting the degradation as well as by the usual factors of temperature, concentration and media.

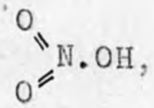
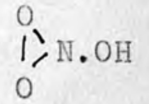
That such degradation embraces that property of the acid known as Nitration is apparent if, as seems ligitimate, we consider nitration as a complementary oxidation-reduction process in which the nitro-compound is the reduction product.

i.e. $HNO_3 + 2H = HNO_2 + H_2O$ i

$HNO_3 + RH = RNO_2 + H_2O$ ii

By assuming hydroxyl ion dissociation, Ostwald, ("Grundriss d allgem. Chemie", 1899. S 440), accounts for the oxidising action of nitric acid as follows:-

$$NO_3H \rightarrow NO_2^{\cdot} + OH' \longrightarrow NO_2 + OH' + [+]$$

the accepted structural formula for nitric acid  $\mathrm{O{=}N(=O).OH}$, or ( $\mathrm{O_2{>}N.OH}$) finding justification in such dissociation.

Hence,

$$\mathrm{HO}^{\prime} + \mathrm{NO}_2^{\cdot} + 2\mathrm{H} = \mathrm{H.OH} + \mathrm{R.NO}_2 \qquad \text{iii}$$

By analogy equation (ii) may be expressed

$$\mathrm{HO}^{\prime} + \mathrm{NO}_2^{\cdot} + \mathrm{RH} = \overset{H}{\mathbf{R}}\mathrm{.OH} + \mathrm{R.NO}_2 \qquad \text{iv}$$

and similarly the reduction of nitric acid by an organic compound would be

$$\mathrm{HO}^{\prime} + \mathrm{NO}_2^{\cdot} + \mathrm{RH} = \mathrm{R.OH} + \mathrm{HNO}_2 \qquad \text{v}$$

Thus the course of reaction between an organic compound and nitric acid must depend primarily on the nature of R in the expression RH, nitration or oxidation being promoted as the case may be.

The primary product of reduction of nitric acid by an organic compound is then nitrous acid, which may wholly or in part undergo further decomposition with evolution of oxides of nitrogen. The primary products of the nitrating action are water and nitrocompounds, and no gaseous reduction products of nitric acid can arise except by secondary reduction reactions.

Though for a considerable period the action of metals on nitric acid was attributed to a simple reduction of the acid, with evolution of the gaseous products of reduction, the metallic oxide then dissolving in the excess acid as nitrate, there seems no reason to doubt that the oxides of nitrogen evolved by such interaction are here also the products of secondary reaction, and that the primary reaction occurs by virtue of hydrogen ion dissociation and is a simple dis-

-placement of hydrogen by the metal with direct formation of the metallic nitrate. The highly oxidised compound, nitric acid, which is present in excess, immediately promotes a secondary reaction with the displaced hydrogen, with formation of reduced nitrogen compounds.

The assumption that a dissociating medium is essential for the oxidation reaction is substantiated by the fact that pure, anhydrous acid, containing only undissociated molecules, does not attack pure homogeneous metal, and a trace of water is essential for interaction. (Stansbie. Jour. Soc. Chem.Ind. 32. 311. 1913.)

At first sight, however, there would appear to be no grounds for assuming that nitration proceeds by an analogous reaction according to equation (iv). High concentration of acid and the presence of dehydrating agents are essestial factors of complete nitration, essentials which are, however, easily understood when it is remembered that such reactions involve the formation of water, and are governed by the Mass Law. But there is reason to believe that, even in such media, the reaction preceeds by virtue of hydroxyl ion dissociation, though the concentration of such would be extremely small. In certain aromatic nitrations, and in the interaction between concentrated sulphuric acid and compounds containing a doubly linked carbon atom, the addition of NO_2 is accompanied by addition of OH. A full discussion of this reaction is reserved for a later section, but it is important to emphasise at this stage the very definite part played, as will be shown from experimental evidence, in organic nitrations by the radicle OH.

Factors Causing Reduction of Nitric Acid.

Metals. The degradation of nitric acid is illustrated in so many of its aspects by its action on metals that the whole problem can with advantage be surveyed primarily from this point of view.

A brief examination is sufficient to show that the reaction is complex, and that it cannot be fully explained by the simple hypothesis that the primary rection is one of liberation of hydrogen, which in its nascent state interacts with nitric acid causing reduction. Rather must it be considered as a complicated oxidation-reduction r process, more nearly analogous to such a reaction as that between nitric acid and sugars than to the behaviour towards ~~mineral acids~~ metals of mineral acids in general.

The reducing action of a metal depends on the concentration of hydrogen which would be required to precipitate the metal from its salts, and dissolution of the metal in an acid can only occur in a dissociating medium in which hydrogen ions are present, but in which their concentration is below this precipitation value. It may be supposed that, in contact with such an acid, there is a spearation of metallic ions from the usrface of the metal due to a definite solution pressure which varies with the nature of the metal and the solution. But the concentration of such positive ions is limited on the one hand by their osmotic pressure and by their attraction to the undissociated negative metal, and on the other by hydrion concentration.

Hence, any factor which decreases the hydrogen ion concentration promotes the dissolution of the metal. Such a factor is nitric acid itself, which, by its oxidation of hydrogen to water, removes hydrogen ions from the solution.

The nature of the secondary products arising from this reducing action of the hydrogen is dependent on its concentration, on temperature, on the dilution of the acid and on the presence and nature of other substances.

The possible primary reduction products arising by the direct action of hydrogen on nitric acid may be set out as follows:-

$$
HNO_3 \quad + \quad \begin{array}{lllll}
H & \longrightarrow & NO_2 & + H_2O & \quad \text{i} \\
2H & \longrightarrow & HNO_2 & + H_2O & \quad \text{ii} \\
4H & \longrightarrow & HNO & + 2\ H_2O & \quad \text{iii} \\
6H & \longrightarrow & NH_2OH & + 2\ H_2O & \quad \text{iv} \\
8H & \longrightarrow & NH_3 & + 3\ H_2O & \quad \text{v}
\end{array}
$$

and, with the exception of nitrogen peroxide, the possibility of the existence of which as a primary product will be discussed later, nitrous acid, hydroxylamine, ammonia and water can be the only primary products of the reaction, apart from nitrates and nitrites, though by decomposition of these primary products, and by their action on each other, nitrous oxide, nitric oxide, nitrogen peroxide and nitrogen may arise as secondary products, and in varying mixtures and proportions represent the sole ultimate products.

The subject is one which has received attention for a considerable time, and much experimental evidence, though often of a conflicting nature, is avaliable.

A preliminary classification of the metals on the basis of the appearance or non-appearance of these primary products in the final mixture can be made, and it appears that the dissolution ~~of the metal~~ in nitric acid of the metals iron, nickel, cobalt, cadmium, tin, lead, zinc and magnesium and metals of a strongly basic character give rise to appreciable quantities of ammonia or hydroxylamine or both, though these substances are never the sole ultimate products of the reaction. While in the solution of silver, mercury, copper and bismuth in nitric acid ammonia and hydroxylamine can never be detected. (Acworth & Armstrong. Jour.Chem.Soc. 32. 54. 1877; Divers. ibid. 1883. 443., 1885. 0 231. 445. Jour.SOc.Chem.Ind. 1904. 1182.; Montemartini. Gazz. 22. i. 250. 1891.; Freer & Higley. Amer.Chem.Jour. 15. 71. 1893.) N.B. Under certain conditions traces of ammonia can be detected in copper-nitric acid and in bismuth-nitric acid mixtures. Stansbie. Jour. Soc.Chem.Ind. 1906. 25. 1071; 1908. 27. 365.)

It seems justifiable to suppose that there is a much greater formation of ammonia, and possibly also of hydroxylamine, in reactions involving metals of this second class, but that there is usually complete oxidation to nitrogen, and only under abnormal conditions do traces of ammonia become evident owing to the incompleteness of this oxidation. The evolution of ammonia is not confined to dilute solutions of the acid. At ordinary and higher temperatures ammonia is formed by the dissolution in nitric acid of iron, cobalt, cadmium, zinc, lead and tin whatever the concentration of the acid, though the amount tends to fall off with increase of concentration. This decrease becomes very marked at 3 - 8°C, at which temperature the evolution of ammonia reaches a maximum at a concentration of 40-45% nitric acid, and falls off rapidly, only a trace being detectable, at a concentration of 50%. (Montemartini. ibid.)

Though the formation of ammonia represents a further stage of reduction than does hydroxylamine, equations (4) and (5), the latter compound occurs much less frequently than does ammonia. Under varying conditions of concentration and temperature iron, cadmium and cobalt do not yield hydroxylamine at all. On the other hand, hydroxylamine never occurs unaccompanied by ammonia. But that such behaviour is to be expected is evident when one considers the conditions under which ammonia may be formed.

A reduction potential sufficiently high to promote the direct reduction of nitric acid to ammonia would be favourable to the reduction of any oxygen containing nitrogen compound. Consequently the primary products, nitrous acid, hydroxamic acid and hydroxylamine could by such reduction yield ammonia. Hydroxylamine is in all probability a prolific source of ammonia, not only by reduction

$$NH_2OH + H_2 \rightarrow NH_3 + H_2O \qquad 6.$$

but also by further interaction with the metal

$$NH_2OH + Zn \rightarrow ZnH_2NOH \qquad (a)$$

$$ZnH_2NOH + H_2O \rightarrow Zn(OH)_2 + NH_3 \qquad (b)$$

Reaction (b) takes place in neutral or alkaline solutions as well as in acid media, and the presence of such an intermediate compound as ZnH_2NOH in alkaline solution has actually been determined. (Divers. Jour.Chem.Soc. 1883. 455.)

That some source of ammonia other than the direct reduction of nitric acid by nascent hydrogen is evident when one considers that lead, the reducing activity of which is not high, readily yields ammonia with nitric acid, but no hydroxylamine can be detected.

It must be noted, however, that the absence of ammonia can in no way be taken as evidence of its non-formation.

In an analogous manner hydroxylamine may be produced by routes other than the primary reduction of nitric acid. Any metal, such as tin, which by its capacity for further oxidation acts as a reducing agent, can undergo reaction with the undecomposed nitric acid with formation of hydroxylamine. Nevertheless, the hydroxylamine produced by either of these routes is liable to decomposition, not only to ammonia, as previously indicated by further reduction by hydrogen, or by interaction with the metal, but also by oxidation by nitric acid to nitric oxide,

$$HNO_3 + NH_2OH \rightarrow 2NO + 2H_2O \qquad 7.$$

and by a reaction which is of the nature of a condensation with nitrous with the formation of hydroxamic acid,

$$HO.NH_2 + O.NOH \rightarrow HON{=}NOH + H_2O \qquad 8.$$

(Wislicenus. B. 26. 771. 1893.)

In fact, the presence or absence in the solution of hydroxylamine furnishes somewhat uncertain evidence of the occurence of reactions resulting in its formation. At no time does its presence signify more than the difference between what has been formed and what has been destroyed, and the latter may or may not predominate.

Nitrous acid and oxides of nitrogen may arise as the products of secondary reaction between metals of this class and nitric acid as follows:-

$$HNO_3 + 2M \rightarrow 2\,M.OH + M.NO_2 \qquad 9.$$

$$HNO_3 + M.NO_2 \rightarrow M.NO_3 + HNO_2 \qquad 10.$$

Nitrous acid therefore arises as a secondary product by the action of the metal on its own nitrate in the presence of water, and is proportional in amount to the formation of nitrate and to the decomposition of the nitric acid.

Nitrous oxide may arise either by decomposition of hydroxamic acid,

$$2\,HNO \rightarrow N_2O + H_2O \qquad 11.$$

or by decomposition of hydroxylamine, by nitrous acid,

$$NH_2OH + HNO_2 \rightarrow N_2O + 2\,H_2O \qquad 12.$$

in both cases nitrous oxide would be given off in the evolved gases. An examination of the gaseous products of the dissolution of lead and iron in nitric acid, (Freer and Higley. Amer.Chem.Jour. 21, 277. 1899.) shows that nitrous oxide increases with decrease in concentration of acid, and only becomes apparent at concentrations below 1.3%. Concurrently the formation of nitrogen peroxide falls off, suggesting that nitrous oxide and further reduction products of nitrogen arise by reduction not of nitric acid but of nitrogen peroxide.

Nitrogen trioxide, together with ammonia, is in all probability formed as a decomposition product of hydroxamic acid,

$$3\ HNO \rightarrow NH_3 + N_2O_3$$ 13.

In the end products ammonia and nitrogen trioxide would in all probability be present, but the amount available for estimation would not, as has been shown for hydroxylamine, be a measure of the amount produced.

Possibilities of further reaction may be represented as follows:-

i $NH_3 + N_2O_3 \rightarrow N_2 + H_2O + HNO_2$

ii $4\ NH_3 + 6\ NO \rightarrow 5\ N_2 + 6\ H_2O$

(Nitric oxide may arise by interaction of nitric acid and hydroxylamine.)

iii $N_2O_3 + H_2O \rightarrow 2\ HNO_2$

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

It is probable that the appearance of nitrous acid or nitrite is always a secondary phenomenon with metals of this class, the reducing activity of which is such that the reduction is never arrested at the first stage of nitrite formation, equation (2). To a certain extent, also, nitrous acid is a product of the direct decomposition of hydroxamic acid, a reaction which is a reversal of Wislicenus's synthesis of this acid.

$$2\ HNO + H_2O \rightarrow HONO + NH_2OH \qquad 14.$$

(Hantzsch & Kaufmann. Ann. 292. 332.)

Consideration of the action of nitric acid on the weakly basic metals, copper, silver, mercury and bismuth reveals a correspondingly variable mixture of reduction products of nitrogen, with the distinguishing feature that the ultimate stages of reduction, hydroxylamine and ammonia, are never reached, and that there is apparently always an arrest ~~of~~ at stage I with the formation of nitrous acid or nitrite as the primary product. Contrary to the behaviour of the strongly basic metals the hydrogen of the acid, except in the initial formation of nitrous acid, is entirely detached from the nitrogen as water.

Nitrogen, nitrous oxide, nitric oxide, nitrogen trioxide and nitrogen peroxide can be detected, however, in varying proportions, nitric oxide in the majority of cases largely predominating. There is evidence, (Freer and Higley. Amer.Chem.Jour. 15. 71; ibid. 17. 18.) that the sole products of the secondary reduction of excess of nitric acid, (d 1'4.), by copper are nitrogen trioxide and nitrogen peroxide, the latter very much predominating, and that ~~the~~ nitrous and nitric oxides and nitrogen are the result of secondary reactions which occur only in dilute media. It is further shown that nitric oxide, the presence of which has so frequently been observed, is in the dissolution of copper in nitric acid, the product of decomposition of nitrogen trioxide and nitrogen peroxide when the specific gravity of the acid is 1'25 or greater, and of nitrogen trioxide alone when it is less than 1'25. Thus, as the amount of nitrogen trioxide produced is always considerably below that of nitrogen peroxide, the former gas will not in general appear in the final products. With decreasing concentration of acid nitrous oxide, (at sp.gr. 1'3) and nitrogen, (at sp.gr. 1'25) appear.

The whole question of the formation of nitrogen peroxide as upheld by Freer and Higley, (ibid), is an uncertain one, but on the face of it it is doubtful if the conclusions of these authors can be accepted unreservedly. Inconsistencies are seen to exist between their various results. Moreover, if, as they affirm, nitric oxide is a secondary product of the decomposition of nitrogen trioxide and nitrogen peroxide, there should be a marked difference in the amounts of these gases produced in the iron-nitric acid and in the copper-nitric acid solutions; the former, by reason of its greater reducing power, would be expected to furnish a higher proportion of nitrogen trioxide, and hence of nitric oxide. But a more serious criticism is that no account is taken of the probable formation of nitrous acid, together with the fact that the products are expelled from the solution for estimation at a temperature of 100°C, no account being taken of secondarily induced temperature reactions.

It is doubtful if under any conditions nitrogen peroxide can be considered as a primary reduction product of nitric acid, witness the ordinary method of formation by oxidation of nitric oxide, and its formation in concentrated solution fromnitric acid and nitrite by a process analogous to a condensation,

$$\mathrm{R.NO_2} + \mathrm{HO.NO_2} \rightarrow \mathrm{R.OH} + 2\,\mathrm{NO_2} \qquad 15.$$

This reaction probably largely accounts for its formation in the systems under discussion, the nitrous acid being first formed by direct reduction of nitric acid. In confirmation of this Stansbie, (Jour.Soc.Chem.Ind. <u>28</u>. 268. 1909), has shown that in the dissolution of copper, silver or bismuth in nitric acid nitrogen peroxide increases in amount as the reaction proceeds, ~~I~~.i.e. as nitrite accumulates in the solution.

Effect of External Factors.

Temperature:- Little quantitative knowledge of the effect of temperature of the products of interaction between metals and nitric acid is available. Statements that the effect of temperature is negligible are found on examination to be based on faulty experimental conditions. ~~In~~ For this reason must be discounted the conclusions respecting the effect of temperature of Freer and Higley, (ibid), in that whatever the temperature of reaction the removal of gaseous products from the solution was carried out at 100o C.

That temperature would have considerable effect on the varied and complicated decompositions of nitric acid is only to be expected. All our knowledge of reactions involving nitric acid points to a profound effect, and it is generally recognised that concordant results can only be obtained by rigid definition of the temperature of reaction. This conclusion is borne out in the reactions under discussion by the results of Stansbie, (Jour.Soc.Chem.Ind. 25. 1071 1906.), who, in his investigation of the action of nitric acid on copper, has shown marked sensitiveness to temperature. Over a series of experiments undertaken at different temperatures it is seen that while the total evolution of nitric oxide in the gaseous product, obtained by direct displacement from the reaction vessel, does not vary appreciably, the amount of nitrous acid ~~in~~decreases with rise of temperature. Stansbie somewhat arroneously concludes from this that the main reaction by which nitric oxide is produced is uninfluenced by temperature, whereas rise of temperature is unfavourable to the reaction determining the formation of nitrous acid. The two statements are inconsistent, for the decrease of nitrous acid is in the main accompanied by a concomitant increase in the amount of nitric oxide, the decomposition of nitrous acid proceeding largely as follows:-

$$3\ HNO_2 \rightarrow 2\ NO + HNO_3 + H_2O \qquad \text{I}$$

There must, therefore, with the decrease of nitrous acid, be a corresponding increase of nitric oxide with rise of temperature, but, since the final volume of nitric oxide is unaltered, such increase must be balanced by a corresponding removal, porbably by interaction with nitrous acid,

$$2\ NO + HNO_2 + H_2O \rightarrow 2\ HNO + HNO_3 \qquad II$$

the hydroxamic acid decomposing into nitrous oxide, or into ammonia and nitrogen trioxide, equations (11) and (12). The ammonia thus produced would probably react with more nitric oxide as follows:-

$$6\ NO + 4\ NH_3 \rightarrow 5\ N_2 + 6\ H_2O \qquad III$$

The total effect on the final product might, therefore, by a neutralisation of the effect, with respect to nitric oxide, of equation (I) by equations (II) and (III) display itself in a decrease of nitrous acid, the ultimate volume of nitric oxide being unaffected.

This is evident from the results of Veley, (Proc.Roy.Soc. <u>52</u>. 27. 1892.), in his study of the formation and decomposition of nitrous acid. Nitrous acid, formed by the passage of nitric oxide through nitric acid at different temperatures, increases slightly up to a temperature of 32°C, from which point it decreases, showing clearly the effect of secondary reactions at the higher temperatures.

<u>Concentration</u>. The same variability of experimental conditions, with the consequent variation in composition of the product, confronts us when we compare the results of different investigators. Acworth and Armstrong, (ibid), show that, given similar conditions, the gaseous product by their treatment and analysis is always a mixture, but of variable proportions, of nitrous and nitric oxides

and nitrogen, whatever the concentration of the acid. In a copper-nitric acid mixture nitrous oxide increases and nitric oxide decreases as the concentration of the acid decreases. In a similar reaction with zinc there is a similar decrease of nitric oxide with decrease of concentration, but the amounts of nitrous oxide and nitrogen seem independent of the strength of the acid. The dissolution of iron in nitric acid of increasing dilution causes first a considerable decrease in the volume of nitric oxide, followed by an increase, while nitrogen peroxide first increases and then decreases.

Montemartini, (ibid), studying the action of nitric acid on zinc, shows that at a temperature of 3 - 8°C the formation of ammonia increases with concentration to a maximum at 49 - 45 per cent, then falls steeply to zero, only a trace being perceptible at an acid concentration of 53 per cent. There is an increase in formation, rapidly increasing in speed, of nitrogen peroxide which first appears at an acid concentration of 27 per cent, and reaches a constant value at 80 per cent. The amount of nitrous oxide increases to a maximum at a concentration of 40 per cent, then declines to a minimum at 80 per cent. But in the action of concentrated nitric acid on silver the product is nearly pure nitrogen peroxide, no nitrous or nitric oxides being formed. (Higley and Davies. Amer.Chem.Jour. 18. 587. 1896)

Consequently, whether nitric oxide be a product of the decomposition of nitrogen peroxide and nitrogen trioxide, or of nitrogen trioxide or nitrogen peroxide independently,

$$N_2O_3 \longrightarrow NO + NO_2$$

$$6\ NO_2 + 3\ H_2O \longrightarrow 3\ HNO_2 + 3\ HNO_3$$

$$\downarrow$$

$$2\ NO + HNO_3 + H_2O$$

it would be expected to decrease in amount with dilution of the acid.

An interesting variation appears when one considers the effect of varying amounts of solvent on the proportions of the reduction products. In nitric acid, sp.gr. 1'4, iron gives rise to nitrogen peroxide and nitric oxide in proportions varying with the quantity of acid used. Thus,

7 cc of acid gives NO_2 / NO = 60 / 40
10 cc ,, ,, ,, = 90 / 10

(Freer and Higley. ibid. 21. 377. 1899.)

This may be a phenomenon merely of relative solubility. It is difficult to accept the conclusion of the authors that concentrated nitric acid acts as an oxidising agent here, giving off oxygen to form the peroxide, which in the greater mass of acid and hence greater oxygen concentration is then formed preferentially. Rather is it interpretable by the fact that with increased dilution nitric acid becomes more susceptible to reduction and yields reduction products representing a further stage of reduction than nitrogen peroxide.

Comparison of the relative proportions of reduction products observed for the different metals of the two groups shows that considerable uniformity of behaviour exists in the more concentrated acid media, specific action only becoming marked in acids of low concentration. The products of the lower concentration are secondary decomposition products, mainly of hydroxamic acid, equations (11) and (13), a substance representing a fairly advanced stage of reduction of nitric acid, equation (3). Hence its formation would befavoured by the more dilute reducing acid, and in the dilute medium its decomposition into nitrous oxide and nitrogen trioxide would predominate overits oxidation by nitric acid.

But little count has been taken of the relative solubilities of the gaseous products in nitric acid of varying dilutions, and until our knowledge of such is considerably extended it is difficult to estimate with any accuracy the effect of concentration of acid on the composition of the ultimate product.

Catalysts. That the course of the interaction between nitric acid and metals, and the composition of the ultimate gasesus products can be profoundly influenced by factors other than temperature and concentration has long been regocnised.

Acworth, (Jour.Chem.Soc. 28. 828. 1875.), observed that in the dissolution of copper in dilute nitric acid the formation of nitrous oxide was much influenced by the presence of metallic salts, and that previous saturation of the solution with cupric nitrate could convert a product containing 90 - 95 per cent nitric oxide to one containing 85 per cent nitrous oxide.

Later, in conjunction with Armstrong, (Acworth and Armstrong, Jour.Chem.Soc. <u>32</u>. 54. 1877.), he shows that the presence of cupric nitrate leads to an increased production of nitrous oxide up to stauration of the solution with the nitrate, and suggests that the effect is due to a preliminary reduction of cupric to cuprous nitrate, the nitrous oxide being a direct product of the re-oxidation of cuprous nitrate by nitric acid.

Rennie, Higgins and Cooke, (T. 1908. 1171; 1911. 1035.), show very conclusively that addition of metallic nitrates to a ~~neutral~~ metal - nitric acid mixture accelerates or retards the solution of the metal according to conditions of temperature and concentration. In a copper - nitric acid mixture the presence of nitrates, and of cupric nitrate in particular, cause a marked acceleration of the time of solution of the metal. The specific action of the cupric nitrate in this respect provides an explanation of the autocatalysis observed when copper is dissolved in nitric acid. It is of value to state the author's further conclusions as to the influence of metallic nitrates. " With the same concentration of acid, and with potassium nitrate, the lower the temperature the less the acceler--ation, (it may even become retardation), whereas the higher the temperature the greater the acceleration. With the same temperature increased concentration of acid tends to lessen acceleration.

Caesium and rubidium nitrates cause marked retardation. The acceleration produced by the nitrates of any one group of metals decreases as the atomic weight of the metal increases."

This last observation confirms what had previously been suggested by several workers, that the action of the metallic nitrate is due to the formation of some third substance, independent of the metal, which is the effective agent in bringing about the dissolution of the metal. The observation of Reynold's, (Jour.Soc.Chem.Ind. 1906. 512.)[3] that nitrous-free nitric acid has no action on copper, with or without the addition of nitrates, is significant.

That this third substance is nitrous acid had practically been established by Veley, Proc.Roy.Soc. 46.216. 1889.), when he found that substances such as urea, potassium chlorate and hydrogen peroxide can for a time entirely prevent the dissolution of copper, mercury and bismuth in nitric acid, and further, that in excess nitric acid the amount of metal dissolved and the amount of nitrous acid present are concomitant variables. Veley explains the course of reaction as follows. The initial quantity of nitrous acid dissolves a certain amount of metal with the formation of the metallic nitrate and nitric oxide. The nitric oxide, which would obviously remain in solution owing to its high solubility in nitric acid, reacts with nitric acid to form more nitrous acid, while the metallic nitrite is oxidised to the nitrate by excess of nitric acid which is itself reduced to nitrous acid.

Thus:-

i $Cu + 4 HNO_2 \rightarrow Cu(NO_2)_2 + 2 NO + 2 H_2O$

ii $Cu(NO_2)2 + 2 HNO_3 \rightarrow Cu(NO_3)_2 + 2 HNO_2$

iii $HNO_3 + 2 NO + H_2O \rightarrow 3 HNO_2$

Similar equations represent the behaviour of mercury, silver and bismuth.

The amount of nitrous acid is therefore increased by two independent reactions, and, given a certain concentration, it would be expected that the reversal of equation (iii) would occur with the liberation of nitric oxide.

That the speed of solution of copper in ~~nitric acid~~ pure nitrous acid is considerably greater than in nitric acid, and that the addition of even small quantities of nitric acid ~~the~~ to the nitrous acid merkedly retards the dissolution of the metal is sufficient proof that nitrous acid is the effective agent. But one cannot conclude, therefore, that the scheme of reaction represented above is necessarily correct. It is, however, a significant fact that agitation of the liquid during solution retards the rate of solution, a phenomenon which can be explained on the above assumption in that agitation would reduce the local concentration of the third factor, nitrous acid, round the metal.

Further confirmation of the part played by nitrous acid is given by Petit and Dhar, (Zeit.anorg.Chem. 1924. <u>134</u>. 191.), by their examination of the action of different catalysts on the solution of mercury in nitric acid. Previous addition to the nitric acid of mercurous or ferric nitrite considerably increases the yield of nitrate, the formation of which is, however, entirely prevented if urea or sodium nitrite be first added to the mixture, the former acting by removal of nitrous acid by decomposition, and the latter by the formation of a complex sodium mercurinitrite. Ferrous sulphate, either by direct reduction of nitric acid, or by formation of the ferrous sulphate-nitric oxide complex which then yields nitric oxide and, by reaction with nitric acid, nitrous acid, also accelerates the dissolution of the metal. It would seem, therefore, that nitrous acid is an essential constituent, whether as catalyst or otherwise, of the dissolution of metals in nitric acid. It will, however, be more profitable to discuss the mechanism of its action with the whole question of the catalysis of nitric acid reactions.

Reduction of Nitric Acid by Compounds other than Metals.

Whether the course of reaction initiated by nitric acid in contact with any substance capable of interaction be one of oxidation or of nitration or of both, such reaction is invariably accompanied by secondary degradation involving further reduction of the nitric acid to any or all of the possible reduction products, with resultant oxidation of the compound. Such oxidation, if the degrading agentbe organic, proceeds in part, completely, with evolution of carbon dioxide, and the formation of oxalic acid and other less fully oxidised products depending on the nature of the organic compound. But though this degradation may take place independently, factors which influence such reaction cannot fail to Be of influence on the simultaneous reactions of oxidation and nitration.

Little evidence is forthcoming in the literature as to the nature of the degradation products formed by interaction between nitric acid and organic compounds. With one exception, (Rice. Jour. Amer. Chem. Soc. 1920. 2665.), no examination has been made of either the gaseous products or any possible reduction products of nitric acid present in the solution. In the present investigation, during which a considerable number of reactions between organic compounds and nitric acid have been examined, this aspect of the course of reaction has been taken into account.

Secondary reactions must occur, in the absence of other factors, by virtue of the oxidisable capacity of the organic compound, and consequently may be expected to take place more extensively in a system undergoing oxidation than in a nitrating medium. This is borne out by experiemnt. The reduction products of nitric acid, whether as oxides of nitrogen or as nitrite, decrease as the nitrating action of the acid becomes more pronounced.

Nitrous acid, nitric oxide, nitrous oxide, nitrogen peroxide and nitrogen in varying proportions according to the nature of the organic compound and temperature of reaction are products of both systems, but there is a marked preponderance of nitrous oxide and nitrogen in a system which is undeggoing nitration, while, on the other hand, oxidation by nitric acid determines a high percentage of nitric oxide, nitrogen peroxide and nitrous acid in the reduction products. Similarly, in the latter system, oxalic acid, carbon dioxide and carbon monoxide are increasingly present in varying but considerable amounts, whereas these substances are formed to only a very small extent as secondary products of a nitrating reaction.

Such differentiation is observed, too, if one compares the early and subsequent stages of a nitrating reaction. In the nitration of benzene nitrous oxide and nitrogen account for two thirds of the nitric acid decomposed other than by actual nitration, during the first stage corresponding to the introduction of one nitro group. During further nitration to the di- and trinitro compounds there is a marked falling off in the proportion of these gases, and a corresponding increase in the amounts of nitrogen peroxide and nitric oxide formed as nitration proceeds. In such a system this behaviour is undoubtedly dependent, partially at least, on the gradual dilution of the acid by water. Two factors play an important part here. High concentrations of nitric acid, as was observed in the examination of the degradation of nitric acid by metals, favours the formation of the lower reduction products nitrous oxide and nitrogen, which tend to decrease in amount with a corresponding increase of nitric oxide and nitrogen peroxide as concentration diminishes. But, also, the solubility of nitric oxide and nitrogen peroxide is considerably greater in concentrated nitric acid than in water, and dilution of the acid would necessarily release more of these gases. It is impossible at this stage to dissociate the influence of these two conditions. It is certain, however, that temperature plays an important part, and in general it can be stated that the lower the temperature during the critical stages the less will be the proportion of the higher reduction products.

It is interesting to compare the~~r~~se results with the figures obtained by Rice, (Jour.Amer.Chem.Soc. 1920. 2665.), in the nitration of phenol, where the same distinction between the first and later stages of the reaction is noticeable. While he gives no data as to the effect of temperature on the amount of nitrated product, he observes that low temperature during the early stages of the reaction is a factor for the lower yield of nitrous oxide and nitrogen.

<u>The Effect of the Presence of Metallic Salts</u>:- As can be predicted from the preliminary examination of the action of metals and metallic salts on nitric acid, ~~into a system containing nitric acid and an organic compound,~~ the introduction of such salts into a system containing nitric acid and an organic compound has considerable influence on the course of the reaction.

At the outset it would be expected that those metals which, in their interaction with nitric acid, cause the most extensive degradation would, by virtue of such degradation, tend to promote the oxidising function of the acid. While, on the contrary, oxidation might be decreased and even prevented, possibly in favour of nitration, in the presence of metals or their salts whose power of promoting degradation is less. The products of degradation of nitric acid in the presence of an organic compound by the metals silver, mercury, copper and bismuth, which promote the formation of nitrogen trioxide and nitrogen peroxide, with secondary formation of nitric oxide, and the effect of these metals on the processes of nitration and oxidation, should be clearly distinguishable from that of the metals iron, tin and lead which are powerful agents of reduction of nitric acid, giving rise to the ultimate products of reduction, nitrous oxide, nitrogen and ammonia.

The effect of the addition of small quantities of salts of copper, silver, mercury, tin and iron to the nitration mixtures of various organic compounds strikingly confirms this supposition. In the nitration of phenol, (v. table 16 B), silver, copper and mercury, increasingly in the order named, not only do not promote oxidation of the organic compound, but actually cause an increase in the proportion of phenol undergoing nitration, though for silver this increase is very small. The proportion of nitric acid represented as nitrocompound is greater, and the proportion of nitric acid as oxides of nitrogen is less in the presence of these metals than in normal nitrations when they are absent. On the other hand, iron and tin salts both promote oxidation of the phenol, the former to a considerable extent. And while there is an increase in the proportion of organic compound entering into reaction, such increase is due to destructive oxidation at the expense of nitration, and the proportion of nitric acid represented as nitrated compound is less, and that as oxides of nitrogen greater than is the case in normal, uncatalysed nitrations.

In the interaction between nitric acid and the unsaturated hydrocarbons ethylene and acetylene the course of the reaction is even more susceptible to the presence of metallic salts. As before, mercury has the most marked effect, and causes the greatest increase in the proportion of carbon becoming nitrated, Copper produces the same effect, though to a less degree, while silver, without promoting oxidation at the expense of nitration, seems to carry the reaction ~~to~~ only to the intermediate stages of the nitroalcohol and allied compounds. (v. table 50
Of the other metals examined, all promote oxidation at the direct expense of nitration.

In this survey two metals stand out by reason of the marked influence which they exert on the course of the reaction between organic compounds and nitric acid, and each, mercury and iron, is representative though in an extreme degree, of the two types of metals outlined above.

Iron salts in all the examples studied increase the decomposition of the nitric acid, giving an increased formation of nitrous oxide and nitrogen at the expense of the nitrated compound. In other words, iron salts may be said to be positive catalysts of the oxidising action of nitric acid, the decreased formation of nitrated product being directly proportional. (v. table 16.c).

The effect of mercury salts is much more subtle. At first sight it would appear that the first or immediate effect of the addition of these compounds to a nitric acid system is to increase simultaneously both the oxidising and the nitrating action of the acid, with the formation of an oxidised nitro compound. Evidence from ~~other~~ previous work in the main substantiates this view.

Holdermann, (B. 39.1250. 1906.), examining the effect of mercurous nitrate on the nitration of anthraquinone, and its derivatives, shows that the yield of 1-nitro-2-methylanthraquinone, the nitrated product of β-methylanthraquinone, is considerably increased by the presence of the mercury salt. The effect, however, of such addition to the nitration mixture of anthraquinone is uniformly negative, no nitro compound being produced at all. It is interesting to compare this result with a similar observation of the author that the addition of mercury to a sulphonation of anthraquinone gives mainly the alpha sulphonic acid. Also, sulphonation of toluene in the presence of mercury gives thirty one per cent of ortho compound, as compared with the forty to fifty per cent obtained in normal nitrations.

The nitration in~~t~~ the presence of mercuric nitrate of benzene and its homologues has been examined by Wolffenstein and Boters, (B. 46. 586. 1913.), but their evidence is not substantiated by quantitative data. No modification of the reaction is observed when concentrated acid is used, the yield of nitro compound being unaffected. The effect on the action of more dilute acid, (1'31), is, however, marked. The yield of simple nitro compound is decreased, but the principal product of the reaction is an oxidised, nitrated compound, the nitrophenol, in the formation of which it would appear that oxidation preceeds nitration since no nitrophenol can be obtained from nitrobenzene under similar conditions.

Confirmation of this behaviour is given by Vignon, (Bull.Soc. 1920. 27. 547.), who obtained considerable quantities of picric acid from benzene under these conditions, and by Davies and Worrall, (Jour.Amer. Chem.Soc. 1921. 43. 594.), The latter authors show that, in the presence of mercuric nitrate, benzene is converted completely into nitrobenzene and picric acid, under conditions which otherwise leave a residue of unconverted benzene. The process has, moreover, been patented for the preparation of picric acid from benzene, (D.R.P.194,883 1908; D.R.P. 214,045, 1909; Brit.Pat. 125,461.) It is noteworthy that the phenol formation is a function of the more dilute acids. At concentrations of nitric acid of 70 per cent and over, nitration predominates to the almost complete exclusion of the nitrophenol. [~~The presence of mercury~~] Consequently, the oxidation in the presence of mercury salts, so frequently observed in the literature must not be confused with the oxidising function of dilute nitric acid. There is little evidence that mercury salts can to any appreciable extent exert a negative catalytic influence on the process of nitration.

Examination of the nitration of aromatic sunstances under varying conditions shows that, with the exception of aromatic aldehydes, a decrease in the yield of the nitrated, unoxidised compound is observable only -among the examples studied- in the nitration of anthracene, bromobenzene and salicylic acid.

On the contrary, in a concentrated nitric acid mixture not only is the formation of the hydroxylic nitro compound not favoured, but the yield of simple nitro compound is frequwntly appreciably increased. Such positive catalysis of nitration has been observed in the nitration of phenol, chlorophenol, ortho-, meta- and para- cresols, dinitronaphthol, naphthalene, phenanthrene, benzoic acid and cinnamic acid.

This positive effect is produced by very small amounts of the mercury salt. In normal experiments the relative proportion varied from 0'03 to 9'2 moles of mercuric nitrate to one mole of nitratable substance. Increase in the proportion of nitrate has a varying effect on different nitrations, but above a concentration of 9'93 moles the effect of such increase is slight. Davies, Worrall &c, (ibid), have shown that below this concentration addition of mercuric nitrate to a nitration mixture of benzene, in quantities varying from 0'0046 moles to 0'26 moles, produces at the lowest concentration a slight increase of yield of picric acid, which rapidly increases with increase of mercury until an approximately constsnt maximum value is reached.at a concentration of 0'23 moles of mercury salt. The reaction is not strictly comparable for mercury would seem to increase the yield of the hydroxylated nitro compound -picric acid- at the expense of the simple nitro compound, nitrobenzene. But this is not actually the case. The first very small additions of mercury do actually produce a rapid increase in the yield of nitrobenzene. The increase is not, however, continuously maintained, and the amount of nitrobenzene as the concentration of the mercury salt is increased from 0'0023 moles to 0'046 moles falls steeply to a value representing half the initial yield, and less than one third the maximum yield promoted by 0'0023 moles of mercuric oxide. Further increase of mercury, however, reverses this effect, and the yield of nitrobenzene again stedily rises to a constsnt value equal to the initial value at a concentration of 0'263 moles of mercuric oxide. Thus, the striking fact emerges that the presence of the mercury salt at a concentration varying from 0'0023 to 0'00046 moles in the nitration of benzene has a positive catalytic effect on the formation both of picric acid and of mononitrobenzene. Between concentrations of 0'0023 to 0'046 moles of mercuric oxide the yield of picric acid is increased, while that of nitrobenzne is rapidly decreased. But between concentrations 0'046 and 0'263 moles the formation both of picric acid and of nitrobenzene is again increased.

In examining the effect of mercury in nitration, both from the point of view of the nature of the compound nitrated and also from that of the character of the nitrating medium, one is led to the conclusion that, while the catalytic effect of mercury varies considerably with the nature of the compound nitrated, its effect seems independent of the medium.

Though it is impossible to make any comparable study of the nitration of any one substance in different nitrating media, since there is always an optimum condition for each, nevertheless the examination of a large number of nitrations, carried out under very different conditions, shows that mercury may exert a positive or a negative catalytic effect, or be without any apparent influence, whether the nitration be carried out in concentrated or dilute nitric acid, concentrated nitric plus sulphuric acids, nitric acid plus acetic acid, nitrous acid or potassium nitrate and sulphuric acid. No prediction of the behaviour of mercury in any given medium can be made. This is the more surprising when one considers how different is the physical condition of the mercury salt in the different media. In all completely non-aqueous media only a minute porportion of the mercury salt can exist in solution, the bulk of it remains undissolved as nitrate in concentrated nitric or nitric plus acetic acid media, or as sulphate in a concentrated sulphuric-nitric acid medium, and there is no evidence that the catalytic effect is in any way proportional to the amount which is actually present in solution in the nitrating mixture.

But there is considerable variation in the susceptibility of different types of aromatic compounds to catalytic influence, though here, too, with the exception of phenolic compounds, there is little specific behaviour of type. All the different phenols examined, however, show an increase in the yield of nitro compound, which may amount to as much as thirty per cent, (m-cresol)., and this positive catalysis is maintained in a nitric-acetic acid medium, (nitration of cresols), in a nitric-sulphuric acid medium, (nitration of dinitronaphthol), and in a medium in which nitrous acid is the nitrating agent, (nitration of salicylic acid).

In the nitration of hydrocarbons the effect of mercury is variable. Increase of yield of mononitro compound is found in the nitration of naphthalene, (to the dinitro stage), phenanthrene and chlorobenzene. Benzene, toluene, xylene and methyl and ethylbenzenes in concentrated nitric acid or concentrated nitric-sulphuric acid media give normal yields of nitrated product. In the nitration of bromobenzene on the other hand, addition of mercury causes a depression of yield. v. Tables 1 - 13

Acetanilide and methylacetanilide have been examined, and the influence of mercury, though mainly positive, is irregular, while in the nitration of the base, dimethylaniline, the effect is uniformly positive, a slight increase of yield of total mononitro compound amounting to 5 - 11 per cent being obtained.

Contrary to the statement of Wolffenstein and Paar, (B. <u>46</u>. 589. 1913), there is an appreciable increase, amounting to 10 - 20 per cent, when benzoic acid is nitrated in the presence of mercuric nitrate. These authors appear, however, though little quantitative data is given, to have examined the effect of the metallic salt only in a dilute acid, (nitric acid 1'35), medium in which the nitrating action of the acid is low, and the natural oxidising function would in any case begin to be operative. Using the non-aqueous medium of a potassium-sulphuric acid mixture I have found no trace of oxidised product -the hydroxy nitro acid- but only a larger percentage of the nitro acid. On the other hand, I have been unable to discover any evidence that mercuric nitrate has any constsnt effect on the nitration of sal~~y~~icylic acid, the yield of nitrated product of which is frequently depressed by the presence of mercury. In the nitration of cinnamic acid there is a slight increase in yield of nitrated product.

It would appear from the behaviour of aromatic aldehydes in nitrating media containing mercuric nitrate that this substance possesses the capacity for promoting oxidation, which, however, only becomes operative in the presence of an easily oxidisable compound. Such susceptibility to oxidation exists in the aromatic aldehydes, and these compounds are uniformly simultaneously oxidised and nitrated to the correspodding mononitro acid, i.e. benzaldehyde yields m-nitro-benzoic acid, salicylic aldehyde 3-nitro- and 5-nitrosalicylic acids, p-oxybenzaldehyde 3-nitro-p-oxybenzoic acid.

Examination of an entirely different reaction - the addition of nitric acid to unsaturated hydrocarbons - at once indicates a marked susceptibility to the influence of metallic salts. The course of the reaction is fully discussed in a later section; it is sufficient to indicate here that the reaction provides confirmation of the hypothesis that the influence of mercury salts in nitration is rarely, if ever, to promote oxidation at the expense of the nitrating function. These slats, in the interaction between nitric acid and unsaturated hydro--carbons have a positive catalytic effect on the addition of the groups (OH) and (NO_2) to the double bond, resulting in the first instance in an increased yield of the intermediate compound the nitro--alcohol. In the subsequent rupture and further nitration of this compound there is consequently a proportionate increase in the yield of fully nitrated product, corresponding in amount to an increase in the formation of oxidised products. Thus, in the formation of tetra--nitromethane from acetylene by the direct addition of nitric acid, the ultimate effect of mercuric nitrate in the reacting mixture is to increase the yield of tetranitromethane by as much as 32'8 per cent.

When one examines the whole course of the reactions which organic compounds undergo in a nitrating medium, both in the presence and absence of mercury salts, it is obvious that various factors other than the actual yield of nitrated product have to be taken into acc--ount if one is to form any estimate of the favourable or unfavourable effect of the metallic salt in the actual process of nitration. Conditions of temperature, of purity of rpoduct, the presence or absence of other compounds and the ultimate fate of the nitric acid are all involved.

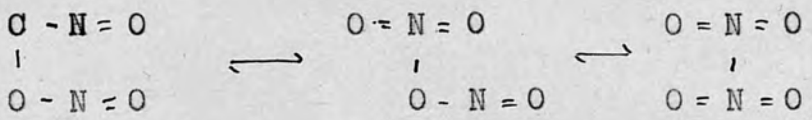
It is proposed at this stage to discuss at some length the action of nitric acid on a double and a treble bond as revealed by the interaction of nitric acid and ethylene and acetylene, and the effect on this reaction of mercury salts. From a detailed study of the effect of such salts in the nitration of aromatic compounds certain evidence is forthcoming as to the mechanism of their catalytic action in nitration.

It has been possible in the light of such evidence, and of the knowledge which has been obtained of the mechanism of the action of nitric acid on the unsaturated linkage to develope to some extent our knowledge of the whole course of the interaction between nitric acid and organic compounds.

The Interaction between Oxides of Nitrogen and Unsaturated Compounds.

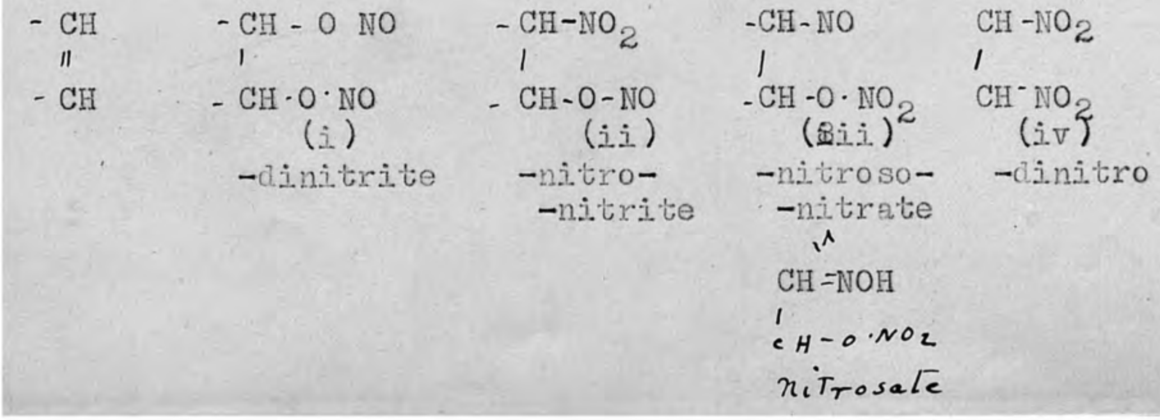
A survey of the literature of the interaction between oxides of nitrogen and the double or triple bond of unsaturated compounds, aliphatic or hydroaromatic, shows at once that we have to deal with a complex series of reactions, depending not only on the composition of the nitrous gases, but to a certain extent on the nature of the unsaturated compound.

The Action of Nitrogen Peroxide. The behaviour towards an ethylene link of pure nitrogen peroxide suggests that this compound exists in solution in three different forms in equilibrium with each other, the proportion of each form depending upon temperature and concentration.



$$\begin{matrix} O-N=O \\ | \\ O-N=O \end{matrix} \longleftrightarrow \begin{matrix} O=N=O \\ | \\ O-N=O \end{matrix} \longleftrightarrow \begin{matrix} O=N=O \\ | \\ O=N=O \end{matrix}$$

According to the predominance of one or other of these forms the following types of addition to the ethylene link may occur:-



$$\begin{matrix} -CH \\ \| \\ -CH \end{matrix} \qquad \begin{matrix} -CH-O\,NO \\ | \\ -CH\cdot O\cdot NO \end{matrix} \qquad \begin{matrix} -CH-NO_2 \\ | \\ -CH-O-NO \end{matrix} \qquad \begin{matrix} -CH-NO \\ | \\ -CH-O\cdot NO_2 \end{matrix} \qquad \begin{matrix} CH-NO_2 \\ | \\ CH-NO_2 \end{matrix}$$

(i) -dinitrite

(ii) -nitro- -nitrite

(iii) -nitroso- -nitrate

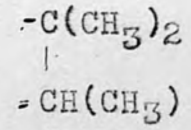
(iv) -dinitro

$$\begin{matrix} CH=NOH \\ | \\ CH-O\cdot NO_2 \end{matrix}$$

nitrosate

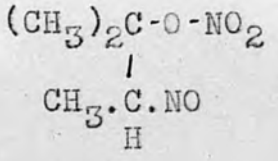
Probably the higher unsaturated aliphatic and hydroaromatic hydrocarbons give with nitrogen peroxide a mixture of all these four types, one or other predominating under specific conditions, though it would appear that, as the tendency to form the nitroso-chloride with nitrosyl chloride increases as the weight of the radicle in the neighbourhood of the reactive carbon increases, (Tilden & Sudborough. T. 1893. 479.), so the tendency to form the nitroso-nitrate increases. Hence, with such compounds, this form is the principal product. Compounds containing a secondary carbon atom can also yield an isomeric oximido compound, which is the true nitrosate.

Thus:-



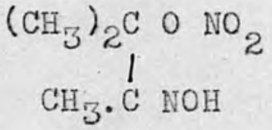
$$\begin{array}{l} -C(CH_3)_2 \\ \,| \\ =CH(CH_3) \end{array}$$

Amylene



$$\begin{array}{l} (CH_3)_2C\text{-}O\text{-}NO_2 \\ \qquad | \\ CH_3.\underset{H}{C}.NO \end{array}$$

Amylene nitroso-nitrate.

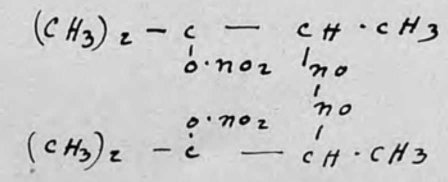


$$\begin{array}{l} (CH_3)_2C\ O\ NO_2 \\ \qquad | \\ CH_3.C\ NOH \end{array}$$

Amylene nitrosate.

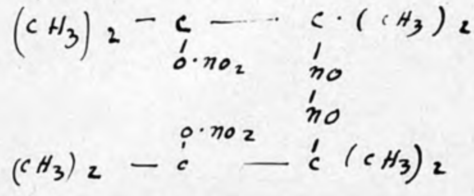
(Wallach. Ann. 248. 161. 1888.)

When the double bond is situated between a secondary and a tertiary, or between two tertiary carbon atoms, there is a general tendency to form a bimolecular bisnitrosate; solid, crystalline compounds which separate from solution, the unimolecular form, when present, remaining in solution. (Klingstedt. Ber. 58. 2363. B. 1925.) Thus amylene bisnitrosate has the constitution



$$\begin{array}{l} (CH_3)_2-\underset{O\cdot NO_2}{C}\ -\ \underset{NO}{CH}\cdot CH_3 \\ \qquad\qquad\qquad\quad | \\ (CH_3)_2-\overset{O\cdot NO_2}{C}\ -\ \overset{NO}{CH}\cdot CH_3 \end{array}$$

and tetramethylethylene bisnitrosate



In the bimolecular state, the bisnitrosate of a compound containing a secondary carbon atom cannot exist in the oximido form.

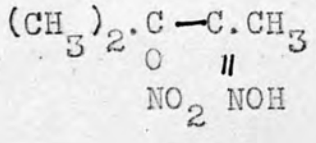
It would appear also, that when each carbon of the ethylene link is fully alkylated the capacity for nitrosate formation is weakened, and varying quamtities of dinitrite and of nitro-nitrate are formed. Schmidt, (Ber. <u>36</u>. 1775. 1903.) fails to detect any nitrosate formation at all in the product of the action of nitrous fumes on tetramethylethylene, but Demjanoff, (Ann. Inst. Agron. Moscow. <u>4.</u> 155. 1899.) shows the formation of nitrosate and of nitro-nitrate by the action of nitrogen peroxide on this compound.

$$(CH_3)_2C-C(CH_3)_2 + 2NO_2 \longrightarrow NO_2C.(CH_3)_2-C.(CH_3)_2.O.NO_2$$

$$\longrightarrow NO_2.C.(CH_3)_2-C.(CH_3)_2.O.NO_2$$

$$\longrightarrow NO.O.C.(CH_3)_2-C.(CH_3)_2.O.NO$$

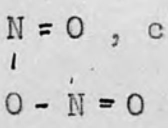
The existence of these bimolecular compounds was known as early as 1860, when Guthrie, (Ann. <u>116</u>. 248. 1860.), obtained a bimolecular compound from amylene and nitric acid, the constitution, and even the empirical composition of which, however, he was unable definitely to ascertain.

Schmidt, (Ber. 35. 2336. 1902.) obtained from trimethylethylene, by treating it in ethereal solution with nitrogen peroxide, two products, - a liquid, monomolecular compound, which he showed to be the nitrosate  $(CH_3)_2.\underset{\underset{NO_2}{O}}{C}-\underset{\underset{NOH}{\|}}{C}.CH_3$, and a solid, bimolecular bisnitrosate, $(C_5H_{10}N_2O_4)_2$, and he demonstrated that the two forms are interconvertible. I is polymerised to II on standing at ordinary temperature, but slight warming causes the decomposition in solution of II into I.

$$2\ C_5H_{10}N_2O_4 \rightleftharpoons (C_5H_{10}N_2O_4)_2$$

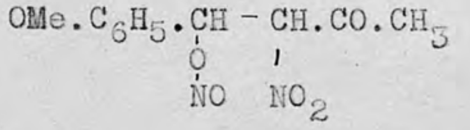
Thus a balanced reaction is set up, comparable to the change

$$2\ NO_2 \rightleftharpoons N_2O_4$$

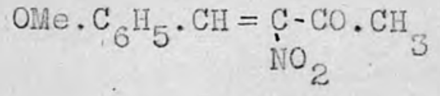
According as pure nitrogen peroxide, or a solution of this gas in nitric acid is used, so the yield of bisnitrosate varies, the higher yield of amylene nitrosate is given in the nitric acid medium. (Klingstedt. ibid.). It is possible that in a dissociating medium that form of nitrogen peroxide which is most favourable to nitrosate formation,  $\begin{matrix} O=N=O \\ | \\ O-N=O \end{matrix}$, can the more easily exist. But the behaviuor seems to be specific for each compound, and the yield of hexene nitrosate is slightly greater in the non-acid, (N_2O_4 in ether) medium. The bisnitrosate in either medium is not stable, and may finally completely disappear by secondary reactions, (Klingstedt, ibid.).

Phenyl-substituted Olefines

Phenyl-substituted Olefines and Nitrogen Peroxide. The substitution of phenyl for alkyl radicles adjacent to the double bond initiates a still further type of addition. When phenylethylene is treated with nitrous gases, containing mainly nitrogen trioxide and nitrogen peroxide, the first and principal product is a bimolecular pseudo-nitrosite, an addition compound involving the addition of N_2O_3. (These compounds are more fully discussed among the addition compounds of nitrogen trioxide.) The filtrate from this reaction mixture, freed from nitrous gases and ether, yields a second addition compound, the product of addition of N_2O_4 to the original unsaturated compound, with either the constitution of a nitro-nitrite, or of a dinitro- compound. The reaction has been examined in detail for anisylidene acetone and for anisylidene acetophenone, (Wieland. Ann. 340. 63. 1905.), and here, where, in the expression R.CH = CH.R', R is aromatic with a positive substituent, and R' is negative, i.e. CO.CH$_3$ or CO.Ph, the addition compound shows such a marked tendency to lose nitrous acid that the isolated product is the nitroketone.

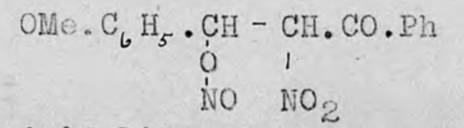


$$OMe.C_6H_5.\underset{\substack{O\\NO}}{CH} - \underset{NO_2}{CH}.CO.CH_3$$

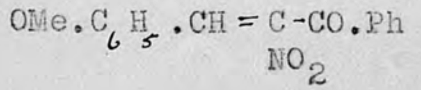


$$OMe.C_6H_5.CH = \underset{NO_2}{C}-CO.CH_3$$

Anisylidene nitro-nitrite.



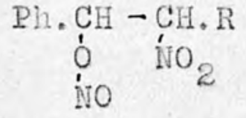
$$OMe.C_6H_5.\underset{\substack{O\\NO}}{CH} - \underset{NO_2}{CH}.CO.Ph$$



$$OMe.C_6H_5.CH = \underset{NO_2}{C}-CO.Ph$$

Anisylideneacetophenone
nitro-nitrite

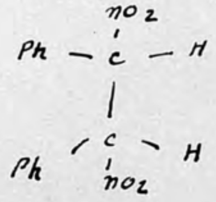
The secondary addition product of the compound $Ph.CH = CH.R$, where R is positive, would be the nitro-nitrite



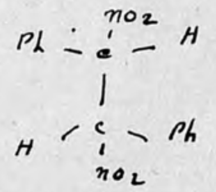
$$\underset{\substack{| \\ O \\ | \\ NO}}{Ph.CH} - \underset{\substack{| \\ NO_2}}{CH.R}$$

which, according to the nature of R, might or might not lose nitrous acid, forming the unsaturated nitro-compound $Ph.CH = C(NO_2).R$.

The product of the interaction of nitrogen peroxide and stilbene is a mixture of two symmetrical dinitro compounds, s-α-diphenyl-dinitroethane and s-β-dinitrodiphenylethane. (Schmidt. Ber. 34. 3536. 1901; Wieland & Blumich. Ann. 424. 75.1921.)



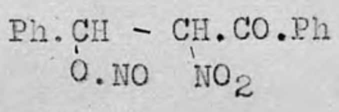
s-α-dinitrodiphenylethene



s-β-dinitrodiphenylethane

ixxs in addition to the normal, primary product stilbene- -nitrosite.

In the expression $R.CH = CH.R'$, where R'is negative, and R is unsubstituted or negatively substituted phenyl, addition both of nitrogen trioxide and of nitrogen peroxide takes place differently, the latter giving mainly a dinitro compound, but one in which only one nitro group attaches itself to the double bond, while the other nitrates the phenyl nucleus. Thus the principal product of the addition of 2 NO_2 to benzylidene acetophenone in cooled benzene solution, is p-nitro-α-nitrobenzylidene acetophenone $NO_2C_6H_5.C(NO_2) - CH.CO.Ph$, together with a small amount of the nitro-nitrite



$$\underset{\substack{| \\ O.NO}}{Ph.CH} - \underset{\substack{| \\ NO_2}}{CH.CO.Ph}$$

Unsaturated compounds with conjugated double bonds readily add two molecules of NO_2 in the 1:4 position when treated with nitrous gases, (Wieland & Stenzl. Ann. <u>360</u>. 299. 1908.).

Thus:-

$$Ph.CH=CH-CH=CH.Ph + 2NO_2 \rightarrow Ph.CH(NO_2).CH=CH.CH(NO_2).Ph$$

But dibenzylidene acetone, with unconjugated double bonds, adds two molecules of NO_2 in the 1:2 position, (Wieland & Blumich. Ann. <u>424</u>. 75. 1921.).

Thus:-

$$Ph.CH=CH.CO.CH=CH.Ph + 2NO_2 \rightarrow Ph.CH(NO_2)CH(NO_2).CO.CH=CH.Ph$$

Dicyclopentadiene undergoes a similar addition, saturating one of its double bonds by the addition of two NO_2 groups, (Wieland & Stenzl. ibid.)

The action of the higher oxides of nitrogen on acetylenic compounds has been very little studied. Schmidt, (Ber. <u>34</u>. 619. 1901), suggests that the addition of two NO_2 groups to the double bond of stilbene with the formation of a dinitro compound, foreshadows the manner of reaction with acetylene. This was confirmed (for phenyl acetylene by Wieland & Blumich. ibid. 100.), who obtained α-β-dinitro-phenylethylene by treatment with nitrogen peroxide.

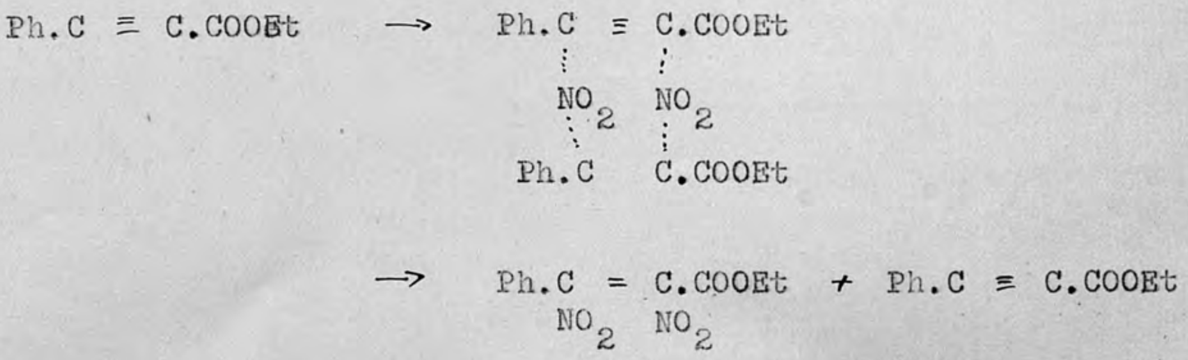
Thus, addition of oxides of nitrogen to the triple bond takes place usually to the incomplete saturation of the bond, an ethyleneic compound being formed. Nothing comparable to the addition of NO NO_2 followed by polymerisation is known. The reaction appears to involve the simple addition of $2NO_2$, (with nitrogen peroxide), or of 2NO, (with nitrogen trioxide), sometimes followed in the latter case by the formation of a ring compound, a furoxane.

Thus, phenyl acetylene and tolan, treated with nitrogen peroxide, add to the triple bond $2NO_2$ forming the unsaturated dinitro compound.

$$\mathrm{Ph.C \equiv CH} \longrightarrow \underset{NO_2}{\mathrm{Ph.C}} = \underset{NO_2}{\mathrm{CH}}$$

$$\mathrm{Ph.C \equiv C.Ph} \longrightarrow \underset{NO_2}{\mathrm{Ph.C}} = \underset{NO_2}{\mathrm{C.Ph}}$$

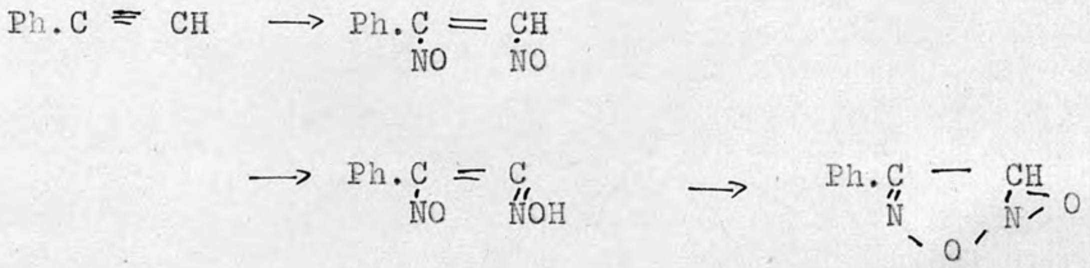
But evidence of an intermediate ~~stage~~ bimolecular stage is obtained in the reaction with ethylphenylpropiolate, which adds the groups $2NO_2$ to two molecules forming as easily dissociable compound which decomposes to equal parts of the unsaturated dinitro ester and the original ester.



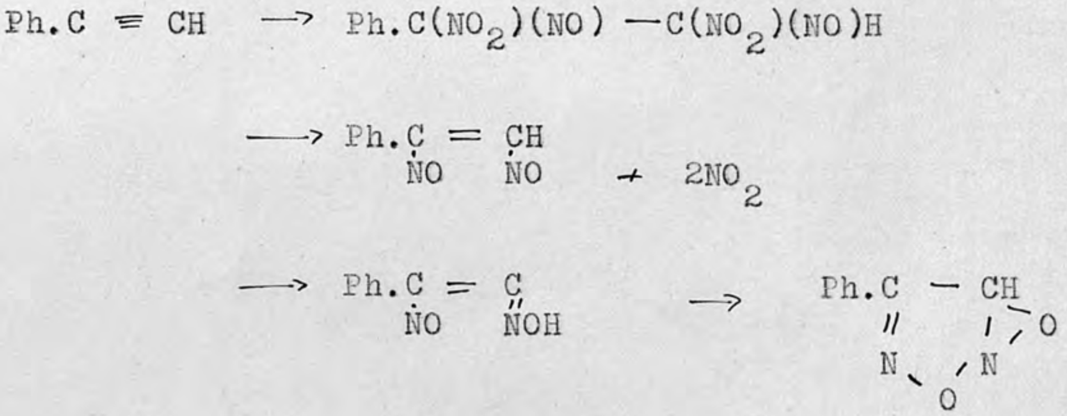
$$\mathrm{Ph.C \equiv C.COOEt} \longrightarrow \begin{array}{ccc} \mathrm{Ph.C} & \equiv & \mathrm{C.COOEt} \\ \vdots & & \vdots \\ NO_2 & & NO_2 \\ \vdots & & \vdots \\ \mathrm{Ph.C} & & \mathrm{C.COOEt} \end{array}$$

$$\longrightarrow \underset{NO_2}{\mathrm{Ph.C}} = \underset{NO_2}{\mathrm{C.COOEt}} + \mathrm{Ph.C \equiv C.COOEt}$$

The action of nitrogen trioxide on phenyl acetylene gives ultimately phenyl furoxane, a condensed dinitroso compound which may arise either by direct addition of two nitroso groups



or by addition of $2(NO_2\ NO)$, followed by elimination of $2NO_2$.

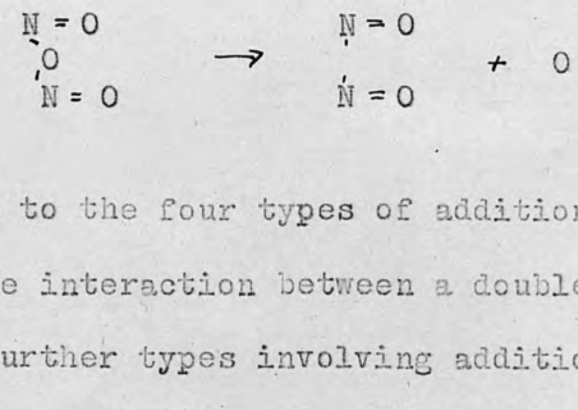


While fundamentally the reaction with oxides of nitrogen involves simple addition to the unsaturated linkage, secondary and more complex reactions can occur. This, as will be shown, applies even more considerably to the reaction between acetylenic compounds and nitric acid. But these reactions are susceptible to the influence of catalysts, and under certain conditions the course of reaction can be simplified so that the primary, simple addition predominates. The discussion of the effect of catalysts is reserved for a later section.

$$Ph.C \equiv CH + 2NO_2 \rightarrow Ph.C(NO_2) - CH(NO_2)$$

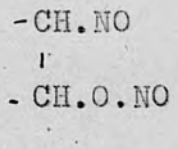
The Action of Nitrogen Trioxide. With equal readiness does nitrogen trioxide react with the double bond of unsaturated compounds. But, inasmuch as the composition of solutions of nitrogen trioxide is variable, the reaction may take place in several ways. According to the temperature and concentration of the mixture there may be a preponderance of nitric oxide or nitrogen dioxide, and in general, such a solution behaves towards unsaturated compounds as a mixture of $NO + NO_2$, and addition takes place as such, though at the same time a dissociation of nitrogen trioxide into $O + 2NO$ undoubtedly in small part, occurs.

i.e.



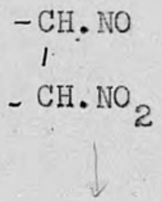
$$\begin{matrix} N=O \\ O \\ N=O \end{matrix} \rightarrow \begin{matrix} N=O \\ \\ N=O \end{matrix} + O$$

In addition to the four types of addition compounds which are possible in the interaction between a double bond and nitrogen peroxide, three further types involving addition of (i) $NO + O.NO$, (ii) $NO + NO_2$, or, if nitrogen pentoxide be present, of (iii) $NO_2 + ONO_2$ are possible, and doubtless occur in varying degrees.

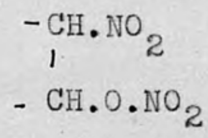


$$\begin{matrix} -CH.NO \\ | \\ -CH.O.NO \end{matrix}$$

nitroso-nitrite



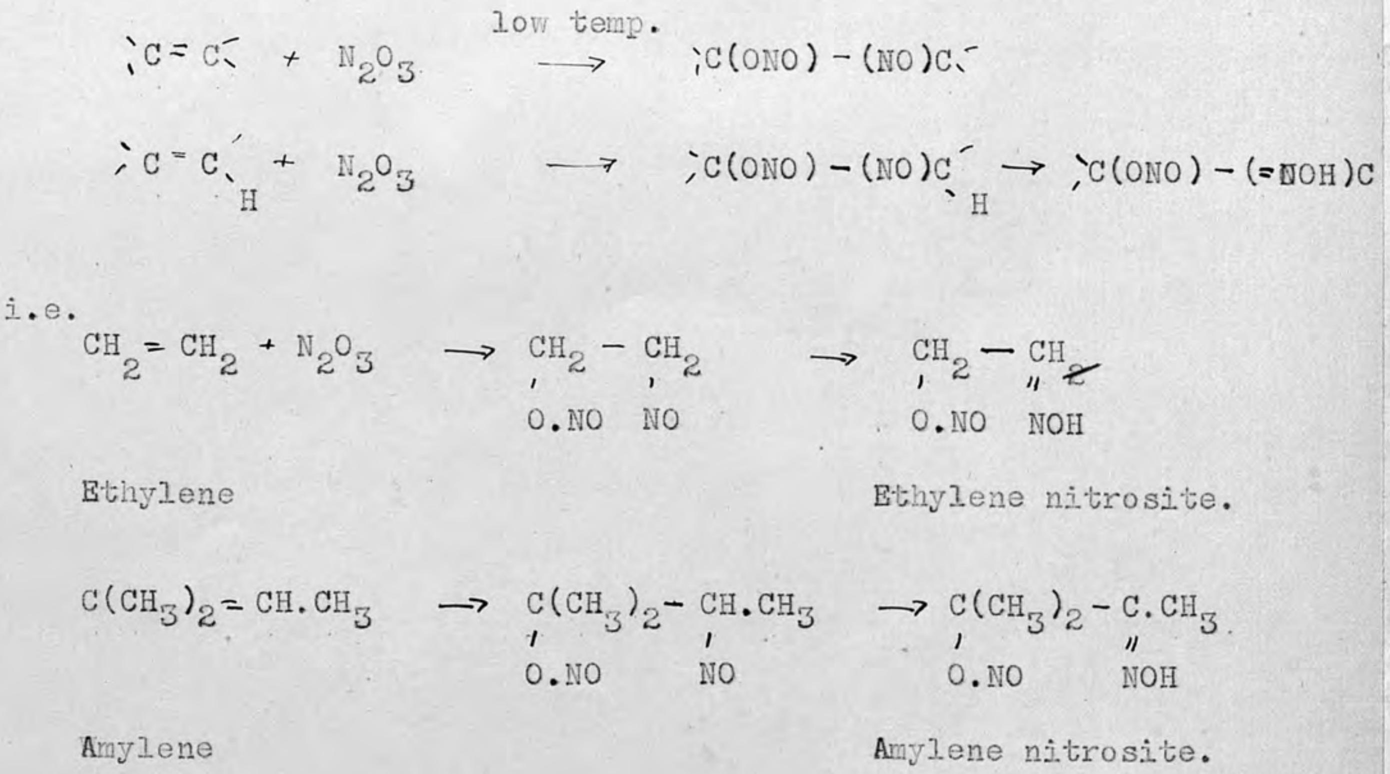
$$\begin{matrix} -CH.NO \\ | \\ -CH.NO_2 \end{matrix}$$



$$\begin{matrix} -CH.NO_2 \\ | \\ -CH.O.NO_2 \end{matrix}$$

nitro-nitrate

Nitrous fumes, prepared from arsenic trioxide and nitric acid, contain mainly nitrogen trioxide and nitrogen peroxide, together with some nitric oxide, the proportions varying with experimental conditions. Consequently, the addition products are, in part, those of the addition of nitrogen peroxide. The principal product of the interaction between nitrogen trioxide and olefinic compounds represents the direct addition of $NO + O.NO$, and is a nitroso-nitrite, or nitrosite, corresponding to the nitrosate involving the addition of $NO + O.NO_2$.



$$\rangle C=C\langle \; + \; N_2O_3 \xrightarrow{\text{low temp.}} \rangle C(ONO)-(NO)C\langle$$

$$\rangle C=C\langle_{H} \; + \; N_2O_3 \longrightarrow \rangle C(ONO)-(NO)C\langle_{H} \longrightarrow \rangle C(ONO)-(=NOH)C$$

i.e.

$$CH_2=CH_2 + N_2O_3 \longrightarrow \underset{O.NO}{\underset{|}{CH_2}}-\underset{NO}{\underset{|}{CH_2}} \longrightarrow \underset{O.NO}{\underset{|}{CH_2}}-\underset{NOH}{\underset{\|}{CH_{\cancel{2}}}}$$

Ethylene — Ethylene nitrosite.

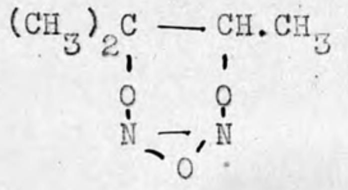
$$C(CH_3)_2=CH.CH_3 \longrightarrow \underset{O.NO}{\underset{|}{C(CH_3)_2}}-\underset{NO}{\underset{|}{CH.CH_3}} \longrightarrow \underset{O.NO}{\underset{|}{C(CH_3)_2}}-\underset{NOH}{\underset{\|}{C.CH_3}}$$

Amylene — Amylene nitrosite.

Wallach, (ibid), and Schmidt, (Ber. 35. 2323. 1902), have both studies this reaction, and have shown that the product of the interaction of nitrous fumes and amylene is a nitroso-nitrite, or the oximido isomeride, having the above constitution. At ordinary temperatures this polymerises to a bisnitrosite, a balanced reaction being set up, analogous to the polymerisation of the corresponding nitrosate.

$$2\ C_5H_{10}N_2O_3 \longleftrightarrow (C_5H_{10}N_2O_3)_2$$

Hantzsch, (Ber. <u>35</u>. 2978. 1902), criticises the nitroso-nitrite formula for amylene nitrosite, and suggests There seems little justification for such a formula, and the formation of the oximido isomeride and of the bisnitrosite are by it less easily explicable.



<u>Phenyl-substituted Unsaturated Compounds and Nitrogen Trioxide</u>:- As in the addition of nitrogen peroxide, analogous distinctions hold between the varying behaviour of higher and lower olefines, hydro--aromatic compounds and phenyl-substituted unsaturated compounds. IN both types of reaction it is noteworthy that the lower, simple olefines show little capacity for addition other than that of the ordinary nitrite or nitrate.

i.e. Ethylene tends to give $O.NO.CH_2-CH_2.O.NO$

Ethylene dinitrite

or

$NO.CH_2-CH_2.O.NO_2$

Ethylene nitroso nitrate

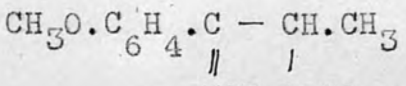
rather than $(NOH)CH-CH_2.O.NO$

Ethylene nitrosite.

As has been indicated above, the principal product of the inter--action of nitrous gases with phenyl-substituted olefines of the type

Ph.CH CH.R is a pseudo nitrosite, a compound differing from nitrosites and nitrosates, which are respectively nitrites and nitrates, in being a true nitro compound, (Wieland. Ann. 329. 225. 1903.), i.e. the two nitrogen atoms of the combining oxides are linked directly to carbon.

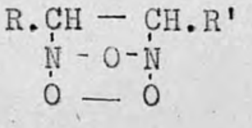
The existence of the nitrogen trioxide addition compound of such substances as anethol, styrol and phenyl substituted butylenes was recognised as long ago as 1878 by Tonnies, (Ber. 11. 1511. 1878.), who, however, failed to realise their true constitution; i.e. he postulated for the addition compound of anethol the constitution of a nitrosite,



$$CH_3O.C_6H_4.\underset{NOH}{\overset{\|}{C}} - \underset{O.NO}{\overset{|}{CH}}.CH_3$$

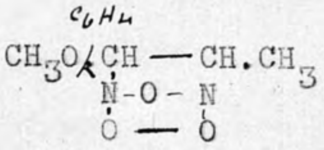
(Tonnies. Ber. 20. 2982.1887.)

Later, Angeli, (Gazz. 23. ii. 124. 1893; 25. ii. 188. 1895.) examining in more detail the action of nitrous fumes on the derivatives of aromatic ethers, as safrole, isosafrole, anethol and styrol, realised the true nitronic nature of these compounds, but gave them the general formula their characteristic property, the ready loss of water, then occuring as follows:-



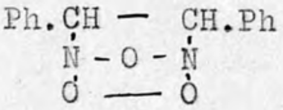
$$\begin{array}{c} R.CH - CH.R' \\ N - O - N \\ O - O \end{array}$$

Hence anethol nitrosite has the formula



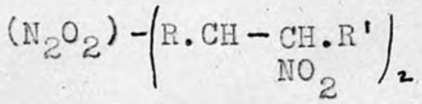
$$\begin{array}{ccc} \mathrm{CH_3O}\overset{\mathrm{C_6H_4}}{\wedge}\mathrm{CH} & - & \mathrm{CH.CH_3} \\ \mathrm{N} & -\mathrm{O}- & \mathrm{N} \\ \mathrm{O} & - & \mathrm{O} \end{array}$$

Schmidt, (Ber. 34. 623. 3536. 1901), obtained from stilbene, together with a small quantity of s-$\alpha\beta$-diphenylnitroethane, a similar pseudo nitrosite, to which he assigned the formula



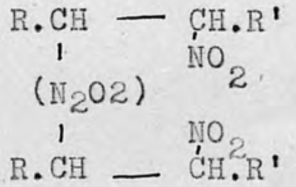
$$\begin{array}{ccc} \mathrm{Ph.CH} & - & \mathrm{CH.Ph} \\ \mathrm{N} & -\mathrm{O}- & \mathrm{N} \\ \mathrm{O} & - & \mathrm{O} \end{array}$$

The constitution of the pseudo nitrosites has been finally settled by ~~E~~ Wieland, (Ann. 329. 225. 1903.), who has conclusively demonstrated them to be bimolecular, nitro compounds,



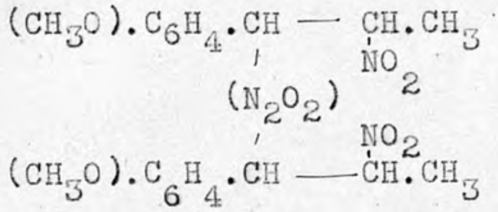
$$(\mathrm{N_2O_2})-\left(\begin{array}{l}\mathrm{R.CH-CH.R'} \\ \qquad\quad \mathrm{NO_2}\end{array}\right)_2$$

the constitution of which is probably best represented by



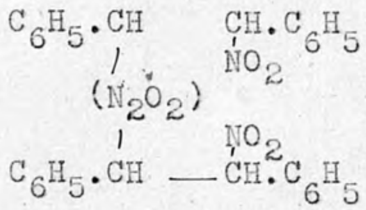
$$\begin{array}{lcl} \mathrm{R.CH} & - & \mathrm{CH.R'} \\ \mid & & \mathrm{NO_2} \\ (\mathrm{N_2O2}) & & \\ \mid & & \mathrm{NO_2} \\ \mathrm{R.CH} & - & \mathrm{CH.R'} \end{array}$$

The bimolecular nature of both nitrosites, (and nitrosates), and pseudo nitrosites is therefore demonstrated. The intermolecular linking takes place, in all probability, in the same way in each type of compound, the nitrite structure of the nitrosite and the nitro structure of the pseudo nitrosite being determined by the NO_2 constituent of nitrogen trioxide.



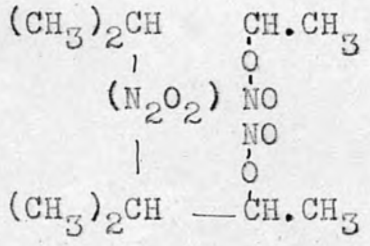
$$\begin{array}{lll}(CH_3O).C_6H_4.CH & - & \underset{NO_2}{CH}.CH_3 \\ \mid & & \\ (N_2O_2) & & \\ \mid & & NO_2 \\ (CH_3O).C_6H_4.CH & - & \overset{|}{CH}.CH_3\end{array}$$

Anethol nitrosite.



$$\begin{array}{lll}C_6H_5.CH & & \underset{NO_2}{CH}.C_6H_5 \\ \mid & & \\ (N_2O_2) & & \\ \mid & & NO_2 \\ C_6H_5.CH & - & \overset{|}{CH}.C_6H_5\end{array}$$

Stilbene nitrosite

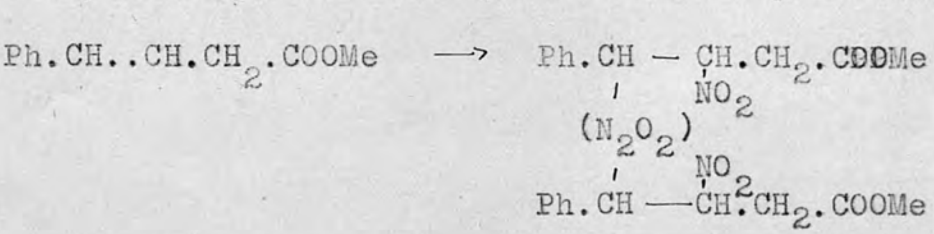


$$\begin{array}{lll}(CH_3)_2CH & & CH.CH_3 \\ \mid & & O \\ (N_2O_2) & & NO \\ & & NO \\ \mid & & O \\ (CH_3)_2CH & - & CH.CH_3\end{array}$$

Amylene nitrosite.

Such a pseudo nitrosite is not, however, an invariable product of the action of nitrous fumes. The capacity for pseudo nitrosite formation weakens as the negative character of the neighbouring radicles increases, (Wieland. Ann. <u>328</u>. 154. 1903.).

Thus Phenylisocrotonic ester gives a normal pseudo nitrosite,



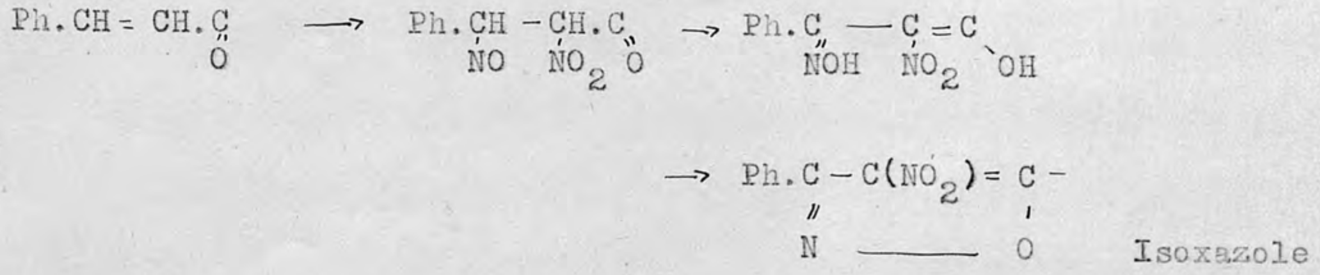
$$Ph.CH..CH.CH_2.COOMe \longrightarrow \begin{array}{lll}Ph.CH & - & \underset{NO_2}{CH}.CH_2.COOMe \\ \mid & & \\ (N_2O_2) & & \\ \mid & & NO_2 \\ Ph.CH & - & \overset{|}{CH}.CH_2.COOMe\end{array}$$

Benzalacetone yields only a very small quantity, while Benzal-acetophenone and Cinnamic aldehyde give none, and instead give a mixture of nitro- and oximido compounds.

Hence it would appear that the immediate proximity of the group C = O to the double bond in compounds of the type $Ph.C = C.\underset{O}{\overset{}{C}}$ almost entirely prevents the formation of the pseudo entirely prevents the formation of the pseudo nitrosite. This may be due to a reduced capacity for pseudo nitrosite formation as R becomes increasingly negative in the expression $Ph.CH = CH.R$, or there may be formation of the nitrosite, followed by its removal by secondary changes. Examination of the products of interaction of nitrogen trioxide and benzalacetophenone, and of nitrogen trioxide and cinnamic aldehyde, (Wieland. loc cit.), would seem to favour the former hypothesis.

Wieland, (loc cit), postulates three types of addition of nitrogen trioxide to the system $Ph.CH = CH.\underset{\overset{\|}{O}}{C}$.

(a) Addition of NO_2 to the α, and of (NO) to the β carbon atoms occurs, forming a compound which then undergoes the following changes:-



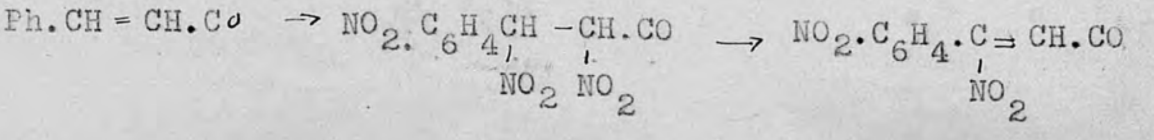
$$Ph.CH = CH.\underset{\overset{\|}{O}}{C} \longrightarrow Ph.\underset{NO}{CH} - \underset{NO_2}{CH}.\underset{\overset{\|}{O}}{C} \longrightarrow Ph.\underset{NOH}{\overset{}{C}} - \underset{NO_2}{C} = C\diagdown OH$$

$$\longrightarrow Ph.\underset{\overset{\|}{N}}{C} - C(NO_2) = \underset{\overset{|}{O}}{C} -$$

Isoxazole

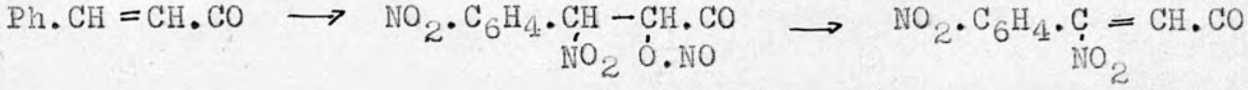
Molecular rearrangement with hydrogen results in the formation of the oxime of the diketone, which loses water giving an isoxazole.

(b) Direct nitration of the side chain may occur, together with nitration of the aromatic nucleus, giving the unsaturated nitro-compound.



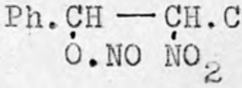
$$Ph.CH = CH.CO \rightarrow NO_2.C_6H_4\underset{NO_2}{CH} - \underset{NO_2}{CH}.CO \longrightarrow NO_2.C_6H_4.\underset{NO_2}{C} = CH.CO$$

or, more probably



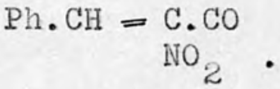
$$\mathrm{Ph.CH{=}CH.CO} \longrightarrow \mathrm{NO_2.C_6H_4.}\underset{\mathrm{NO_2}}{\mathrm{CH}}-\underset{\mathrm{O.NO}}{\mathrm{CH}}\mathrm{.CO} \longrightarrow \mathrm{NO_2.C_6H_4.}\underset{\mathrm{NO_2}}{\mathrm{C}}=\mathrm{CH.CO}$$

(c) Addition of N_2O_4 gives also the nitro-nitrite



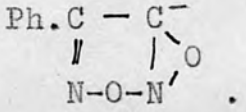
$$\mathrm{Ph.}\underset{\mathrm{O.NO}}{\mathrm{CH}}-\underset{\mathrm{NO_2}}{\mathrm{CH}}\mathrm{.CO}$$

, the tendency of which to lose nitrous acid is often so marked that the product may be the nitro-ketone.



$$\mathrm{Ph.CH}=\underset{\mathrm{NO_2}}{\mathrm{C}}\mathrm{.CO} \quad .$$

Dependent on the addition of nitrogen trioxide as NO NO_2 yet a fourth rearrangement may occur, the product being a glyoxime per-oxide,



Thus a strongly cooled solution of benzalacetophenone gives with nitrous fumes as principal product ultimately the isoxazole. But an intermediate bimolecular stage is arrested here, and there first crystallises out from the reaction mixture a compound in which two molecules of the original ketone have combined with the complex N_6O_{11}, ($4NO_2 + N_2O_3$).

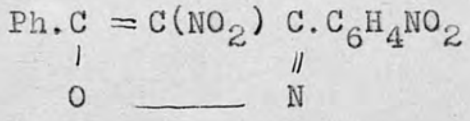
From a detailed stude of the reactions of this compound Wieland, (Ann. 328. 154. 1903.), has assigned to it the formula:-

$$\begin{array}{l} \mathrm{Ph.C(OH)}\ \underset{\mathrm{NO_2}}{\mathrm{CH}}-\underset{\mathrm{NOH}}{\overset{}{\mathrm{C}}}-\mathrm{C_6H_4NO_2} \\ \quad\ | \\ \quad\ \mathrm{O} \\ \quad\ | \\ \mathrm{Ph.C(OH)}\ \overset{\mathrm{NO_2}}{\mathrm{CH}}-\overset{\mathrm{NOH}}{\mathrm{C}}-\mathrm{C_6H_4NO_2} \end{array}$$

It is interesting to compare this witht the action of nitrous gases on phenanthrene, whereby an oxy addition compound in which the intermolecular linking i~~t~~s through the medium of oxygen is produced, (Schmidt. Ber. 33. 3252.).

Probably the normal reaction of addition of NO_2 of NO is followed in both cases by one of oxidation, brought about by the oxidising action of the higher oxides of nitrogen. Wieland, to account for the established formula of the nitrogen-oxygen compound of benzalacetophenone, assumes an actual dissociation of the molecule of nitrogen trioxide into O + 2NO.

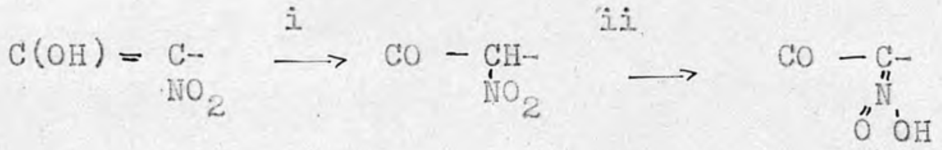
This addition compound readily loses water and passes into the final product, the isoxazole.



$$\begin{array}{l}Ph.\underset{\displaystyle O}{\underset{|}{C}} = C(NO_2)\ \underset{\displaystyle N}{\underset{\|}{C}}.C_6H_4NO_2\end{array}$$

A stable monomolecular oxime, which is the monoxime of a 1:3-diketone, can be isolated by treatment of the oxy-addition compound with ethereal ammonia. But once the reaction has been arrested at this stage the monoxime, thus formed, shows no tendency to give the anhydride, the isoxazole.

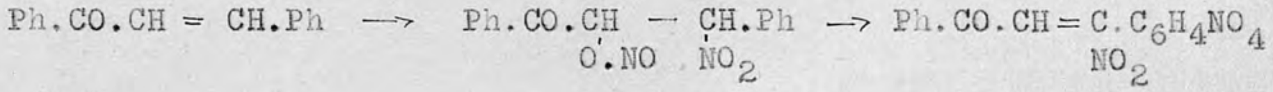
The stability of this monoxime is noteworthy, for among the class of ordinary 1:3-diketones no monoxime can be isolated, so easily does it pass into the anhydride. Wieland, (ibid), attributes this, probably rightly, to a decreased mobility of hydrogen in the expression $-CO-\underset{NO_2}{CH}-$, due to the opposing negative attraction of the nitro group, whereby the enolisation of the carbonyl group requisite for dehydration is prevented.



$$C(OH)=\underset{NO_2}{C}- \xrightarrow{i} CO-\underset{NO_2}{CH}- \xrightarrow{ii} CO-\underset{\underset{O\;\;OH}{\overset{\|}{N}}}{C}-$$

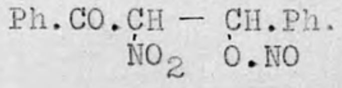
i.e. reaction (i) is counterbalanced by reaction (ii), and hence the nitro-ketone is stable.

Secondary products of the interaction with benzalacetophenone involve the addition of $2NO_2$, and are (b) p-nitro-β- nitrobenzalacetophenone, probably through the intermediate addition compound, the nitro-nitrite, which then loses nitrous acid.

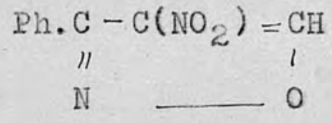


$$Ph.CO.CH=CH.Ph \longrightarrow Ph.CO.\underset{O.NO}{CH}-\underset{NO_2}{CH}.Ph \longrightarrow Ph.CO.CH=\underset{NO_2}{C}.C_6H_4NO_4$$

and (c) Benzalacetophenonenitronitrite, $Ph.CO.\underset{NO_2}{CH}-\underset{O.NO}{CH}.Ph.$

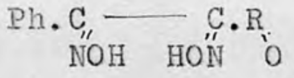


No such intermediate product as the bimolecular oxy-oximido addition compound of benzalacetophenone can be isolated from cinnamic aldehyde by the action of nitrous fumes. The primary product is the isoxazole, phenylnitroisoxazole,

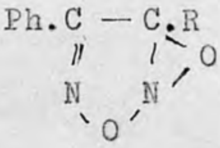


one secondary product only, the nitro-glyoxime peroxide, and that in small quantity, being isolated.

The formation of a second anhydride, the glyoxime peroxide, is a reaction which assumes much greater importance when in the expression Ph.CH=CH.CO.R the phenyl nucleus is positively substituted. Such substitution completely counteracts the influence inhibitory to poly-merisation, and these compounds undergo the normal pseudo nitrosite formation with nitrous fumes. Following on the decomposition of the bimolecular pseudo nitrosite to the monomolecular nitro-oxime form, $\underset{\text{NOH}}{\overset{\|}{\text{Ph.C}\cancel{\text{H}}}} — \underset{\text{NO}_2}{\text{CH.R}}$, a decomposition which is readily brought about by heating with alcohol, dehydration can take place between the nitro and the oximido groups, the product being the glyoxime peroxide.



$\underset{\text{NOH}}{\text{Ph.C}} — \underset{\text{HON}\ \ \text{O}}{\text{C.R}}$



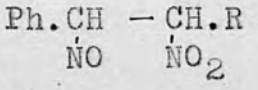
and this dehydration can occur regardless of whether R is positive or negative, provided that in the latter case the phenyl nucleus is positively substituted. Thus the peroxide formation is dependent only on the nitro-oximido formation, and occurs regardless of the presence of a carbonyl group, provided, as will be more fully discussed in considering the decompositions of these compounds, the negative influenee of this group is counteracted by positive substitution on the phenyl nucleus. Dehydration to the isoxazole, on the other hand, is structurally dependent on the presence of a carbonyl group in the enol form. This dehydration is, however, independent of phenyl substitution; when both anhydrides are theoretically possible, both are formed. Thus anisylideneacetophenone yields both a peroxide and an isoxazole by the action of alcohol on the pseudo nitrosite.

If one examines the mechanism of reaction with nitrogen trioxide and nitrogen peroxide in the three types

$$Ph.CH = CH.R, \quad Ph.CH = CH.CO.R, \quad R'.C_6H_4.CH = CH.CO.R$$

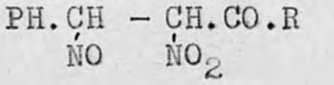
(R' -ve)

it is at once apparent that there must be considerable similarity of behaviour in the initial stages, the different ultimate products arising largely from subsequent molecular rearrangements specific to the nature of the original compound. Thus it seems probable that the primary addition products with these three types are respectively



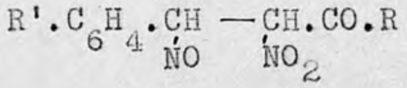
$$\underset{NO}{Ph.CH} - \underset{NO_2}{CH.R}$$

,



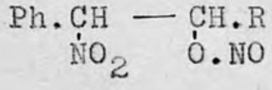
$$\underset{NO}{PH.CH} - \underset{NO_2}{CH.CO.R}$$

,



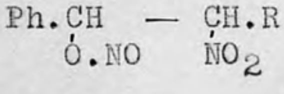
$$R'.C_6H_4.\underset{NO}{CH} - \underset{NO_2}{CH.CO.R}$$

and with nitrogen peroxide



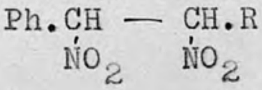
$$\underset{NO_2}{Ph.CH} - \underset{O.NO}{CH.R}$$

,



$$\underset{O.NO}{Ph.CH} - \underset{NO_2}{CH.R}$$

together with a small varying amount of the dinitro compound

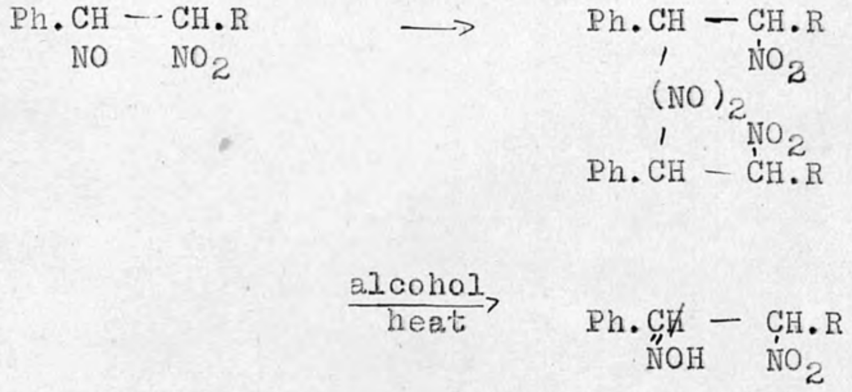


$$\underset{NO_2}{Ph.CH} - \underset{NO_2}{CH.R}$$

and that these latter products are formed regardless of whether R is positive or negative. Thus in all cases simple addition to the double bond of $NO + NO_2$, $NO_2 + O.NO$, or $NO_2 + NO_2$ takes place.

Secondary reaction then occurs as follows:-

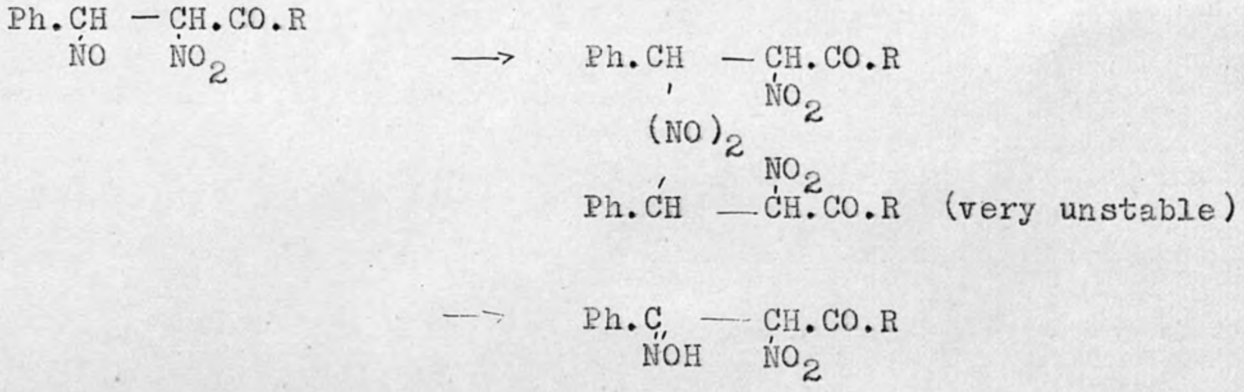
i.



$$\underset{NO}{Ph.CH} - \underset{NO_2}{CH.R} \longrightarrow \begin{array}{ll} Ph.CH & -\ CH.R \\ \quad / & \quad NO_2 \\ (NO)_2 & \\ \quad / & \quad NO_2 \\ Ph.CH & -\ CH.R \end{array}$$

$$\xrightarrow[heat]{alcohol} \underset{\overset{\|}{NOH}}{Ph.C\cancel{H}} - \underset{NO_2}{CH.R}$$

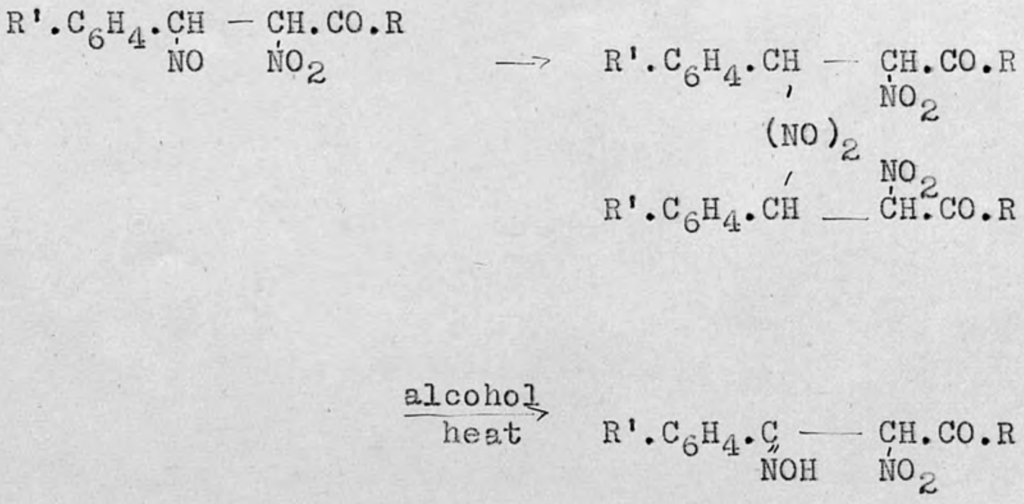
ii.



$$\underset{NO}{Ph.CH} - \underset{NO_2}{CH.CO.R} \longrightarrow \begin{array}{ll} Ph.CH & -\ CH.CO.R \\ \quad / & \quad NO_2 \\ (NO)_2 & \\ \quad / & \quad NO_2 \\ Ph.CH & -\ CH.CO.R \end{array} \text{(very unstable)}$$

$$\longrightarrow \underset{\overset{\|}{NOH}}{Ph.C} - \underset{NO_2}{CH.CO.R}$$

iii.

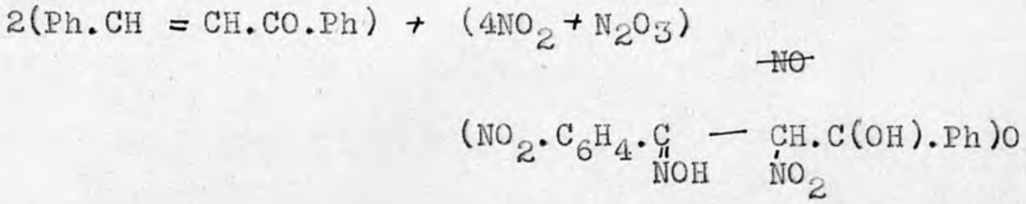


$$R'.C_6H_4.\underset{NO}{CH} - \underset{NO_2}{CH.CO.R} \longrightarrow \begin{array}{ll} R'.C_6H_4.CH & -\ CH.CO.R \\ \quad / & \quad NO_2 \\ (NO)_2 & \\ \quad / & \quad NO_2 \\ R'.C_6H_4.CH & -\ CH.CO.R \end{array}$$

$$\xrightarrow[heat]{alcohol} R'.C_6H_4.\underset{\overset{\|}{NOH}}{C} - \underset{NO_2}{CH.CO.R}$$

Thus the ease with which the subsequent decomposition to the oxime takes place varies considerably, and the stability of the pseudo nitrosite is dependent on the specific nature of the compound.

As has been shown, benzalacetophenone reacts with nitrous gases according to the equation



$$2(\mathrm{Ph.CH = CH.CO.Ph}) + (4\mathrm{NO_2} + \mathrm{N_2O_3}) \quad \cancel{\mathrm{NO}}$$

$$(\mathrm{NO_2.C_6H_4.}\underset{\mathrm{NOH}}{\underset{\|}{\mathrm{C}}} - \underset{\mathrm{NO_2}}{\underset{|}{\mathrm{CH}}}\mathrm{.C(OH).Ph})\mathrm{O}$$

and though a pseudo nitrosite is not stable, a stable, bimolecular compound is formed.

It is possible that such is the normal reaction when R is negative, and that according to the nature of R the stability of the intermediate bimolecular compound varies greatly, and only in certain cases can it be isolated, (i.e. when R = CO.H no trace of the bimolecular compound has been detected). But this is unlikely, for it would appear that we are in benzalacetophenone dealing with a specific reaction dependent on the presence of the complex CO.Ph.

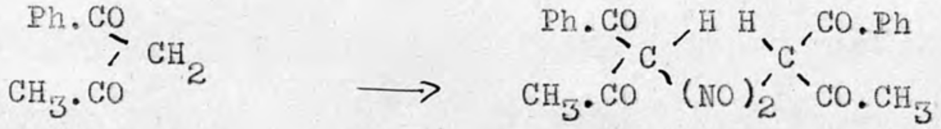
The great tendency to polymerise shown by the NO group is weakened, and hence the stability of the bimolecular compound is considerably decreased, when the compound contains an adjacent negative group, i.e. carbonyl, and the oxime is the more stable form. This is completely analogous to the behaviour of the compounds bromnitrosopropane and chlornitroseethane; the former cannot exist in the bimolecular form, while the bimolecular compound of the latter very readily dissociates to the monomolecular state.

But benzalacetophenone undergoes a subsequent reaction with oxides of nitrogen by which the second phenyl nucleus is nitrated, probably by nitrogen pentoxide which dissociates into nitrogen peroxide and oxygen nitrates two phenyl nuclei of two molecules and simultaneously promotes oxidation and condensation between the two molecules, inter-molecular linking being set up through the additional oxygen.

Hence, when R is positive, or when R is negative but the phenyl nucleus is positively substituted, the primary addition product with nitrogen trioxide is able, by direct coupling of the unsaturated nitroso groups of two molecules, to form a stable product, the pseudo nitrosite, from which the monomolecular oximido compound can only be obtained by treatment with reagents. When R is negative and the phenyl nucleus is unsubstituted or negatively substituted the addition product with nitrogen trioxide is unstable and cannot be isolated as immediate, spontaneous decomposition to the monomolecular oxime takes place.

<u>1:3-Diketones and Nitrous Gases</u>. It is interesting to compare the behaviour towards nitrous gases of such unsaturated ketones as benzal-acetone and anisylidene acetone with that of 1:3-diketones. These compounds react only with the nitroso constituent of nitrogen trioxide giving a bisnitroso compound, bimolecular compounds in which, ~~the~~ as in pseudo nitrosites, intermolecular linking is established by means of the nitroso group. Thus dibenzoyl methane yields bisnitroso-dibenzoyl methane, benzoyl acetone gives bisnitrosobenzoyl acetone.

Bisnitrosodibenzoylmethane.



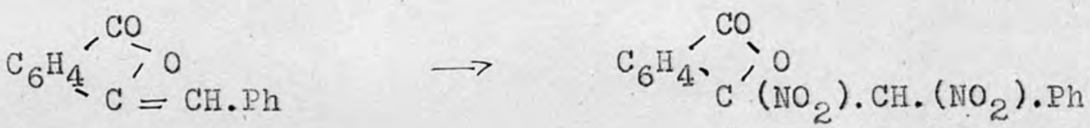
Bisnitrosobenzoylacetone.

But negative substitution of one of the phenyl nuclei attached to a carbonyl group prevents this, thus, p-nitro-dibenzoylmethane gives no bisnitroso compound, (Wieland & Bloch. Ber. 37. 1524. 1904) The mechanism of this reaction is not analogous to the additive formation of nitrosites and pseudo nitrosites in which the constituents of nitrogen trioxide are added to a double bond. The reaction between 1:3-diketones and oxides of nitrogen is one os simple substitution of the group NO for H. But the subsequent polymerisation of the nitroso compound is subject to the same influences as is the formation of the bimolecular pseudo nitrosite, and the presence of an adjacent negative group, such as the nitro group on the phenyl nucleus prevents the polymerisation.

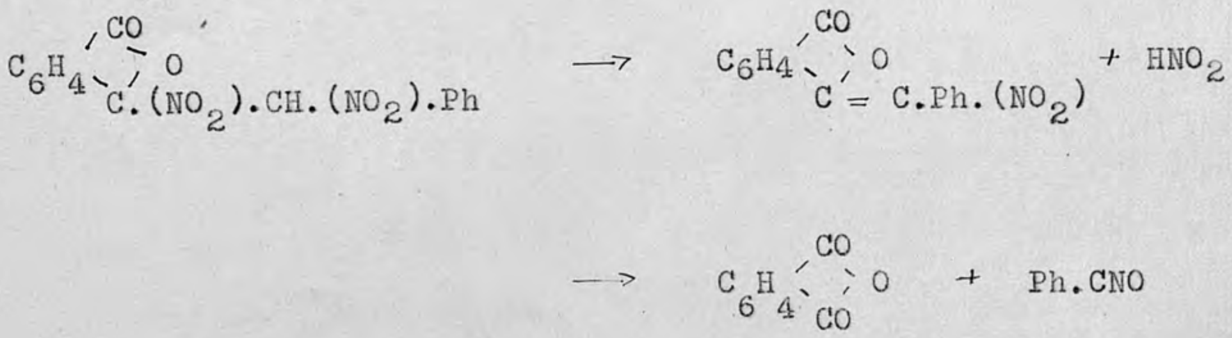
The Inetraction between Nitrous Acid and Unsaturated Compounds.

In such reactions with nitrous acid as have been investigated it is clear that the reaction frequently involves merely the addition of NO NO_2, and in such cases conforms in every respect with the behaviour of nitrogen trioxide. Angeli and Rimini, (Gazz. 1895. 25 ii. 188), obtained a pseudo nitrosite by the action of nitrous acid on safrole. Tonnies, (Ber. 20. 2982. 1887.), obtained pseudo nitrosites from styrol and anethol, while Schmidt, (Ber. 34. 3536. 1901), obtained from stilbene by the action of nitrous acid on the one hand and of nitrogen trioxide on the other identical pseudo nitrosites.

There is evidence, however, that the addition may also be that of $2NO_2$. Gabriel, (Ber. 18. 1251. 2435. 1885), shows that benzylidenephthalide, by treatment with nitrous acid yields an unstable dinitro compound.



This compound decomposes with loss of nitrous acid on heating or standing giving an unsaturated mononitro compound and finally phthalic anhydride.



Benzalphthalimidine yields a corresponding dinitrocompound by the action of either nitrous acid or of nitrogen peroxide.

The conclusion deduced by the author from this behaviour that an initial decomposition of nitrous acid into the radicle NO_2 must be presupposed is unjustifiable. The reaction can be accounted for by the normal decomposition of nitrous acid into nitric acid and nitric oxide, $3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$, atmospheric oxidation of the nitric oxide then furnishing the necessary nitrogen peroxide radicle.

Though undoubtedly involving the addition of $2NO_2$, the dinitronic structure of these compounds is criticised by Wallach, (Ann. 241. 288, 1887), who, from the reactions of the addition compounds of benzylidenephthalide and -phthalimidine and of aethinediphthalide, prefers the nitronitrite constitution.

The Decompositions of the Nitrogen-oxygen Addition Compounds of Unsaturated Bodies.

The addition compounds formed between double or triple linked carbon atoms and oxides of nitrogen or nitrous or nitric acids may undergo further reaction, the stability of the addition compound depending largely on the character of the addition, as well as on the nature of the original compound.

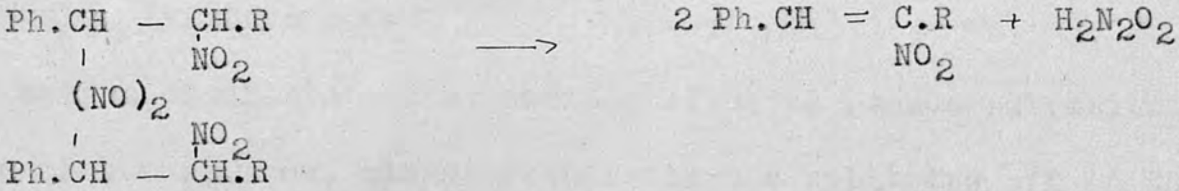
In certain cases, i.e. when the addition compound contains a nitroso group, the remarkable tendency to polymerisation of the nitroso group usually produces a bimolecular compound which is comparatively stable. Thus nitro-nitroso, nitroso-nitrite and nitroso-nitrate compounds, where addition has taken place as $NO + NO_2$, $NO + O.NO$ or $NO + O.NO_2$ readily polymerise to the stable bimolecular pseudo nitrosite, bisnitrosite and bisnitrosate respectively, intermolecular linking taking place as has been indicated by means of the nitroso group.

The characteristic property of polymerisation possessed by the nitroso group displays itself wherever this group is found, irrespective of the organic residue to which it may be attached. But the stability of the so-formed bimolecular compound varies considerably. Only in a few cases of halogen fatty nitroso compounds is, however, an independent existence precluded by great instability. From the easily dissociable chlornitrosoethane to the completely stable terpene nitroso derivatives, i.e. bisnitrosyl carone, $C_{10}H_{15}.O(NO)_2.C_{10}H_{15}O$, varying degrees of ~~stability are~~ ease of dissociation are met with, the pseudo nitrosite occupyihg a position mid-way between the easily dissociable type and the stable bisnitrosyl compounds.

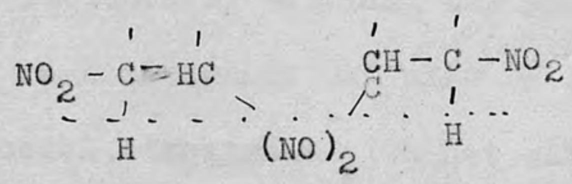
Two lines of decomposition of pseudo nitrosites, brought about by acids and alkalis respectively, give rise to several types of decomposition products.

I. The first action of dilute alkali is to depolymerise the addition compound to the monomolecular form. This, like all secondary nitroso compounds in the presence of alkali, then gives the oxime.

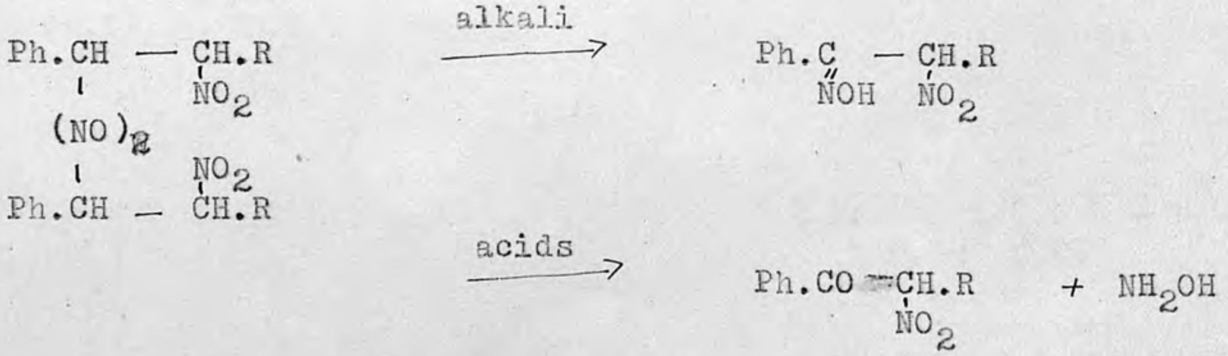
II. Mineral acids split off the polymerised nitroso group as hydroxamic acid, giving an unsaturated nitro compound



The nitro-olefine formation can be expressed thus:-



But it seems more probable that the two reactions are primarily identical, the first action of the decomposing agent being in each case the formation of the monomolecular nitroso compound, which rearranges to the stable oxime under the influence of alkali. Such a grouping undergoes the ordinary oxime reaction on heating with mineral acids and is decomposed with elimination of hydroxamic acid, and the formation of the unsaturated nitro compouhd, behaviour that finds comfirmation in the formation by mineral acids of a nitro ketone from the corresponding oxime.

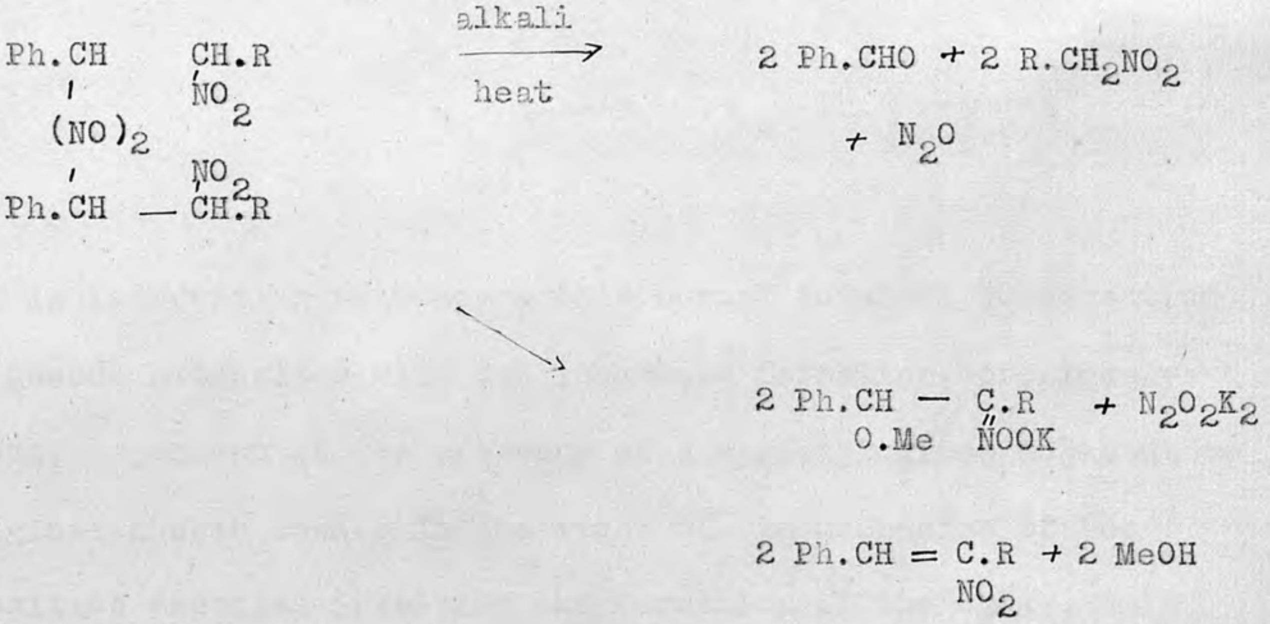


$$\begin{array}{l} Ph.CH - \underset{NO_2}{CH}.R \\ \quad | \\ \;(NO)_2 \\ \quad | \\ Ph.CH - \overset{NO_2}{CH}.R \end{array} \xrightarrow{\text{alkali}} Ph.\underset{NOH}{C} - \underset{NO_2}{CH}.R$$

$$\xrightarrow{\text{acids}} Ph.CO - \underset{NO_2}{CH}.R \quad + \quad NH_2OH$$

Concentrated acids act as dehydrating agents, and from the pseudo nitrosites of unsaturated ketonic compounds such dehydration produces the isoxazole, (v.above p 52)

The action of dilute acids, whether with the pseudo nitrosite itself or with the oxime, always results in the splitting off of the nitroso group either as hydroxamic acid or as hydroxylamine. While the oxime can be isolated by treating the pseudo nitrosite with cold dilute alkali, a reaction which can also be brought about by heating with absolute alcohol, treatment with hot alkali, or with alcoholic alkali, also brings about the alimination of the nitroso group, in the former case, accompanied by hydrolysis, as nitrous oxide, the compound being completely broken up into the aldehyde and nitro compound of the side-chain residue, and in the latter as hydroxamic acid, a decomposition analogous to that brought about by heating with mineral acids, except that here an intermediate stage of an alkoxy compound can be isolated.



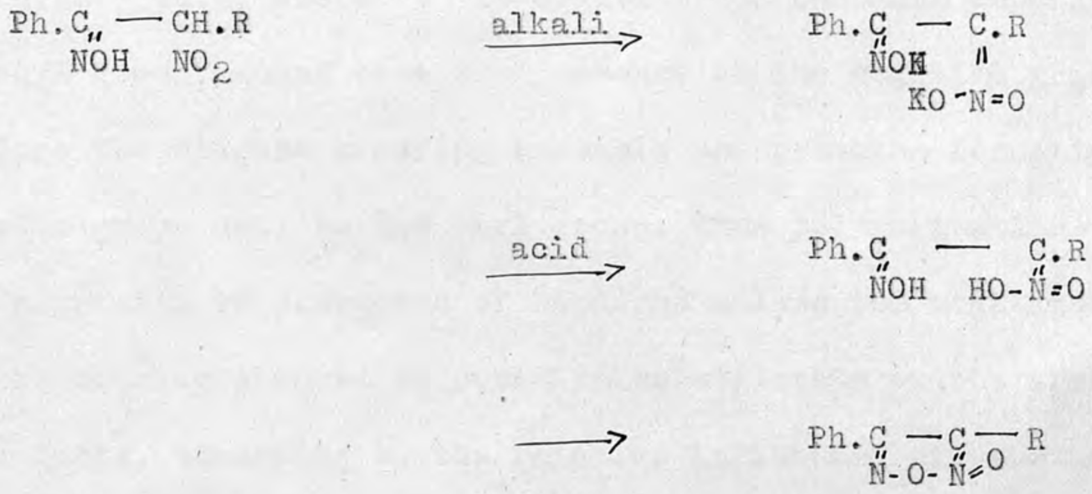
$$\begin{matrix} Ph.CH & CH.R \\ | & NO_2 \\ (NO)_2 & \\ | & NO_2 \\ Ph.CH & - CH.R \end{matrix} \xrightarrow[heat]{alkali} 2\,Ph.CHO + 2\,R.CH_2NO_2 + N_2O$$

$$\searrow \quad 2\,Ph.\underset{O.Me}{CH} - \underset{NOOK}{\overset{}{C}}.R + N_2O_2K_2$$

$$2\,Ph.CH = \underset{NO_2}{C}.R + 2\,MeOH$$

The ease with which the formation of the oxime from the pseudo nitrosite takes place varies considerably, and in certain cases, i.e. benzalacetone, no pseudo nitrosite can be isolated so great is its isnatbility that spontaneous decomposition to the oxime occurs in the initial reaction between the ketone and oxides of nitrogen.

Under certain conditions, by conversion of the oxime into its potassium salt and acidification, or by alkali treatment of the pseudo nitrosite followed by acidification, further condensation occurs between the oximido and the aci-nitro groups involving ring formation of a cyclic peroxide.



It is interesting to compare this normal internal condensation of the pseudo nitrosites with the isoxazole formation, previously described, dependent on the presence of a carbonyl group adjacent to the original double bond. In the light of the mechanism of the decomposition reaction involving the formation of the oxime, this behaviour can readily be explained.

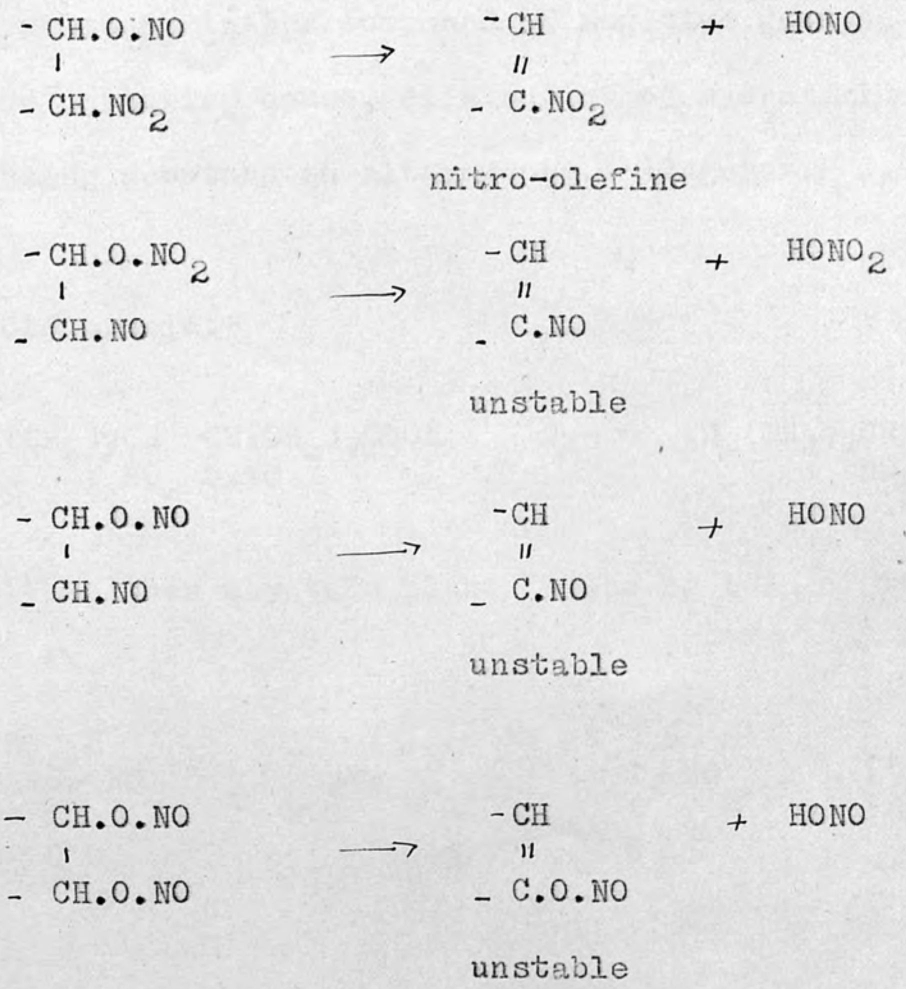
It is evident that ready peroxide formation can only occur when the oxime is present in that form which is anti to the aromatic residue. This configuration, in that the oxime group contains hydroxyl, will be favoured by positive substituents on the benzene nucleus, and will be hindered if such substituents are negative, i.e. the more negative the aromatic residue the more stable will be the oxime form syn to ~~kx~~ it. Under such circumstances the nitro-oxime will be stable, and will resist peroxide formation.

The non-formation of a pseudo nitrosite in compounds of the type Ph.CH = CH.R, where R is negative and contains especially a carbonyl group, means that the presence of the negative group in R renders the nitroso grouping unstable and promotes formation of an oximido group anti to the aryl group. Thus polymerisation to the pseudo nitrosite is prevented or hindered unless the negative influence of R is counterbalanced by positive substituents on the aryl nucleus. In such cases, according to the relative influences of substituted phenyl and R, pseudo nitrosite formation occurs to a greater or less degree. At the same time, the anti oxime form stabilised by the presence of carbonyl facilitates condensation between the oximido and the carbonyl groups, and isoxazole formation occurs.

But in general, subsequent reactions of the nitrogen-oxygen addition compounds, whether polymerisation has taken place or not, involves elimination of nitrogen-containing, (or, from the addition compounds with nitric acid, of hydroxyl-containing), groups with the formation of an unsaturated nitro- or nitroso-compound. Only when addition occurs as $NO + NO_2$, or as $NO_2 + NO_2$ is the resulting addition compound capable of existing as such.

All addition compounds containing the ester group O.NO or $O.NO_2$ tend to eliminate this as the corresponding acid, the tendency to lose nitrous acid from a nitro-nitrite being so marked, particularly if adjacent negative groups are present, that the primary product is often the unsaturated nitro compound.

Thus:-



$$\begin{array}{l}\mathrm{-CH.O.NO}\\ \;|\\ \mathrm{-CH.NO_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{-CH}\\ \;\|\\ \mathrm{-C.NO_2}\end{array} + \mathrm{HONO}$$

nitro-olefine

$$\begin{array}{l}\mathrm{-CH.O.NO_2}\\ \;|\\ \mathrm{-CH.NO}\end{array} \longrightarrow \begin{array}{l}\mathrm{-CH}\\ \;\|\\ \mathrm{-C.NO}\end{array} + \mathrm{HONO_2}$$

unstable

$$\begin{array}{l}\mathrm{-CH.O.NO}\\ \;|\\ \mathrm{-CH.NO}\end{array} \longrightarrow \begin{array}{l}\mathrm{-CH}\\ \;\|\\ \mathrm{-C.NO}\end{array} + \mathrm{HONO}$$

unstable

$$\begin{array}{l}\mathrm{-CH.O.NO}\\ \;|\\ \mathrm{-CH.O.NO}\end{array} \longrightarrow \begin{array}{l}\mathrm{-CH}\\ \;\|\\ \mathrm{-C.O.NO}\end{array} + \mathrm{HONO}$$

unstable

The unsaturated nitrite tends again to lose nitrous acid, reverting to the original olefine.

In the presence of hydrochloric acid the unsaturated nitro compounds undergo further decomposition involving the final elimination of the nitro group.

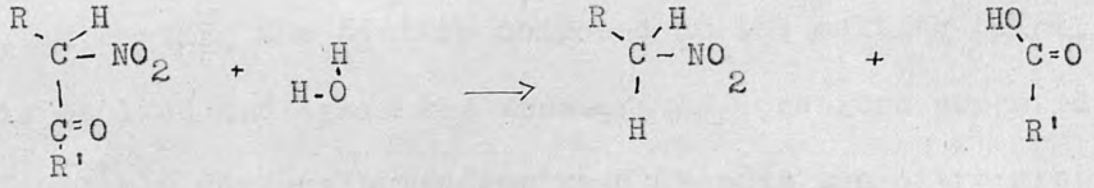
The formation of a nitro-olefine here is not always the inevitable product of decomposition. Under certain conditions, it would appear that the presence in the compound of negative groups, i.e. carboxyl, can be the promoting cause, elimination of hydroxamic acid occurs, the product being a saturated nitroketone. (Jagorov. J.Pr.Ch.1912.(ii). 86. 521.)

e.g. Oleic acid:-

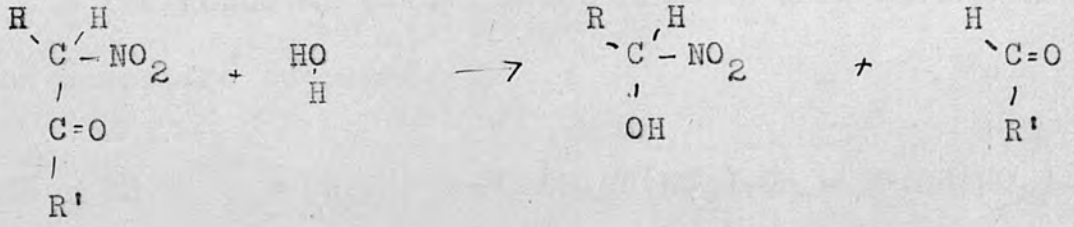
$$CH_3(CH_2)_7\underset{NO_2}{CH}-\underset{O.NO}{CH}(CH_2)_7COOH \longrightarrow CH_3(CH_2)_7\underset{NO_2}{CH}-\underset{\overset{\|}{O}}{C}.(CH_2)_7COOH$$

Hydrolysis then may take place in one or both of two ways:-

1.

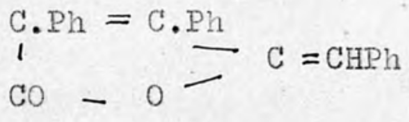


2.

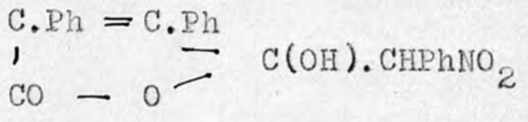


The normal stability of such dinitro compounds as may be pro-duced by addition of nitrogen peroxide is considerably weakened if adjacent negative groups are present in the addition compound, and elimination of one nitro group usually occurs. Thus, Benzaldiphenyl-

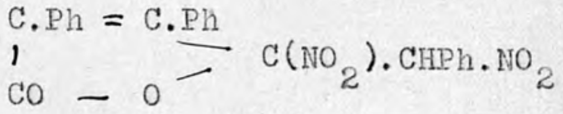
-maleide gives two addition products when treated with nitrous fumes: a hydroxy-nitro- and a dinitro-maleide. (Cohn. B. 24. 3865.1891)



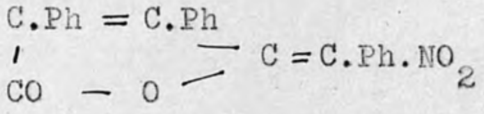
1.



2.



Water is readily eliminated from (1), i.e. by treating with acetyl chloride, giving:-



while, on heating the dinitro compound at the melting point, nitrous acid is evolved and again the unsaturated mononitro compound formed.

Similarly diphenylbutadiene readily adds two nitro groups when treated with nitrous gases, and the dinitro compound thus formed, under the influence of alkali loses nitrous acid giving an unsaturated mononitro compound.

$$\mathrm{Ph.CH = CH - CH = CH.Ph} \longrightarrow \mathrm{Ph.CH(NO_2).CH = CH.CH(NO_2).Ph}$$

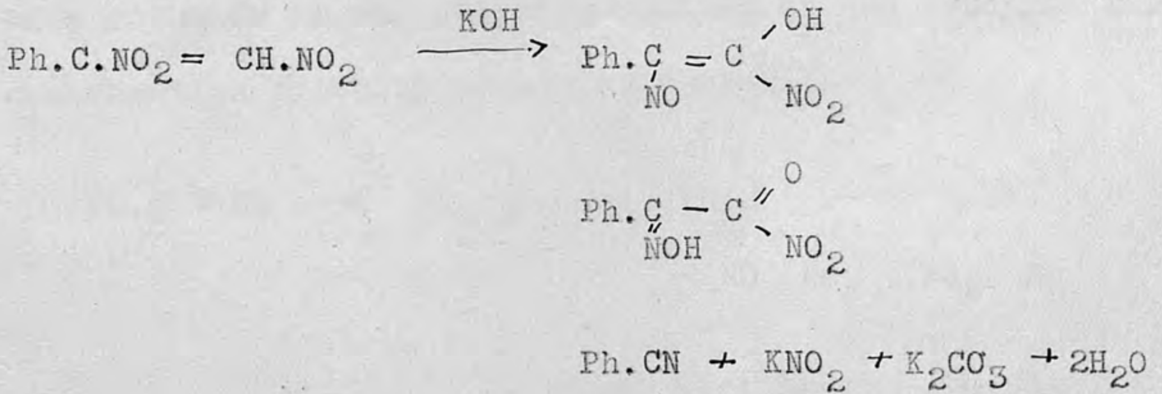
$$\longrightarrow \mathrm{Ph.C(NO_2) = CH - CH = CH.Ph}$$

From cinnamic acid a very unstable dinitro compound can be obtained, which decomposes immediately in the presence of water giving an unsaturated nitro compound:-

$$\mathrm{Ph.CH = CH.COOH \longrightarrow Ph.CH(NO_2)-C(NO_2)H.COOH}$$

$$\mathrm{\longrightarrow Ph.CH = CH.(NO_2) + CO_2 + HNO_2}$$

Acetylenic Addition Compounds. The addition compounds of acetylenic compounds with oxides of nitrogen are subject fundamentally to the same type of decomposition as are ethylenic compounds, though, owing to the greater reactivity of the acetylenic addition compound which is still unsaturated it may be more profound and involve cleavage. Thus, Wieland and Blumich, (A. 424. 100. 1921.), have shown that dinitrophenyl-acetylene, obtained by direct addition of nitrogen peroxide, hydrolyses with rupture of the molecule and elimination of one nitro group as metallic nitrate, a reaction which probably occurs as follows:-

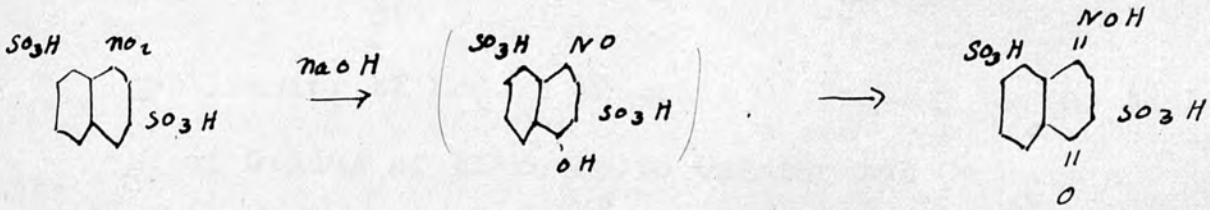


$$\mathrm{Ph.C.NO_2 = CH.NO_2 \xrightarrow{KOH} Ph.\underset{NO}{C} = C\begin{smallmatrix} OH \\ NO_2 \end{smallmatrix}}$$

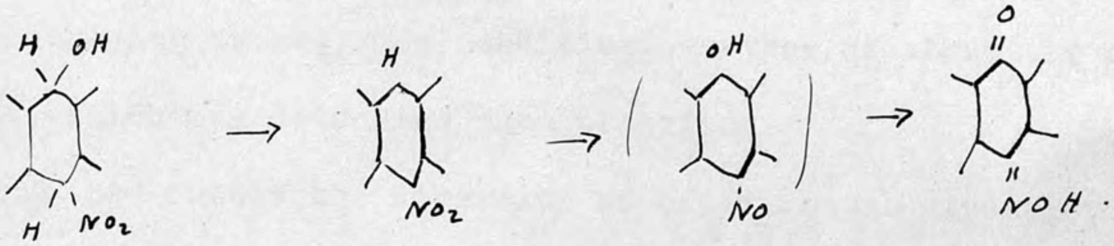
$$\mathrm{Ph.\underset{NOH}{C} - C\begin{smallmatrix} O \\ NO_2 \end{smallmatrix}}$$

$$\mathrm{Ph.CN + KNO_2 + K_2CO_3 + 2H_2O}$$

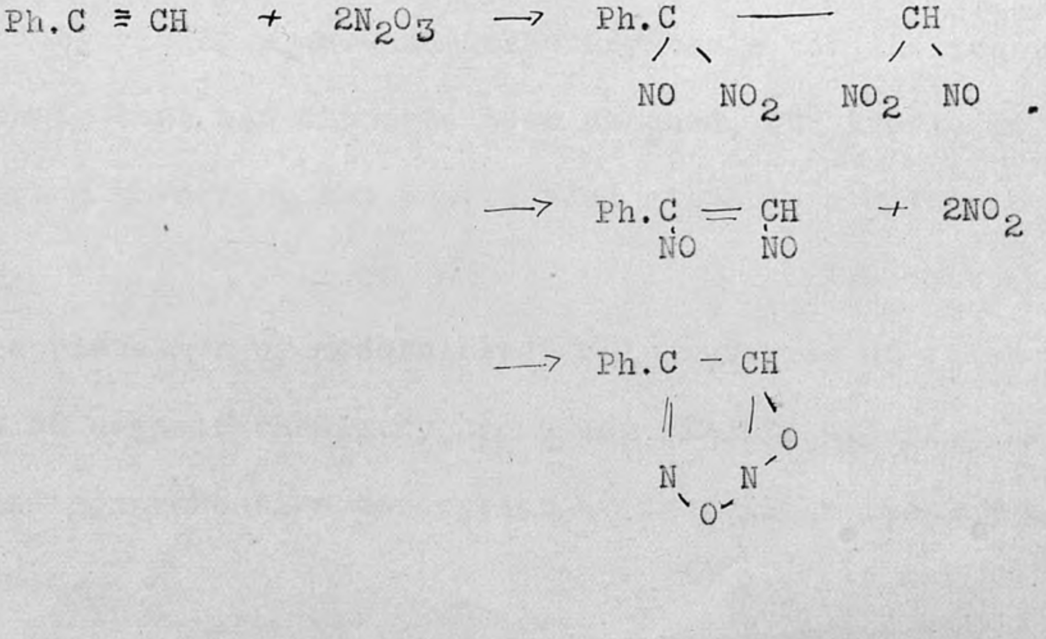
The intramolecular change of a nitro to a nitroso group with the corresponding formation of a hydroxy group on the adjacent carbon finds analogy in the conversion by alkali of the disulphonic acid of nitronaphthalene into the oxime of the corresponding quinone. (Friedlander. B. 28. 1535. 1895)



and in the similar conversion of nitroanthraquinone into anthraquinone monoxime. (Meisenheimer. A.<u>323</u>. 205. 1902.)



The addition compound with nitrogen trioxide undergoes a peroxide condensation to phenyl furoxane, but a normal course of reaction via the oxime cannot obviously take place here, and in that nitrogen peroxide is an undoubted product of the reaction ~~in the~~ the condensation probably occurs as follows:-



$$\mathrm{Ph.C \equiv CH + 2N_2O_3 \longrightarrow \underset{NO\ \ NO_2}{Ph.C} - \underset{NO_2\ \ NO}{CH}}\ .$$

$$\mathrm{\longrightarrow \underset{NO}{Ph.C} = \underset{NO}{CH} + 2NO_2}$$

$\longrightarrow$ Ph.C – CH

Application of Modern Theories of Valency to the Addition of Oxides of Nitrogen to Unsaturated Compounds.

If we are to interpret in the light of the foregoing the addition of nitric acid to an unsaturated linkage, it is necessary to seek for some underlying cause, some condition, whether of structure or environment, which may determine such behaviour.

From the outset the diversity of experimental conditions precludes any profound environmental influence, and explanation must perforce be sought for in the peculiar grouping of molecular forces constituting an unsaturated linkage.

No advancement of chemical science has done more to elucidate such a complex than the developement, arising from our recent knowledge of atomic structure, of the electronic conception of valency. But, while advancing considerably our conception of double and triple bonds, and providing a more satisfactory basis for the reactions of such linkages than had hitherto been reached, our knowledge of the actual forces governing the unsaturated state in a molecule are still tentative.

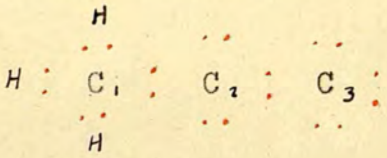
The application of modern electronic theories of valency to the reactions of organic chemistry has given rise to a perfectly intelligible and comprehensive conception of the single linking between carbon atoms.

The acceptance of the electron as the fundamental unit of chemical union has now been placed beyond question. While the actual structure of the atom, and the arrangement of its planetary electrons, each in its orbit, in groups of energy levels, is still in process of flux, the phenonemon of chemical union seems fairly clearly established, and independent of any present developement of the quantum theory.

Without attempting to enter into a detailed examination of atomic and molecular structure, a discussion which would be irrelevant here, one may say briefly that chemical combination between atoms takes place by virtue of the polarised electro-magnetic force fields surrounding each atom. Condensation between points of opposite polarity occurs with loss of energy and the formation of a condensed field. By such condensation a potential gradient will be established between the two atoms, which, if sufficiently steep, will cause a transference of an electron from the atom of positive polarity to the negative atom. Before such a union can be ruptured there must be reabsorption of energy sufficient to open up the closed force fields.

In this union the outer sheath of planetary electrons alone plays a part, and the marked tendency to establish in this outer shell a group of eight electrons offers at once an explanation of atomic union, for a deficiency of electrons in the one outer sheath may be made up by combination with another atom or atoms in whose outer sheath there in an excess. The coupling of the two electronic orbits, and the formation of an electronic pair between two electrons of two different atoms is then the physical unit of union. This~~s~~ union may assume a different character according as the electron pair is equally or unequally shared by the two atoms, an arrangement depending mainly on the electrochemical character of the original atoms or radicles. Such atoms or radicles which can form negative ions, tend to draw towards themselves electrons from the outer sheath of other atoms. Those which can form positive ions tend to repel such electrons. Hence, atoms in which the difference between the number of electrons in the outer sheath and the number eight is small tend to complete their sheath by appropriating the electrons from the outer sheath of those atoms where such difference is great, or where the number of ungrouped electrons is small, negative and positive ions respectively being formed. Such ionic formation actually means a transference of electrons, and the bond between the two ions is then purely an electrostatic one, the bonding pair being entirely shifted towards the nucleus of the negative ion. It is conceivable that numerous stages exist intermediate between such a completely polar union and the union established between neutral elements such as carbon where each of the four odd electrons in the outer shell of each carbon atom can form one of a bonding pair of electrons with the electrons of other carbon or other neutral atoms, such pairs being shared equally by the atoms concerned, forming a co-valent, non-polar union. Thus the single bonds of a saturated carbon chain are of this co-valent character., involving no appropriation of electrons. Only when the atoms linked to carbon are themselves markedly polar will there be a shifting of the electron pair towards the element of negative polarity, or away from that of positive polarity. It is important to realise, however, that only in a few exceptional cases can such shifting in the unions of carbon atoms amount to complete polarisation and ionisation of the molecule.

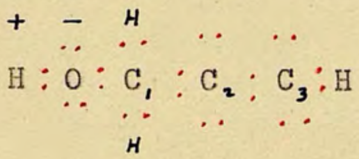
Hence the electronic state of such a saturated system as propane may be graphically represented as



$$H\,:\,\underset{H}{\overset{H}{\underset{..}{\overset{..}{C_1}}}}\,:\,\underset{..}{\overset{..}{C_2}}\,:\,\underset{..}{\overset{..}{C_3}}\,:$$

Each carbon atom is therefore surrounded by a complete sheath of eight electrons, each of which is involced in a bonding pair which is shared equally by two atoms, and the members of each of which are furnished by two different atoms. Thus, in the octet of electrons surrounding C_1 the electrons of each pair are furnished, one by C_1 and the other by one of the four attached atoms.

Substitution of one of the hydrogen atoms of such a system by a polar group, e.g. hydroxyl, immediately polarises the carbon atom to which it becomes attached, and this polarisation must be reflected, though probably very weakly, through the system. Consequently the electronic state of propyl alcohol may be represented

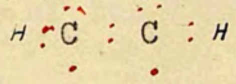


$$\overset{+}{H}\,:\,\overset{-}{\underset{..}{\overset{..}{O}}}\,:\,\underset{H}{\overset{H}{\underset{..}{\overset{..}{C_1}}}}\,:\,\underset{..}{\overset{..}{C_2}}\,:\,\underset{..}{\overset{..}{C_3}}\,:\,H$$

The polar or key atom, oxygen, tends to complete its octet at the expense of C_1, and a hydrogen atom, the bonding pairs thus formed tending to shift from a midway position to one nearer the oxygen nucleus. A negative polarity is thus established on the oxygen complex, which confers opposite, positive polarity on the adjacent hydrogen and carbon atoms. The proximity of the positively polarised carbon atom to the neutral carbon will undoubtedly cause a slight shifting towards C_2 of the bonding pair between C_1 and C_2, though it is unlikely that the shift will be sufficient to polarise C_2

In its application, however, to unsaturated systems, or to what is by common consent known as the double or triple bond of such systems, conflicting ideas have arisen.

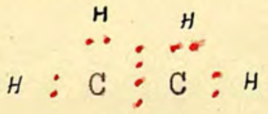
When two carbon atoms or groups are united in such a way that a single by an electronic pair still leaves one electron of each carbon atom unaccounted for,

i.e. 

$$H:\overset{H}{\underset{\cdot}{C}}:\overset{H}{\underset{\cdot}{C}}:H$$

the electronic condition of the unsaturated molecule thus produced has not yet been placed wholly outside the field of speculation.

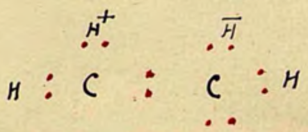
If the old conception of the double bond between two such groups is realised physically we have to assume that the four, probably binuclear orbits of four electrons unite the two carbon atoms. Rach orbit of each external electron of a carbon atom is normally inclined to each other orbit at an angle of 109° 28', thus confirming the old tetrahedral conception of the valency lines of the carbon atom, and it is not possible to conceive of a union in which four such orbits are involved without considerable strain. In other words, the old conception embodied in Baeyer's Strain Theory is revived, the distortion being not of lines of force proceeding from the nucleus, but of the actual planetary orbit of the electron. Suchbwould be the condition -one of considerable strain- graphically represented by



$H : \overset{H}{C} \vdots \overset{H}{C} : H$

Such a conception seems unjustifiable and far more rigid than our present knowledge warrants. If the orbits of a bonding pair of electrons between two atoms involve the two nuclei of the atoms, i.e. are binuclear, whether the path is external to both nuclei or not, there seems no reason why a similar pair of binuclear orbits should not be established between another pair of electrons involving the same atoms, the planes of the first pair being set at an angle of 109° 28' to the second.

In striking contrast to this conception Lowry, (T. 1923. <u>123</u>. 822) postulates a "mixed double bond", i.e. one in which the carbon atoms are united by one ordinary co-valent bonding pair of electrons and by one electrovalent pair or a bond in which one electron of one carbon atom has been appropriated by the other atom, thus establishing a highly polar structure.



$H : \overset{H^+}{C} : \underset{..}{\overset{\overline{H}}{C}} : H$

Hence one carbon atom of the bond has a completed octet of electrons and functionally negatively, while the other possesses only a sextet and functions positively.

The universality of the pairing of odd electrons prejudices the third alternative in which each carbon atom possesses an odd unpaired electron.

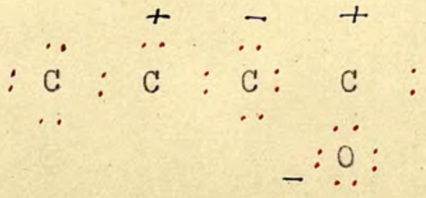
But while the mixed bond consisting of a co-valent and an electro-valent pair by virtue of its highly polar nature expresses admirably the behaviour of the unsaturated linkage, there is no ground for assuming that such is the normal resting condition of the ~~nucleus~~ of the unsaturated molecule. All available evidence, on the contrary, points to an inert state which is best represented by a double or triple co-valent bond, and the measure of reactivity of the compound depends on the readiness with which a co-valency is transformed into an electrovalency. With equal truth can it be said that the reactivity of any compound depends on the readiness of this transformation from co-valent to electrovalent state, the polarisation thus set up producing latent or actual ionisation in which state chemical union is facilitated. The following diagramatic representation of the addition of bromine to ethylene illustrates this conception.

One criticism can relevantly be made in respect of such a theory of mixed double bonds. A sharp distinction is drawn between the two bonds, electrovalent and co-valent, of the unsaturated link, whereas it seems unnecessary to postulate more than a difference of degree a difference which is exhibited in all its phases in the conversion by external agency of a co-valent into an~~d~~ electrovalent bond.

The latent polarity of a system may, however, become permanantly established by the presence of a polar or key atom. In the system

$$CH_3.CH = CH.CO -$$

the oxygen of the carbonyl bond acts as a negatively polar key atom; the latent polarity of the double bond is established, and a alter--nating polarity is set up throughout the system as follows:-



In the absence of such an atom the non-polar candition may be supposed stable, and the influence of ~~the~~ activating agents become of considerable importance. Thus, while a non-polar compound such as ethylene in its resting and inert condition is capable of reacting with a polar compound, e.g. hydrobromic acid, in other words, the polar field produced by the hydrobromic acid is sufficient to activate the molecule and hence facilitate interaction, interaction between two non-polar bodies such as ethylene and molecular bromine can only occur in the ~~the~~ presence of an activating agent or polar catalyst. The whole problem of catalysis at once assumes a new aspect. As the question of catalysis is one which looms very large in the influence of mercury salts in nitration reactions, it is proposed to reserve that aspect of the subject for a later section.

For the purpose of this work Lowry's conception of mixed double bonds as representing the state of the molecules in their reacting condition has been adopted. It has the great merit of expressing clearly and convincingly the specific reactions, and in particular the addition reactions of unsaturated compounds with which this work is concerned.

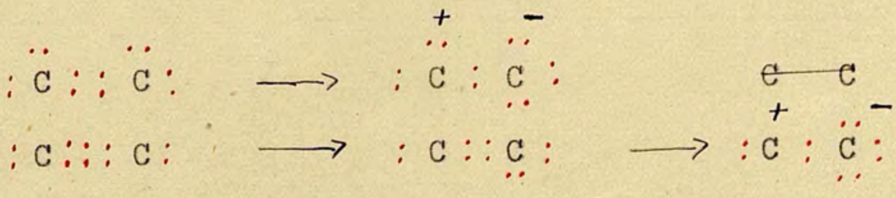
Triple Bond. It is possible to postulate for the triple bond, in contradistinction to the double bond, an electronic condition in which the union is entirely unpolarised, each carbon atom being surrounded by a sextet of paired electrons.

$$\mathrm{H} : \overset{\cdot\cdot}{\mathrm{C}} : \overset{\cdot\cdot}{\mathrm{C}} : \mathrm{H}$$

Whether this or a triple co-valent state

$$\mathrm{H} : \mathrm{C} \vdots\vdots \mathrm{C} : \mathrm{H}$$

represents the inert condition of the molecule, Lowry conceives of the successive reactions of the acetylene molecule as the successive con--versions of two co-valencies into electrovalencies, thus:-



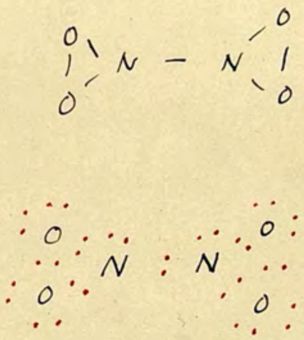
However the triple bond be visualised, and some common conception must be sought for such trebly linked groups as CO-, N_2-, ~~+;~~ CN',

$CH \equiv CH$, it seems evident that the high degree of unsaturation exemplified by the ready polarisation of the double bond is not reached in the triple bond.

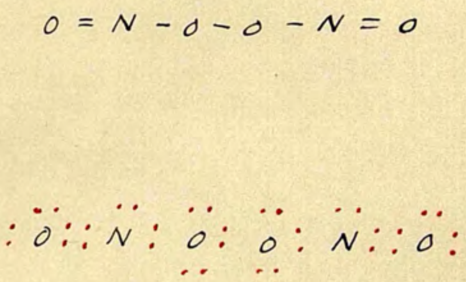
Application to the Reactions of Oxides of Nitrogen and of Nitric Acid.

Application of the octet theory of valency to the structure of the oxides of nitrogen shows very clearly the possibility of three tautameric formulae for nitrogen peroxide.

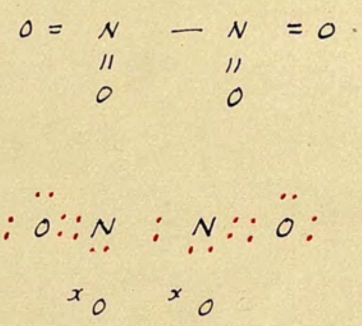
(a)



(b)



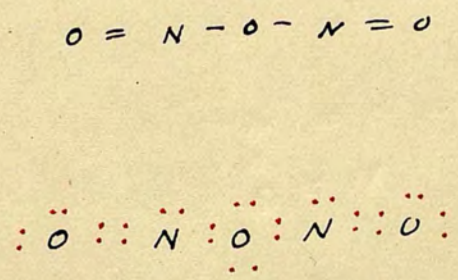
(c)



Formula (a) represents an electronic state of six octets all shared by single co-valencies, while the electronic arrangement of the form (b), though involving six shared octets, does so in four of these octets by double co-valent bonds. In the state represented by (c) no perfect octet of single co-valencies exists, there being only four octets shared each by a double co-valent bond, possibly augmented by two, supposing the bonds (x(to partake in octet formation. Hence (a) would represent the most stable form, and may possibly represent the state of the non-reacting molecule.

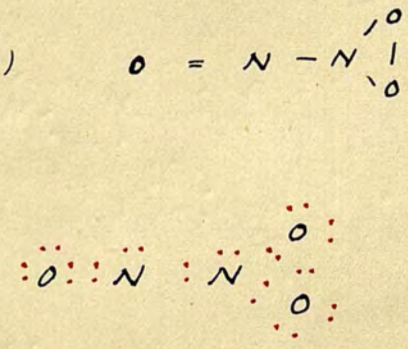
Consideration of similar formulae for the molecule of nitrogen trioxide allows of four possible formulae.

(a')

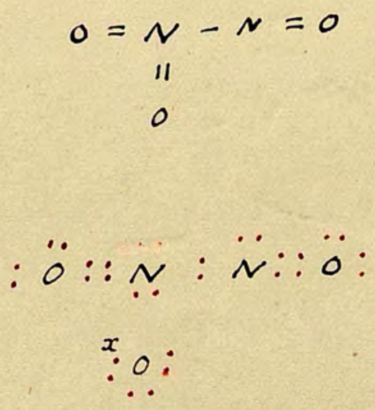


$O = N - O - N = O$

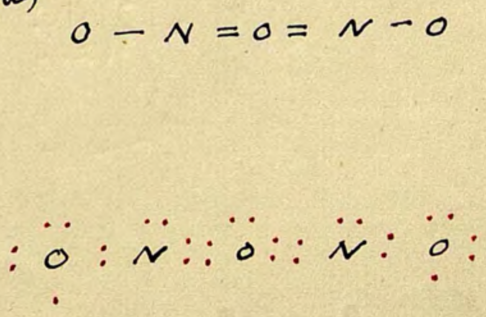
(b')



(c')



(d)



$O - N = O = N - O$

In formula (a') one central oxygen atom, surrounded by a complete actet of electrons, exhibits a single co-valence with each of the nitrogen atoms, th~~us~~ese in this form exhibiting double co-valencies with each of the remaining two oxygen atoms. In ~~a~~ (b') three completed octets are shared by single co-valent bonds between two oxygen and one nitrogen atom, which latter is united by one co-valent bond to the second nitrogen carrying the third oxygen by a double co-valency. A third alternative is represented by formula (c') in which a non-polar bond, not strictly co-valent, is established between oxygen and nitrogen, the pair of electrons which thus completes the octet of the oxygen atom being part of the sphere of the adjacent nitrogen atom. Such a bond might conceivably readjust itself so that two co-valent bonds were established by the breaking of this nitrogen pair and of an odd oxygen pair and consequent rearrangement. The state of qunique-co-valent nitrogen arrived at would be peculiar to such types of compounds, and quite distinct from the quadri-co-valency of the ammonium ion, and similarly constituted compounds where the attachment of the fifth atom is established by means of an electrostatic attraction between charged ions. But in fundamental opposition to such a postulate we have the fact that an arrangement of this nature would allot ten electrons to the outer sphere of the central oxygen atom. A similar objection applies to the condition expressed by (d'), as the arrangement of co-valencies would necessitate the presence of two odd electrons, one attached to each terminal oxygen atom, and the presence of ten electrons associated with the central oxygen ~~carbon~~ atom.

It seems probable that, in a non-reacting condition at least, the atoms in the molecule of nitrogen trioxide will take up that position in which the strong tendency to octet formation possessed by each atom is most fully satisfied. Further, an octet in which pairs of electrons are shared by four single co-valent bonds would conceivably be more stable than one in which double co-valencies played a part. From these considerations formula (b′) would be the most stable representation of the molecule. (a′), with one such octet of single co-valencies, would rank next in order of stability, while (c′) would be the least stable, there being no octet arrangement in such a condition in which double co-valencies do not play a part. Langmuir postulates a fourth formula for nitrogen trioxide, O-N=O=N-O, a condition represented by formula (d) above, but from the ready decomposition of nitrogen trioxide into nitric oxide and nitrogen peroxide he gives preference to (c′) as the more easily expressive of this decomposition than (a′). He does not suggest the possibility of (b′). It is possible, however, that, whatever view be taken of the bond (x) in (c′), the two nitrogen electrons of the bond are sufficiently shared by the two atoms for a stable octet to be established in the oxygen sphere, in which case form (c′) might approach form (a′) in stability.

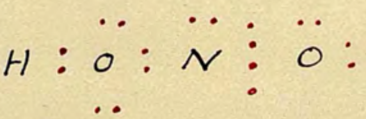
It is impossible to consider on the basis of the electron theory any formula for nitrogen peroxide in relation to its decomposition into (NO_2), since, by such a theory, in that the nitrogen molecule possesses five electrons in its outer shell, molecules of oxides of nitrogen can only be stable when two atoms of nitrogen are involved, unless such a group as (NO_2) can exist as an ion. Without some graphical proof of the stability of the compound formed by such a decomposition, it is of little value to postulate probable lines of cleavage of the different molecular complexes. But from consideration of octet stability in the original molecules of nitrogen trioxide and nitrogen peroxide, formulae (b') or (c') for the former, and formula (a) for the latter might be expected to allow most readily for the decomposition into nitric oxide and nitrogen peroxide on the one hand, and into two molecules of nitrogen peroxide, (NO_2), on the other. THe molecular states represented by (b), (a') and (c) would most readily, it would appear, dissociate into oxygen and nitric oxide.

It is important to emphasise in this connection that dissociation can only occur in any compound when, under the influence of some force or forces, the co-valent bond of the neutral compound is converted into an electrovalency, or, in other words, dissociation is preceded by a temporary appropriation of the co-valent electron pair. But it is conceivable that in such a condition postulated by the bond (x) in (c') or (c), supposing such a bond can exist, since there is no true co-valent union, dissociation and separation of the two atoms may be brought about by a force which is much less than that required to rupture a co-valent bond. Such dissociation could only lead in the molecular states represented by formulae (c) and (c') to cleavage into oxygen and nitric oxide, a conclusion which has already been arrived at for (c) by a priori reasoning. Hence formula (b') may be taken to represent most adequately the behaviour of nitrogen trioxide.

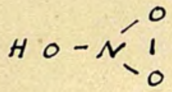
Acceptance of the above formulae, (b') and (a) for nitrogen trioxide and nitrogen peroxide respectively makes the electronic conception of nitrous and nitric acids perfectly straightforward, and these two acids may be simply represented as follows:-

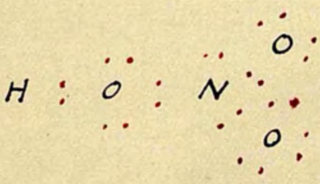
HNO_2

$H-O-N=O$



HNO_3

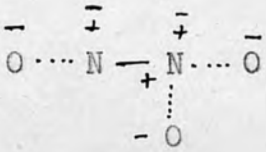




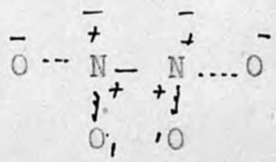
So far, it has been assumed that in the electronic arrangements of the molecules of oxides of nitrogen the bonds of union between the atoms are completely co-valent or non-polar. But this is not strictly correct, since any linking between oxygen and nitrogen must be conditioned by the relative polarities of the two atoms, and ~~the~~ an incipient polarity or weak electrovalence must be recognised. Relative to oxygen nitrogen is the less electronegative element, and in the linking N - O a latent polarity $\overset{+}{N}\cdots\overset{-}{O}$ is set up. In other words, the electron pair binding the two atoms is shifted in each case towards the oxygen nucleus, thus effecting a contortion of the molecule in which the resultant condition of strain is the agent of chemical action. Where a double co-valency exists, a double similar shifting would, in a resting state, presumably occur, which, in the initiation of chemical union, would divide into one slightly polar co-valency and one electrovalency.

In his definition of the electronic condition of a double bond Lowry, (ibid), adopts a nomenclature of positive and negative signs to indicate the electrovalent, polarised bond of the unsaturated union, and the ordinary (-) sign between atoms bound by an unpolarised co-valency. Thus ethylene is written $\overset{+}{CH_2} - \overset{-}{CH_2}$. While I am anxious not to add to already existing confusion by adopting still another nomenclature, it will be convenient for the moment to denote a single co-valent bond, which is however slightly polarised in the sense that the electron pair is shifted somewhat towards the nucleus of negative polarity, by the sign $\overset{+}{X}\cdots\overset{-}{Y}$. Obviously this expresses a different conception to $\overset{+}{X}\ :\overset{-}{Y}$ where polarisation has taken place, and an electrostatic union alone binds the two atoms, as it does also to $\overset{+}{X}--\overset{-}{Y}$, where by Lowry's definition the bestowal of positive and negative signs in conjunction with the normal, simple bond (-) denotes a second, electro- valence and an unsaturated molecule.

In this sense nitrogen trioxide and nitrogen peroxide may be written

i 

$$\begin{array}{c}\overset{-}{O}\cdots\overset{\mp}{N}\underset{+}{-}\overset{\mp}{N}\cdots\overset{-}{O}\\ \qquad\ \vdots\\ \qquad -O\end{array}$$

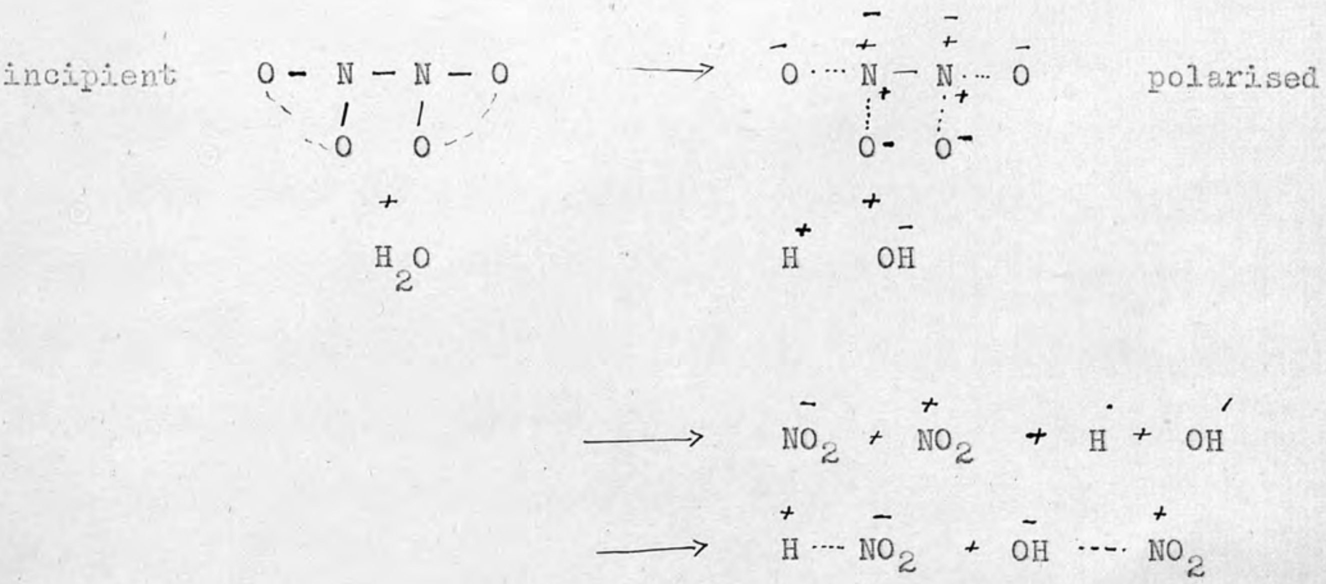
ii 

$$\begin{array}{c}\overset{-}{O}\cdots\overset{\mp}{N}-\overset{\mp}{N}\cdots\overset{-}{O}\\ \ \ \overset{+}{\vdots}\quad\overset{+}{\vdots}\\ \ \ O\quad\ O\end{array}$$

Taking oxygen in each case as the key atom of strongest polarity, we arrive at a state of crossed polarities such as Lowry has postulated for maleic acid, (ibid)

$$\overset{o}{O}-\overset{+}{C}(OH)-\overset{\pm}{C}H-\overset{\pm}{C}H-\overset{+}{C}(OH)-\overset{-}{O}$$

Accepting, as Lowry suggests, such a condition as evidence of a state of instability, we arrive at once at a simple explanation of the dissociation of the molecules represented by (i) and (ii) into nitric oxide and (NO_2) and twice (NO_2) respectively. Such dissociation would, however, only take place if the requisite energy providable by heat or a polarised medium were available to establish permanantly the otherwise latent polarities. But the dissociation in aqueous solution of the molecules of N_2O_4 into nitrous and nitric acids receives a convincing demonstration.

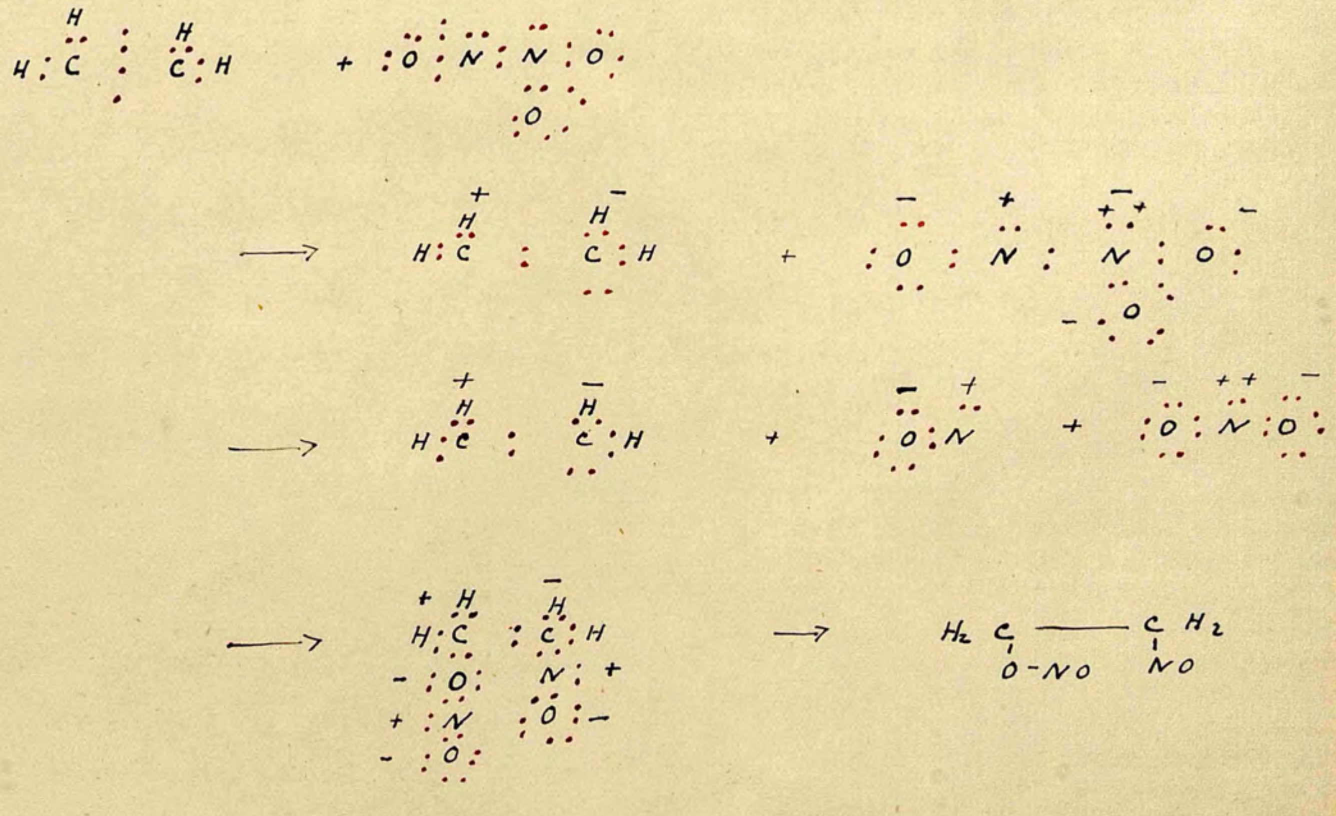


Application to Addition Reactions.

In applying such conceptions of molecular structure to the addition of nitrogen trioxide, nitrogen peroxide and nitric acid to unsaturated compounds of ethylenic and acetylenic types it is at once apparent that not only does it offer a satisfactory explanation of the reaction and hence the addition, but that the decomposition and cleavage reactions which follow are fully accounted for, and can with fair certainty be predicted.

In the cleavage of the molecules of nitrogen trioxide preceding addition it seems probable from an examination of the selective addition of the decomposition products to polarised double bonds that the group (NO_2) is polarised in the positive sense and the group(NO) in the negative sense. Thus, in the addition of nitrogen trioxide to compounds of the type Ph.CH = CH.CO, which may, on the basis of the key group (CO), be written

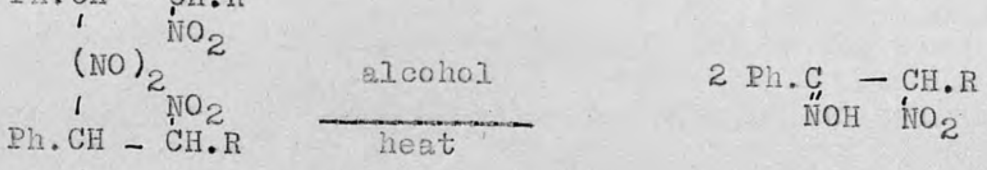
$\text{Ph.}\overset{+}{\text{CH}} = \overset{-}{\text{CH}}.\overset{+}{\text{C}}\overset{-}{\text{O}}$, the group (NO) always attaches itself to the carbon of positive polarity. This is reasonable if it is recognised that in the radicle (NO_2) as compared with (NO) the octet of the nitrogen atom is subject to greater strain from two negatively polarised oxygen atoms than is the nitrogen of the (NO) group from one. On the other hand, addition of the cleavage products of nitrogen trioxide to weakly polarised double bonds as are present presumably in ethylene and amylene seems to point to a dissociation into $(\text{NO})^{+}$ + (O.NO)', and the positively polarised group $(\text{NO})^{+}$ then attaches itself to the negative carbon pole, (c.f. p 47). Hence, the interaction of nitrogen trioxide with ethylene may be expressed



Polarisation and dissociation of the molecule of nitrogen trioxide into (NO) and (NO_2) promotes addition of (NO) to the negative pole of ethylene and of (NO_2) to the positive pole.

The contortion produced at one end of a carbon chain by the double co-valent bond of the nitroso group, and the marked asymmetry produced would undoubtedly lead to instability, and a readjustment between two adjacent molecules would tend to occur, (equation 3). That this the factor promoting the universal polymerisation of the nitroso group seems a not unjustifiable conclusion.

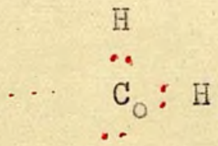
On the other handm though the formation of the monomolecular oximido form, possible in all compounds which contain a hydrogen atom attached to the nitroso-bearing carbon, is not precluded, the bimolecular compound is, in the absence of external energy, except in special cases, the stable form. The presence of elements of marked polarity, such as halogen, seem to facilitate the formation of the group =N-O-H, in inself more definitely polar than -N=O, and in such cases the monomolecular oxime is produced. But in general, by the use of suitable agents, the bimolecular nitroso compound can give way to the oxime.



$$\begin{matrix} \text{Ph.CH} - \underset{\text{NO}_2}{\text{CH.R}} \\ | \\ (\text{NO})_2 \\ | \\ \text{Ph.CH} - \overset{\text{NO}_2}{\text{CH.R}} \end{matrix} \xrightarrow[\text{heat}]{\text{alcohol}} 2\ \text{Ph.}\underset{\text{NOH}}{\text{C}} - \underset{\text{NO}_2}{\text{CH.R}}$$

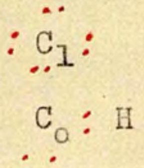
It is possible on this basis to advance an explanation of the distinction which exists in the tendency to form addition compounds with nitrogen trioxide and nitrogen peroxide respectively. It is known, as has been already stated, that the lower olefines do not readily form nitrosites by the addition of nitrogen trioxide, but show a greater inclination to add the component parts of nitrogen peroxide forming a dinitrite or nitrosate, (c.f. p ~~47~~ 38). If one considers the nagatively polarised carbon group of the ethylene double bond in ethylene and an alkyl substituted ethylene as amylene, we have the following arrangement of electrons:-

Ethylene, i



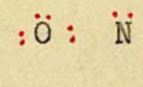
$$\begin{matrix} & H & \\ & \cdot\cdot & \\ \cdots & C_o & : H \\ & \cdot\cdot & \end{matrix}$$

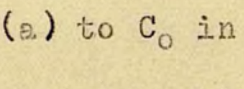
Amylene, ii



$$\begin{matrix} & \cdot\cdot & \\ : & C_1 & : \\ & \cdot\cdot & \\ & C_o & : H \\ & \cdot\cdot & \end{matrix}$$

and the addition to either of these systems of nitrogen peroxide or trioxide would involve the linking to these negative carbon atoms of the positively polarised constituent of the oxide, i.e. either

(a)  $:\underset{\cdot\cdot}{\ddot{O}}:\ddot{N}$ from nitrogen trioxide

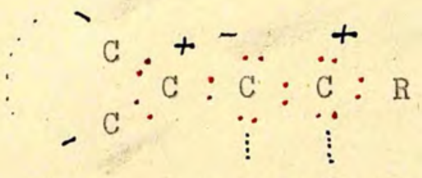
or (b)  $:\ddot{O}:\ddot{N}\vdots\ddot{O}:$,, ,, peroxide

The attachment of (a) to C_o in (i) would allot sixteen electrons to the sharing of five atoms, while that of (b) to the same carbon atom would allot twenty-two electrons to the sharing of six atoms, and it is obvious that the latter would constitute the more stable system. Hence, in a reaction with mixed nitrous gases, ethylene would preferentially form the dinitrite or nitrosate. Consideration of the carbon complex (ii), however, shows the influence of other factors. The presence of a stable octet round the carbon nucleus, C_1, and adjacent to the negatively polarised nucleus, C_0, would tend to reduce the negative polarity of C_0. This carbon atom would therefore tend to unite with that group which by the more ready loss of its electron would the more easily re-establish its own octet. Hence, addition would then take place between C_0 and the nitroso group, rather than bewteen the less positive complex $\overset{-}{O}-\overset{+}{N}-\overset{-}{O}$.

Phenyl Substituted Olefines. Pseudo nitrosite formation.

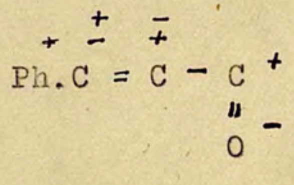
Viewed from the electronic standpoint, an explanation of the preferential pseudo nitrosite formation exhibited by this group, involving the addition of the groups (NO) and (NO), and subsequent polymerisation of the nitroso group, when a carbon atom of the unsaturated group bears a phenyl substituent, must be sought for in the relative polarities of the carbon atom bearing the phenyl group and of the groups O.NO and NO_2. Taking the generally accepted ring of alternating positive and negative polarities as best representative of the phenyl nucleus, it is most probable that the carbon atom of the ethylene molecule on which phenyl substitution takes place will, owing to the state of strain and hence reactivity of the substituted ethylene system, attach itself to that carbon of the phenyl nucleus which is negatively polarised, or in other words, which is already displaying a tendency to ~~lose~~ gain an electron.

An alternating polarity will thus be set up throughout the ethylene system as follows:-



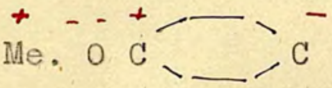
In the interaction with nitrogen trioxide the addition of the nitroso group to the positive carbon pole may be supposed to take place normayyl. The distinction of behaviour then lies in the addition of the radicle (NO_2) to the negative pole in preference to the radicle (O.NO) to this pole when phenyl is absent.

Negative Substitution. The inhibition to pseudo nitrosite formation, and the preferential formation, by addition of nitrogen trioxide, of the oximido group when a markedly negative group, i.e. carbonyl, is present adjacent to the double bond, may possibly be accounted for, (v. p 42), by the presence of this polar group, carbonyl, which promotes rearrangement to the radicle (NOH) in preference to the polymerised nitroso group. But it is difficult to visualise this clearly. It seems more probable that the system of crossed polarities which is inevitably set up by this substitution, and which, as is known is a factor of instability, Ƶ (Lowry. ibid.), is the main cause inhibiting pseudo nitrosite formation. i.e.



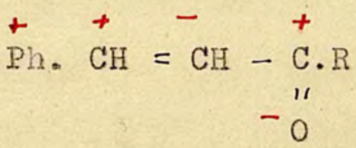
$$\overset{+}{\text{Ph.}}\overset{\overset{+}{-}}{\text{C}} = \overset{\overset{-}{+}}{\text{C}} - \underset{\underset{\text{O}\,^{-}}{\|}}{\text{C}^{\,+}}$$

That positive substitution on the phenyl nucleus should over-come this inhibition to pseudo nitrosite formation is less easy to interpret. The substitution for hydrogen of a group such as alkoxyl would undoubtedly stabilise the polarities of the phenyl nucleus, and consequently those of the side chain. If such substituents are present in the para position to the unsaturated chain, i.e. anethol, which readily forms a pseudo nitrosute, then the carbon atom para to the alkoxyl group will be negative, since the carbon bearing it must be positive.



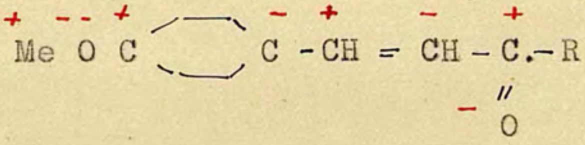
Hence, an induced positive polarity will be set up on the carbon atom alpha to phenyl in the side chain, and the polarities of the whole system will be reversed.

i.e.



$$\overset{+}{\text{Ph}}.\ \overset{+}{\text{CH}} = \overset{-}{\text{CH}} - \underset{\overset{\|}{{}^{-}\text{O}}}{\overset{+}{\text{C}}}.\text{R}$$

and



This would seem to necessitate a reverse process of addition of the elements (NO) and (NO_2), which does not actually occur. But it is unprofitable to push this conception too far. Our knowledge of the electronic state of molecules is as yet too incomplete to interpret conclusively the more subtle reactions of organic chemistry. Where, however, our knowledge of atomic structure can be applied without p postulating conditions which are still, owing to insufficient data, matters of controversy, considerable light has been thrown on problems hitherto obscure.

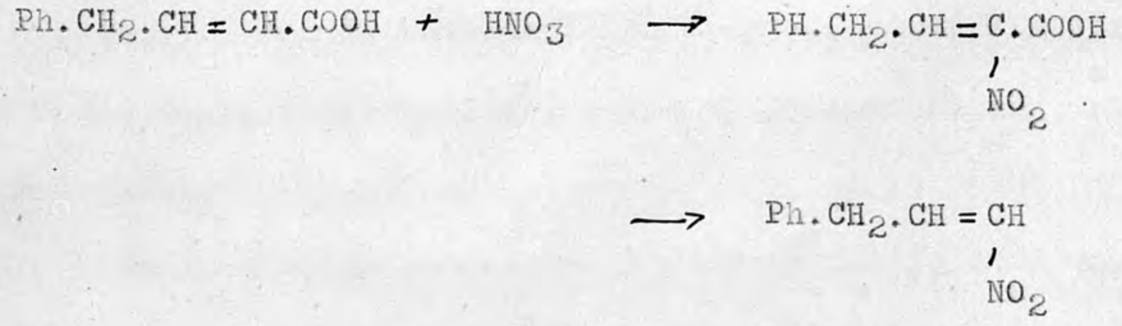
The Addition of Nitric Acid to Unsaturated Systems.

The way has now been prepared for a detailed examination of the addition of nitric acid to unsaturated systems.

The possibility of the addition of the component parts of nitric acid to the double bond of unsaturated compounds has long been recognised in a few isolated cases, though the products of the interaction have only recently been elucidated.

Haitinger, (A. 193. 366. 1878), obtained from thimethyl carbinol, by the action of fuming nitric acid, a nitroisobutylene, which he proved identical with the nitro butylene obtained by the same action with butylene. The mechanism of the reaction was, however, not examined.

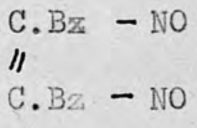
Erdmann, (B. 17. 412. 1884), examining the same reaction with phenyl-iso-crotonic acid obtained not the expected nitropropylene but phenylnitroethylene, $Ph.CH = CH.NO_2$, evidence of the simultaneous oxidising action of nitric acid.



$$Ph.CH_2.CH=CH.COOH + HNO_3 \longrightarrow PH.CH_2.CH=\underset{NO_2}{C}.COOH \longrightarrow Ph.CH_2.CH=\underset{NO_2}{CH}$$

It is significame however, that it is nitration and not oxidation which takes place at the double bond, the latter being confined to the terminal carbon group. He observed later, (B. 24. 2771. 1891.), that phenylnitroethylene is also formed in very small amount when cinnamic acid is stirred into warm, fuming nitric acid, a reaction which preceeds to a greater extent when cinnamic acid is treated in ethereal solution with nitrous gases.

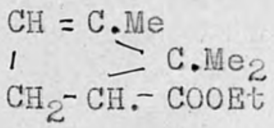
Hollemann in 1887, (B. 20. 3359.), obtained from acetophenone, by treatment with nitric acid, a compound of the empirical formula $C_2N_2O_2(CO.Ph)_2$, to which he later, (B. 21. 2835. 1888), assigned the constitution This reaction was later confirmed by Angeli, (B. 26. 527. 1893).



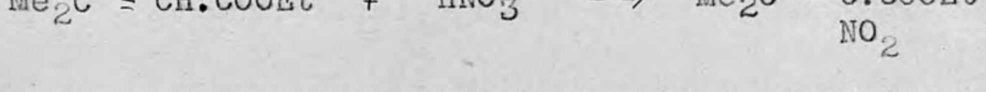
$$\begin{matrix} C.Bz - NO \\ \| \\ C.Bz - NO \end{matrix}$$

Anschutz and Romig, (A. 233. 327. 1033. 1886), investigated the action of nitric acid on diphenylethane, and later, (Anschutz and Hilbert. B. 54. 1854. 1921), the nature of the products was definitely established to be β-nitro-αα-diphenylethyl alcohol, [illegible]-nitro-αα-diphenylethylene and ββ-dinitro-αα-diphenylethylene. At the same time it was shown that the same reaction occurs with αα-diphenylethylene, a result which points to a preliminary oxidising effect of nitric acid on the saturetd nitric acid on the saturated hydrocarbon, converting it into α.α -diphenylmethylcarbinol, which by loss of water gives αα -diphenyl-ethylene.

As an examination of the action of nitric acid on the double bond, Bouveault and Wahl, (C.r. <u>131</u>. 687. 1900; C.r. <u>136</u>. 159. 1903; also Bouveault and Bongest, C.r. <u>132</u>. 1569. 1901), have carried out a series of investigations of the products formed by the action of fuming nitric acid on unsaturated esters. Of the following types which were studies:-

Ethyldimethylacrylate. →	$Me_2C = CH.COOEt$
Ethylcrotonate	$CH_3CH = CH.COOEt$
Ethyl tiglinate	$Me.CH = C.Me.COOEt$
Ethyl-iso-lauronolate	

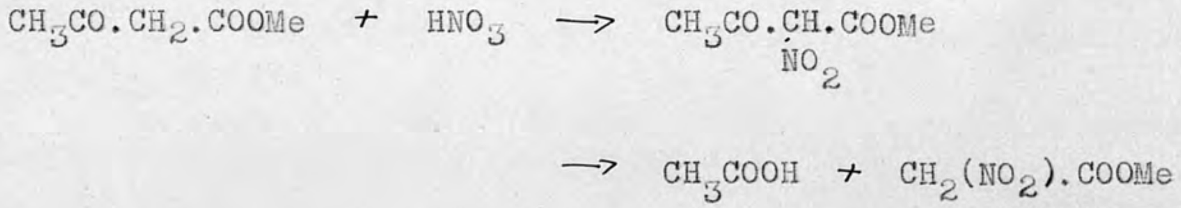
the first alone gives a nitro compound, and it is interesting to note that it is a substituted compound which is formed under the influence of nitric acid, and that the reaction does not involve addition to the double bond.



$$Me_2C = CH.COOEt + HNO_3 \longrightarrow Me_2C = \underset{NO_2}{C}.COOEt$$

Fixation of nitric acid without nitration, followed in most cases by extensive oxidation, was observed with all the other esters examined.

Clear evidence of simple nitration by substitution was also obtained by these authors, (ibid. 132. 1069. 1901; 136. 159. 1903), who, by treatment of the esters ethylhydrogen- and diethyl malonate and methylacetyl acetate, obtained true nitro compounds, i.e. ethyl-dinitroacetate, $CH(NO_2)_2.COOEt$, from the two esters of malonic acid, and as an intermediate product from methylacetyl acetate, methylnitroacetate.



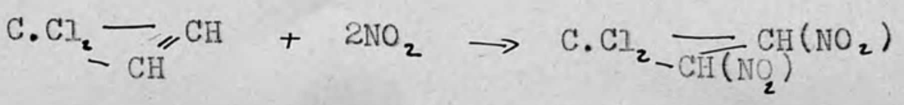
$$CH_3CO.CH_2.COOMe + HNO_3 \longrightarrow CH_3CO.\underset{NO_2}{CH}.COOMe$$

$$\longrightarrow CH_3COOH + CH_2(NO_2).COOMe$$

Addition to Unsaturated Linkages. Of the direct addition of nitric acid to unsaturated linkages little information has been available.

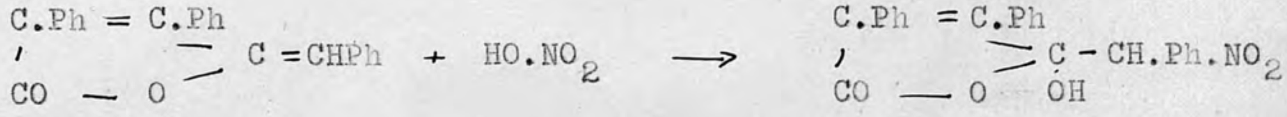
In 1876 Lorenz and Blumenthall, (B. 8. 1050. 1876.), showed that stilbene in ethereal solution yields with nitric acid a crystalline, nitrogen-containing compound, which breaks up on hydrolysis into nitric oxide, nitrobenzene and non-nitrogenous bodies.

Dichlorallylene reacts vigorously with fuming nitric acid, (Pinner. B. 8. 959. 1876), giving trichlorpropylene and trichlornitro-propylene, from which the author deduces that the interaction probably consists in the addition to the double bond of two molecules of nitrogen dioxide. Thus

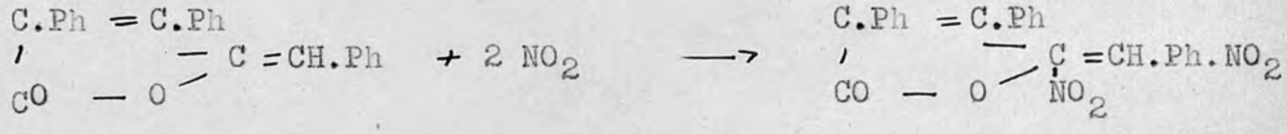


This appears to be the first recognised instance of the direct addition to an unsaturated linkage of nitro groups, with consequent saturation of the bond.

The formation of a hydroxy nitro compound by the interaction of nitrous gases with benzaldiphenylmaleide led Cohn, (B. 24, 3865. 1891), to the conclusion that the reaction is one which actually involves the addition of nitric acid, the formation of which acid in the nitrogen oxide medium he attributes to the possible absorption of water from the air. The reaction then becomes

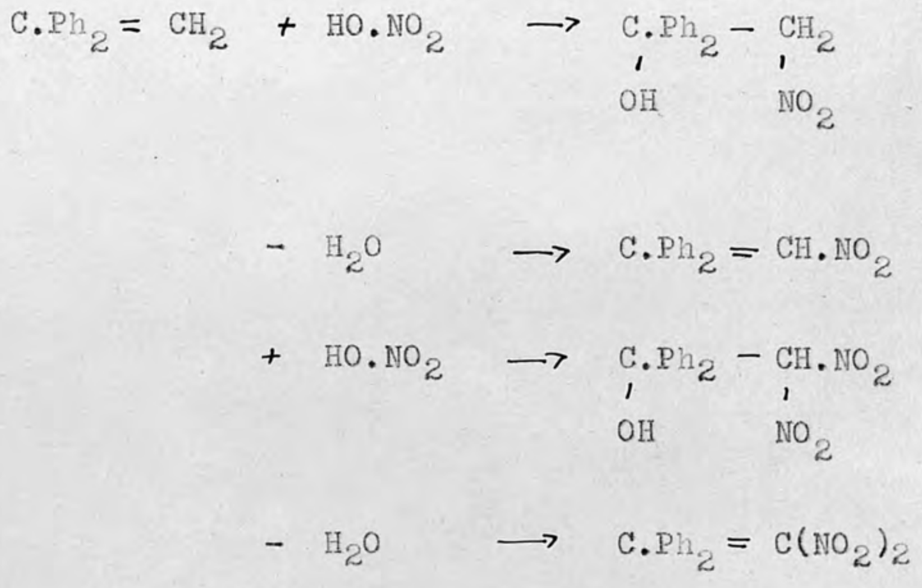


though at the same time addition of two nitro groups can also occur.



evidence that the interaction between nitric acid and unsaturated ethylenic compounds follows fundamentally the same course as that with oxides of nitrogen, but, in that the compound of the addition contains in the former case hydroxyl together with nitro groups, the primary product of the reaction is not a nitro nitrite or corresponding body but a nitro alcohol.

Following on the work of Wieland and Salellarios, (B. 53. B.201.1920 on the nitration of ethylene by a nitric-sulphuric acid mixture, Anschutz and Hilbert, (ibid), showed that the action of nitric acid on αα-diphenylethylene is to give first a saturated hydroxy-nitro compound, which by loss of water yields the unsaturated -nitrodiphenylethylene. Further addition of nitric acid then takes place giving a dinitrohydroxy compound, the double bond being again saturated by hydroxyl and nitro groups. Finally, a second dehydration yields the asymmetric dinitrodiphenylethylene.



$$C.Ph_2 = CH_2 + HO.NO_2 \longrightarrow \underset{OH}{C.Ph_2} - \underset{NO_2}{CH_2}$$

$$- H_2O \longrightarrow C.Ph_2 = CH.NO_2$$

$$+ HO.NO_2 \longrightarrow \underset{OH}{C.Ph_2} - \underset{NO_2}{CH.NO_2}$$

$$- H_2O \longrightarrow C.Ph_2 = C(NO_2)_2$$

While the action of nitric acid alone on ethylene and similar compounds has scarcely been examined, Wieland and Sakellarios, (ibid), have studied a similar reaction with ethylene using a nitric-sulphuric acid mixture. The action of such a reagent is found to be purely additive with respect to nitric acid. The primary product is β-nitroethyl alcohol, $CH_2OH - CH_2NO_2$, which by the further action of the nitric acid in the presence of sulphuric acid etherified, the final products being ethylene dinitrate, $CH_2O(NO_2) - CH_2.NO$

and β-nitroethyl nitrate, $CH_2O(NO_2)-CH_2NO_2$, a reaction which is exactly analogous to the interaction between ethylene and sulphuric acid, the concentrated sulphuric acid preventing further oxidation and hence facilitating etherification.

$$CH_2=CH_2 + H_2SO_4 \longrightarrow CH_2OH - CH_2.SO_3H$$

$$\longrightarrow CH_2(O.SO_3H)\ \ CH_2.SO_3H$$

thus the course of the reaction is represented by

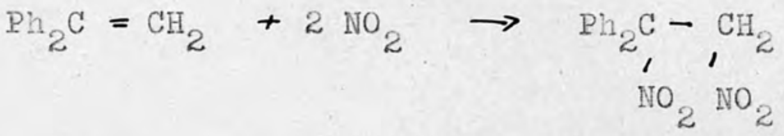
$$CH_2=CH_2 + HO.NO_2 \longrightarrow CH_2OH - CH_2.NO_2$$

$$\longrightarrow \begin{array}{c} CH_2(O.NO_2)\ \ CH_2.NO_2 \\ + \\ CH_2(O.NO_2)\ \ CH_2(O.NO_2) \end{array}$$

That some oxidation occurs is recognised by the authors in the presence of nitroacetaldehyde, of ehich they obtained evidence, though they were unable to isolate this.

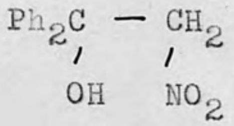
That the formation of the primary addition product, the nitro-alcohol, is probably independent of the presence of sulphuric acid is shown by the further examination of the action of fuming nitric nitric on αα-diphenylethylene, carried out by Wieland and Rahn, (B. 54. 1770. 1921), simultaneously with the work of Anschutz and Hilbert on the same substance. In both the formation of the nitroalcohol by direct addition is fully established. Further light is thrown on this reaction, however, by Wieland and Rahn, (ibid), who by a compar-

-ative study of the reaction of anhydrous nitrogen peroxide and of nitric acid with $\alpha\alpha$-diphenylethylene reveal the extraordinary ease of addition of hydroxyl and nitro groups to the double bond. $\alpha\alpha$-diphenylethylene, by the action of nitrogen peroxide in light petroleum in the complete absence of water, yields a dinitro compound by the addition of two nitro groups.



$$Ph_2C = CH_2 + 2\,NO_2 \rightarrow \underset{NO_2}{Ph_2C} - \underset{NO_2}{CH_2}$$

But if water be not rigidly excluded the addition is that of hydroxyl and one nitro group, and the product is the nitro alcohol,

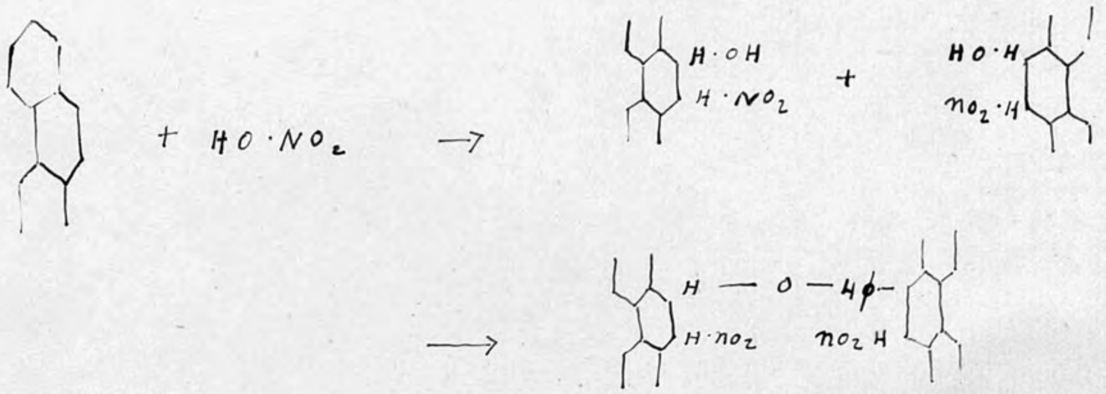


$$\underset{OH}{Ph_2C} - \underset{NO_2}{CH_2}$$

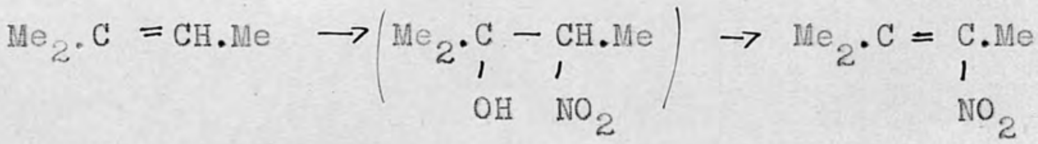
The stability of the nitroalcohol varies, as would be expected, with the nature of the original compound. The nitroalcohol of all phenyl substituted olefines which have been examined shows a marked tendency to lose water, and pass either into an unsaturated nitro-compound or, by condensation between two molecules, into a bimolecular nitro ether.

$C.Ph_2OH - CH_2NO_2 \rightarrow C.Ph_2 = CH.NO_2$ or $(CPh_2 = CH\,NO_2)_2O$

Phenanthrene reacts instantly with nitric acid, but the product isolated is the bimolecular condensation product.

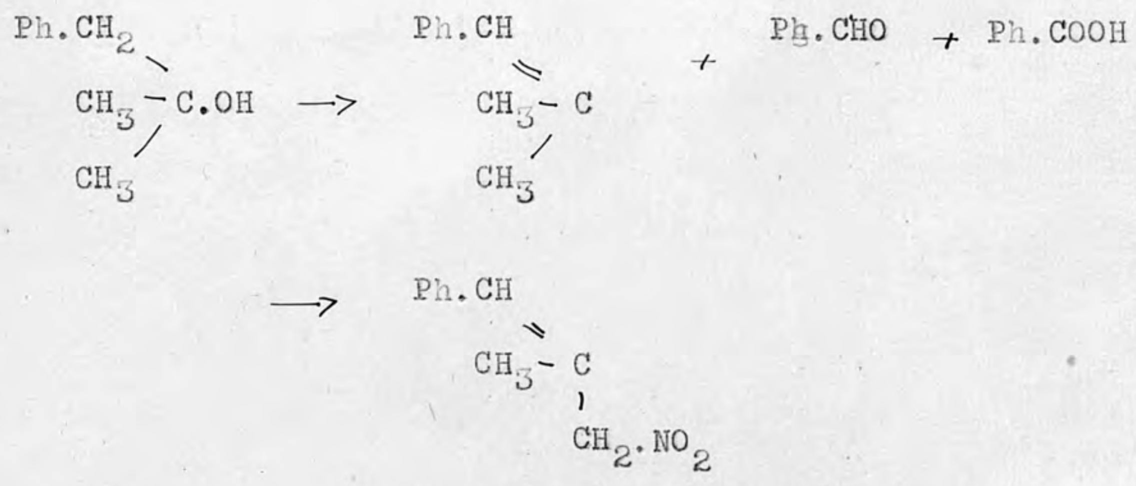


The nitroalcohol of trimethyl ethylene loses water equally rapidly with the formation of nitro-iso-amylene.



$$Me_2.C = CH.Me \rightarrow \left(Me_2.\underset{OH}{\underset{|}{C}} - \underset{NO_2}{\underset{|}{CH}}.Me \right) \rightarrow Me_2.C = \underset{NO_2}{\underset{|}{C}}.Me$$

It is interesting in this connection to compare this behaviour wiht the action of dilute nitric acid on tertiary alcohols. The primary action of the acid is the removal of water, with the formation of an unsaturated hydrocarbon, and this is followed by the immediate nitration of the hydrocarbon so produced. (Konowalow and Manewsky. Jour.Russ.Phys.Chem.Ges. 1904. 36. 224). But the nitration affects not the double bond but one of the alkyl groups attached to the central carbon atom.



(c.f. also the similar action of nitric acid with tertiary halogen compounds, (Konowolow. ibid. 1904. 36. 220)

Prior to 1920 nothing of a quantitative nature was known of the corresponding interaction between acetylene and nitric acid. Such references as are found in the literature indicate that complete oxidation to oxalic acid and carbon dioxide usually occur, though a qualitative examination of the reaction involving the detection and isolation of certain nitrogen-containing products was carried out by Baschieri, (Atti.R. Accad. Lincei, 1901.(v). 9. i. 391), and by Testoni and Mascarelli, (ibid. 1902.(v).9xxx391 10.i.442; Gazzetta, 1903, 33. ii. 319), who, by the action of fuming nitric acid on acetylene, obtained nitroform and a series of condensed, neutral and acid substances, some explosive, in only one of which, $C_4H_2O_3N_4$, a neutral oil, which readily loses oxides of nitrogen on warming, could nitro or nitroso groups be detected.

Our attention was first directed to this problem in 1917 when, under the direction of Professor Orton, I carried out, with the object of preparing the explosive, tetranitromethane, an investigation on the action of nitric acid on acetylene. Our object at that time was to find for war purposes a source of tetranitromethane from inexpensive materials, and the investigation was concentrated on the formation and yields of this substance. At the same time much interesting light was thrown on the mechanism of the reaction. (Orton and McKie. T. 1920. <u>117</u>. 283)

I have now considerably extended this investigation, and from a detailed examination of the action of nitric acid on ethylene and acetylene the mechanism of the reaction between nitric and an unsaturated linkage can be with fair certainty explained.

If fuming nitric acid is treated, under conditions when gaseous absorption is facilitated, with a slow stream of dried ethylene or acetylene gas, a marked absorption of the gas, which is increased by rise of temperature, takes place. As the passage of the gas is continued marked decomposition of the nitric acid, ~~indicated by~~ indicative of interaction, and accompanied by evolution of nitrous fumes and considerable darkening in colour is observed. At the same time, gaseous products of the reaction, of which carbon dioxide is the most prominent constituent, appear. A point is reached when the nitric acid remaining becomes too diluted by the products of the reaction for further absorption, and it is disadvantageous to continue the passage of the gas beyond this stage.

An investigation of the reaction under varying conditions of temperature, concentration and the presence of catalysts or sulphuric acid has shown that the nitric acid is able to exercise its function both as an oxidising and as a nitrating agent, and according to these conditions so does one or other function predominate. It is not possible, however, to eliminate either of these reaction types altogether.

The combined products of the oxidising and of the nitrating action of the nitric acid are varied. The direct products of the oxidation by nitric acid of ethylene and acetylene are in both cases oxalic acid and carbon dioxide, and the greater the tendency to oxidation the more, as is usual, does the oxalic acid become completely oxidised to carbon dioxide.

But though, under suitable conditions, the amount of oxidation, and hence of its immediate products, can be reduced very considerably, carbon dioxide persists, as will be shown, as a feature of the nitrating reaction. Whatever the conditions, therefore, the gaseous products of the action of nitric acid on ethylene and acetylene are carbon dioxide, a small amount of carbon monoxide and the products of reduction of nitric acid - nitrogen peroxide, nitrogen trioxide, nitric oxide and nitrous oxide, together with any excess hydrocarbon.

From the nitric acid mixture, when the absorption of the hydrocarbon is complete, only two products can, as a rule, be isolated, nitroform, (trinitromethane) and oxalic acid, though, as will be shown from the ethylene-nitric acid reaction mixture the primary product, the nitro alcohol, β-nitroethyl alcohol, $CH_2NO_2-CH_2OH$, can in small amount be isolated; c.f. the isolation of the corresponding addition product of αα-diphenylethylene, (Wieland and Rahn. B. 54. 1770.1921).

It is significant that as the reaction prodeeds the ratio of nitroform to nitroalcohol increases, an indication that the latter is a preliminary and intermediate stage of nitration. If, however, the reaction is carried out in the presence of concentrated sulphuric acid etherification of the nitroalcohol takes place and ethyl dinitrate and β-nitroethyl nitrate are produced; c.f. also Wieland and Sakellarios, (B. 1920. 53. B. 201), a reaction which supercedes the formation of nitroform as only a very slight trace of this substance can ever be detected in the sulphuric - nitric acid medium.

Possible routes of the formation of nitroform from acetylene and ethylene.

The principal and characteristic product of nitration in each case is therefore nitroform. The formation of this compound from the hydrocarbons must therefore be considered.

In the examination of the action of nitric acid on the double bond of various unsaturated compounds it was seen that, except in a few cases of substitution, there is a marked tendency for addition to take place at the double bond, this addition involving the saturation of the bond by the taking up of the constituent~~s~~ parts, hydroxyl and nitro, of nitric acid, forming a nitro alcohol.

e.g. ~~Ph .C CH~~ ~~Ph .C(OH)~~

e.g. $Ph_2.C = C.H_2 \longrightarrow Ph_2.C(OH) - CH_2.NO_2$

(Anschutz and Hilbert. ibid.)

though at the same time a small varying amount of nitration by substitution may also occur, e.g.

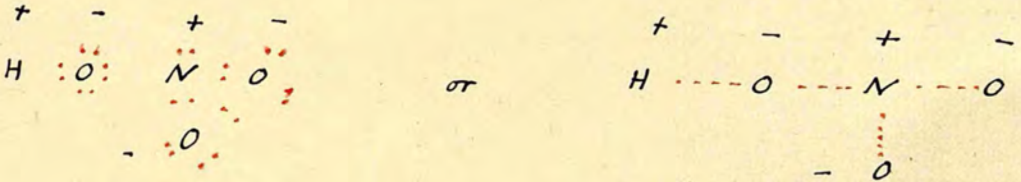
$$Ph_2.C = CH_2 \longrightarrow Ph_2.C = CH.NO_2$$

$$\longrightarrow Ph_2.C = C(NO_2)_2$$

(Anschutz and Hilbert. ibid.)

From the formation of ethylene dinitrate and β-nitroethyl nitrate by the action of concentrated sulphuric and nitric acids on ethylene, Wieland and Sakellarios, (ibid), have concluded that the primary product of the reaction must be the addition product, the nitro alcohol, and it is obvious that in the observed formation of a nitro alcohol from ethylene by treatment with nitric acid, we are dealing with a similar primary addition of hydroxyl and nitro groups. β-nitroethyl alcohol is a comparatively stable compound which, provided other reagents, such as the etherifying agent, sulphuric acid, are absent, can be isolated from the reaction by fractional distillation under reduced pressure. It is clear, however, that acetylene cannot give rise to an analogous stable compound. The primary product of addition of nitric acid would be the unsaturated compound, $CH(OH) = CH(NO_2)$, which, in the nitrous-nitric acid medium, might be expected to be highly susceptible to further addition and interaction. This will be more readily understood from a consideration of the electrovalent condition of the compounds participating in the reaction.

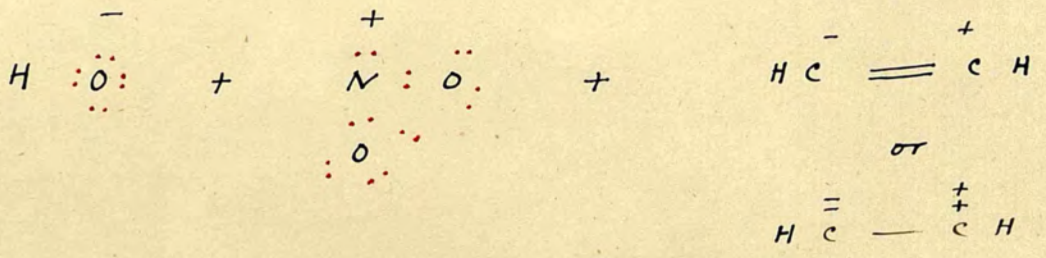
The electrovalent formula of nitric acid, (v. p 89), shows that this acid, analogous to nitrous acid, exists in a state of latent, simple polarity, thus:-



There are no crossed polarities, and in the absence of the requisite dissociating energy, this would be the stable state. In the ethylene and acetylene molecules we have a similar state of latent polarity, which is also stable in the absence of polarising agents; but the high degree of unsaturation, or the incipient polarity of the ethylene molecule, as shown by its ready polarisation, is not realised in acetylene, and the interaction between the inactive polar fields, or fields of latent polarisation, of nitric acid and the hydrocarbon must conceivably, therefore, be slower for acetylene than for ethylene. In both cases it is obvious that a polarising catalyst should have considerable influence on the reaction.

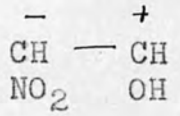
And here one must note a fact of considerable importance, that absorption of the hydrocarbon by nitrous-free nitric acid only proceeds to a very limited extent. In other words, there is little capacity for interaction between the inert, unpolarised molecules of acetylene or ethylene and nitric acid. Directly, however, nitrous acid or a metallic polarising catalyst is introduced, absorption of the hydrocarbon takes place with great readiness, a readiness which is increased by rise of temperature, or other additional energy, and interaction is promoted. It is proposed in a subsequent section this effect of polarising catalysts on an inert systen.

Whatever may be the activating force, the state of the system in which interaction takes place may be represented by



and interaction occurs thus:-

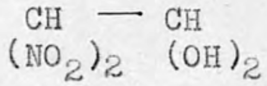
It is conceivable that th~~is~~e unsaturated addition compound, owing to the polarisation of the molecule by the addition of the polar groups hydroxyl and nitro will exist in the still polarised, ethylenic condition,



$$\overset{-}{\underset{NO_2}{CH}} - \overset{+}{\underset{OH}{CH}} \quad (11)$$

(Lowry's notation)

in which state further addition would be facilitated and the double addition compound be formed.

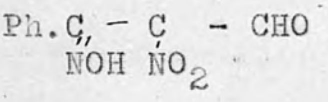


$$\underset{(NO_2)_2}{CH} - \underset{(OH)_2}{CH}$$

It is obviously unlikely that the compound, (11), would add the polar elements, OH and NO_2, in the reverse oredr. The usual chemical reaction between two adjacent hydroxyl groups would then occur giving the aldehyde, $(NO_2)_2CH - CHO$, which in the nitric acid medium would become the corresponding acid, $(NO_2)_2CH.COOH$. (That oxidation occurs simultaneously to a considerable extent is shown by the copious evol--ution of the reduction products of nitric acid.) The course of the subsequent stages is conditioned, both for acetylene and ethylene, by the formation of nitroform and carbon dioxide. As was suggested, (Orton and McKie. T. 1920. <u>117</u>. 283.), there are two possible routes by which both these compounds can be produced from the dinitro addition compound of acetylene. (1) Loss of carbon dioxide would give the nitroparaffin, dinitromethane, which by interaction with nitrous acid would yield the isonitroso compound, $(NO_2)_2C = NOH$.

$$HC(NO_2)_2.COOH \longrightarrow H_2C(NO_2)_2 + CO_2$$

$$+ \ HO.NO \longrightarrow NOH = C(NO_2)_2$$

Though the nitrolic acids are extremely unstable compounds, and decompose by hydrolysis in aqueous acid media to carbon dioxide and oxides of nitrogen, it is probable that, in the concentrated acid medium, this may be averted. Analogous to this is the behaviour towards concentrated acids of the oximido compounds of the type  $Ph.\underset{NOH}{C} - \underset{NO_2}{C} - CHO$, where, instead of the decomposition with the splitting off of the oxinido group which is the normal reaction in dilute acid media, dehydration and formation of a cyclic isoxazole occurs, (v. p 55). Whether dehydration occurs between two molecules a compound of a nitrogen-ether type, i.e.

$$(NO_2)_2G = NOH \ + \ HON = C(NO_2)_2 \longrightarrow (NO_2)2C = N - O - N = C(NO_2)_2$$

which then takes up two molecules of nitric acid at the double bonds, subsequent hydrolysis giving nitroform and nitrous acid, or whether nitroform arises by direct oxidation of the isonitroso compound,

$$(NO_2)_2.C = NOH \longrightarrow (NO_2)_2.C\begin{smallmatrix}\diagup NO_2\\ \diagdown H\end{smallmatrix}$$

must be left an open question for the moment.

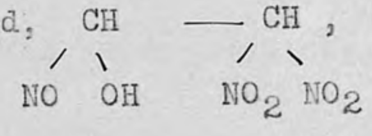
(2) Further nitration and formation of a trinitroacetic acid,

and immediate loss of carbon dioxide would give the compound, nitroform,

$$HC(NO_2)_2.COOH \longrightarrow (NO_2)_3.C.COOH$$
$$\longrightarrow (NO_2)_3.CH + CO_2$$

It is, however, unlikely that dinitroacetic acid, showing as it would in its possession of two nitro groups adjacent to carboxyl, a marked tendency to lose carbon dioxide, would remain sufficiently stable to undergo further nitration, and the most probable alternative for the formation of nitroform is therefore one of the two routes outlined in (1).

It is conceivable, though, that under the influence of nitrous acid, which, as has been seen, tends to react towards the double bond as an addition of nitroso and nitro groups, addition of these radicles to the double bond of the unsaturated nitroalcohol may occur. A further possibility is indicated by the formation of glycoldinitrate and of β-nitroethylnitrate under the etherifying influence of concentrated sulphuric acid, (Wieland and Sakellarios, ibid,). That such etherification tales place, but that the compound is immediately decomposed in the absence of sulphuric acid is conceivable. Both alternatives would lead ultimately to the same result as (1) described above, for the addition compound,



$$\underset{NO\quad OH}{CH} — \underset{NO_2\quad NO_2}{CH}$$

, (and the polarisation of nitrogen trioxide in the groups $\overset{-}{NO_2} + \overset{+}{NO}$ would direct the addition in this order,) would conceivably lose nitrous acid or nitric acid respectively, the unsaturated compound thus produced then undergoing oxidation to carbon dioxide and dinitromethane. (c.f. p 62) It is known, however, that a nitro acid can react with nitrous acid, eliminating carbon dioxide and water and giving rise to a nitrolic acid, (c.f. p 69). Hence, at the concentration of nitric acid which is reached in the medium under consideration, such interaction with dinitroacetic acid would in all probability occur, and the same di-nitro oximido compound, $C(NO_2)_2 = NOH$, would be formed. Such a compound, as has been indicated, would be expected to undergo further oxidation to nitroform.

The formation of nitroform from ethylene under similar conditions is less obvious. The primary product is undoubtedly the nitroalcohol, $CH_2OH.CH_2.NO_2$, and nitroform is produced at the direct expense of this compound. In the light, however, of the reaction between a nitro fatty acid and nitrous acid just described, a possible route becomes evident, involving a preliminary oxidation of nitroethylalcohol to nitroacetic acid. Granted that such an oxidation is possible, interaction with nitrous acid would then take place giving methylnitrolic acid, which, analogous to the compound, $C(NO_2)_2 = NOH$, could undergo oxidation to dinitromethane. The subsequent stages would then occur as already described for acetylene.

Comparison of the subsequent courses of reaction of the addition compounds with oxides of nitrogen and of nitric acid reveals two distinct lines of decomposition. The survey of the effect of acid media on the addition compounds with oxides of nitrogen shows that no cleavage occurs between the two carbon~~s~~ atoms involved in the unsaturated linkage; the products of decomposition are invariably products of the nitrogen-oxide radicle, one or both of which are eliminated. Only in one observed reaction, and that in alkaline medium, is a carbon atom of the double bond eliminated, i.e. the decomposition of pseudo-nitrosites by hot alkali, (v. p 67). On the other hand, the addition compound of nitric acid with the simple hydrocarbons, ethylene and acetylene ultimately, under the further influence of nitric acid, loses by oxidation one carbon atom of the unsaturated bond, the second carbon of the bond being nitrated. If, however, the ethylene molecule carries phenyl substituents this oxidation is prevented, and the final product is a nitro compound containing both carbon atoms, (Anschutx and Hilbert. ibid). This difference is obviously intrinsic to the relative valuse of the oxidising and nitrating function of the two types of reagent, the latter predominating in interaction with oxides of nitrogen. But it is important to emphasise that it is not as nitrating or oxidising agents that oxides of nitrogen on the one hand, and nitric acid on~~e~~ the other, undergo the initial reaction, which in both types is purely additive. Both components of the nitrogen oxides in their addition to the double or triple bond involve nitration, or some addition of a nitrogen-containing group, whereas in the addition of the hydroxyl constituent of nitric acid we are dealing with a group which readily undergoes oxidation, and it is only at this subsequent stage that this second, oxidising function of the acid comes into play. Simultaneously, however, it functions equally in promoting nitration of the second carbon atom.

In the interaction, therefore, between nitric acid and an unsaturated linkage the sequence of reactions is -(1) addition to the unsaturated linkage, followed in acetylene by a second similar addition, (11) simultaneous oxidation of one carbon atom and nitration of the other. Independently, and this may also occur, though to a less degree, in the interaction with oxides of nitrogen, simple oxidation involving complete decomposition and oxidation to oxalic acid and finally carbon dioxide may and usually does occur. The carbon dioxide evolved in any such reaction with oxides of nitrogen is therefore a simple measure of that independent oxidation, but in the analogous reaction with nitric acid it is more than this, and is in part a measure of the nitration. The total amount of carbon dioxide represents the extent of the independent oxidation plus that of the simultaneous oxidation and nitration of the unsaturated bond, and may be represented thus:-

$$\begin{array}{lcl} & \xrightarrow{HO + NO_2} & C(NO_2)_3H + CO_2 \\ >C = C< & \xrightarrow[HNO_3\ (\text{oxidising})]{} & 2\ CO_2 \\ \text{or } (-C \equiv C-) & & \end{array}$$

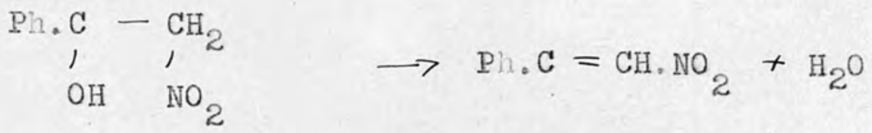
The extreme instability in the nitrous acid-containing acid medium of dinitromethane and the corresponding nitrolic acid precludes any definite isolation and recognition of these compounds. But there is a certain amount of evidence for their existence, and hence for the scheme of reaction described above, in the blood-red colour obtained when the reaction mixture is made alkaline, a colour characteristic of the nitrolic acids. This colour has been observed in various cases, and is a comparatively constant product of the ethylene-nitric acid reaction mixture. In no case would one expect to get more than a transitory appearance of such compounds.

There are undoubtedly present in the reaction mixture, when the absorption of the hydrocarbon is completed, compounds intermediate to the formation of nitroform. If the product be mixed with sulphuric acid or oleum and heated, the nitroform is further nitrated, quantitatively, to tetranitromethane, but the amount of tetranitromethane obtained is always in excess of the amount of nitroform in the product. The quantity of nitroform, determined by titration with potassium permanganate, a method which I have exhaustively tested, does not represent under the best conditions more than 85 - 87 per cent of the tetranitromethane which can be obtained in the second stage, and is often much less. If the product be left for some days, or be heated for some hours before mixing with oleum, the amount of nitroform is found practical ly unaltered, whereas the amount of tetranitromethane which can then be isolated is much less, and is now nearly equal to the nitroform. It appears, therefore, that there is present in the product an unstable substance which is capable of further nitration to give ultimately tetranitromethane, but which, failing the conditions and medium for such nitration, decomposes.

The possibility of the presence of nitrogen peroxide or of nitrogen trioxide in the concentrated nitric - nitrous acid mixture, and the consequent addition of either or both of these substances to the unsaturated linkage must not be overlooked. Since we are only concerned with the simple primary hydrocarbons, addition to either the ethylenic or acetylenic link would occur, (v. p 37), as 2 (O.NO), or less readily as (NO + O.NO). In the strong acid medium the di-nitrite addition compound would be extremely unstable, and would lose nitrous acid, reverting to the original olefine. As has been seen, the primary hydrocarbons show little capacity for forming nitroso compounds, but should addition take place as (NO + O.NO) the oxime into which the nitroso compound would pass would, under the influence of acids, lose the nitroso group as hydroxylamine, and the residual compound, the nitroaldehyde, undergoing oxidation to the corresponding acid, would constitute the same nitroacetic acid as is produced by other routes. But there is no evidence of either the oxime or of its decomposition product, hydroxylamine, and it is unlikely that this reaction occurs to any appreciable extent.

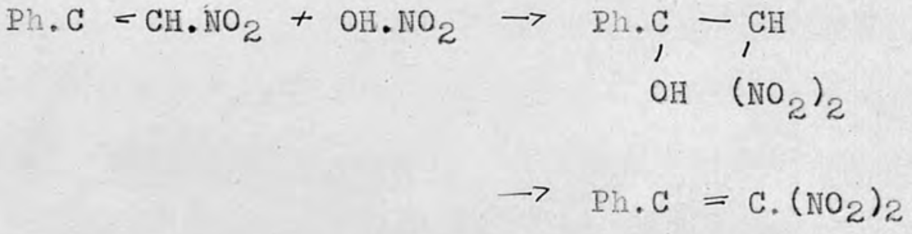
Stability of the Addition Compounds. In the absence of nitroso groups there is little capacity for polymerisation, and there is a marked absence of such compounds among the addition products. No evidence has ever been obtained of the complex condensation products observed by Testoni and Mascarelli, (ibid), by passing pure acetylene into cooled nitric acid.

Anschutz and Hilbert, (ibid), have shown that the nitroalcohol addition compound of αα -diphenylethylene and nitric acid loses water and passes into the unsaturated nitro compound,



$$\begin{array}{ll}\text{Ph.C} - & \text{CH}_2\\ \;\;| & \;\;|\\ \text{OH} & \text{NO}_2\end{array} \longrightarrow \text{Ph.C} = \text{CH.NO}_2 + H_2O$$

which again undergoes addition at the double bond, adding the elements hydroxyl and nitro groups, and giving rise to α -hydroxy- ββ-dinitro- - -diphenylethylene. Water is lost from this compound, and the primary product is the unsaturated $\overset{\beta\beta}{\cancel{\alpha\beta}}$-dinitro-αα -diphenylethylene.



$$\text{Ph.C} = \text{CH.NO}_2 + \text{OH.NO}_2 \longrightarrow \begin{array}{ll}\text{Ph.C} - & \text{CH}\\ \;\;| & \;\;|\\ \text{OH} & (\text{NO}_2)_2\end{array}$$

$$\longrightarrow \text{Ph.C} = \text{C.}(\text{NO}_2)_2$$

This is exactly analogous to the loss of nitrous acid from the addition compound, $\begin{array}{l}\text{-CH.NO}_2\\ \;|\\ \text{-CH.O.NO}\end{array}$ giving the nitro-olefine $\begin{array}{l}\text{-C.NO}_2\\ \;\|\\ \text{-CH.}\cancel{\text{O.NO}}\end{array}$ (Schaarschmidt and Hofmeier. B. 58. 1047. 1925.), and to a similar loss of nitrous acid from the addition compound, $\begin{array}{ll}\text{Ph.CH} - & \text{CH.CO} -\\ \;\;| & \;\;|\\ \text{O.NO} & \text{NO}_2\end{array}$ where, however, the loss of the nitrogen--containing groups is facilitated by the presence of the adjacent, negative carbonyl group, (Wieland. A. 328. 154. 1923.).

By analohy, therefore, the nitroalcohol addition compound of ethylene might be expected to undergo reaction in the following way:-

$$\begin{aligned} H_2C = CH_2 \quad &\xrightarrow{HNO_3} \quad H_2C(OH) - CH_2(NO_2) \\ &\xrightarrow{-H_2O} \quad H_2C = CH.NO_2 \\ &\xrightarrow{HNO_3} \quad H_2C(OH) - CH(NO_2)_2 \\ &\xrightarrow{-H_2O} \quad H_2C = C(NO_2)_2 \end{aligned}$$

The final product, the unsaturated αα-dinitroethylene, by simultaneous oxidation and nitration, would then break up into carbon dioxide and nitroform.

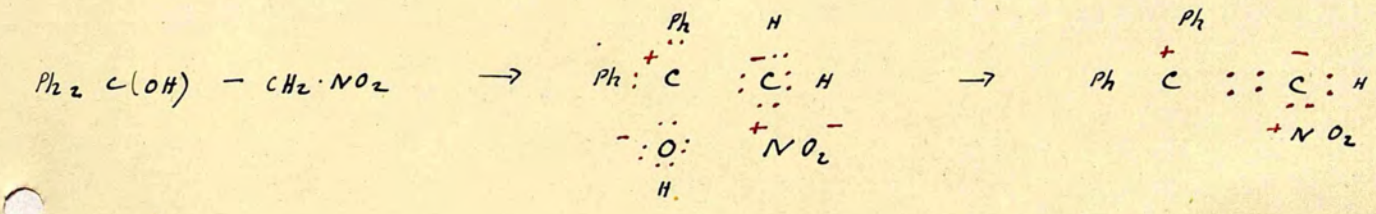
Applying this series of reactions to acetylene, the final pro-duct might conceivably, also, be nitroform and carbon dioxide, as follows:-

$$\begin{aligned} HC \equiv CH \quad &\xrightarrow{HNO_3} \quad HC(OH) = CH(NO_2) \\ &\xrightarrow{-H_2O} \quad HC \equiv C.NO_2 \\ &\xrightarrow{HNO_3} \quad HC(OH) = C(NO_2)_2 \\ &\longrightarrow \quad CO_2 + CH(NO_2)_3 \end{aligned}$$

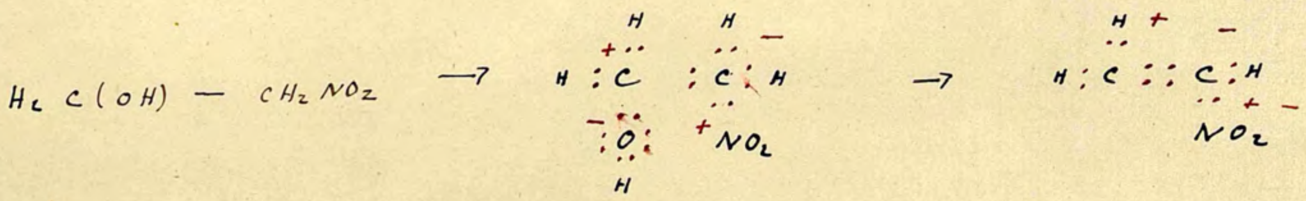
or, if double addition preceeded the loss of water, dinitromethane or isonitrosodinitromethane would be formed.

Consideration of the relative stability of the addition compounds $Ph_2.C(OH) - CH_2NO_2$, $H_2C(OH) - CH.NO_{2\,2}$ and $HC(OH) = CH.NO_2$, and the subsequent reactions which are determined by such stability, enables one to decide in favour of one or other of these alternative routes.

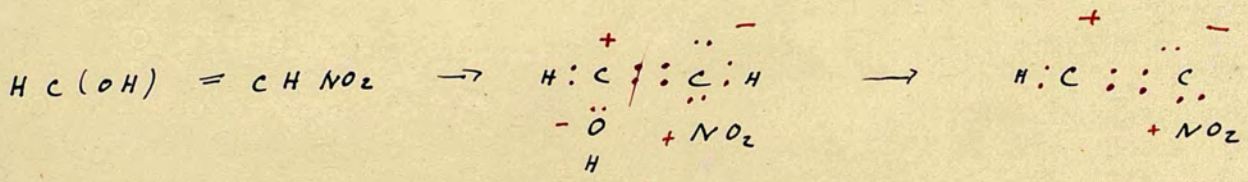
These compounds can be represented electronically as follows:-



$= Ph_2C = CH \cdot NO_2$

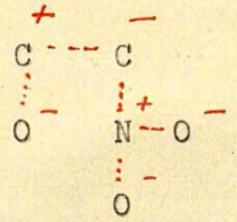


$= (CH_2 = CH\,NO_2)$



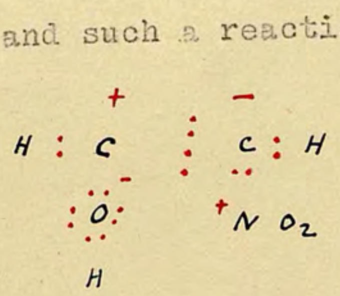
$= CH \equiv C \cdot NO_2$

Accepting the alternate polarity of a substituted phenyl nucleus, which in the most recent communication of Lowry, (Boll.Soc. (4) 35. 815. 1924), is considered the most adequate representation of the distribution of the lectrons, -diphenylethylene is seen to be a highly polar structure, the key atoms oxygen and nitrogen polarising the carbon atom of the ethylene molecule thus- so that the incipient polarity of the phenyl nuclei attached to the positive ethylene carbon atom becomes stabilised in a negative sense. The accumulation of negatively polarised groups in the neighbourhood of the ~~beta~~ alpha carbon atom is, however, owing to the lower positive polarity of nitrogen and hydrogen, not balanced by a corresponding opposite polarisation of the ~~alpha~~ beta carbon atom. Moreover, in the nitric acid medium, reversion to a stable, unpolarised condition would not be facilitated, and hence such a compound would be unstable, and by loss of one of its more negative radicles could adjust itself to a more stable condition.



This unsaturated compound, in the nitric acid medium, would, however, undergo the same addition reaction as the original unsaturated diphenylethylene, in this case rather more readily owing to greater polarisation, and the dihydroxy-dinitro addition compound would be formed.

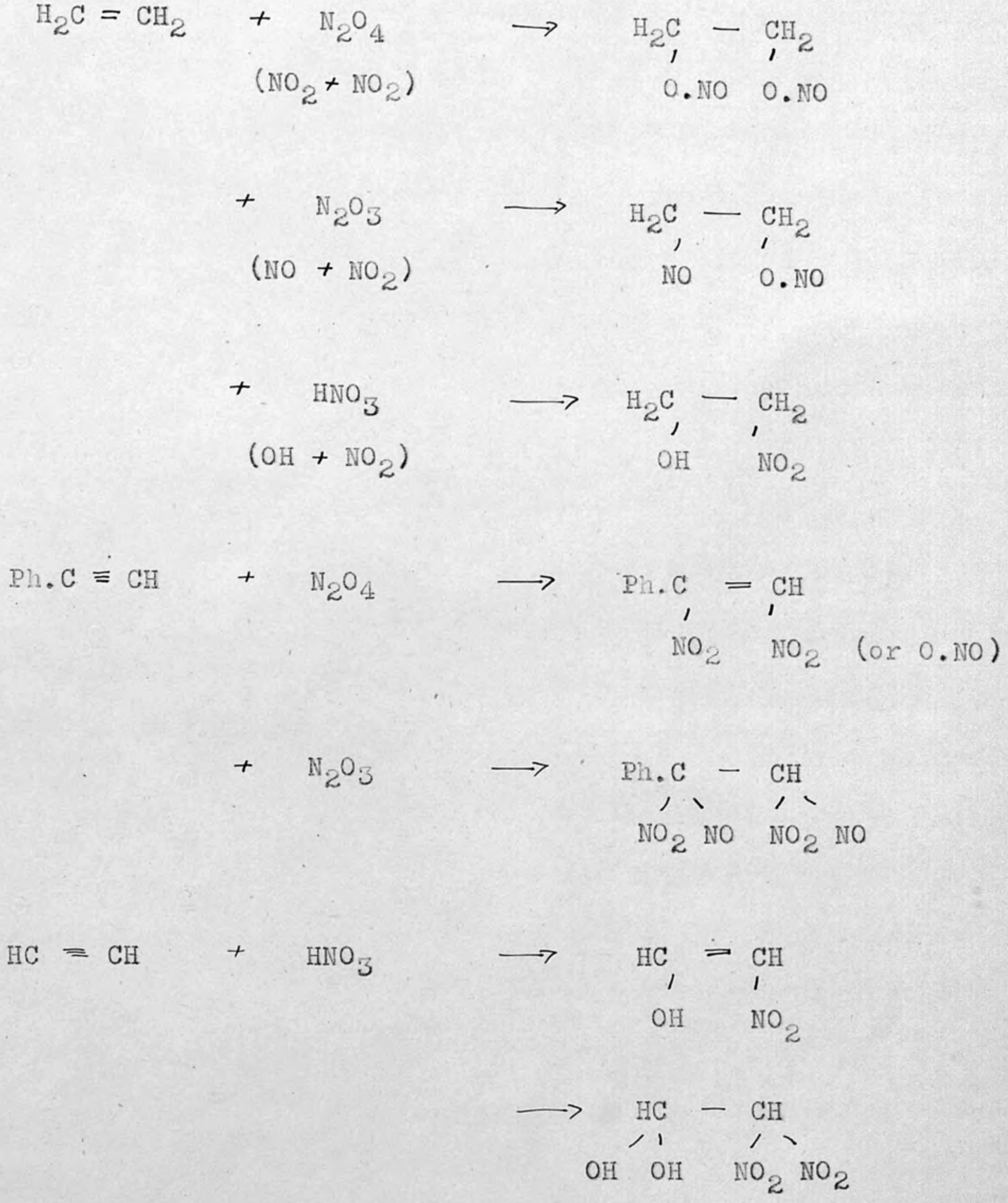
Nitroethyl alcohol, on the other hand, is seen to be a comparatively symmetrical polar structure, so that there is little tendency to lose water. Moreover, should such an abstraction of elements occur, the compound $CH_2 = CH.NO_2$, owing to the polarisation of the beta carbon atom by the nitro group, would, in the absence of any group which could stabilise the positive polarity of the alpha carbon atom, be unstable, and would tend to break up by oxidation. Oxidation of the original nitroethyl alcohol, however, would represent a perfectly stable, (electronically), series of reactions, and consequently this must be taken to constitute the normal course of reaction.

The argument of electronic stability applies with even greater force to the hypothetical addition compound which would be formed by elimination of water from the nitro-hydroxy addition compound of acetylene, and such a reaction is not conceivable. But, in the molecule  owing to polarisation by the oxygen and nitrogen groups, it is probable that at least one of the co-valent bonds is transformed into an electrovalent one, and consequently further addition is initiated. Hence, the double addition compound, $CH(OH)_2 - CH(NO_2)_2$, is formed in preference to the immediate oxidation of the primary, unsaturated nitro alcohol.

Thus, both for acetylene and for ethylene the reaction with nitric acid follows fundamentally the same course, as is shwon graphically in the accompanying diagram. Addition of hydroxyl and of nitro groups occurs at the unsaturated linkage giving the nitro alcohol. For acetylene this becomes by further addition the dinitro-dihydroxy compound. Oxidation to the aldehyde, and finally to the acid occurs. This acid, from ethylene, mononitro- and from acetylene, dinitroacetic acid, may then by reaction with nitrous acid, or by other routes, eliminate one molecule of carbon dioxide and become the corresponding nitrolic acid. The dinitro nitrolic acid from acetylene by oxidation becomes nitroform, while methyl nitrolic acid, from ethylene, by a similar process of oxidation becomes dinitromethane, a repetition of the reaction with nitrous acid then giving the dinitro nitrolic acid and finally trinitromethane, nitroform.

That this behaviour is fundamentally in harmony with the addition reactions of nitrogen peroxide and of nitrogen trioxide is seen when we compare it with the interaction of these gases with simple ethylenic and acetylenic compounds. Whatever the subsequent course of the reaction the primary interaction involves in all cases the simple addition to the unsaturated linkage of the component radicles of the reagent.

i.e.



$$H_2C = CH_2 \quad + \quad \underset{(NO_2 + NO_2)}{N_2O_4} \quad \longrightarrow \quad \underset{O.NO}{H_2C} - \underset{O.NO}{CH_2}$$

$$+ \quad \underset{(NO + NO_2)}{N_2O_3} \quad \longrightarrow \quad \underset{NO}{H_2C} - \underset{O.NO}{CH_2}$$

$$+ \quad \underset{(OH + NO_2)}{HNO_3} \quad \longrightarrow \quad \underset{OH}{H_2C} - \underset{NO_2}{CH_2}$$

$$Ph.C \equiv CH \quad + \quad N_2O_4 \quad \longrightarrow \quad \underset{NO_2}{Ph.C} = \underset{NO_2}{CH} \quad \text{(or O.NO)}$$

$$+ \quad N_2O_3 \quad \longrightarrow \quad \underset{NO_2\ NO}{Ph.C} - \underset{NO_2\ NO}{CH}$$

$$HC \equiv CH \quad + \quad HNO_3 \quad \longrightarrow \quad \underset{OH}{HC} = \underset{NO_2}{CH}$$

$$\longrightarrow \quad \underset{OH\ OH}{HC} - \underset{NO_2\ NO_2}{CH}$$

Simple, unpolymerised addition compounds are formed, which are are comparatively stable, except when addition takes place as an ester group, ie. as (O.NO) or ($O.NO_2$), when this radicle tends to split off as the corresponding acid, (V. p 55)

Effect of External Factors. It is not proposed here to discuss more than briefly the effect of external factors, temperature, concentration &c, except in so far as they modify or alter the course of the reaction. Their influence will be dealt with in detail in the experimental section.

Temperature. No effect beyond that of the normal increase of the speed of the reaction is observed by carrying out the reaction between such limits of temperature as -3° and 50°C. Above a temperature of 50°C the reaction becomes difficult to manipulate, owing to the copious evolution of gaseous products. In that the reaction proceeds by various stages, the lower the temperature the less will the final stages of the reaction be attained, and this is made evident by a decreasing yield of nitroform and carbon dioxide as the temperature is lowered, and a relatively greater proportion of the intermediate products, (Table XLVII). At the same time there is a definite decrease in the amount of hydrocarbon absorbed at the lower temperature. The ratio of final product, nitroform or carbon dioxide, to hydrocarbon absorbed increases with rise of temperature.

Concentration. With decreased concentration of the acid, absorption of acetylene of ethylene takes place more slowly, and in diminishing amount. At a concentration of seventy percent nitric acid less than forty percent of the hydrocarbon passed through is absorbed, but, relative to the hydrocarbon absorbed, the yield of nitroform at this concentration is almost negligible. If the yield of nitroform is plotted against the proportion of hydrocarbon absorbed at varying concentrations of nitric acid between 100 and 70 per cent, a curve is obtained which reaches a maximum, for acetylene at a concentration of 95 per cent nitric acid, and for ethylene at 90 per cent, and a minimum for both at 70 per cent. It is noteworthy that the curve reaches a point at a concentration of 100 per cent nitric acid which is not appreciably above the minimum point, though the absorption of the acetylene or ethylene at this concentration is high. If, however, the yield of carbon dioxide be taken as the ordinate there is a progressive increase of carbon dioxide relative to hydrocarbon absorbed as the concentration of the acid is diminished. Oxalic acid and carbon dioxide predominate. Thus the fall in amount of nitroform on both sides of the concentration curve is due to two different causes. On the ascending curve at high concentrations of acid a small proportion of water is found to be necessary in order that the reaction may proceed from the first stage of the nitroalcohol to the final stages. Actually, however, in the interaction with ethylene the yield of nitroalcohol does not reach a maximum value unless a small proportion of water is present, though the optimum value to promote addition, i.e. for the maximal formation of nitro alcohol, is less than that for the formation of nitroform. When it is remembered that a preliminary dissociation of nitric acid into the groups (OH) and (NO_2) is necessary beföre addition can take place this is obvious.

In the more concentrated acids substances are produced which do not under any subsequent conditions yield nitroform, and though all efforts to isolate these substances have so far been unsuccessful, it is possible that they are the complex condensation products isolated by Mascarelli and his co-workers, (ibid). Thus in 100 per cent nitric acid at 14°C such compounds may represent 80 per cent of the hydrocarbon absorbed.

It will be seen, therefore, that, since in the interaction of nitric acid and the hydrocarbon water is formed, and hence the nitric acid pregressively diluted, that the relative proportions of the products changes with the increasing dilution. Starting with an acid of 97'5 per cent concentration, in which nitration appears to reach a maximum, one very soon arrives at dilutions at which oxidation and also ~~the~~ possibly the formation of other substances play the prominent part. One is apt, therefore, by passing in excessive amounts of hydrocarbon, and hence carrying the reaction over too extended a period, to confuse the main issue, and instead of dealing with an acid of one particular dilution one is in reality observing the effects of successive dilutions. The following diagrams will help

Fig I

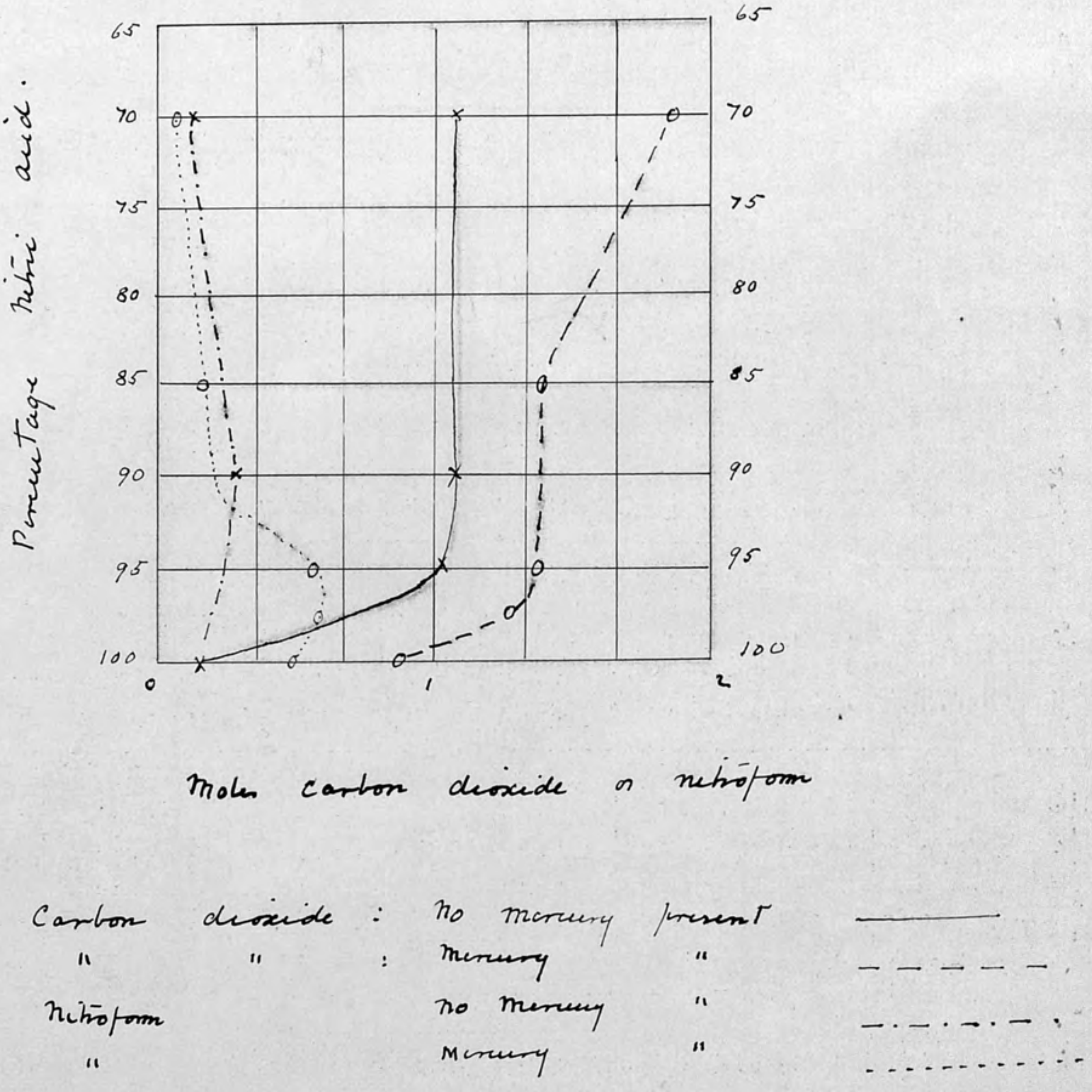
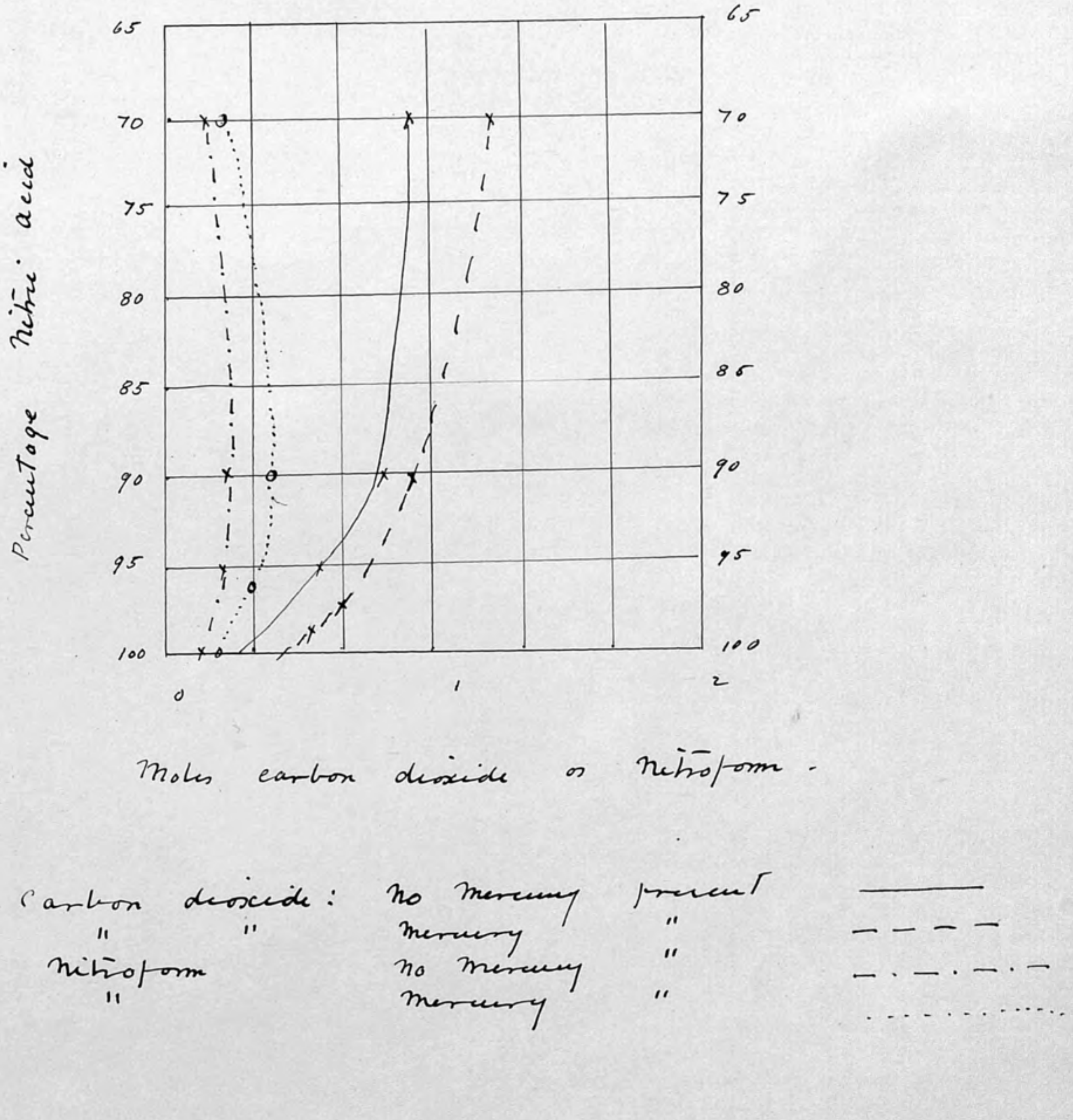
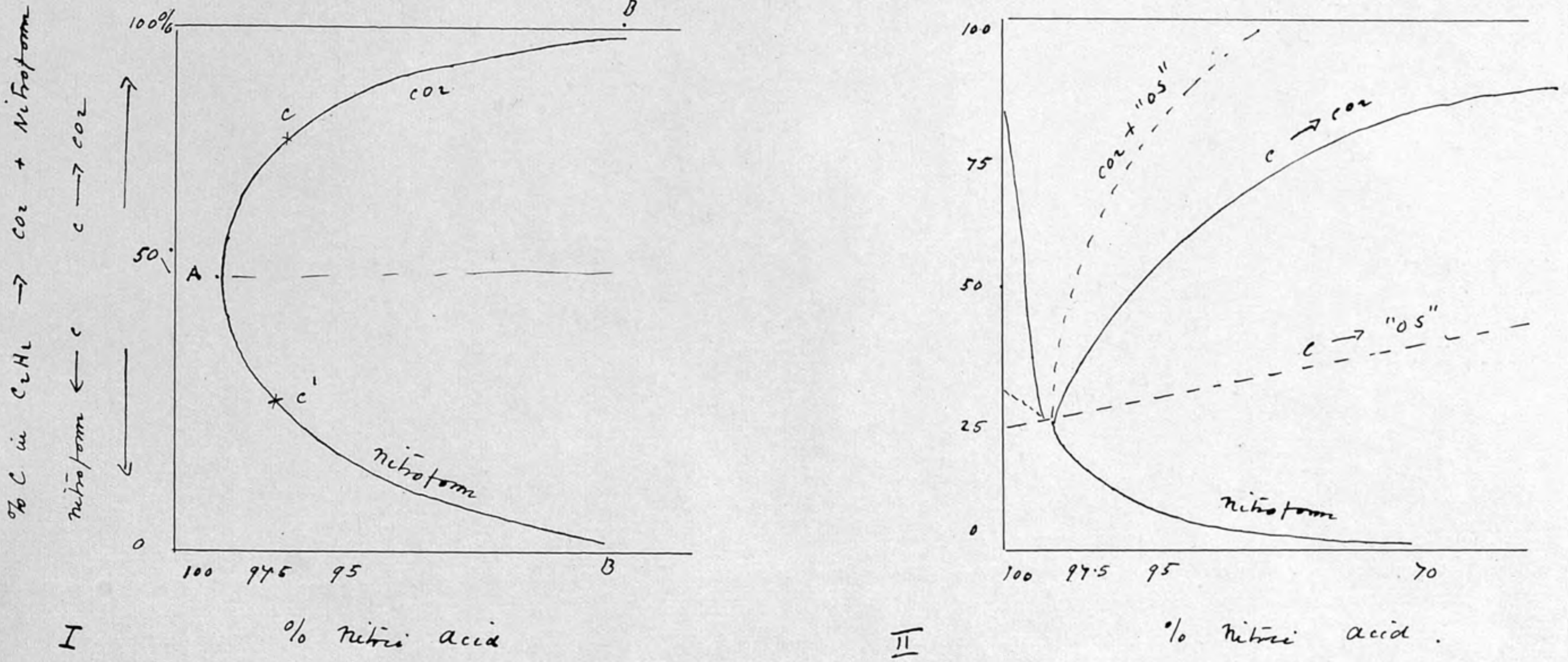

Percentage nitric acid
65
70
75
80
85
90
95
100
0
1
2
Moles carbon dioxide or nitroform
Carbon dioxide : no mercury present
" " : mercury "
nitroform no mercury "
" mercury "

Fig I A

Ethylene.

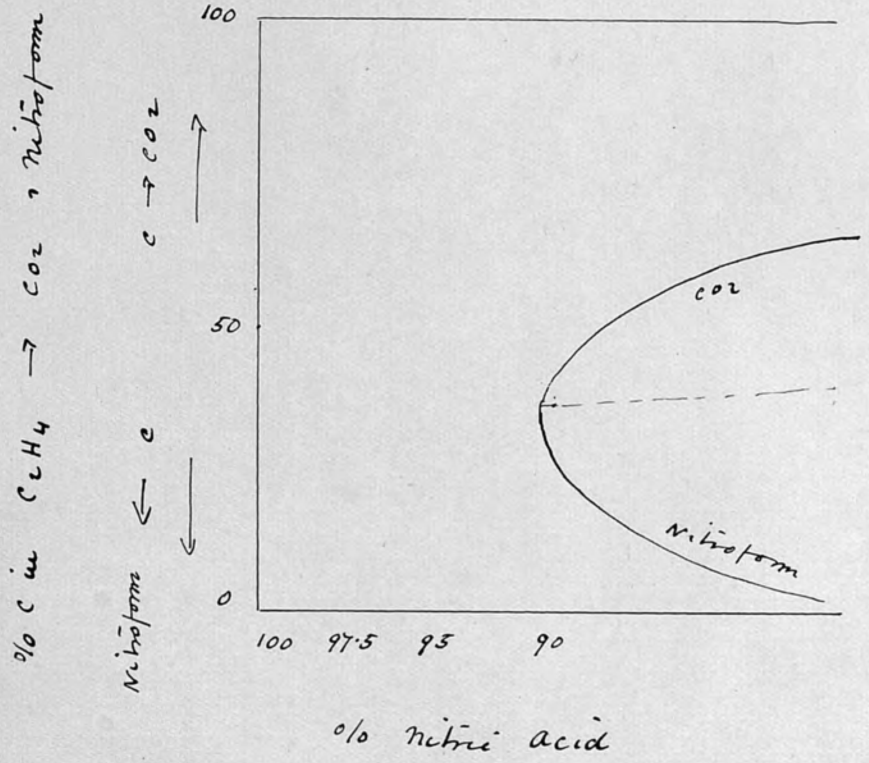




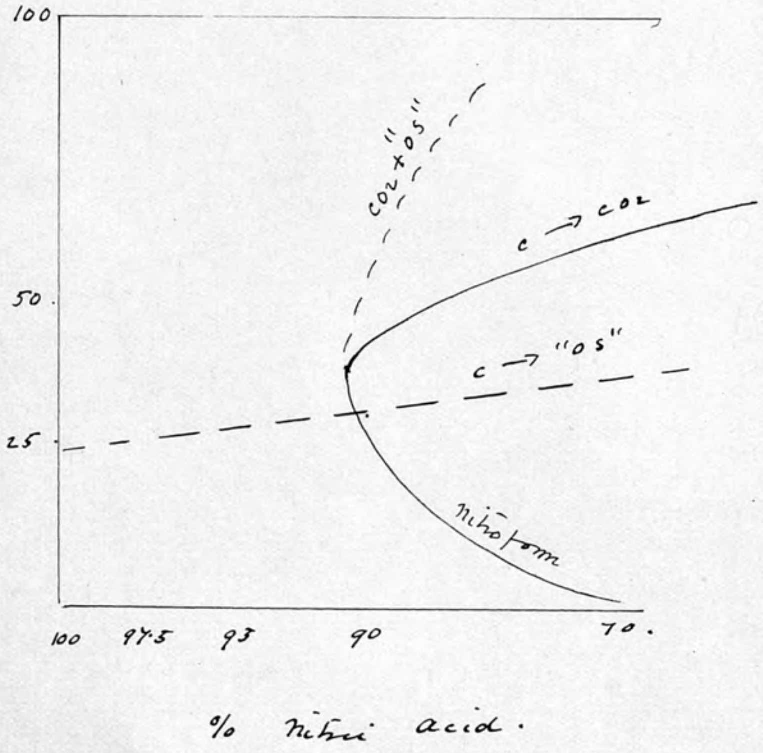
Extent of "OS"

Fig. II

Fig II A
Ethylene.



III



IV

Extent of "OS"

At the point A, fig. II, therefore, in acid of 97'5 per cent concentration, fifty per cent of the carbon reacting becomes nitroform and fifty per cent becomes carbon dioxide. As the reaction proceeds and the acid becomes more diluted, the percentage carbon becoming carbon dioxide increases and that becoming nitroform decreases. (Note the points B and B', 100 per cent nitric acid and no nitration, and C and C' at which fifty per cent of the acetylene becomes nitrated and fifty per cent oxidised, and hence the amount of carbon becoming carbondioxide is seventy-five and that becoming nitroform is twenty-five per cent. By the time a dilution of 70 per cent acid has been reached the formation of nitroform has ceased, and hence the nitroform curve falls away steeply.

On the descending curve of decreasing concentration of acid in fig. I, the fall in the yield of nitroform is due, not to an arrested reaction and a halt at the stage of the nitroalcohol, but, as would be expected, to an increased facility for the alternative reaction of oxidation. The proportion of nitroalcohol in the reaction with ethyene falls off markedly, and at a concentration of 70 per cent acid only 8'4 per cent of nitroform is formed, while at the same time, the yield of carbon dioxide, which can only therefore arise as a product of oxidation, shows a marked increase.

Sulphuric Acid. The course of the reaction is considerably modified by the addition to the reaction mixture of concentrated sulphuric acid. Such mixtures do not give rise to the normal cleavage products of the reaction with pure nitric acid, i.e. the second stage of simultaneous nitration and oxidation, with the consequent formation of nitroform and carbon dioxide does not, exceptin certain limiting cases with nitric acid largely in excess, occur. An analogy to this may be found in experiments carried out by Davis ahd Worrall, (J.Amer. Chem.Soc. 1921. <u>43</u>. 594), in which the formation of picric acid, initiated by the addition of merzuric nitrate to the nitration of benzene is eliminated by addition of sulphuric acid.

It is worth while, before examining this reaction in detail, to recapitulate briefly our knowledge of the action of pure, concentrated sulphuric acid on unsaturated hydrocarbons.

Investigation of the reaction of mineral acids with such compounds has dealt mainly with two aspects, (1) the action of dilute mineral acids, (including phosphoric and acetic acids), in aqueous solution, and (2) the interaction with concentrated or fuming sulphuric acid, the latter receiving attention mainly on the grounds of its analytical importance.

<u>Action of Sulphuric Acid on Acetylene</u>. One finds in the literature varied statements regarding the action both of concentrated and of fuming sulphuric acid on acetylene. Berthelot, (Ann.Chim.Phys. (3). <u>57</u>. 82. 1856), first examined this reaction, and stated that he obtained acetylene hydrate, or vinyl alcohol. Later, (Ann. <u>154</u>. 132. 1870), he confirmed this, showing that the action of concentrated

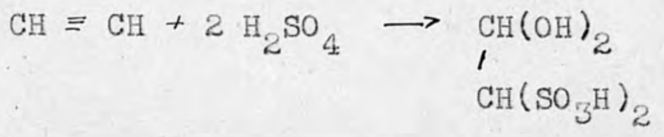
sulphuric acid on acetylene is analogous to its interaction with hydrocarbons of the formula C_nH_{2n}, giving acetylsulphuric acid, which, on distilling with water, yields acetylene hydrate and sulphuric acid. In contradistinction, the action of fuming sulphuric acid, (Berthelot ibid), produces acetylene sulphuric acid, $C_4H_2S_2O_6$.

Lagermack's and Eltkoff's later investigation of this reaction, (B. 10. 687. 1877), led to the statement that crotonaldehyde is the main product of the interactikn of acetylene and concentrated sulphuric acid, but Zeisel, (Ann. 191. 366. 1878), who had previously arrived at the same result, proved conclusively that this was erroneous the crotonaldehyde being formed from the vinyl bromide with which the acetylene was contaminated. He was unable to obtain anybcrotonaldehyde from acethlene freed from vinyl bromide.

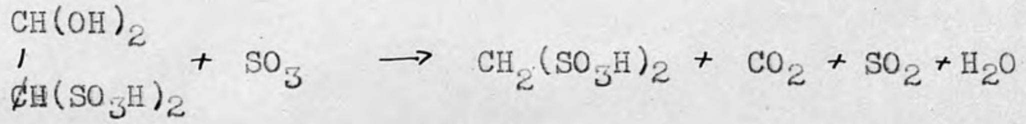
Zeisel consdiered that acetylene is only attacked very slowly by concentrated sulphuric acid, and he was only able to obtain a small quantity of the product, too small for further investigation, which he assumed to be ethylene sulphuric acid. Muthmann, (B. 31. 1802. 1898), while confirming Zeisel's denial of the formation of crotonaldehyde, was unable to isolate sufficient of the product to prove its constitution definitely as the stable methanesulphonic acid, or methionic acid.

Much more rapid is the interaction between fuming sulphuric acid and acetylene; much heat is evolved, and the reaction proceeds the

the more energetically, (Muthmann, ibid), the higher the content of sulphur trioxide. The same product -methanedisulphonic acid- as is got in the absence of sulphur trioxide is obtained. Carbon dioxide and sulphur dioxide, (no carbon monoxide), are both gaseous products of the reaction, there are no side products or reactions, and this behaviour can be correlated with that of methane disulphonic acid as follows:-



$$CH \equiv CH + 2\ H_2SO_4 \longrightarrow \begin{array}{l} CH(OH)_2 \\ | \\ CH(SO_3H)_2 \end{array}$$



$$\begin{array}{l} CH(OH)_2 \\ | \\ CH(SO_3H)_2 \end{array} + SO_3 \longrightarrow CH_2(SO_3H)_2 + CO_2 + SO_2 + H_2O$$

the first step being an addition of hydroxyl and dithonic acid. The subsequent oxidising action of the sulphuric acid is probably due to the effect of high temperature, which, in spite of ice-cooling, cannot be kept down locally.

The formation of methanedisulphonic acid and other sulphonic acids in this reaction involves, according to Shroeter, (Ber. 31. 2189. 1898), the formation of carbon monoxide,

$$CH \equiv CH + 2\ SO_3 + H_2O \longrightarrow CH_2(SO_3H)_2 + CO$$

but this is denied by Knorre and Arendt, (Verh. Gewerft. 1900. 166), as carbon monoxide is never observed.

On analogy with other fatty hydrocarbons, the form of addition suggested by Muthmann seems to be the most probable, but Shroeter, (ibid. and Ann. 303. 114. 1898), investigating the nature of the other sulphonic acids formed simultaneously with methionic acid, showed that aldehydosulphonic acid, which he had previously suggested as an intermediate stage in the formation of methionic acid, can by avoiding hydrolysis, be made to predominate in the product at the direct expense of methionic acid. By hydrolysis, aldehydodisulphonic acid yields methionic acid and formic acid.

$$CH \equiv CH + O(SO_3H)_2 \longrightarrow OCH.CH(SO_3H)_2 \qquad \text{i}$$

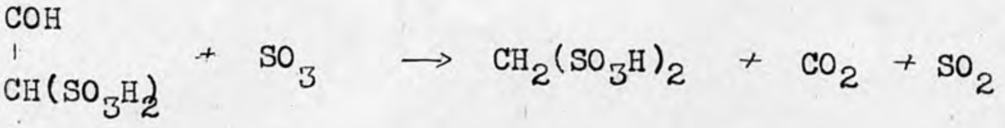
$$+ H_2O$$

$$\longrightarrow H.COOH + CH_2(SO_3H)_2 \qquad \text{ii}$$

(N.B. Stage ii occurs in such dilution, and at such temperature that carbon monoxide is never ~~observed~~ formed).

If aldehydodisulphonic acid is actually an intermediate stage, and not a second reaction which takes place independently of the first, its formation may be harmonised with Muthmann's equation, which alone accounts for the actual observed evolution of carbon dioxide and sulphur dioxide, as follows:-

$$CH \equiv CH + 2\,H_2SO_4 \longrightarrow \begin{array}{c} COH \\ | \\ CH(SO_3H)_2 \end{array} + H_2O$$



$$\begin{matrix}\mathrm{COH}\\ |\\ \mathrm{CH(SO_3H)_2}\end{matrix} + SO_3 \longrightarrow CH_2(SO_3H)_2 + CO_2 + SO_2$$

To a certain extent, also, hydrolysis of aldehydodisulphonic acid occurs, with the formation of methionic acid and formic acid, both of which substances were isolated by Shroeter.

The respective actions of concentrated sulphuric and concentrated nitric acids on acetylene thus reveal considerable analogy. In both the process seems to be one of simple addition, with the formation of a hydroxo-nitro compound, or a hydroxy-sulphonic compound, subsequent elimination of water giving the aldehyde compound, and finally a nitrohydrocarbon or sulphonic acid, with the splitting off of carbon dioxide. In both cases the evolution of carbon dioxide may also be the result of direct oxidation.

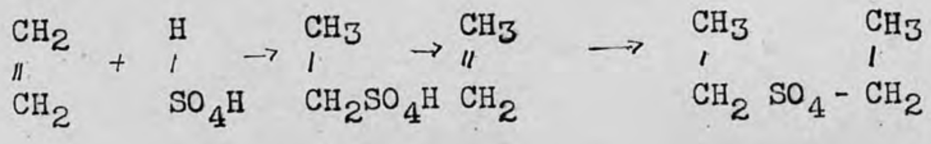
The Action of Sulphuric Acid on Ethylene Hydrocarbons. We again owe to Berthelot, (Ann.Chim. (3) 43. 385. 1855)$\frac{3}{\ast}$ the first examination of the reaction which occurs when ethylene is absorbed by concentrated sulphuric acid. He established the formation of ethyl sulphuric acid, and, further, the hydrolysis of the compound to ethyl~~e~~ alcohol on pouring the product into water. Berthelot showed, (ANN. 94. 78. 1855) that propylene undergoes even more readily a similar reaction, and by hydrolysis of the sulphuric acid addition compound can be made to yield a theoretical quantity of propyl alcohol. This reaction was shown by Fritzsche, (Zeit. Angw. Chem. 9. 456. 1866), to be sufficiently regular and complete to serve as a quantitative method of estimation of the hydrocarbon. The formation of diethyl sulphate, involving as it does the further acetylation of the addition compound, ethyl sulphuric acid, and hence the prevention of hydrolysis, was recognised, and late Plant and Sidgewick, (J.SOC. Chem.Ind. 1921. 40. 147) examined the reaction in more detail and showed that the absorption of ethylene by 99'3 per cent sulphuric acid at 70° gives a product whish, on pouring into water, yields am oil which is practically pure diethyl sulphate. A small quantity of ethyl sulphuric acid is also present, but this shows little tendency to hydrolyse, as only traces of ethyl alcohol could be detected.

But it is to Damiens, (C.r. 175. 585. 1922), that we owe our complete knowledge of this reaction, and the conditions of formation of ethyl sulphuric acid, and from it ethyl alcohol on the one hand and diethyl sulphate on the other. Absorption of acid of 99 - 100 per cent strength gives mainly diethyl sulphate, but equilibrium in the equation

$$H_2SO4 + SO_4.C_2H_5 \longrightarrow 2\ C_2H_5.SO_4H$$

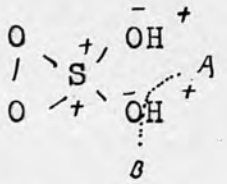
is displaced in favour of ethyl sulphuric acid by rise of temperature, and by hydration of the acid when further hydrolysis of the ester and formation of ethyl alcohol occurs.

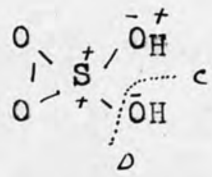
At first sight there seems to be little analogy between the reactions initiated by the absorption by concentrated sulphuric acid of acetylene and of ethylene. In the former addition to the unsaturated link takes place largely, (and this predominates as the concentration of the acid becomes high), as hydroxyl and the group (SO_3H), leading ultimately, by a subsequent process of oxidation to the production of methane disulphonic acid. Only, apparently, in the slihgtly hydrated acid, i,e. in the absence of sulphuric trioxide, does a dissociation of the acid into the groups (H) and (SO_4H) occur, and addition take place as such. On the contrary, absorption of ethylene by anhydrous sulphuric acid, as well as by more dilute acids, promotes addition to the double bond in all cases of the elements (H) and (SO_4H). The addition in more dilute acid of the elements (OH) and (SO_3H) giving the addition compound, $CH_2OH - CH_2SO_3H$, which by hydrolysis yields ethyl alcohol and sulphuric acid, is not precluded, but, in that ethyl sulphuric acid is an observed product in such reactions, and by hydrolysis yields directly ethyl alcohol, such an addition is improbable. In highly concentrated and anhydrous acids, however, the formation of diethyl sulphate from ethyl sulphuric acid by prolonged absorption of ethylene definitely precludes this form of addition, for it is difficult to conceive of the formation of this compound other than by the following route:-

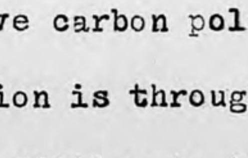
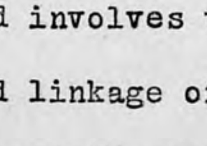


$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + \begin{matrix}H\\ |\\ SO_4H\end{matrix} \rightarrow \begin{matrix}CH_3\\ |\\ CH_2SO_4H\end{matrix} \rightarrow \begin{matrix}CH_3\\ \|\\ CH_2\end{matrix} \longrightarrow \begin{matrix}CH_3 & & CH_3\\ | & & |\\ CH_2 & SO_4 - & CH_2\end{matrix}$$

A probable explanation may be sought in the relative intensities of the electric fields of the two systems. The dissociation of sulphuric acid into positive hydrogen and the nagatively polarised radicle (SO_4H) involves cleavage of the molecule along the dotted line AB,





while by dissociation into the radicles (OH) and the positively polarsied group (SO_3H) the cleavage line CD is produced. In the first case union with carbon is established through oxygen, and involves the positive carbon pole of the ethylene molecule, while in the second the union is through sulphur, and involves the negative carbon pole. Since addition to the unsaturated linkage of acetylene or ethylene must be preceeded by a conversion of the co-valency of either carbon atom into an electrovalency, and hence the creation of a polar field, and since acetylene is less readily, and hence more feebly polarised than ethylene, that addition to acetylene will take place the most readily which involves radicles of highest polarity. In the relative dissociation of sulphuric acid into (OH) and (SO_3H) or into (H) and (SO_4H) it is obvious that, other things being equal, the group~~s~~  is in a highly positively polar condition, while the group  , owing to the proximity of three strongly negative groups, owes its polarity, a nagative one, to one atom only. Hydroxyl, by virtue of its key atom, oxygen, may be supposed more highly polar than is hydrogen, and hence the addition to acetylene of the groups (OH) and (SO_3H) is preferred to the alternative addition of (H) and (SO_4H).

Acetylene and a ''Mixed Acid'' Preliminary examination of the effect of the addition of concentrated sulphuric acid to mixtures of nitric acid and acetylene showed that in the main the reaction followed quite another course to that undergone in the presence of nitric acid alone. No nitroform or other coloured nitro compounds are observed, nor can tetranitromethane be obtained from the product on further nitration, showing that all precursors of this substance are absent. Only in the presence of mercury, or in a large excess of nitric acid over sulphuric acid, (of 75 per cent and upwards by weight of the mixture), is nitroform, and subsequently tetranitromethane, formed, and then only in very small quantity.

Kekulé, (B. 6. 329. 1869), had examined the action of a nitric-sulphuric acid mixture on ethylene and had isolated, besides the products of simple oxidation, an oil, to which he gave the constitution of an ethylene glycol-nitrite-nitrate, but with this exception no previous knowledge was available, though while the investigation was in progress a brief examination of the products of the reaction of ethyelne and a "mixed acid" was made by Mareschi, (Atti. Accad.Lincei.

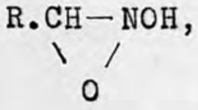
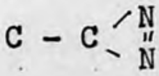
1919. (v). 28.i. 393), who showed that ethylene dinitrate, -dinitro-glccol- was the principal product.

Subsequent to our study of the absorption of acetylene by a "mixed acid", Wieland and Sakellarios, (ibid), examined in considerable detail the similar absorption of ethylene by a mixed acid containing sulphur trioxide, (20%), confirming the formation of ethylene dinitrate and β-nitroethyl nitrate. Identification of the nitric ester of pure nitroethyl alcohol with this nitroethyl nitrate points to the formation of nitroethyl alcohol as an intermediate stage. In the light of the addition of nitric acid to the unsaturated linkage of acetylene and etyylene this reaction is of considerable interest, for it is, as with nitric acid and sulphuric acid independently, primarily additive, giving rise to the addition product~~s~~ β-nitroethyl alcohol, the same addition product as is obtained from ethylene by the interaction with pure nitric acid. But in the nitric acid medium this compound would be readily oxidised to nitroacetic acid, and its isolation as the alcohol is a matter of some difficulty. Traces of the intermediate nitroaldehyde have also been observed. The presence of sulphuric acid promotes the etherification of this hydroxy compound, and β-nitroeethyl nitrate, $CH_2.NO_2 - CH_2.O.NO_2$, is produced, together with the dinitrate $CH_2.O.NO_2 - CH_2.O.NO_2$, arising obviously by a second process of addition i.e. of the groups (OH) and (O.NO), which compound then undergoes simultaneous etherification and oxidation to the dinitrate.

In the following year Wieland and Rahn, (B. 54. 1770. 1921.) extended their study of this reaction to the interaction between --diphenylethylene and pure nitric acid, and here the primary addition follows exactly the lines of the addition to the ~~unsaturated~~ unsubstituted hydrocarbon giving $\alpha\alpha$-diphenylethyl alcohol. The rapidity and ease of addition to the double bond is brought out here very clearly, for by heating ~~ethylene~~ $\alpha\alpha$ -diphenyl ethylene in light petroleum with gaseous nitrogen peroxide the addition of two nitro groups takes place, and the dinitro compound, $\beta\beta$-dinitro-$\alpha\alpha$ -diphenyl ethylene, is produced. BUt in the presence of a trace of water, this reaction is almost entirely superceded by the addition of hydroxyl and nitro groups, with the formation of a nitroalcohol. This compound is a crystalline solid, which can readily be isolated from the reaction mixture, and in that the presence of the phenyl nuclei stabilises the compound towsrds oxidation there is no detruction of the alcohol in the nitric acid medium, and an almost theoretical yield is obtained.

Rxamination of the action of a "mixed acid" on acetylene and ethylene reveals, as has been said, several marked differences of behaviour to the normal reaction with pure nitric acid. There is a considerable increase in the proportion of hydrocarbon absorbed relative to the volume of acid. The absence of gaseous products of the reaction other than a very slight evolution of nitrous fumes, indicated that oxidation reactions do not occur, while corresponding with this the products of nitration involved in the various stages leading to the ultimate formation of nitroform are absent also; a fact which receives confirmation in the non-formation of even a trace of tetra-nitromethane, except by the further nitration of mixtures in which nitric acid has been largely in excess. The most characteristic reaction of the water-diluted product is the formation of the intensely coloured alkali salt, characteristic of dinitromethane, on making alkaline, which on hydrolysis readily liberates the volatile base, ammonia.

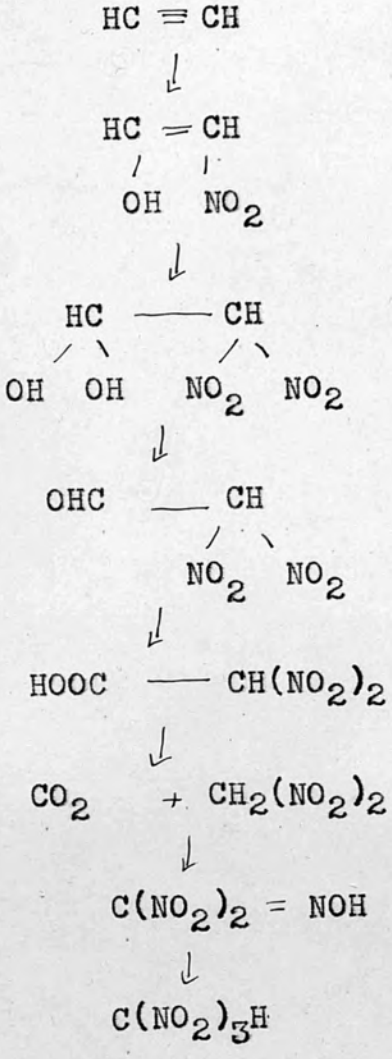
The problem is much more complicated than the isolation of simple sulphonic acids or nitrohydrocarbon derivatives. The presence of both nitrate and nitrite renders the isolation of the not very in-soluble barium salts of methionic acid and like substances -supposing such substances to be formed- extremely difficult. On the other hand most pseudo-acid nitrogen compounds, -and there are various indications that such compounds occur in the product - are extremely sensitive to nitrous acid. Nitroform is completely decomposed by heating in aqueous solution containing nitrous acid, while the formation of nitroso alcohols and nitrolic acids in this way is well known.

But the behaviour of the product suggests that we have present as an intermediate stage at least, one of the unsatble nitrolic acids, investigated by V.Meyer, (Ann.175. 88; 180. 170; 214. 320), and later extremely fully by Hantzsch, (B. 31. 2754. 1898) 32. 3037.1899) These acids dissolve in alkalis with an intense red colour, changing immediately to the colourless acid on addition of mineral acids, or on standing, and by acid or alkaline hydrolysis yielding ammonia. This behaviour is quite distinct from that of true aci-nitro compounds,  $R.CH{-}NOH$ with O bridging CH and N, (Hantzsch, ibid), which decompose into the corresponding aldehyde and the residue (:NOH), combination then occurring with the formation of the nitroso alcohol. None of these compounds give any but pale or colourless salts. The property of forming intensely coloured red-brown salts, the marked intensification of colour with ferruc chloride and the formation of a volatile base on boiling with acids or alkalis are all, therefore, characteristic of the linking ~~NxIxCxIxCxIxNx~~ N - N - C - N, or  $C - C{\diagup N \atop \diagdown \overset{\|}{N}}$,(containing at least one nitro and one oximido group), and their derivatives, as distinct from aci-nitro compounds.

In the sulphuric acid medium, therefore, the principal products of the reaction are (1) nitric esters, formed by etherification of the nitro alcohol in the presence of concentrated sulphuric awid, and (2) a nitrolic acid corresponding to the hydrocarbon used. The first is the predominating reaction, and from the quantities of esters which can be isolated it accounts for a large proportion of the hydrocarbon. It is in complete harmony with the course of the reaction which has beeh described as taking place in pure nitric acid and in pure sulphuric acid. The primary reaction consists in all cases of a simple addition to the unsaturated linkage of the component parts of the acid. Whether sulphuric acid be present or not it is possible that this nitro-alcohol addition product of the action of nitric acid is etherified to a slight extent by the acid, though in such circumstances this reaction is subordinate to the formation of nitroform. But if sulphuric acid be present etherification is facilitated and becomes the predominating reaction to the complete exclusion of nitroform, though not to such exclusion of certain intermediate products of that reaction. For, as will be remembered, however the formation of nitroform from acetylene or ethylene be viewed, it involves at some stage the intermediate formation of a nitrolic acid, which, in the concentrated acid medium is oxidised, according to its kind, either to dinitromethane or to trinitromethane. It is obvious, therefore, that in the presence of a considerable quantity of concentrated sulphuric a acid, the oxidation of such acids would largely or entirely be prevented, and at the same time their stability in the highly concentrated acid medium would be increased, and they would actually, therefore, appear as partial products of the reaction. The following outline of the reactions involved in the three media will show this more clearly.

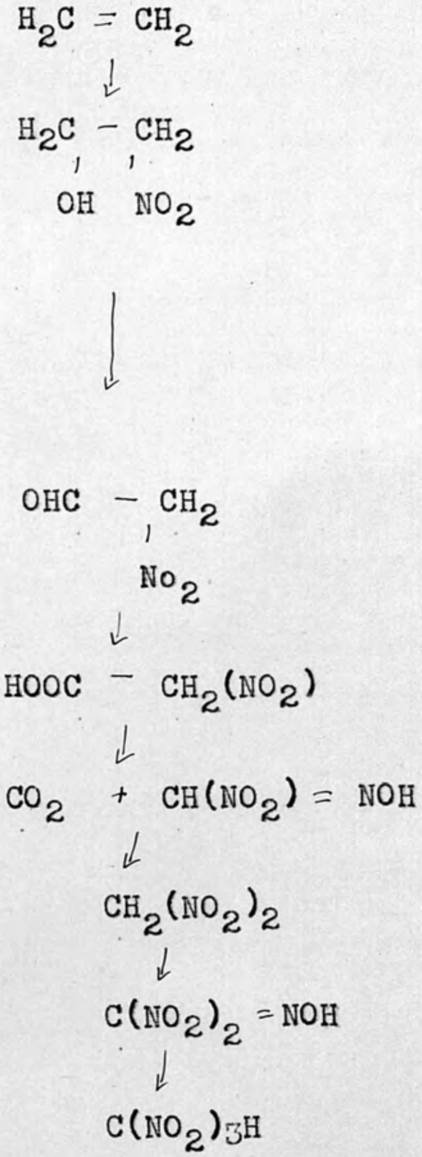
However the reaction with these two types of hydrocarbon be viewed it is essentially one of simple addition to the unsaturated bond of the dissociated products of the acid.

Acetylene.

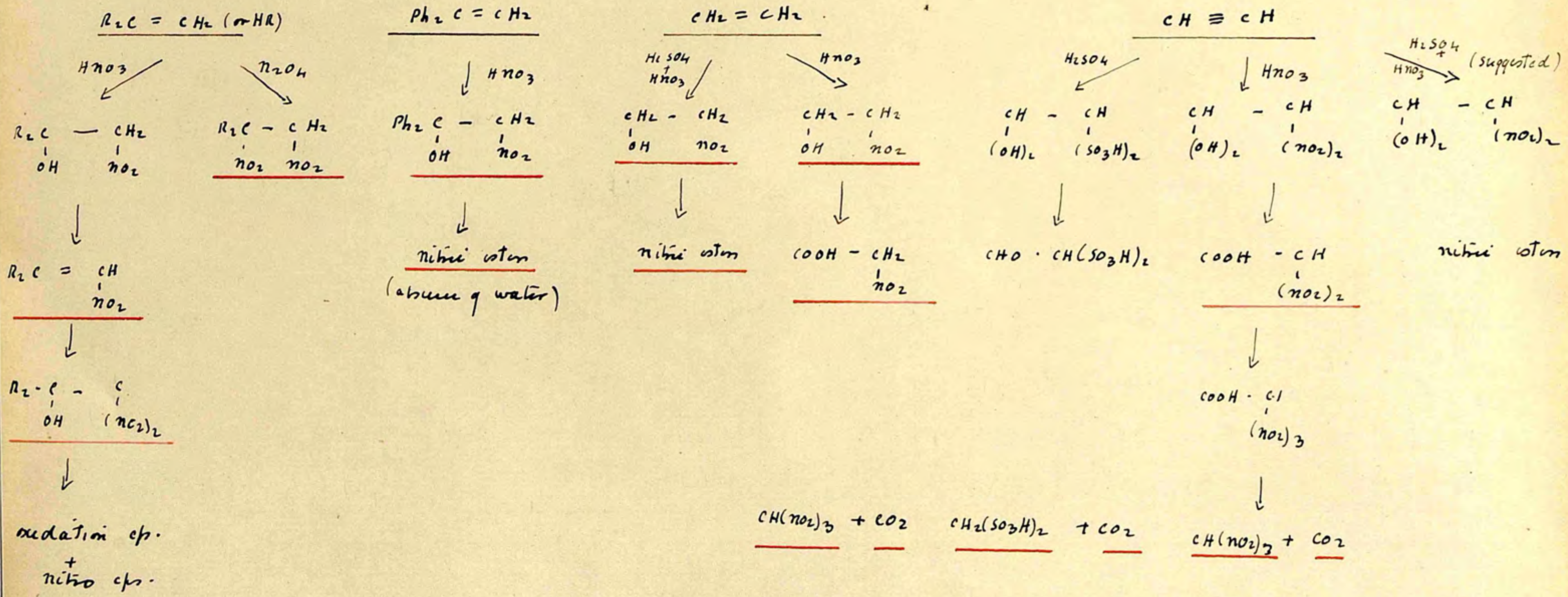


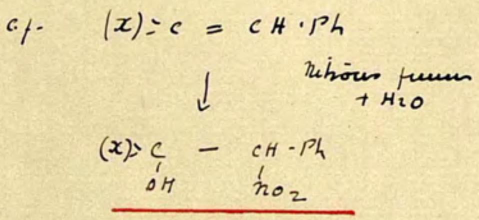
$$\begin{gathered}
HC \equiv CH \\
\downarrow \\
\underset{OH}{HC} = \underset{NO_2}{CH} \\
\downarrow \\
\underset{OH\ \ OH}{HC} - \underset{NO_2\ \ NO_2}{CH} \\
\downarrow \\
OHC - \underset{NO_2\ \ NO_2}{CH} \\
\downarrow \\
HOOC - CH(NO_2)_2 \\
\downarrow \\
CO_2 + CH_2(NO_2)_2 \\
\downarrow \\
C(NO_2)_2 = NOH \\
\downarrow \\
C(NO_2)_3H
\end{gathered}$$

Ethylene.

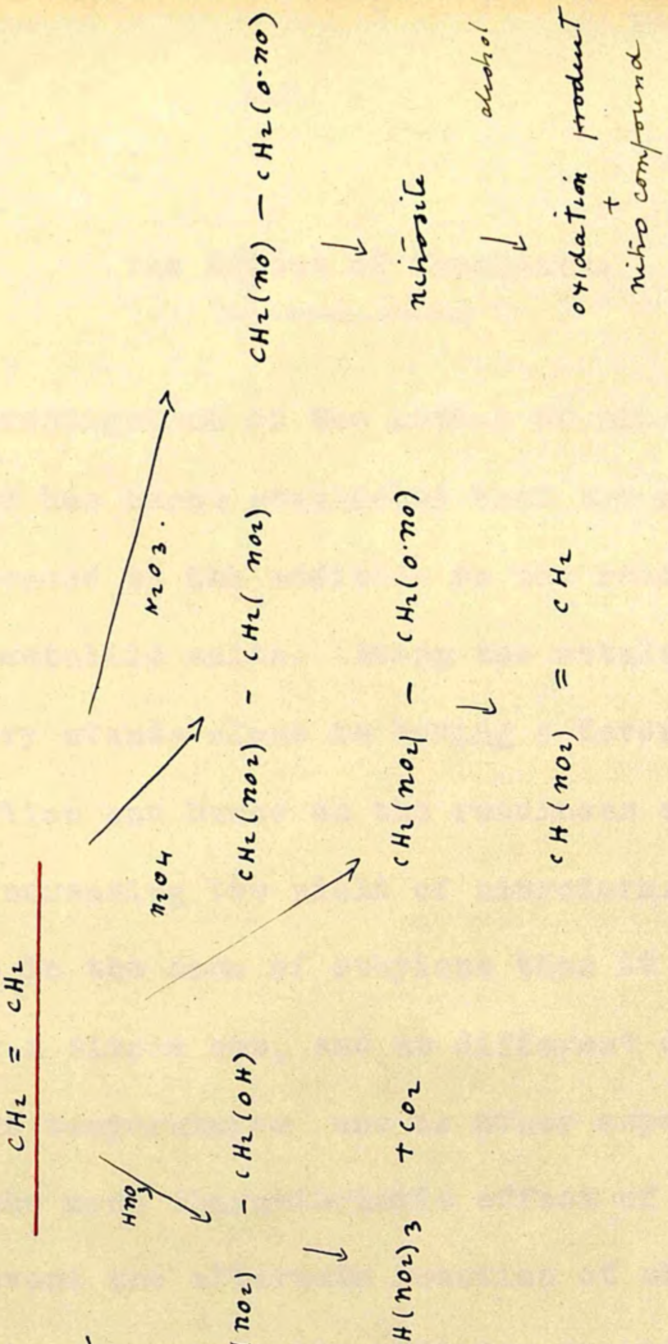


$$\begin{gathered}
H_2C = CH_2 \\
\downarrow \\
\underset{OH}{H_2C} - \underset{NO_2}{CH_2} \\
\downarrow \\
OHC - \underset{No_2}{CH_2} \\
\downarrow \\
HOOC - CH_2(NO_2) \\
\downarrow \\
CO_2 + CH(NO_2) = NOH \\
\downarrow \\
CH_2(NO_2)_2 \\
\downarrow \\
C(NO_2)_2 = NOH \\
\downarrow \\
C(NO_2)_3H
\end{gathered}$$





[Known compounds underlined in red]


$CH_2 = CH_2$
$H_2SO_4 + HNO_3$
HNO_3
N_2O_4
N_2O_3.
$CH_2(NO_2) - CH_2(OH)$
$CH_2(NO_2) - CH_2(OH)$
$CH_2(NO_2) - CH_2(NO_2)$
$CH_2(NO) - CH_2(O \cdot NO)$
$CH_2(NO_2) - CH_2(O \cdot NO_2)$
$CH(NO_2)_3 + CO_2$
$CH_2(NO_2) - CH_2(O \cdot NO)$
nitrosite
alcohol
$CH(NO_2) = CH_2$
oxidation product
+
nitro compound

The Effect of Catalysts.

In the investigation of the action of nitric acid on acetylene and ethylene it has been established that the reaction is very ~~kxx~~ merkedly influenced by the addition to the reaction mixture of small quantities of metallic salts. Among the metals which have been examined mercury stands alone in having a favourable effect on the rate of absorption and hance on the readiness of interaction, and in considerably increasing the yield of nitroform. This effect, which is rather less in the case of ethylene than it is for acetylene, is not altogether a simple one, and at different concentrations as well as at different temperatures one or other aspects may be the more marked. But the most characteristic effect of the mercury salt is largely to prevent the alternate reaction of simple oxidation, and to increase proportionately the addition reaction producing the nitro-alcohol, and further the extent of the subsequent nitration-oxidation reaction producing nitroform. Among the metals platinum, uranium, silver and copper which have been examined in this connection, all depresss the absorption of the hydrocarbon, and all save copper favour simple oxidation of the hydrocarbon at the expense of the production of nitroform, while platinum causes an increase in the formation of by products.

The effect of caralysts on the addition reactions of unsaturated hydrocarbons and concentrated mineral acids has been little studied. In 1913 Lebeau and Damiens, (C.r. <u>156</u>. 557.), showed that the speed of absorption of ethylene by sulphuric acid is considerably increased by certain metallic salts, e.g. vanadium and uranium. A one per cent solution of vanadic acid in concentrated sulphuric acid absorbs one hundred and fifty times its volume of ethylene in a few minutes, while a one per cent solution of uranyl sulphate behaves similarly. Tungsten and molybdenum similarly increase the reate of absorption, but more slowly. These experiments were, however, carried out with the object of finding a ralid absorbent of ethylene for analytical purposes, and therefore involved the presence of mercury in the gas burette in which the absorption was carried out. Later, Damiens, (ibid <u>175</u>. 585. 1922) submitted this reaction to a detailed study, and showed that an equally marked increase of absorption of ethylene takes place in the presence of cuprous oxide, this substance being more efficacious as a catalyst for this reaction than any of the substances examined. Damiens postulates the preliminary formation of a complex, which is partially soluble in sulphuric acid.

$$C_2H_4 + H_2SO_4 + CuSO_4 \longrightarrow SO_4Cu_2.n(C_2H_4)$$

He gives no evidence of having actually isolated this addition compound. The complex is attacked by the acid with the formation of ethylsulph-

-uric acid, and either ethyl alcohol or diethyl sulphate according to the conditions. Hence the function of the catalyst is here conceived to be that of an intermediate agent, through the medium of which a loose complex of the two reacting substances is established.

Many instances are known, of course, of the catalysis of the addition of elements, - of halogen, of halogen acid or of water - to unsaturated systems. Such catalytically influenced reactions form the basis of many of our common laboratory and industrial methods of preparation of the resulting addition compounds, but the mechanism of the chemical action of the catalyst has received little attention, and beyond the more obvious effect of accelerating the speed of reaction, has been ignored.

It is obvious from the study of the action of mercury in the absorption of acetylene and ethylene by nitric acid, and by mixtures with sulphuric acid, that the metal has a far-reaching effect, not only on the speed of the reaction, but also on the actual course of the reaction. Before discussing this effect in more detail it is worth while examining some of the reactions in strong acid media in which mercury or its salts have been known to play a part.

The use of mercury as a catalyst of the oxidising function of concentrated sulphuric acid at high tenperatures is well known, and in such cases the action of the metal seems purely catalytis of the velocity of oxidation, the sulphuric acid, at the temperature em-

-ployed acting specifically as an oxidising agent, whethervthe catalyst is present or not.

As a catalyst of the sulphonation by cold, concentrated sulphuric acid, the use of mercury is also not unknown, though here its use has been even less explored. Iljinsky, (B. 36. 4194. 1903), showed that sulphonation of anthraquinone takes place mush more easily in the presence of mercury. Besides the -monosulphonic acid, which is formed in considerable yield, the 1 : 5-, 1 : 8-, 1 : 7- and 1 : 6-disulphonic acids also appear among the products. The process has been patented, D.R.P. 149. 801. Freid. Bayer &Co. 1902., for the preparation of anthraquinone- -monosulphonic acid, and for anthraquinone-1 : 5- and 1 : 8-disulphonic acids, as described by Schmidt, (B. 37. 66. 1903) The significance of the action of mercury in this reaction lies, however, in the change in orientation from anthraquinone- -monosulphonic acid, the normal product of sulphonation, to anthraquinone- -monosulphonic acid in the presence of mercury. A similar, though slighter effect has been onserved in the sulphonation of toluene, where the presence of mercury decreases the ratio of ortho and para isomers from $\frac{40 - 50}{60 - 50}$ tp 31 ¢ 69, (Holdermann. B. 39. 1250. 1906). But examination of the sulphonation of benzoic acid, of -naphthol and of the nitration of toluene, nitrobenzene and anthraquinone reveals the absence of any effect of the mercury salt, (Holdermann, ibid). The effect of mercury in the sulphonation of anthraquinone is, however, parallelled by that of boric acid in the sulphonation of 1 : 4-amidooxyanthraquinone, by the addition of which substitution of the sulphonic group on the already substituted nucleus is superceded by substitution on the unsubstituted nucleus.

The use of mercury salts in reactions involving nitric acid has received a certain measure of attention, though little other than purely qualitative investigation has been extablished. One frequently finds in the literature of the subject statements to the effect that the action of mercury in such reactions has a purely oxidative function, and that when nitration occurs at all, its extent is very much diminished. As has been shown, this is by no means always the case.

Wolffebstein and Boters, (B. 1913. 46. 586), examining the action of mercury salts in the nitration of benzoic acid and its homologues, state that in highly concentrated acid media the salt is entirely without effect, but that in more dilute acid media the yield of nitro product is diminished and oxidation reactions lead to the formation of nitrophenols. A similar effect in the nitration of benzoic acid in the presence of mercuric nitrate is observed by Wolffenstein and Paar, (B. 1913. 46. 589)

Vignon, (Bull.Soc. 1920. 27. 547), observes that a considerable yield of picric acid is obtained by addition of ten per cent of mercuric nitrate to a benzene nitration mixture.

A lengthy investigation of the role of mercuric nitrate in the nitration of benzene, carried out by Davis, Worrall, Drake, Helmkamp and Young, (J.Amer.Chem.Soc. 1921. 43. 594), loses much of its value as the authors fail to distinguish between the relative nitrating effect of concentrated and dilute nitric acidsm and nitration and oxidation effects are attributed to the action of mercury which can readily be interpreted as functions of the concentration of the acid. Certain facts of significance, however, emerge. It seems clear that, in the nitration of benzene by commercial nitric acid in the presence of mercuric nitrate, (in quantity equal to ten per cent of the benzene used), brings about a complete conversion of the benzene into mononitrobenzene and picric acid, while in the absence of mercury, in a similar medium, much of the benzene is unaffected. Moreover, the recovery of unchanged nitro compound from a series of experiments in which mononitro, dinitro- and symmetrical trinitro- benzene and trinitrotoluene respectively were boiled with nitric acid, (1'4), containing mercuric nitrate indicates that at least in the presence of previously substituted nitro groups, mercury in no way facilitates the oxidising action of the nitric acid. In the nitration of mononitro benzene to dinitrobenzene the addition of mercuric nitrate decreases the yield of dinitrobenzene. Increase in the proportion of the mercury salt from 0'00046 moles to 0'263 moles in the nitration of benzene by a large excess of nitric acid, (1'4), causes a marked, though not proportional, increase in the yield of picric acid, and, except with very small concentrations of mercuric nitrate, where a preliminary rapid incraese is obtained, decreases the yield of nitrobenzene. The subsequent increase in this yield by increase of the mercury concentration above 0'046 moles of mercuric nitrate, is only substantiated in the graph given by the authors by one point. There is little evidence for the statement that mercury takes part in the reaction, forming an intermediate complex.

In a similar reaction with naphthalene, (Davis&c ibid. 44. 1588. 1922), the product contains, in addition to the normal products of nitration, a small proportion of the nitration products of α-naphthol.

A detailed study of the relative oxidising and nitrating functions of nitric acid in its interaction with organic compounds, and the effect on such systems of mercuric nitrate, has recently been made by Klemenc and Scholler, (Zeit.Anorg.Chem. 141. 231. 1924)¾ Klemenc and Pollak, (ibid. 115. 131. 1921), had previously shown that traces of mercuric nitrate negatively catalyse the oxidation of arsenious acid by nitric acid. Regarding nitration as a reduction-oxidation process, in which the nitro body is the reduced product,

i.e. $HNO_3 + 2H \rightarrow HNO_2 + H_2O$

so $HNO_3 + RH \rightarrow R.NO_2 + H_2O$

mercuric nitrate, as examined ~~bxxh~~ by these authors in the nitration of phenol, has a similar, though less extensive, effect in nitration. The second process of oxidation, shown to accompany nitration, is also influenced by mercury, and the supposition is put forward that the action of the mercury ions lie in postponing, or bringing to a stand@ -still, this secondary oxidation process with which nitration is intimately bound up. But nitration of phenol does not occur in the presence of a large excess of nitrous acid and mercury, and the authors find it impossible to assign a definite role to the action of the mercury salt.

Thus we are faced with two directly opposing statements, i.e. that the oxidising action of nitric acid is considerably increased by the presence of mercuric nitrate, and, on the other hand, that the oxidising, (and nitrating)m action of the acid is depressed by mercury.

There are isolated examples in the literature of the use of other metals as catalysts of reactions of nitric acid. Copper, silver, manganese and aluminium have all benn patented as promoters of the preparation of nitrophenols by the action of nitric acid on benzene. Davis, Worrall &c, (ibid), comparing the effect of these and other metals with that of mercury, show that it is in all cases less.

In the nitration of phenol to picric acid iron salts accelerate the decomposition of the acid, and diminish the yield of picric acid. The nitration here is carried out in 60 - 70 per cent aqueous nitric acid media, and the negative catalytic effect of the iron salt is correlated with the known decomposing effect of metals in solution in nitric acid. Other examples of the catalytic effect of iron salts in acid media are not lacking. In the liberation of iodine from potassium iodide by hydrogen peroxide in the presence of ferrous salts, the iron does not act catalytically, but is itself oxidised, but in acid solution the iron is a positive catalyst, (Manchot and Wickelm. B. 34. 2479. 1901). Mummery, (J.Soc.Chem.Ind. 32. 889. 1913), attempts an explanation of this catalytic function of ferrous ion by supposing the formation of a perhydrol, Fe.O.OH, which promotes oxidation by alternate production from and reconversion into ferrous salt, when an oxidisable substance is present.

In dilute nitric acid ferric salts retard the solvent action of the acid on mercury, while manganese and sodium nitrates are positive catalysts for this reaction, (Ray. T. 99. 1012. 1911). Ferrous salts, on the other hand, are positive catalysts of the solution of copper, silver, nickel and mercury in nitric acid, an effect to be attributed to the formation of nitrous acid by the action of ferrous ion on nitric acid, (Banerji and Dhar. Zeit.Anorg. 122. 73. 1922). Oxidising agents are therefore negative catalysts, since they prevent the formation of nitrous acid. By the reducing action, however, of of copper and silver on ferric salts, ferrous ion is produced, and hence ferric salts are positive catalysts of this reaction.

From these somewhat isolated data two tentative hypotheses of the effect of metals on the action of nitric acid, neither substantiated by careful quantitative investugation, emerge. (1) The effect of metals is purely one of degradation. Reduction of nitric acid to nitrous acid and oxides of nitrogen takes place, and the acid thus diluted is rendered less efficient as a nitrating agent, the products of which are necessarily diminished. (2) As well as serving to decompose the nitric acid, it is suggested that metals, and in particular mercury, catalyse~~s~~ the oxidising function of the acid with respect to the organic compound interacting. Oxidation products of the compound are therefore obtained at the direct expense of the nitrated products. Neither of these hypotheses, though embodying certain elements of truth, are correct.

In order to establish definitely the effect of mercury salts on the process of nitration I have carried out a series of experiments on the nitration of varying types of organic compounds, both in the presence and absence of mercury salts. For this purpose I have examined in turn all the main types of nitration methods involving nitric acid, (a) concentrated and fuming nitric acid, (b) dilute nitric acid, (c) "mixed acid", (d) nitric acid plus acetic anhydride or acetic acid, (e) sodium nitrate plus sulphuric acid, (f) nitrous acid, and have extended my investigation as far as possible to most of the principal groups of nitratable organic compounds. The reactions have been examined for (1) yield of nitrated product, (2) nature of nitrated product, (3) yield, if any, of other products specific to the mercury-influenced reaction, (4) gaseous products, in particular carbon dioxide and other evidences of oxidation.

The evidence is conclusive that, except in the nitration of such organic compounds as are particularly susceptible to oxidation, i.e. aldehydes, marcury does not favour oxidation at the expense of nitration, that in general it does not hinder nitration, but in certain groups of compounds -phenols-, can even act as a positive catalyst of nitration, and that the presence of the metal causes increased interaction of the organic compound. This behaviour, moreover, is fundamentally in agreeement with the effect of mercury on the addition of nitric acid to unsaturated linkages. It is proposed, therefore, to discuss at some lenght the observed results in relation to the possible mechanism of the mercury-influenced reaction.

The question as to how all the conflicting evidence of the literature can be harmonised, and how, in the light of our knowledge of the effect of mercury on the addition of nitric acid to unsaturated linkages and on the nitration of aromatic systems, the true function of the metal is to be interpreted must depend for its complete answer on an intimate knowledge of the reacting condition of solutions of nitric acid containing mercury, and at present such knowledge is far from being complete or firmly established. But here too suggestive light is thrown upon the reaction by the application of modern structural views, and this conception, together with the observed effect of mercury, enable us to suggest with a considerable measure of probablitiy a definite course of reaction.

The effect of the addition of mercuric nitrate to various types of reaction can be briefly summarised:-

	Nitrating Mixture.	Effect of Mercury.	
		Maximum effect on Total Nitration	
1.	Nitric acid. concentrated	+ 26·7 %	(o-cresol)
2.	,, ,, dilute.	+ 41·6 %	(phenol)
3.	Nitrous acid.	— ve	
4.	Sodium nitrate plus sulphuric acid.	+ 19·1 %	(benzoic acid)
5.	"Mixed acid".	+ 18·5 %	(naphthol)
6.	Addition of nitric acid to unsaturated linkages.	+ ve	
7.	Addition of nitric acid in a "mixed acid" to unsaturated linkages.	+ ve	
8.	Solution of mercury in nitric acid.	≑ 15%	
	Comcentrated.		
	Dilute.	≑ 30%	

Obviously, therefore, the effect of mercury in such reactions is rarely negligible; it is frequently considerable, and there is undoubted evidence that simultaneously or not, both the nitrating and oxidising functions of the acid can be catalysed.

A brief recapitulation of the reactions which take place on the dissolution of a metal, and in particular of mercury, in nitric acid will show the composition of the nitric acid-mercuric nitrate mixture we are dealing with.

It has been shown that the same reactions are initiated, though more slowly and to a less extent, by the dissolution of mercury salts, copper &c in concentrated nitric acid as in more dilute acid. In the majority of experiments carried out for this research the quantity of mercuric nitrate used was small, - 0'5 - 2 per cent of the weight of the nitric acid, but it has been established that the reaction is fundamentallyunaltered in character, and practically in extent by even large increase in the amount of mercury salt used.

The presence, therefore, in the concentrated nitric-nitrous acid mixture of small quantities of mercuric nitrate produces primarily in corresponding amount mercurous or mercuric nitrite and nitric oxide. The nitrite formed is decomposed by the nitric acid, reproducing nitrous acid and mercuric nitrate, while the nitric oxide, owing to its high solubility, reaching a high concentration in the nitric acid, reduces the excess nitric acid, thus providing a further source of nitrous acid. (c.f. p 11). The reaction is therefore, if nitrous acid be regarded as the effective agent, autocatalytic.

The ionic condition of the mixture when an appreciable quant-

-tity of the mercuric salt ~~g~~ has dissolved, may be represented as consisting of mercurous and mercuric ions, a low concentration of NO_3' ions, and an increasing concentration of NO_2' ions. In the absence ~~presence~~ of mercury or other metallic salt, the concentrated acid mixture would contain merely a low concentration of nitrate and nitrite ions. Further, the accumulation of nitrous acid in the solution as the reaction proceeds probably initiates the formation of nitrogen peroxide, (v. p 13.)

Consideration of the polar conditions of the two systems, in the presence and absence of metallic salts respectively, shows that in the mixture of nitric acid with an aromatic compound we have an unpolarised compound in the presence of two substances, nitric and nitrous acids, in both of which the component radicles are held by electrovalencies, and in which a certain ~~amount~~ low concentration of actual dissociated, polarised radicles exists. There is, therefore, a weakly polar field, potentially capable of becomingly increasingly polar with respect to the acid as more of the acid molecules completely dissociate, but with respect to the aromatic compound, only capable of exhibiting actual polarity in a field of high potential. The presence of an organic, unsaturated compound would, however, increase the potential polarity of the system, for, as has been shown, the conversion of the co-valencies of an unsaturated linkage into polarised electrovalencies takes place with extreme readiness. Any

Any process of addition to a double bond should therefore require less energy than a process of substitution in aromatic compounds with the same reagent. Both systems are capable of catalysis, however, in the opening up of their potentially polar fields of the organic compounds, and in increasing the dissociation of the acid. It therefore remains to determine whether the presence of mercury in such systems can bring about this change, - its relation to other metals in this respect must also be considered - and whether the observed catalytic effect on nitration or oxidation can be interpreted on this basis or by some other hypothesis.

However the action of nitric acid be viewed, whether as nitration or oxidation of any organic compound, or of addition to such a compound of the component parts of the acid, such action implies polarisation of the compound, and potential dissociation into the elements (OH') and (NO_2.), (v. p 2, and equations i - v), the relative extent of the two processes of nitration and oxidation depending primarily on the nature of (R). It would be expected that nitration would be the predominating reaction when (R) is negative, and that oxidation would be favoured if (R) were positive, a rough basis of classification of the relative functions of nitric acid in aliphatic and aromatic compounds being thereby obtained.

Catalysis of any one of these reactions must, therefore, consist in durectly influencing the hydroxyl dissociation or polarisation of the acid, or in facilitating the conversion of the co-valencies of the organic compound into electrovalencies. The ready tendency shown by mercuric salts to combine with hydroxyl to form basic compounds is of significance in this connection. The formation of such a basic salt as $Hg(NO_3)_2.2H_2O$ would increase the partial dissociation of nitric acid into the ions (OH') and (NO_2). This would be of value only in so far as it created a greater tendency to such dissociation independent of the actual withdrawal of hydroxyl by the basic salt, and it is doubtful whether any appreciable effect can be attributed to this cause.

An interpretation of this specific case of catalysis must be sought for in some conception of catalysis in general, and must be based fundamentally on the mechanism of chemical change, ideas of which, in the light of our present knowledge, have had to be materially altered.

Chemical combination, which occurs by virtue of the polarised, electromagnetic force fields of which each atom forms the centre, involves the condensation with evolution of energy, of these fields, for each atom, at points of opposite polarity, the loss of energy being in terms of the elementary quantum. Such primary condensation will not involve the residual poles of the fields pertaining to each atom, and a secondary condensation between these fields must obviously occur if the molecules are to stable, and ~~it~~ on the completeness or incompleteness of this secondary condensation will depend o the relative reactivity of the molecules. It is obvious that a number of stages of reactivity must exist between a molecule which is completely inactive, through complete secondary condensation, and one in which the residual magnetic fields of each atom of the molecule are so different that secondary condensation can only occur to a very slight extent, giving a highly unstable molecule. "The force field condensation will take place in stages, each stage corresponding to the loss of one molar quantum of energy. A freshly synthesised molecule is unstable, and must lose one or more quanta of energy by the condensation of its atomic force fields, and so must pass into one of a number of possible phases, each consecutive phase differing in energy content by one molecular quantum. ....It is evident that if the positive or negative affinities of the external force fields are equal and opposite, the molecular force field condensation will proceed far, with the escape of many molecular quanta. In such a case the phase formed will be characterised by a highly condensed field, with its frequency situated in the extreme ultraviolet. On the other hand, if the atomic fields are unequally balanced the condensation will not preceed very far, and a balance of one type of affinity will remain uncompensated", (Baly. T. 1922. 17. 590). It follows, therefore, that the compounds whose molecules have arrived at the completely condensed state can only interact if some ecternal source of energy is present by which the lost quanta of energy can be reabsorbed, and the residual force fields thereby opened, and rendered available for further interaction. Such external energy may be radiant energy in the form of heat or light, of frequency equal to the atomic frequency of the element, or it may be supplied by one of the various groups of substances which have been included in the term "catalyst". We have in this conception, therefore, a general hypothesis which can account equally for all the many manifestations of catalytic mechanism.

In order that a substance may function as a catalyst it must possess residual affinity, a term which muat now be re-defined to mean an uncompensated residuum of force lines, or of affinity left over when the maximum condensation and loss of energy hass occured between two atoms whose original force fields were not of equal intensity. This does not imply that such a compound can always function as a catalyst. There are obviously two ways in which such an uncompensated molecule, C, can effect the electromagnetic condition of two completely closed fields of molecules XY and AB. By virtue of its residual affinity C can form an addition compound, or complex, with molecules XY or AB in such a way that the energy given up by C in the condensation is lost, and a second completely closed field is established. In such a case the addition complex will be stable and will represent the end of the reaction. On the other hand, if the infra-red frequencies of the molecules C and AB, or C and XY are identical, or if they possess certain infra-red frequencies in common, the quanta of energy lost by the condensation of C with one on the reagents may be wholly or in part absorbed by the other compound, which, by such absorption, will become more reactive. In other words, catalysis of the reaction between XY and AB, or the activation of the molecules XY or AB, with the opening up of their closed force fields by an external souree of energy supplied by the residual affinity of the compound C, has taken place. The following scheme will illustrate this:-

Given reaction $XY + AB \rightarrow XA + YB$

Add catalyst C.

(a) active molecule with uncompensated field.

(in) inactive molecule with closed field.

Then

$$C_a + XY_{in} \rightarrow CXY_a \qquad \text{i}$$

$$CXY_a + AB_{in} \rightarrow C.XY.AB_a \qquad \text{ii}$$

$$C.XY.AB_a \rightarrow AX + BY + C \qquad \text{iii}$$

It is important to emphasise that reaction (iii) can only occur by virtue of an actual rearrangement of electrons, and that this depends on the presence within the addition compound of a sufficiently sharp potential gradient between the energy level of C.XY.AB and C.XA.YB. Negative catalysis receives a ready interpretation on the lines of this conception, for, in a reaction $A + B$ when one of the molecules A or B is uncompensated,(by virtue of which the) by virtue of which the reaction takes place, any substance, C, which preferentially combines with the uncompensated molecules, and thereby establishes a closed field, hinders the first reaction.

This hypothesis of chemical reaction receives confirmation in the work of Boeschen, (Proc.K.Akad.Wetensch. Amsterdam. 1922. <u>25</u>. 210), on the photo-oxidation of alcohols in the presence of p-benzophenone and oxygen. The author does not, however, give the fullest interpretation to his results. The velocity of oxidation is, above a certain concentration of the ketone, independent of the concentration, but proportional to the square of the intensity of light and to the concentration of the alcohol. The significant feature is the immediate formation of a quantity, $kI(1 - c^{-kcd})$, of activated ketone by absorption of light of intensity I. (k = absorption coefficient, c = concentration of ketone, d = thickness of layer). When k, c, and d are large, the quantity of activated ketone is proportional to the intensity of light and independent of the concentration. Combination then occurs between the activated ketone and the alcohol molecules, and the following sreies of reactions is postulated,

$$\begin{array}{lcl}
\text{Ketone} + \text{light} & \rightarrow & \text{Photo-ketone} \\
\text{Photo-ketone} + \text{alcohol} & \rightarrow & \text{(Photo-ketone)alcohol} \\
\text{(Photo-ketone)alcohol} & \rightarrow & \text{(Photo-ketone)(active alcohol)}
\end{array}$$

$$2\ \text{(photo-ketone, active alcohol)} + O_2 \rightarrow 2\ \text{ketone} + 2\ \text{aldehyde} + 2\ H_2O$$

As well as demonstrating that the energy required for the interaction is derived from the external source, light, the experimental fact that ~~the~~ intimate contact between the catalyst and the reacting molecules is essential is of interest in the present connection.

Viewed in this light, therefore, it must be considered how far metallic salts can function as catalysts in the type of reaction with which we are dealing. That metallic salts can function as catalysts of various reactions there is ample evidence, and that they do actually play this part in reactions in strong acid media, or in reactions involving concentrated acids as reagents, has already been shown.

Any metal which in its salts is capable of forming addition complexes, i.e. with water, organic compounds &c, must possess residual affinity, and by virtue of such should be able to function as a catalyst of certain reactions. But it is to be expected that the catalytic capacity of each metal will be specific, ar at least that it will be more favourable to one type of reaction than another. This is obvious when the nature of the residual affinity is considered. Such affinity is the uncompensated balance of electromagnetic force left over from the condensation of the respective force fields of two or more atoms, and must therefore be polar. In this condition the affinity will tend to display itself the more readily when brought into contact with molecules where there is a residuum, however, slight, of affinity of opposite polarity. Though it is conceivable that, given an entirly closed field, the residual affinity will still be effective, though less readily. And from this point of view the tendency shown by mercury to form basic salts becomes of significance, for it implies that the residual affinity of mercuric salts displays itself most readily when brought into contact with hydroxyl or like groups. Consequently, therefore, the presence of mercuric nitrate in a nitric acid medium will of itself tend to promote the hydroxyl dissociation of the acid. Hence, on general grounds, any function of nitric acid which involves such dissociation will be favoured. Further, it is obvious that the effect of the strongly basic metals of group I, (v. p 6.), will be wholly negative in this respect.

In the particular addition of nitric acid to an unsaturated bond neither reagent possesses a completely closed field. Though in the resting condition of the molecule both types of unsaturated compounds exist in a co-valent and not an electrovalent state, their respective force fields being entirely compensated, yet, as has been shown, the highly unsaturated and hence reactive condition of the ethylene molecule arises by virtue of the very ready convertibility of the co-valencies into electr valencies, a conversion which takes place less readily un the acetylenic type, and hence determines a less reactive state. Hence it would be expected that a catalytic effect would be the more marked in reactions involving the latter type of unsaturated compound than in reactions with ethylenic compounds. Under equivalent experimental conditions of concentration of acid, temperature and concentration of hydrocarbon the effect of addition of mercuric nitrate is 40 per cent greater for acetylene than for ethylene, (tables, 49 + 58), and thus provides striking confirmation not only of this conception of the ethylenic and acetylenci bonds, but also, and this is of fundamental importance, of the hypothesis that chemical reaction occurs by virtue of the conversion of co-valencies into electrovalencies, and proportionally to the ease by which this is effected. The catalytic effect is therefore concerned mainly with the opening up of the condensed fields of the unsaturated bond, and the conversion of the co-valencies into electrovalencies through the medium of the residual affinity of the mercuric nitrate molecules. A secondary effect, - it is difficult to estimate the relative extent of these two functions- lies in the increased hydroxyl dissociation of the acid, arising as a consequence of the positively polar character of the residual affinity of the mercuric salt and its affinity for hydroxyl. It may be supposed, therefore, that by virtue of its residual affinity the mercury salt acts upon the undissociated nitric acid molecules forming an addition complex, the energy lost, absorbed by the acid molecules, being sufficient to cause dissociation. In the presence of the sensitive force field of the ethylene molecule, or to a less degree of the acetylene molecule, condensation then occurs between the activated nitric acid and the hydrocarbon, and the primary addition of the compound, the nitroalcohol, is formed. There seems no necessity to postulate the formation, other than momentarily, of a mercury-nitric acid-hydrocarbon or a marcury-hydrocarbon complex, and no experimental proof of the existence of such a compound is forthcoming. The whole essence of such addition complex formation on our present theory is an enhanced reactivity and hence instability, and any such compound which possessed sufficient stability to appear among the products of the reaction would be functionless in catalytic mechanism.

It would appear, on the other hand, that catalysis of the oxidising function of nitric acid depends mainly on the nature of the organic compound reacting, and less on the nature of the catalyst. Both nitration and oxidation of organic compounds involve, as has been shown, hydroxyl dissociation of the acid, the predominance of one or other reaction for the compound RH depending largely on the nature of R. But any salt which increases the decomposition of the acid, giving an increased formation of nitrous oxide and nitrogen, may be supposed a positive catalyst of the oxidising function of the acid, (v.p 21.) But both oxidation and nitration in the interaction between nitric acid and acetylene or ethylene takes place to a certain extent, the relative proportion of each type of reaction depending on experimental conditions and on the catalyst. (tables 47 58). If, however, ethyelene or acetylene be viewed as the type R.H there is no a priori reason why of the two processes oxidation and nitration there should be a greater tendency to the one than to the other, for in the reactive condition $H_2C = CH_2$ R may be either positive or negative according as the alpha or beta carbon atom is affected and hence, other factors being equal, each reaction should proceed to an approximately equal extent. This is actually shown to be the case for acetylene. In a normal interaction between 95 per cent nitric acid and acetylene, in the absence of a catalyst, the proportion of carbon becoming carbon dioxide by simple oxidation is 32·6 per cent, and by the process of simultaneous nitration and oxidation 22·6 per cent. But in a similar reaction with ethylene this relation is not maintained. Under the same conditions of concentration, temperature &c, the proportion of carbon becoming carbon dioxide by simple oxidation, (route i), is 60 per cent of the value for acetylene, while the extent of the nitrating reaction, (route ii), represents only 65 70-80 per cent of the corresponding acetylene value. It is noteworthy that though in the acetylene system reactions (i) and (ii) proceed to an approximately equal extent, reaction (i), simple oxidation, is always slightly in excess of reaction (ii). (v. tables 50)

The most striking effect of the addition to the reaction mixture of a small quantity of mercuric nitrate is markedly to increase the total proportion of carbon undergoing reaction by either of these two routes; in other words, side reactions are considerably depressed, and for acetylene eliminated. But if the reaction is analysed it is found that in the reaction with acetylene secondary reactions are suppressed to the greater advantage of simple oxidation than of the reaction by route (ii), i.e. the proportion of carbon becoming carbon dioxide by route (i) is 41'6 per cent, while that becoming carbon dioxide by route (ii) is 29'2 per cent. (It must be remembered that by route (ii) an equal percentage of carbon becomes nitrated as is oxidised.) Hence simple oxidation in this reaction is slightly more susceptible to catalysis than is the reaction of route (ii). Again this relation does not hold in the corresponding interaction with ethylene. Addition of mercuric nitrate increases the proportion of carbon reacting by routes (i) and (ii), though to a less extent than was observed for acetylene, but, while direct oxidation is increased porportionally to about the same extent as for acetylene, the addition compound of the nitration reaction is formed to a relatively greater extent, and reaction (ii) is ~~[illegible]~~ increasedvfrom a value which is 65 per cent of that obtained for acetylene to about 75 per cent. Hence for ethylene, that reaction which involves nitration is the more readily catalysed.

Hence, while there is substantial evidence that catalysis of both processes (i) and (ii) takes place, the realtive extent to which these two reactions are affected by catalysis varies, simple oxidation being the more readily catalysed in the reaction with acetylene, while nitration of ethylene is the more susceptible to catalytic influence.

In other words, whereas in the absence of a catalyst oxidation for acetylene represents 50 per cent of the hydrocarbon absorbed, that for ethylene represents 30 per cent, while addition of mercuric nitrate causes an increase of oxidation in each case to an extent approximately 60 per cent of the hydrocarbon absorbed for acetylene, and 40 per cent for ethylene. On the other hand, while addition of a catalyst causes an increase in the proportion of carbon of acetylene undergoing nitration from 1 to 1'23, similar catalysis of the reaction with ethylene raises the nitration value from 1 to 2 . Table 57.

Assuming that the two processes (i) and (ii) both occur by virtue of the dissociation of the acid into (OH') and (NO_2), the only route by which oxidation can be effected is by the addition of these two radicles, and hence the mechanism of the initial catalytic effect in the two reactions must be identical, the specific effect being confined to the subsequent phases of the reaction, which, on the process of simple ~~addition~~ oxidation probably involve elimination of nitrous acid with the formation of an unsaturated hydroxy compound. It is to expected that this elimination of nitrous acid will take place less readily from the acetylene addition compound than from that of ethylene, and is it therefore susceptible to such catalytic influence as facilitates the formation of the nitrated compound, and is the nitration of ethylene intrinsically more susceptible to catalysis than is this process in the reaction with acetylene, are questions which must be asked if we are to explain the catalytic effect on this hypothesis. Actually this implies rather less than would at first appear. If we compare, as a percentage of the carbon absorbed, the proportion of carbon becoming oxidised by route (i), or nitrated by route (ii) in the two reactions, both in the presence and absence of a catalyst, we find, representing the lowest values by 1 and expressing the other values as multiples of this, the following relations:-

	Ethylene.			Acetylene.		
	Carbon becoming oxidised by i	Carbon becoming nitrated by ii	Ratio $\frac{i}{ii}$	Carbon becoming oxidised by i	Carbon becoming nitrated by ii	Ratio $\frac{i}{ii}$
No Hg.	9	1	9 : 1	13	11	1'18 : 1
Hg	12	7	1'7 : 1	20'5	14'8	1'4 : 1
Increase	1'33	7		1'53	1'35	

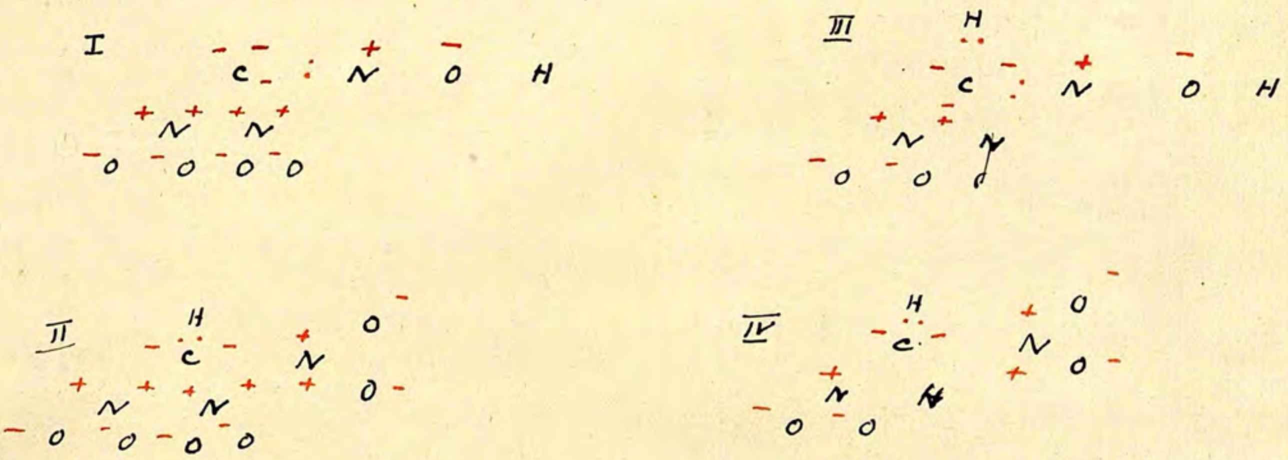
The figurse showing the proportional increase brought about in each case by the addition of the catalyst express the result discussed above. But another relation becomes apparent from these figures. In spite of the very considerable increase of reaction (ii) in the ethylene brought about by mercury, the proportion of carbon becoming nitrated in relation to the hydrocarbon absorbed never quite attains the value which is reached for acetylene in the absence of mercury. The more obvious effect of the metal is to bring the relative proportions of the two reactions in the ethylene system into line with the same reactions in the acetylene system, and the relation of the two reactions in the two systems in the presence of mercury are not very different. The effect of the catalyst must indeed be two-fold. Both processes of nitration and oxidation are ~~simplified~~ susceptible to its influence, and the extent to which each takes place is increased both for ethylene and for acetylene. No negative effect of the addition of marcury has ever been observed. The relatively much greater increase of nitration, (route ii), in the ethylene system is probably a secondary effect of the catalyst due to a stabilisation of the subsequent stages of route (ii), the products of which under normal conditions in the absence of a catalyst are either not formed or are removed by secondary decomposition.

Our question rather becomes, therefore, an investigation of the electromagnetic or other causes which, in the ethylene system largely prevent the occurence of reaction (ii), or lead to decomposition of its products.

The general effect of marcury as a catalyst of the hydroxyl decomposition of nitric acid, and hence of the addition to the unsaturated bond of the elements (OH) and (NO_2) has already been shown. Initially, therefore, the extent of both oxidation, (route i) and nitration, (route ii), and the proportion of carbon in the hydrocarbon undergoing reaction by both routes is, in the absence of other effective agents, proportionally increased.

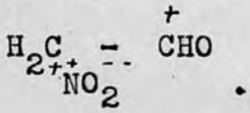
If we examine the route by which nitroform is produced from ethylene, (p 118), it is obvious that the specific effect of the catalyst in this series of reactions must be confined to the changes ii, iii and iv, since the primary addition, i, and the formation of nitroform from dinitromethane are common to both systems. We are faced, therefore, with two alternatives. Either the system, in the absence of mercury, is not sufficiently reactive to proceed to any one of these three successive stages, or the product, methylnitrolic acid, must, under the conditions of the reaction, undergo decomposition rather than oxidation. Decomposition of nitroacetic acid which, in the nitric acid medium could only take the form of oxidation, is excluded for oxidation is not increased under these conditions. To attribute the absence of reaction to decomposition of the nitrolic acid would imply that methylnitrolic acid is less stable than the compound $C(NO_2)_2$ NOH, which in the subsequent stages of the reaction is oxidised to nitroform, or that the oxidation to nitroform requires less energy than the corresponding oxidation of methyl nitrolic acid to dinitromethane. That this undoubtedly plays some part in bringing about the observed effect becomes evident when we examine the electronic condition of these compounds.

In the accompanying diagram,



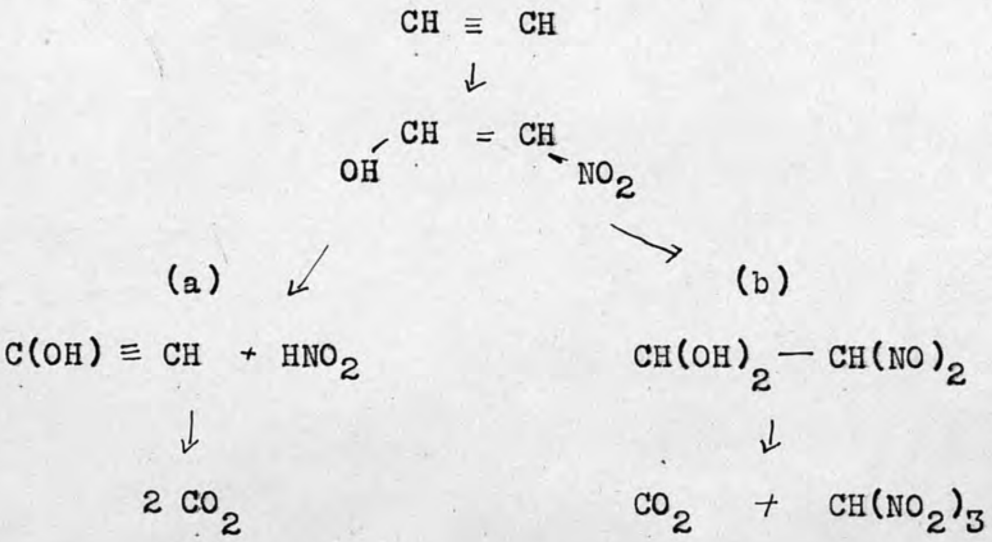
C^{I} is electronegative by virtue of three negative charges, the double bond between carbon and the oxygen group consisting probably of one co-valent and one electrovalent bond, oxygen being the key atom in each case, while C^{III} is negative only to the extent of two negative charges. In passing to the more highly oxidised state, II and IV respectively, each carbon atom acquires an additional negative charge corresponding to the additional positive charge on the more oxidised nitrogen. It is to be expected, therefore, that the nitrogen attached to that carbon which is already the more negative, i.e. C^{I}, will display a greater tendency to oxidation than the corresponding nitrogen atom in III. Consequently, therefore, methylnitrolic acid will be less susceptible to oxidation, and, failing oxidation, will be the ~~more~~ less readily decomposed. The presence of a catalyst, by providing additional energy, will overcome this lesser tendency to oxidation, and the series of reactions leading to the final nitration to nitroform will be promoted.

But an effect must also be attributed to the first alternative, i.e. that the reactions following the formation of the nitroalcohol take place with less readiness than do the corresponding reactions of the acetylene system. The primary nitroalcohol in the latter system is unsaturated and therefore would be expected to undergo ready secondary addition and elimination of water, with formation of dinitroacetaldehyde. Oxidation of the dinitroaldehyde will obviously occur with greater ease than will the corresponding oxid-ation of nitroacetaldehyde produced in the ethylene system, since the presence of the additional nitro group will endow the alpha carbon atom in the expression $\underset{\beta}{H\overset{=}{C}}(\overset{+}{N}O_2)_2 - \underset{\alpha}{\overset{\ddagger}{C}HO}$ with greater positive character, and therefore render it more susceptible to further reaction than the corresponding carbon atom in the expression


$H_2\underset{\overset{++}{NO_2}}{C} \overset{-}{-} \overset{+}{C}HO$.

It is clear, therefore, that both factors contribute to the absence of nitrated product in the ethylene systen, and that the pre-sence of a positive catalyst, by establishing a more highly reactive system will overcome this effect to a greater or less extent.

Turning now to the further catalytic effect of the greater proportional increase of oxidation, (i) over nitration, (ii) which, owing to the specific depression of reaction (ii) in the ethylene mixture, can only be observed for acetylene, explanation must again be looked for in the stages of the reaction subsequent to the primary addition. The two routes may be outlined as follows:-



$$CH \equiv CH$$
$$\downarrow$$
$$\underset{OH}{CH} = \underset{NO_2}{CH}$$

(a)

$$C(OH) \equiv CH + HNO_2 \rightarrow 2\,CO_2$$

(b)

$$CH(OH)_2 - CH(NO)_2 \rightarrow CO_2 + CH(NO_2)_3$$

As for ethylene, the elimination of nitrous acid with the formation of a highly unsaturated body, which immediately succumbs to oxidation, is the simplest interpretation of the formation of carbon dioxide from the nitroalcohol. It is difficult to imagine that this cleavage can the more readily appropriate to itself a greater proportion of the additional energy introduced by the catalyst than does the corresponding process (b/, leading ultimately to nitroform, especially as it already is known to take place with greater ease, and it is rather in the formation of nitrous acid by the oxidation process that this behaviour can be interpreted. As is known, Ihle. Zeit.phys.Chem. 1896. 19. 589), the oxidation potential of a nitric acid system is lowered by the presence of nitrous acid, and the oxidation of [illegible] (a) must therefore become negatively autocatalytic. On the other hand the alternate process, (b), involves the removal of nitrous acid by interaction. Anything, therefore, which increased the extent of this reaction would by causing a greater removal of nitrous acid from the system by any reaction, involve an inc-rease of the oxidation potential, and hence the extent of the oxidation. The oxidation process is therefore subject to two wources of energy, the catalytic source provided by the catalyst, mercuric nitrate, which is also available for nitration, and the increased energy arising from the increase of the oxidation potential.

The effect of mercury salts in the interaction between nitric acid and an unsaturated hydrocarbon is therefore complex. The primarh effect is an enhanced activity throughout the whole system by which an increased yield of both oxidation and nitration porducts is obtained. The extent of both reactions is increased, though not proportionally, and side reactions are considerably reduced. Secondary effects [illegible] specific to each eeaction, i.e. to each individual system, may result in a relatively greater increase of the one series of reactions over the other, though the increased interaction is always at the direct expense of the compound reacting, and never at the mutual expense of one or other product.

The Effect of Mercury in Aromatic Systems. In the behaviour of mercury salts towards the nitration of aromatic compounds there is evidence that we have to do with a very similar series of reactions, providing in this demonstration the existence of certain intermediate stages, confirmation of the behaviour which has been postulated for unsaturated aliphatic systems.

It has been shown that the most obvious effect of the presence of marcuric nitrate on the products of nitration of aromatic compounds, and a number of all the nitratable types have been studied, is an increased reactivity of the whole system, and a larger proportion of the organic compound undergoes reaction than would otherwise be the case. As was found in the reaction with unsaturated compounds, there is a tendency, particularly with hydrocarbons, to form nitrophenolic compounds, (c.f. the addition of nitric acid to the unsaturated bond of ethylene and acetylene forming a nitroalcohol), In the nitration of phenolic compounds themselves nitration alone is susceptible to catalytic influence, and the nitrated pprduct is obtained in greater yield, (v. p 13 & Table 15). Destructive oxidation to oxalic acid and carbon dioxide, usually present to a very slight extent in normal nitrations, is increased by the addition of mercury as was observed i unsaturated systems, though proportionately to a less degree. There is, therefore, a very marked analogy in the superficial effect of mercury on the two systems, an analogy which cannot be without significance in the actual mechanism of the two reactions. Both nitration of a phenyl nucleus and substitutive oxidation, i.e. the formation of phenolic compounds,

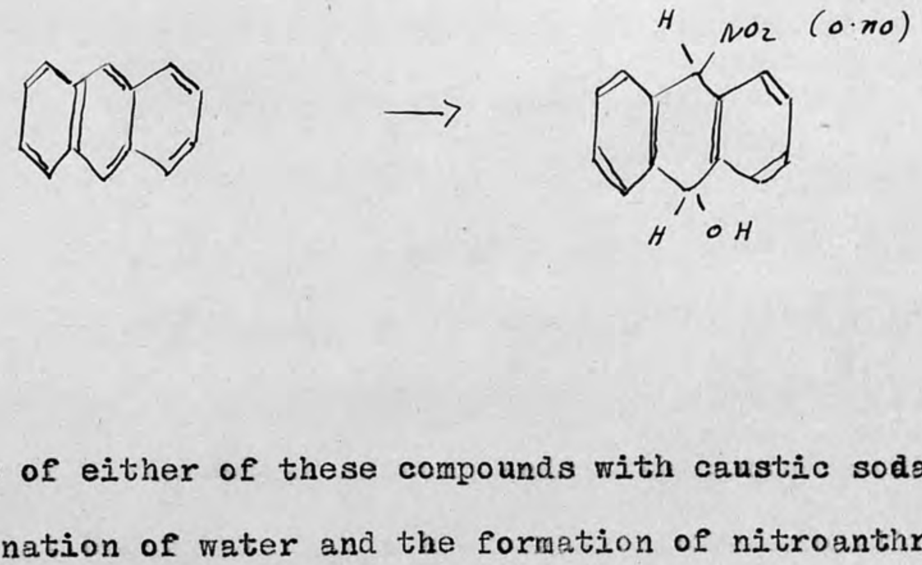
i $Ph.H + HO.NO_2 \rightarrow Ph.NO_2 + H.OH$

ii $Ph.H + HO.NO_2 \rightarrow Ph.OH + HNO_2$

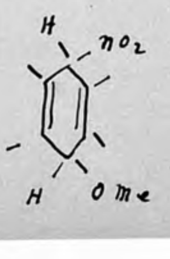
(ii occurs only in conjunction with i)

involves a dissociation of nitric acid into (OH') and (NO_2), whether such dissociation takes place ionically with complete transference of electrons, or whether interaction occurs with molecules of nitric acid in which an electrovalent bond exists between hydroxyl and nitro. Given that any residual affinity which the phenyl nucleus possesses is, in such a mixture, effective in a negative sense by virtue of which the positive (NO_2) radicle is appropriated, and hence nitration accurs, then obviously equation ii, which implies a positive residual affinity on the phenyl nucleus, cannot take place independently in the same medium. The impossibility of forming phenolic compounds in this way confirms this. To what, then, is the hydroxylation which frequently occurs when mercury is present, together with nitration of the same nucleus, due?

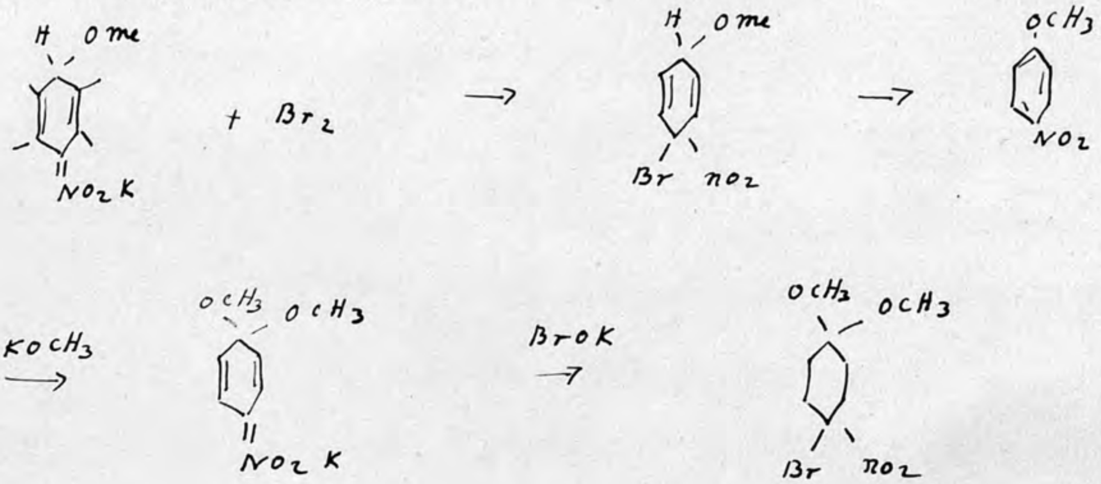
It is becoming increasingly evident that the mechanism of substitution in reactions involving aromatic compounds differs in no way from any organic molecular reaction, the initial stage being a loose addition compound which rearranges forming the usual substitution product. Anthracene, when treated with nitrous gases under conditions when water is not excluded, forms a stable addition compound in which the radicles (OH) and (NO_2) have become attached to the two para positions of the central nucleus forming a dihydro-nitro-anthranol, (Meisenheimer. B. 33. 3547. 1900) Simultaneously a second addition compound in which the nitro radicle rearranges and attaches itself as the ester group O.NO is produced.



Treatment of either of these compounds with caustic soda promotes the elimination of water and the formation of nitroanthracene. The methylsalpetersaure anthracene obtained by Perkin, (T. 1891. 634), and shown to have the constitution is further evidence of this capacity, a

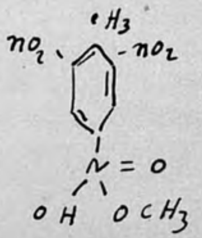


capacity which is strikingly illustrated by the addition reactions of the potassium salt.

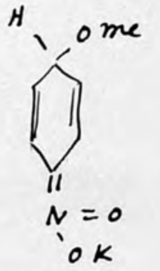


(Meisenheimer. A. 323. 205. 1902)

Several examples had previously been discovered of the existence of unstable, complex, coloured addition compounds between aromatic nitro compounds and alcoholates.by direct interaction. i.e. Lobry de Bruyn and Van Leent, (Rec. trav.Chim. 14. 150. 1895), obtained from trinitrobenzene and potassium methylate the salt, $C_6H_3(NO_2)_3.KOCH_3\cdot \frac{1}{2} H_2O$. Similarly trinitrotoluene yields the addition compound $C_6H_2(NO_2)_3.CH_3.CH_3OK + CH_3OH$, (Hanzsch and Kirsel. B. 32. 3137.), from which the free acid can be isolated. This formation was interpreted by assuming an addition of a molecule of alcoholate to one of the nitro nitrogen atoms, a formula which explained the great instability of the complex and reformation of the original com-

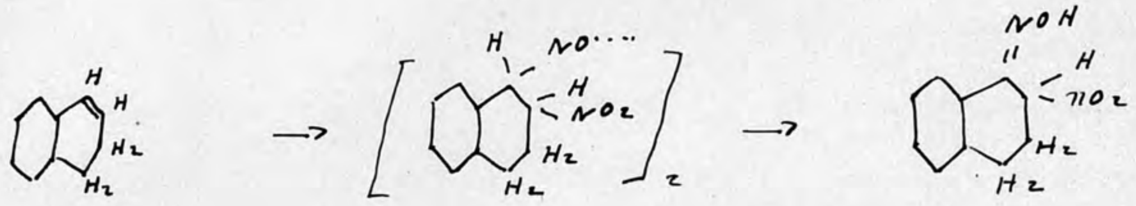


-pound, but was quite inadequate to account for the marked colour of the salts. Meisenheimer, (ibid), on analogy with the addition reactions of anthracene, and the formation in particular of the compound suggested that a more probable formula was one which would involve addition of the metal to the nitro group, and the methoxy group to the para carbon atom, hence creating a quinonoid stnucture, and this he has confirmed conclusively.



A very suggestive light is thrown upon the problem by Wieland, (A. 328. 154. 1903), who shows that only those aromatic systems which possess the capacity to pass into the quinonoid form can react with nitrous gases, e.g. all phenolic compounds can undergo this reaction. Addition, for example in quinone, would them occur:-

The formation of the pseudo-nitrosite of Δ^1-dihydronaphthalene by the addition of nitrous gases involves a similar addition.



(Straus and Ekhard. A. 444. 146. 1925.)

But the most striking evidence that it is through the medium of an addition compound that nitration, and hence other substitution reactions of aromatic compounds, occur is given by the work of Schaarschmidt on the addition of oxides of nitrogen to aromatic hydrocarbons, (B. 57. 2065. 1924.) Nitrogen peroxide, which readily undergoes addition reactions with olefines and acetylenes, reacts scarcely at all with benzene, though more readily with toluene and xylene, and immediately, with evolution of heat, with mesitylene. Such reaction as does occur is complex, and involves the formation of traces of nitro derivatives, nitrophenols and their easily hydrolysable nitrous and nitric esters, and products of oxidation, - oxalic acid and carbon dioxide. By the addition of certain metallic chlorides, - ferric chloride and aluminium chloride, it is possible to cause direct addition to the aromatic nucleus, an intermediate complex addition compound being formed between the hydrocarbon, nitrogen peroxide and the metallic salt.

$$2\ AlCl_3 + 3\ C_6H_6 + 3\ N_2O_4 \rightarrow 3(2/3\ AlCl_3.C_6H_6.N_2O_4)$$

These compounds are characterised by great stability, and can be heated to 100°C without decomposition. But in the presence of water the complex is broken up into a hydroxy chloride of the metal and a very unstable dihydro-nitro-nitrite addition compound of the hydrocarbon, which rapidly loses nitrous acid, with the formation of the simple nitro compound.

$$2(AlCl_3.3\ C_6H_6.3\ N_2O_4) + H_2O \rightarrow 2\ AlCl_3H_2O + 3(C_6H_6\ N_2O_4)$$

$$\rightarrow 3\ C_6H_5.NO_2 + 3\ HO.NO$$

The evidence for the existence of the addition compound, $C_6H_6N_2O_4$, is not, however, clear, for its activity is such that the author was unable to isolate it. The following figures show the very marked increase of yield of nitrated product brought about by the addition of the catalyst.

	No $AlCl_3$	$AlCl_3$
C_6H_5F	No nitro compound	88% nitrofluorbenzene
C_6H_5Br	~~45%~~ 6'5% nitrobrombenzene	90% ,, brom ,,
C_6H_5I	45% ,,iodo ,,	79% ,, iodo ,,

So considerable is the yield of nitro compound by this method that the process is utilised on the commercial scale for the preparation of ortho- and para-nitrochlorbenzene from chlorbenzene. It must be noted here that the ortho/ para ratio of the nitrated product is appreciably lower with respect to ortho- compound than is the corresponding ratio obtainable by a "mixed acid" nitration.

There is, therefore, little doubt that the formation of unstable addition compounds between an aromatic compound and the reagent is a not infrequent phenomenon, such addition leading in all cases ultimately to substitution. Moreover, it is possible by the introduction of a metallic salt to bring about catalysis of such reactions through the medium of an addition complex between the catalyst and the two reacting compounds, a complex which, if isolated in the solid state, may be of comparative stability. It became, therefore, a matter of considerable interest to harmonise this behaviour with the influence of mercury on the nitration of aromatic systems, and in general with the action of nitric acid on organic compounds.

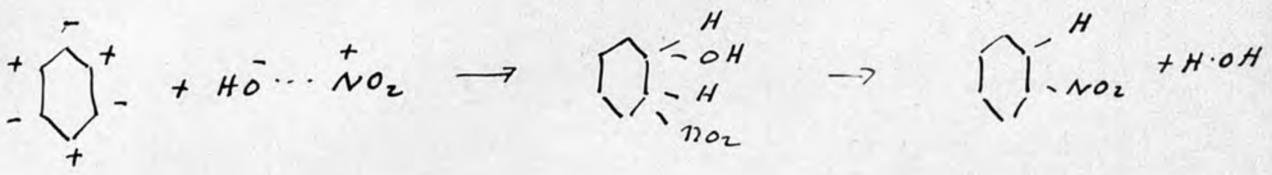
It seems probable that any reaction which is not ionic, and hence occurs by virtue of opposing affinity by simple recombination between ions, takes place through the medium of an inetrmediate addition complex. It has been shown that molecular interaction can only occur between molecules possessing residual affinity, i.e. an uncondensed residium of electromagnetic force, such interaction taking place by the condensation of these hitherto unclosed fields. This must inevitably lead to a temporary, maybe in certain cases momentary, molecular combination, in which, if a sufficiently high electric potential is set up, a rearrangement and transference of electrons is initiated resulting in the condensation of two new force fields and the creation of two new molecules. It is obvious that the time factor of a chemical reaction is determined by this rearrangement and recondensation, it being legitimate to suppose that, if combination occurs at all, the initial stage involving the formation of the addition complex, is a rapid one.

It would appear that the free affinity of the phenyl nucleus, through the agency of which it is enabled to enter into reaction, with various reagents, does not exist normally as active, uncondensed, electromagnetic force which is free to react with any type of compound with which it is brought into contact. The general inertia towards each other displayed by the majority of aromatic compounds points to an almost completely condensed force field in the resting kolecules, and a solvent or other medium possessing free residual affinity is essential if interaction is to take place. The electronic conception of the aromatic nucleus (v. p 96), enables us to conceive of a wholly internally condensed force field, for by the alternate polarisation of the carbon atoms of the nucleus not only is there condensation betwean adjacent pairs of carbon atoms, but also there can be mutual condensation of the residual affinities or uncondensed partial fields of the whole system, thus creating the symmetrical, tempcrarily inactive system with which we are familiar. Once such an internally compensated field is penetrated by the force lines of a molecule possessing residual affinity the balance of mutual compensation is disturbed, and the whole system becomes reactive through the free affinities which are now alotted to each carbon atom. At once, the inner meaning of the Crum Brown rule is seen to lie in this allocation of free affinities to alternately polarised carbon atoms. An aromatic system, therefore, is one which should readily lend itself to catalysis, only extremely reactive compounds such as strong acids being able of themselves to upset by the penetration of the nucleus by their own extremely active force fields, the balance of the aromatic forces. Once this is accepted, intermediate, molecular addition follows as the inev-

-itable behaviour in the reactions of aromatic compounds.

Nitration, or the substitution of the radicle, (NO_2), of the nitric acid molecule, involves the dissociation of this molecule into the groups (OH) and (NO_2). Examination of the interaction of nitric acid with unsaturated compounds has shown that at points where free affinity is displayed, i.e. in unsaturated compounds at the adjacent carbon atoms of the double or treble bonds, addition of each of these radicles takes place, an unstable hydroxy-nitro compound being the primary product of the reaction, and this behaviour finds ample confirmation in the similar addition reactions of nitrous gases and of sulphuric acid with unsaturated compounds. It is to be expected, therefore, that the intermediate addition compound of aromatic reactions, which has been shown to be a probable agent of such reaction, is formed by a similar process of addition of the groups (OH) and (NO_2) to adjacent carbon atoms of the phenyl nucleus, a hypothesis which receives confirmation in the work already discussed of Meisenheimer,)ibid), Wieland, (ibid) and Schaarschmidt, (ibid).

It is suggested, therefore, that the primary stage of nitration is probably represented by the following scheme, penetration of the closed fields of the phenyl nucleus by the force lines of the hydroxyl and nitro groups taking place, resulting in the polarisation of the carbon atoms of the nucleus and the formation of the hydroxy-nitro addition compound.



Both the unsymmetrical loading of the molecule and the juxtaposition of hydroxyl and hydrogen undoubtedly influence the elimination of water involving the return to the aromatic, uncondensed condition.

The hypothesis that substitution in aromatic compounds is preceeded by some form of addition is not a new one. Various theories on this basis have been tentatively put forward, but up to the present have received little measure of proof. Kekule, (Lehrbuch. 1867), and Armstrong and Collie, (1887)) both put forward the suggestion that the primary reaction is one of addition, but imagine that the addition takes place at either the carbon atom to which the directing group is attached, or to the directing group itself, and the idea is extended in much more detail in Lapworth's dyads and tryads. But it is to Flurscheim, (J.pr.Chem. 1902. <u>66</u>. 321; <u>76</u>. 165.), that we owe the clearest conception of substitution through the medium of molecular addition. Based on Claus' and Werner's conception of valency, and of the variability of the affinity content of different bonds, its fundamental postulate of residual affinity as the agent of molecular addition and hence interaction, is a foreshadowing of what has now been rendered much more probable by our modern knowledge of the structure of the atom, and Flurscheim's explanation that by the decreased or increased demands on the available affinity of the nucleus by a substituent an induced alternation of greater or less affinity at successive carbon atoms approaches as nearly as was then possible the conception of induced alternate polarity, involving partial transference of electrons. Flurscheim states clearly that the reactivity of a carbon atom, and hence the rate of substitution, must be governed by the energy supplied by such external factors as temperature and media, as well as by the internal kinetics of the molecule, - quantity and nature of affinity, and the magnitude of steric effects.

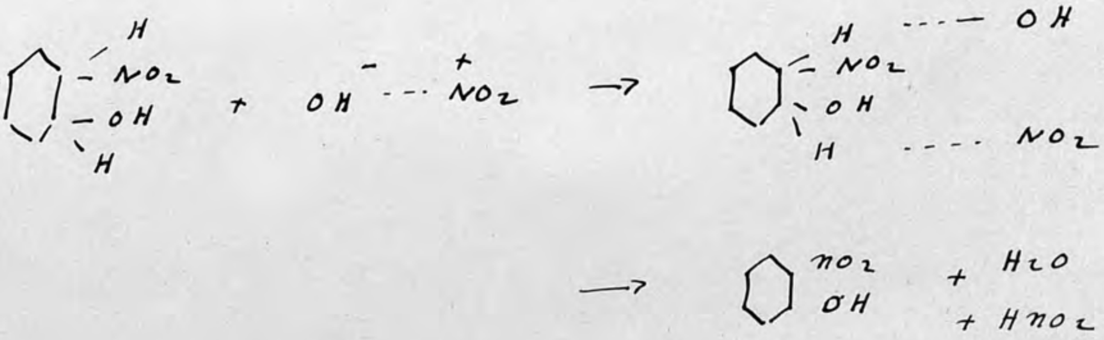
Arising out of our modern conception of reaction in terms of electrons and the ~~1~~ electromagnetic forces resulting therefrom, various theories of substitution have arisen, some postulating addition, others not. Of the former, it is ~~sufficient~~ supposed that the directing group induces an alternation of electrical charge on the carbon atoms of the ring, the hydrogen atoms being similarly polarised. (Fry. Steiglitz, Lowry.) Such theories are merely hypothetical, and up to the present no considered study of the mechanism of the reaction had been made.

In this reaction it is probable that the activating influence of mercury will be functional at both stages, and, as was the case in unsaturated √ systems, will both promote an increased dissociation of the acid, and by creating a more highly reactive medium will facilate and increase the formation of the addition complex. But in the effect of mercury on the subsequent elimination from this addition compound of adjacent radicles we are obviously dealing with a more complex phenomenon.

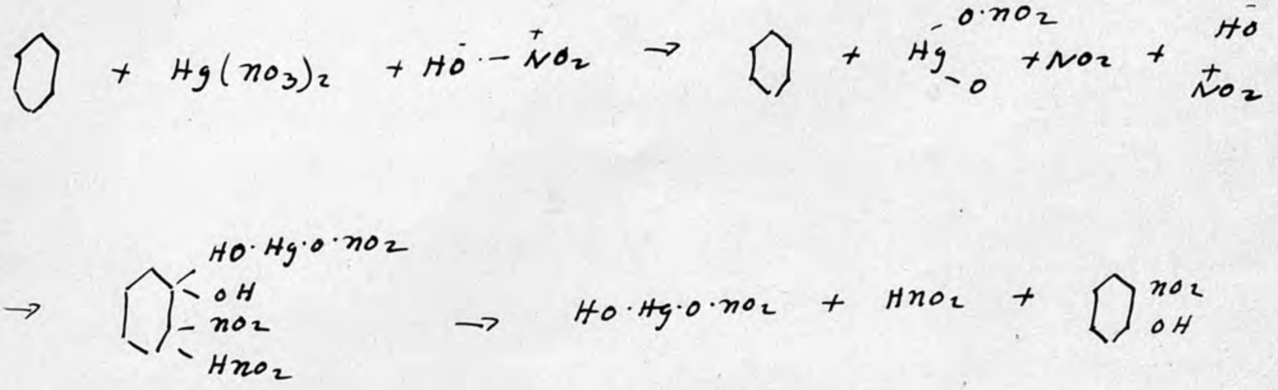
It is suggested that the influence of the metal at this stage is two-fold. There is the general catalytic effect of enhanced activity, and there is the definite directing influence, according to the aromatic compound interacting, on the cleavage products of the addition compound.

Thus, as has been shown, aromatic hydrocarbons, which give normal nitro substitution products in the absence of a catalyst, not only react to a greater extent in the presence of mercury, hence frequently yielding an increased amount of nitrated product, but there is a marked tendency for this product simultaneously to become oxidised, i.e. hydroxylated, such hydroxylation, as is obvious from the nature of the intermediate compound, taking place ortho to the first nitro group. It is significant thst the most marked increase of simple nitration without corresponding hydroxylation is observed in those compounds which already contain a hydroxyl group, i.e. phenols.

It is probable therefore, that in the addition compound of aromatic hydrocarbons at least, whatever may be the actual mechanism of the reaction, that the presence of mercury facilitates the retention by the molecule of both nydroxyl and nitro groups. It is possible that the increased concentration of these radicles resulting from the activating presence of the mercury salt brings about molecular addition between the primary addition compound and these radicles, there being immediate rearrangement or adjustment of forces and elimination of water and nitrous acid. Thus:-



All our evidence has gone to show, however, that the molecular addition in a catalysed reaction involves also the molecules of the catalyst, and it seems more probable that the addition compound is formed between the aromatic nucleus and a molecule of the catalyst, involving at the same time further addition with the component parts of the acid. Thus:-



there being immediate elimination of the newly constituted molecules of HO.Hg.O.NO_2 and HNO_2.

To postulate, as Davis does, (J.Amer.Chem.Soc. 44. 1588. 1922), that the mercuric nitrate is the actual nitrating agent is not in harmony with the most probable views of catalysis, and involves the unnesessary complication of the assumption that the activity of the nitric acid, which is in large excess, and which, in the absence of mercury, displays a great affinity for the aromatic compound, becomes markedly subordinate to that of the catalyst.

It is interesting to compare the deduction which has been arrived at with Baly's conception of aromatic nitration. (J.Amer.Ch.Soc. 37. 990. 1911). He accounts for the interaction between the aromatic compound and nitric acid by the opposing affinities of the nitro group and the phenyl nucleus. Addition compounds are formed between the aromatic compound and nitric acid, in which closed fields are opened up. If a sufficiently steep potential gradient is set up such addition compounds, by transference of electrons, yield the nitro compound and water. Of particular interest with reference to the influence of mercury is this author's interpretation of the influence of other acids in nitration. In cases where the affinity of the nitric acid o is not sufficiently strong to open up the closed fields of the aromatic compound, addition~~al~~ compounds with another strong acid will probide additional affinity. Hence the function of concentrated sulphuric acid or glacial acetic acid in nitration is not only dehydrative but catalytic.

Effect of Nitrous Acid. One frequently in the literature comes across reference to the part played by nitrous acid in reactions involving nitric avid. Many examples are known both of the oxidising and nitrating functions of nitric acid in which reaction only takes place in the presence of nitrous acid, and it has repeatedly been suggested that nitrous acid ia an essential catalyst of the reactions of nitric acid. It becomes of importance, therefore, to determine to what extent, if at all, the catalytic effect of metals in nitric acid media is due to the formation of nitrous acid which they initiate.

In 1842 Millon, (C.r. 14. 904. 1842), had shwon that the dissolution of copper in dilute nitric acid is dependent on the presence of nitrous acid, and that the addition of some substance e.g. potassium permanganate, which can remove nitrous acid, entirely prveents the reaction. Veley, (Phil.Trans. 182 A. 279. 1891)[3] after a lengthy investigation, (v.p. 15), of the dissolut-ion of metals in nitric acid, and the actual significance in this series of reaction of the nitric acid, sums up his evidence and that of other investigators by showing that the amount of nitrous acid present and the amount of metal dissolved by nitric acid are concomitant variables, and concludes that the primary change is between the metal and nitrous acid, producing the metallic nitrite.

The influence of nitrous acid in the interaction of organic compounds with nitric acid is also considerable. Jute is converted into a nitroso derivative by nitric acid containing nitrous acid, but is merely hydrolysed by pure nitric acid. (Cross. Ann. 277. 310.) Nitric acid, (1'4), reacts with aldehydes and ketones in the presence of nitrous acid, giving as initial products, (from acetone), iso-nitrosoacetone and amyl nitrolic acid. (Behrend.A. 283. 209). But Denniger, (J.Pr.Ch.(2). 42. 550), observed that certain hydroxy benzoic acids can benitrated by nitrous acid alone, and his conclusion that the initial products of nitration are nitroso compounds which are decomposed by nitric acid cannot be of general application, for Klemenc and Scholler, (ibid), have shown conclusively that the nitration of phenol, though dependent on the presence of nitrous acid, does not proceed by way of nitroso compounds.

Klemenc and Elk, (Monat. 1918. 39. 641), have shown that the nitration of phenol is an autocatalytic process, the rate of nitration being dependent on the proportion of nitrogen peroxide and of nitrous acid in the acid. No nitration occurs in pure nitric acid free from these two substances.

The presence of nitrous acid is necessary for the nitration of dialkylanilines, (Orton. B. 40. 370. 1907), though this may be a specific case due to the intermediate formation of a nitroso compound.

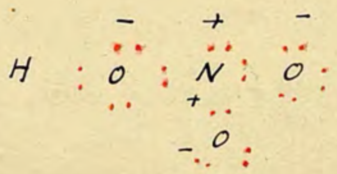
It has been found, too, that the oxidation of arsenious to arsenic acid by nitric acid only occurs in the presence of nitrous acid, (Klemenc and Pollak. (Zeit.anorg.Chem. 115. 131. 1920).

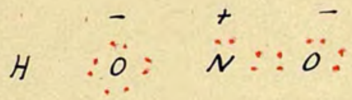
In a lengthy investigation of the mechanism of the action of nitric acid as a nitrating agent, Klemenc and Scholler, (Zeit.anorg. Chem. 141. 231. 1924), have shown for the nitration of phenol that nitration occurs only in the presence of a third substance. The necessity for the formation of a hypothetical "E" acid to account for this does not seem clear. It is shown, however, that the velocity of nitration is proportional to the 5/2 power of the nitric acid concentration, and to the 1/2 power of the concentration of nitrous acid, but the r equilibrium figures indicate that (NO_2) has a stronger accelerating influence than (HNO_2) in which the tension of (NO_2) is smaller. As an oxidising agent the velocity of oxidation by nitric acid is shown by a graph to be proportional to the concentration of nitrous acid, and this value falls off to zero if nitrous acid is removed. It is interesting that the authors, from the rapid, unexplained changes in velocity at equal concentrations and conditions, establish the susceptibility of the oxidising system to strong catalytic influences.

But the suggestion so frequently made that nitrous acid is the effective agent, both in nitrating and oxidising functions of nitric acid, and that its presence is therefore essential in these reactions, is not tenable, though there is ample evidence that when present, it usually plays a significant part. For nitration can take place in the complete absence of nitrous acid. Orton, (T. 1902. 807; B. 40. 370. 1907), has shown that anilines and symmetrical tri-substituted anilines can be readily nitrated, and quantitatively, by nitrous-free nitric acid in a glacial acetic acid -acetic anhydride medium.

Strong support of the view that nitrous acid acts catalytically in reactions of nitric acid is found in data given by Ihle, (Zeit. Elect.Chem. 1895. 174; Zeit.Phys.Chem. 1986. 19. 577), for the polarisation of a Grove's cell. At all concentrations of the acid the velocity of oxidation is proportional to the concentration of the acid, and is increased by small quantities of nitrous acid. In dilute acid, less than 28%, addition of nitrous acid appears to raise the oxidation potential, while at concentration of acid greater than 28% this potential is depressed by such addition. It is obvious, however, that at the low concentrations of acid the velocity of oxidation is considerably retarded, ~~by~~ and addition of nitrous acid increases this, and at the same time raises the electromotive force, but to a lower value than would be attained ultimately in the absence of nitrous acid. Such accelerating influence is typically catalytic, and the results of Veley and others can as well be interpreted on this basis as on any other.

The particular value of nitrous acid in this respect can be estimated when we compare the formulae of nitric acid nitrous acids.





The bond between the nitrogen and the oxygen which is not hydroxylic is different in the two acids, and is obviously more active in nitrous acid when it involves four electrons. As has been shown, such a bond passes with extreme readiness into a heteropolar condition, i.e. one of the bonds tends to become electrovalent, thus establishing an active force field; and all the conditions for catalytic action, (v.p. 166) are fulfilled.

It is possible that the mevhansim of ~~reaction~~ catalysis by nitrous acid in this reaction is specific and exerts its activity through the medium of the reaction

$$HNO_3 + HNO_2 \rightarrow H_2O + 2\ NO_2$$

It is not suggested that by this means a new compound, nitrogen dioxide, which is the effective agent, is produced, but rather that the reversal of the reaction, for an equilibrium is established, provides activated molecules of nitric acid in which the force fields are continually being opened up for interaction. It is difficult to decide in favour of either hypothesis; probably both are effective in this case.

Viewed as a whole, therefore, nitrous acid as a factor in the nitrating or oxidising functions of nitric acid falls into line as one of the several agebts which by their special power of activation can open up the closed fields, or nearly closed fields, of the reacting compound, or can cause an increased activity ~~of~~ in the dissociating molecules of nitric acid. Metals, hitrous acid, possibly also solvents, i.e. glacial acetic acid, acetic anhydride, are all, therefore, effective agents in this respect, and there seems no reason to postulate that the catalytic action of metals is due ultimately to the nitrous acid which is a consequence of their oxidation by nitric acid. Apart from other considerations it has been shown conclusively that metals do not dissolve in nitrous-free nitric acid.

It is possible, however, that there is a regeneration of nitrous acid during the reaction. Experimental results show that this acid does accumulate in the solution, and that such systems become autocatalytic with respect to nitroua acid. The total effect is undoubtedly complex, but the oytstanding feature remains that both the oxidising and the nitrating functionsof the nitric acid are suscpptible to catalytic influence, which may be supplied either by metals or by other agents.

Granted that nitrous acid, when present, can act catalytically, it would seem that strongly basic metals, i.e. metals of the first class,(p. 6), by causing the removal of nitrous acid by reduction would act as negatuve catalysts of the reactions of nitric acid, ar at least could not be positively catalytic. Moreover, the reduction potential established by such metals would be high, (v. p. 7), and consequently would be unfavourable to both the (NO_2) dissociation of the acid and to the stability of any potential nitro compounds that mught be formed. The hydroxylamine formation initiated by these metals, (v.p. 8) would also be effective in removing nitrous acid.

The Effect of Mercury Salts on Orientation in Aromatic Compounds.

Effect of Catalysts on Orientation.

So far as the problem has received attention, it is generally accepted that both the type of aromatic substitution and the relative proportions of the isomers are independent of catalytic influence. Taking the more generally accppted theory or meaning of catalytsis agents as something additional to solvent or medium, thi this conception is still not wholly correct, whereas if we exclude, as from our present understanding of catalysis we are entitled to do, from the phenonemon of catalysis all effects of solvent or medium, then there may be considerable catalytic effect on the order and proportions of substitution.

Outstanding is the work of Iljinsky, (ibid), already discussed, in which he demonstrates the change in orientation from the beta to the alpha isomer by addition of mercury to the sulphonation of anthracene. Similarly, there is an obvious change of orientation though slighter, in the sulphonation of toluene, in which the presence of mercury decreases the ratio of ortho / para isomers from 20 - 50 / 60 - 50 to 31 / 69, (Hollemann, ibid), and a correspond--effect is produced by boric acid on the sulphonation of 1 : 4-amido -anthraquinone.

An examination of the influence of various media on orientation shows that, depending on the type of substitution involved, so may media have very varying effects on the relative proportions of the isomers, though there is no evidence that the substitution type cam be changed by such influence.

Orientation is little effected by variation of organic solvents in the halogenation or nitration of organic compounds, but in nitration in a medium of nitric acid or sulphuric acid, and in sulphonation in concentrated sulphuric acid the proportions of the isomers formed may vary considerably both ~~in~~ with the nature and strenght of the acid used, the relative velocity of formation of isomerides depending frequently on the strenght of the acid. Nitration of phenol with ten per cent nitric acid yields the same proportion of product whatever the medium, but there is a marked variation of the ortho / para ratio, corresponding to variation of concentration of acid, (Arnall. J. 1924. 811).

Medium.	Percentage ortho.	Percentage para.
80 % aqueous HNO_3	40'7	59'3
90 % ,, ,,	23'5	76'5
81 % ,, ,, plus 10% acetic acid	30'0	68'8

while nitration in sulphuric acid yields almost exclusively the para isomer.

In my investigations of the influence of mercury in aromatic nitrations I have explored this question, and have discovered that in certain cases a quite definite variation in the ortho / para ratio can be effected by the addition of a catalyst.

The most marked effect was shown by the formation of the ortho and para isomers of nitrocinnamic acid by concentrated nitric acid. In the absence of mercury the ortho / para ratio varies from 7'4 / 1 to 9'6 / 1, but in the presence of 10 per cent of mercuric nitrate the limits of variability of ortho and para compounds wree 3'77 / 1 tp 4'5 / 1, indicating an appreciable increase, amounting to 41 per cent, in the proportion of ortho compound relative to para, the total amount of nitrated product being little altered.

Nitration of salicylic acid in the presence of mercury by sodium nitrite and sulphuric acid reduced the ortho / para ratio from 2'1 / 1, (varying to 2'4 / 1), to 1'6 / 1, (varying to 1'2 / 1). Here the shift is slighter and is in the opposite sense, the relative proportion of para isomer increasing by about 28 per cent. Here, too the total yield of nitrated product does not appreciably alter.

In the mono-nitration of m-cresol in acetic acid it is impossible, under normal conditions, to estimate the relative proportions of the 2-nitro and 6-nitro compounds, as the product is invariably a sticky oil. In the presence of mercury, however, a solid can be isolated which can be recrystallised for para compound, the relative proportion of the liquid isomer, the 2-nitro compound, being decreased. Mercury nitrate slightly increases the extent of the nitration of phenol in aqueous nitric acid, and at the same time increases the proportion of para compound relative to ortho to about 34 per cent.

Of the monosubstituted hydrocarbons, chloro- and bromo- benzene, examined, only the former shows an appreciable change of the relative proportions of ortho and para isomers. In neither case can the ortho compound be isolated in any way which would make its estimation of mush value, but the amount of p-chlorobenzene decreases on an average by 30'8 per cent in the presence of mercury.

Mercury would appear to be without influence on the nitration of acetanilide; no variation either in the extent of nitration nor in the relative amounts of the isomers was observed. It is noteworthy that both the nitration of acetanilide and of bromobenzene, in neither of which has mercury any influence, were carried out in concentrated nitric-sulphuric acid or in glacial acetic acid media.

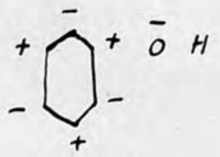
It is clear that appreciable effects are, as a rule, only obtained in the absence of dehydrating agents, i.e. in aqueous media, a result which is in harmony with the general effect of medium on substitution, ~~in~~ organic, non-aqueous solvents being without influence on the ortho / para ratio. But an exception to this is found in the nitration of m-cresol in acetic acid, v. above. On the other hand marcury causes complete change of orientation in the sulphonation of anthracene in concentrated sulphuric acid medium.

One other faeture which emerges from these results is that both types of compound which contain a hydroxy group yield an increased proportion of para compound under the influence of mercury, while cinnamic acid and chlorobenzene show a decrease of para compound relative to ortho.

It becomes, therefore, essential to determine how far orien--tation of entering groups in the benzene nucleus is dependent on external sources of energy, and how far it is directed by available energy within the molecule. Fundamentally the direction of the entering group is determined by the relative reactivities of the ortho and the para carbon atoms of the nucleus, or by the relative accelerating influence of the diretting group on the substituent. The problem, therefore, resolves itself into an estimation of the extent to which these reactivities can be changed by external en--ergy factors, and of these temperature has no, -or at most a very slight- effect, while certain catalysts, including aqueous media, may in certain types of compounds, especially when a hydroxyl group is present, have considerable influence.

If we consiedr the electronic condition of a monosubstituted nucleus it is apparent that polarisation has occured, to an extent depending on the polar intensity of the substituent. For while the unsubstituted benzene nucleus, though possessing latent polarisation, probably exists normally, in the absence of activating agents, in a non-polar form, the introduction of the polar or key atom at once disturbs the balance of the internally compensated system, each carbon atom becoming correspondingly polarised, and free affinity becomes available at the negative poles.

i.e.



This free affinity cannot display itself equally at both ortho and para positions simultaneously in the same molecule, otherwise substitution would be expected at both or all these points, which is contrary to experimental evidence. It is possible, therefore, that the activated compound exists as an equilibrium of electro-magnetic forces, the relative ultimate proportions of the isomers depending on the position of this equilibrium point.

Of the ortho- para- directing groups hydroxyl alone yields on nitration under normal conditions a greater proportion of ortho derivative than of para compound, while for all the other groups of this type the reverse is true. With the exception of the two compounds, bromobenzene and acetanilide, in the mono-nitration of which mercury has no apparent effect, the influence of the metal may be directed in one of two ways, (a) to the increase of para relative to ortho isomer and (b) to the increase of ortho relative to para compound. But in each case examined, whether the increase be of ortho or of para, the significant emerges thatthe variation is towards equilisation of the relative proportions of the two isomers. In both types where negative results were obtained the nitration in the absence of a metal is predominatingly in favour of para isomer, and though the extent of ortho formation cannot in these cases be estimated, the primary effect of the metallic salt is to reduce this proportion of para to a value approaching the 50 per cent level, (v. tables).

This tendency towards equilisation of the reactivity of the ortho and para positions on the nucleus may be the clue to the mechanism of catalysis influence on substitution. It seems impracticable, in the present state of our knowlegde, to pursue further the cause of selective substitution in either ortho or para positions. A further examination of the activating influence of media and catalysts on substitution is needed before a profitable discussion of this aspect of the problem can be made. But, if, as seems probable, a low proportion of one isomer relative to the other is due to a depressed reactivity at that point on the nucleus it is obvious that the activating agency of a catalyst would probably adjust this, and a more equilised partition of affinity would result, but further than this we cannot at present go. That the problem is centered in the relative activation of the several carbon atoms of the nucleus, and that this activation can be markedly altered by the presence of active molecules possessing residual affinity, e.g. metals, aqueous media &c, there can be little doubt, and there would seem no necessity to complicate the question by establishing a dependance on the actual mechanism by which substitution takes place.

SUMMARY.

The principal products of the interaction of fuming nitric acid with acetylene or ethylene are carbon dioxide and trinitromethane, together with a small amount of dinitromethane. As well, in the reaction with ethylene, and intermediate to the formation of trinitromethane, is formed the addition compound, β-nitroethyl alcohol.

The course of the reaction is seen to be fundamentally the same for both compounds, and takes place, though modified in detail, under varying conditions of temperature, concentration of acid and the presence or absence of metallic salts. Other substances, including oxalic acid, are by-products of this reaction, and may represent as much as 35 per cent of the carbon undergoing reaction, but the presence of mercuric nitrate considerably reduces this, -in the reaction with acetylene side reactions are by this means completely, and the carbon of the acetylene absorbed is then entirely represented by carbon dioxide and trinitromethane .

The maximum yield of nitroform, or of tetranitromethane isolated from it by further nitration, in one operation in the absence of a catalyst, is obtained by the absorption of 2'7 - 2'9 liters of acetylene, or of 2'9 - 3'1 liters of ethylene by 100 grams of 95 per cent nitric acid. ~~The~~ yield of ~~tetranitrome~~

The yield of tetranitromethane is then 9 - 10 grams, (from acetylene), or 277 per cent of the acetylene absorbed, or 6 - 7 grams (from ethylene), or 231 per cent. In the presence of mercuric nitrate, (0'33 per cent for acetylene and 0'66 per cent for ethylene), both the absorption of the hydrocarbon is increased as well as the percentage yield of tetranitromethane on the hydrocarbon absorbed.

The carbon dioxide formed under the best conditions still represents more than one half molecular proportion of the hydrocarbon molecule, while the proportion of tetranitromethane is rather less. Consequently a reaction takes place in which fifty per cent of the carbon of the acetylene molecule, (or of ethylene) is nitrated while fifty per cent is oxidised, and this is accompanied to a varying, though never large extent, by a second reaction involving direct oxidation of the hydrocarbon to carbon dioxide.

The tetranitromethane which can be isolated by further nitration from either mixture, always represents considerably more than the trinitromethane which can be estimated in the reaction mixture. Hence there are present in the product substances other than trinitromethane, but possibly intermediate to its formation, which are capable on further nitration of yielding tetranitromethane.

The interaction between oxides of nitrogen and the double or treble bond of unsaturated compounds, though involving a complex series of reactions, resolves itself fundamentally into an addition of the dissociated radicles of the nitrogen oxide to the unsaturated link, with, usually, saturation of the bond.

Whether the reaction be brought about by nitrogen peroxide or by nitrogen trioxide or mixed nitrous gases, this mechanism of reaction is maintained whatever the type of organic compound interacting. The type of compound does, however, influence the preliminary dissociation of the reagent, and addition may take place as $NO_2 + NO_2$, $NO + NO_2$, $NO + O.NO$, $NO_2 + O.NO$ or $O.NO + O.NO$, the particular type being determined by the nature of R and X in the expression R.CH CH.X. Subsequent reaction determined largely by the type of previous addition and may involve elimination of groups as nitrous acid, hydroxamic acid or hydroxylamine, or condensation to bodies of the pseude nitrosite type, the latter being characteristic of compounds in which the carbon atom of the unsaturated link is secondary or tertiary. Thus ~~simple~~ simple non-alkylated or partially alkylated compounds of the ethylene ar acetylene type tend to add nitrogen peroxide and trioxide as $O.NO + O.NO$ or $NO + O.NO$, while ~~fully alkylated~~ alkylation of the compound increases the tendency to add the reagents as $NO + NO_2$ or $NO + O.NO_2$. (v. literature, p 35 et seq.)

An exhaustive study of the literature has shown that only in fully alkylated and phenyl substituted unsaturated compouhds is there any tendency to form with oxides of nitrogen or nitrous acid stable condensation compounds of the type of pseudo nitrosite. In ~~acid or alkaline~~

acid or alkaline solution the decomposition of these products in all cases leads to the formation of the oxime, (with alkali), with final elimination of the nitroso group as hydroxamic acid, and in more concentrated acid to the formation of an isoxazole. In no cases has evidence of these types of compounds been obtained, showing that here too the characteristic reactions are wholly those of the simple, unsaturated aliphatic compounds leading to the formation of the nitroalcohol or corresponding compound.

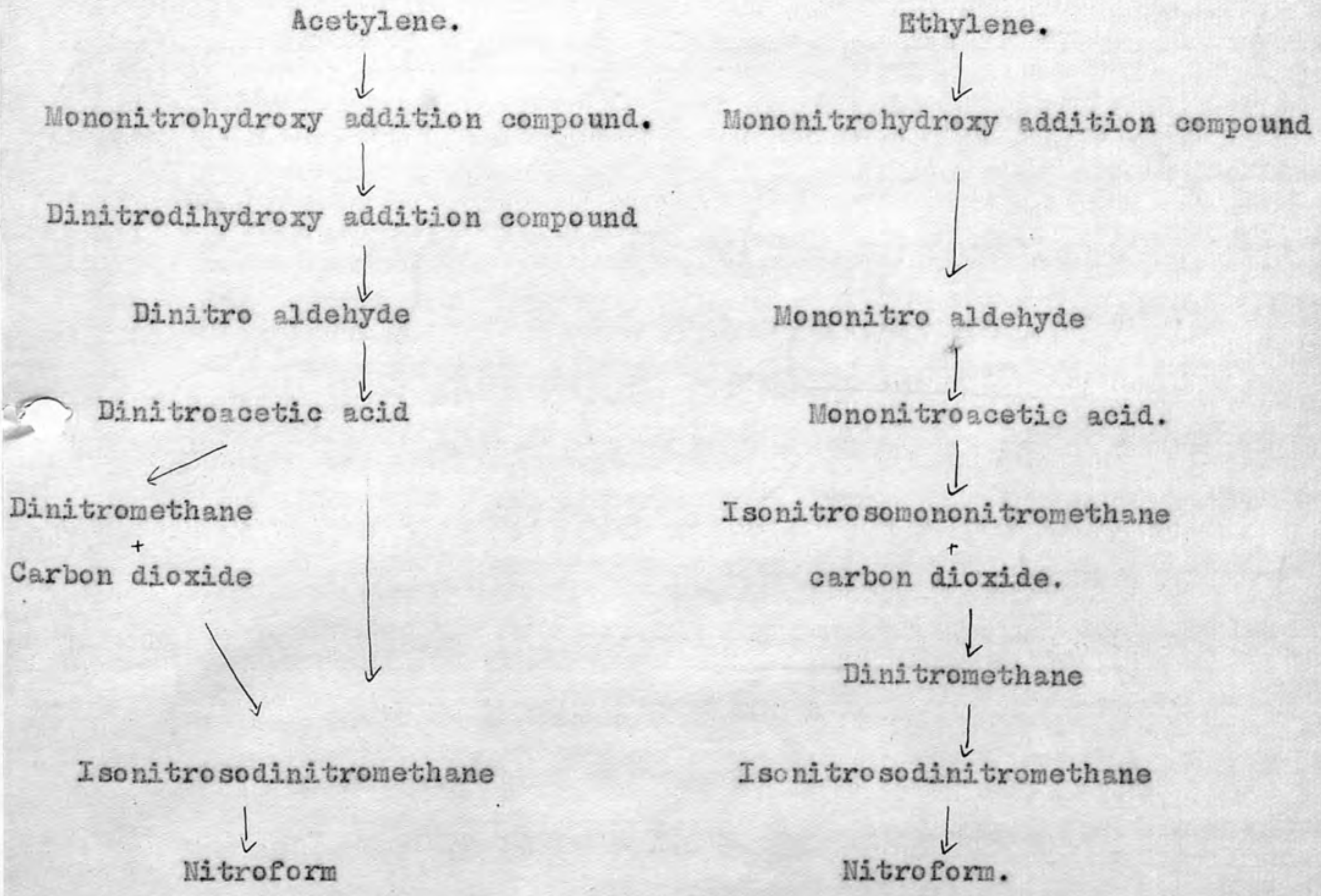
That the primary reaction for ethylene is one of addition to the double bond of the component parts of nitric acid forming the addition compound, β-nitroethyl alcohol is supported by (a) the presence in the reaction mixture of β-nitroethyl alcohol, and by the formation of nitroform at the expense of this compound, and (B) that it is fundamentally in harmony with the reaction between oxides of nitrogen and double or treble bonds, and with the addition of nitric acid to the double bond of various unsaturated compounds , c.f the addition of nitric acid to diphenylethylene giving the addition compound, $Ph_2C(OH)=CH_2NO_2$, (Anschutz and Hilbert, ibid), and to diphenylmaleide, (Cohn. ibid).

This reaction has also been established in the presence of concentrated sulphuric acid where treatment of compounds of the type of phenanthrene with a "mixed acid" yields a nitroalcohol addition compound. (Wieland and Sakellarios, ibid).

Thus the nitric acid, through the medium of addition, is able to exercise its function both as a nitrating agent and as an oxidising agent, one carbon of the hydrocarbon molecule becoming nitrated, the other becoming oxidised, finally to carbon dioxide. One or other of these reactions may predominate, and carbon dioxide as a product of direct oxidation be increased or diminished according to experimental conditions, but in no case can either reaction be entirely eliminated.

Concentrated sulphuric acid entirely prevents the formation of nitroform, and reduces the amount of carbon dioxide to very small proportions, a reaction which is accounted for in the ethylene mixture by etherification of the nitroalcohol to ethylene dinitrate and β-nitroethyl nitrate, a reaction which superceeds the formation of nitroform.

Evidence is adduced for the formation of nitroform and carbon dioxide from acetylene and ethylene under these conditions by the following routes:-



Acetylene.
↓
Mononitrohydroxy addition compound.
↓
Dinitrodihydroxy addition compound
↓
Dinitro aldehyde
↓
Dinitroacetic acid
↙ ↓
Dinitromethane
+
Carbon dioxide
↘ ↓
Isonitrosodinitromethane
↓
Nitroform

Ethylene.
↓
Mononitrohydroxy addition compound
↓
Mononitro aldehyde
↓
Mononitroacetic acid.
↓
Isonitrosomononitromethane
+
carbon dioxide.
↓
Dinitromethane
↓
Isonitrosodinitromethane
↓
Nitroform.

In the presence of sulphuric acid the principal products of the reaction are (1) nitric esters, formed by etherification of the nitroalcohol in the presence of the etherifying agent, sulphuric acid, and (2) nitrolic acids, the first being the predominating reaction.

Hence, the reaction is in all cases one of simple addition to the unsaturated bond of the component parts of the nitric acid molecule.

<u>The Effect of Catalysts</u>. Among the metals which have been examined in this reaction, - platinum, uranium, silver, copper and mercury-, mercury stands alone in having a favourable effect on the rate of absorption and hence on the rate of interaction, and in considerably influencing and increasing the yield of nitroform. The effect of the mercury salt is complex, but is largely to prevent the alternate reaction of simple oxidation, and hence to increase proportionally the addition reaction producing the nitroalcohol. Further, side reactions are considerably reduced, and for acetylene entirely eliminated.

In the nitration of aromatic compounds by various methods the effect of the addition to the nitration mixture of mercuric nitrate is rarely negligible, and may be considerable, and evidence is forthcoming that, under varying conditions, either the nitrating or the oxidising function of the acid can be positively catalysed. In no case does increase of oxidation take place at the expense of nitration, but at the direct expense of the organic compound undergoing reaction, i.e. a larger proportion of carbon undergoes reaction in the presence of mercury. Only in a few cases in the presence of low concentrations of mercury in the nitration of hydrocarbons, and in the nitration of salicylic acid has mercury a definitely negative effect on nitration. Total nitration is usually increased, whether the product isolated in the presence of mercury be the simple nitro- or the hydroxynitro compound. Direct oxidat-

-ation of the aromatic compound is ih every case very slight, and little more than occurs in the absence of mercury.

A comparison of the effect of mercury in the interaction between nitric acid and unsaturated compounds and in the nitration of aromatic compounds has revealed certain obvious points of resemblance in the marked effect on the extent of nitration, and has given support to the theory of nitration of aromatic compounds by preliminary addition of nitric acid as (OH) and (NO_2) to the aromatic nucleus.

It is concluded, further, that mercury salts can, under certaincconditions, act as positive catalysts of nitration.

A theory of catalysis, based on modern conceptions of valency, is put forward.

The Effect of Nitrous Acid. Nitrous acid is shown to fall into line as one of the several agents which by their special power of activation can cause an increased activity of the dissociation of nitric acid, and hence of the functions of nitric acid. The action of nitrous acid is discussed in relation to the degradation of nitric acid in general, and the significance of nitrous acid in the catalytic action of metallic nitrates in promoting the dissolution of metals in nitric acid is emphasised. It is shown that strongly basic metals would be unfavourable both to the dissociation of the nitric acid, and to the formation of stable nitro compounds, and, further, that mercury should be the

the most effective metal in this respect.

Effect of Catalysts on Orientation. Examinatioj of the relative proportions of ortho and para nitro isomers in the nitration of phenol, of m-cresol, of cinnamic and salicylic acids and of chlorobenzene, shows that appreciable variation in the ortho/para ratio can be brought about by the addition of mercuric nitrate. This variation may amount to as much as a 41 per cent increase of ortho compound relative to para, (cinnamic acid), the total amount of nitrated product being little altered.

The variation may be in opposite senses, i.e. in the nitration of salicylic acid the presence of mercury causes an increase of para nitro isomer, the ortho/para ratio decreasing from 2'1/1 to 1'6/1.

From a detailed study of the results the conclusion is drawn that the function of the catalyst is to equalise the relative activities of the two centres of addition, the ratio of isomers being more nearly 1/1 than is realised in the absence of a catalyst.

EXPERIMENTAL.

Experimental.

The Action of Nitric Acid on Aromatic Compouhds.

EXPERIMENTAL.

A. The Influence of Mercuric Nitrate on the Nitration of Aromatic Compounds.

Plan of Experiments:- With the onject of determining the influence of mercuric nitrate on the nitration of aromatic compounds, parallel series of experiments wree carried out for varying types of aromatic nitrations, and for varying types of aromatic compounds. Experiments were run in pairs, one following the normal type of nitration for the pacticular compound, the second involving in addition the presence of a certain quantity, (5 - 10%), of mercuric nitrate.

The following types of nitration were examined:-

i Dilute nitric acid.

ii Concentrated nitric acid.

iii ~~/~~ "Mixed Acid".

iv Potassium nitrate and Sulphuric acid.

v. Nitrous acid.

vi Concentrated nitric plus glacial acetic acids.

and the effect of the addition of mercuric nutrate to the nitration mixture of hydrocarbons, phenols, aldehydes, acids, anilides and amino compounds was investigated.

In order to determine in all its aspects the influence of mercury salts on such nitrations it was necessary to examine the product of nitration not only for yield of nitrated compound, but also for nitrated compounds other than the normal nitro compound, for oxidation products, gaseous or otherwise, and for evidence of side reactions. The relative total degradation of the nitric acid in the presence or absence of mercury had also to be taken into account.

Experimental Procedure:- In all the nitration experiments carried out in this connection the normal or standard process of nitration for each particular compound was adopted. The exact procedure for the admixture of mercuric nitrate was modified according to the nature of the compound to be nitrated, and will be described in each corresponding section.

Examination of the Product.:- (a) Nitrocompounds:- In general the product of nitration was poured onto ice or water and any solid compound filtered under standardiesd conditions, and examined for yield, purity of compound and the presence of one or more nitro compounds. (b) Products of Oxidation:- The presence of mercury as well as affecting the yield of nitrated product frequently also influences the oxidising action of the nitric acid to an extent which is usually slight, but which varies acdording to the type of compound nitrated. Such action is evidenced by an increased degradation of the nitric action and by an increased interaction and hence removal of the compound reacting, resulting in the formation of one or more products of oxidation according to the energy available in the system. Thus, oxides of nitrogen occur in varying amounts as products of the degradation of the acid, as well as hydroxylated nitro compounds, and oxalic acid and carbon dioxide must be looked for as the direct products of the effect of this action.

(i) Hydroxylated Compounds. Such compounds are invariably nitrated and must be looked for among the products of nitration, from which they are isolated by the usual means.

(ii) Oxalic Acid. This acid, to a greater or less extent, is frequently found in nitration mixtures in which mercury has been used, though in the nitratian of certain groups, e.g. $-CHO$ oxidation takes place so readily that the ultimate product of tis reaction is mainly carbon dioxide. But in no type of nitration examined does this oxidation represent more than 7 per cent of the compound reacting. The estimation of oxalic acid is the reaction mixture is simply and quantitatively carried out by neutralising an aliquot portion of the diluted product, after filtration of any solid constituent, and precipitating as calcium oxalzte in the usual way.

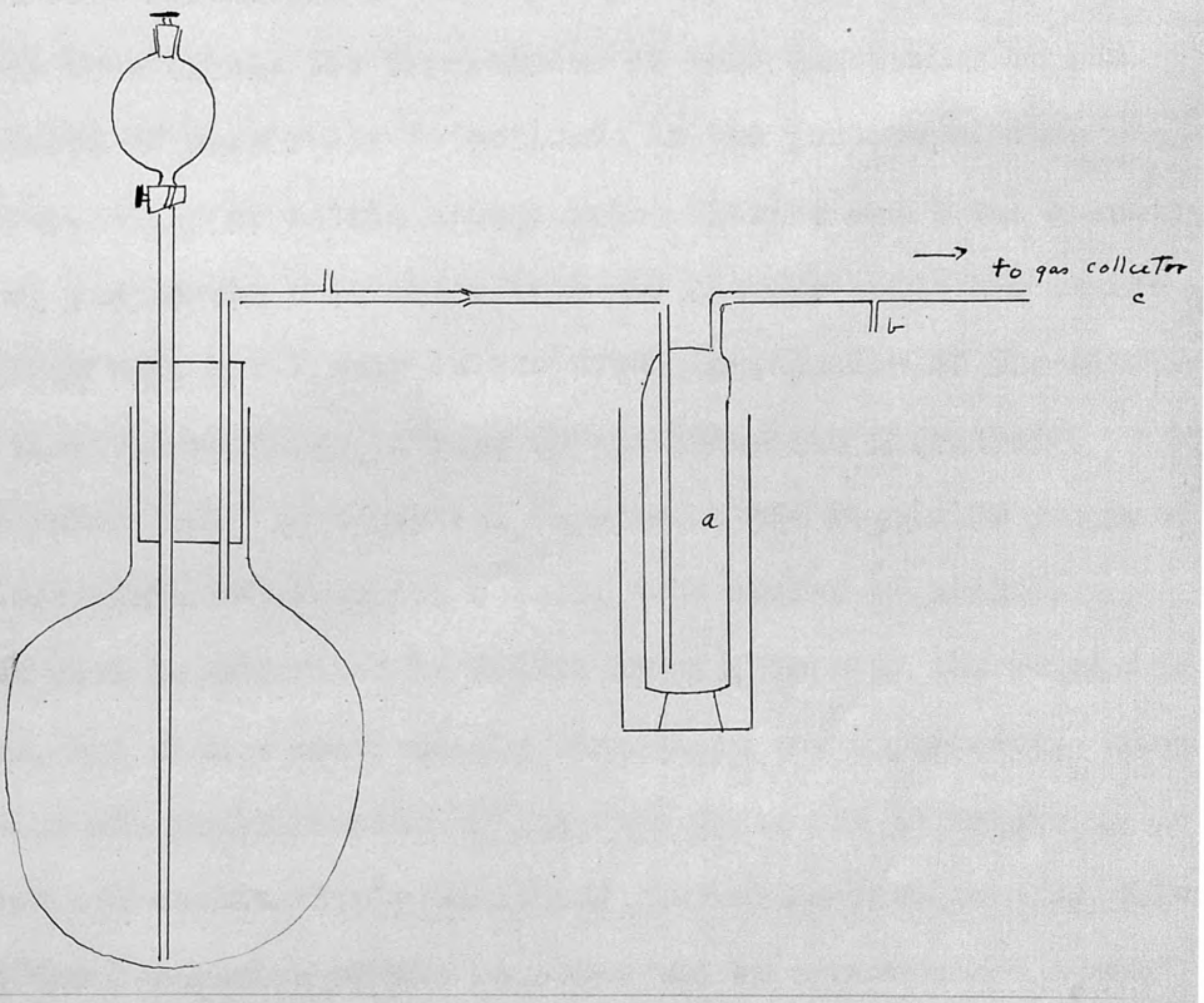
(iii) Gaseous Products. Quantitative examination of the gaseous products of the nitration reactions, when such was possible, showed that oxides of nitrogen, carbon dioxide, carbon monoxide, the latter in very small amount, were produced in varying amounts. It was necessary to devise some form of apparatus by which these gases could be completely drawn off from the nitration vessel in such a way that analysis of the gases could be made at intervals during the course of the experiment.

For the nitration vessel a large flask of about 500 cc capacity, with a neck sufficiently wide to allow of the easy removal of solid was used. The flask was fitted with a double bored, greased stopper, carrying a dropping funnel with drawn-out end reaching to the botgom of the flask, and a gas delivery tube connected to (a) a small wash bottle, cooled, for the condensation of nitrci acid vapour, (b) a T piece and stopcock from which samples of gas could be drawn during the course of the experiment, and (c) a small gas collecting vessel containing and inverted over saturated calcium chloride. Fig IV Calcium chloride, which had been used previously for ethylene nitrations and was therefore saturated with oxides of nitrogen and carbon dioxide, was used.

The different types of nitration which have been carried out tende to arrange themselves into two groups according to the relative amounts of gas given off during the nitration. In some this amount was comparatively large, and evolution occured fairly rapidly, so that not only could the total gas evolution be measured and analysed, but samples could be taken for analysis before the completion of the experiment, thus enabling the change in the composition of the gaseous products as the nitration proceeded to be estimated. In others, however, e.g. the nitration of xylene, and especially in nitrations which have to be carried out in a freezing mixture, the evolution of gas is so small that at the most only one analysis of the final mixture can be made.

Analysis of Gaseous Product:- A qualitative analysis of the gaseous mixture can readily be perofrmed by rapidly withdrawing into a Lunge nitrometer samples of the gas which have previously been freed from nitric acid. By shaking with a small quantity of water in the cold any nitrous, (and nitric) anhydrides and nitrogen peroxide are removed and can be detected as nitrous and nitric acids. In the residual gas carbon dioxide is detected by the usual means. On the scale of the experiments employed it was found difficut to devise a method of quantitative analysis sufficiently accurate to be of much value. Moreover, the final composition of the gaseous mixture with respect to oxides of nitrogen, owing to various possibilities of secondary reaction, oxidation of nitric oxide by the oxygen of the

Fig IV



air present in the apparatus, decomposition of nitrous anhydride and of nitrogen peroxide &c gives little idea of the relative proportions of these compounds as they are evolved from the nitration mixture. Any quantitative estkmation of the ~~sy~~ separate gases can have, there--fore little meaning and for the purpose of this discussion it has been considered of more value to estimate in the gaseous mixture the relative proportions of nitric acid, carbon dioxide and total oxides of nitrogen, and in the solution nitric and nitrous acids and oxalic acid. In this way, not 1 only is the total degradation of the nitric acid, but also the relative amounts of exidation and nitration accurately estimated. In a typical experiment the requisite reagents are introduced into the reaction vessel, (the method of admixture varies, and will be described in detail later), kept at the requisite temperature, and shakem continuously throughout the experiment. When gas evolution was rapid samples of gas were drawn off at intervals of half an hour and qualitatively analysed, the volume thus removed being noted. At the conclusion of the reaction the apparatus was allowed to stand at room temperature for several hours before examination of the products.

I. The Nitration of Naphthalene.

(a) Nitration to mononitro compound. Preparation of nitronaphthalene. Beilstein and Kuhlberg. A. 169. 83. The principal effect of mercury in the nitration of naphthalene to the mononitro stage by a concentrated nitric-sulphuric acid mixture is to convert the otherwise oily product obtained by pouring the nitration mixture into cold water, into a weighable solid form. Examination of both products by submitting them to steam distillation shows, however, that while the total weight of solid material, -unchanged naphthalene plus α-nitronaphthalene - which can be isolated from the distillate and residue of each distillation, is greater, actually less naphthalene is nitrated in the presence of mercury, the weight of unchanged naphthalene being greater in experiments where mercury has been used. As is usually the case in nitrations in concentrated sulphuric acid media, no apparent evolution of gas can ever be observed, and little or no oxidation takes place either in the presence or absence of mercury. Table II.

(b) Nitration to Dinitronaphthalene. In the method of Beilstein and Kurbatow, (A. 202. 219.), for the preparation of 1 : 5-dinitronaphthalene from naphthalene, the nitration mixture containing three parts of fuming nitric acid to one part of naphthalene, after standing at room temperature for twenty four hours, is heated for a further twenty four hours with 1'6 parts of concentrated sulphuric acid. The addition of mercuric nutrate to such a mixture considerably influences the course of the reaction, the most obvious and first effect of which is an increased oxidation resulting in considerable evolution of gas, -carbon dioxide and oxides of nitrogen-. But if the naphthalene is added to the fuming nitric acid containing mercuric nitrate sufficiently slowly to ensure no rise of temperature above that observable in normal experiments in which mercury is absent, this increase of oxidation is very slight, though the effect of marcury on the nitration is not appreciably lessened. Such effect is first noticeable in an increased yield of crude dinitro compound, an increase of from 5 - 10% being obtained. That the effect of marcury is not confined to the first stage of nitration is shown by the following experiments. Parallel experiments were run with and without marcury, in which the product was isolated at the end of the first stage, no sulphuric acid being added. In all cases the yield of dinitro product was increased, but to a less extent than in the complete experiments. Table IV . It is noticeable that if at the completion of such experiments the nitration mixture be warmed before isolation of the dinitro compound, there is a marked evolution of carbon dioxide and the yield of dinitro compound is appreciably lessened in all mixtures which contain mercury. Clear evidence is forthcoming both here and in subsequent nitrations, that with rise of temperature the oxidising function of the nitric acid is more susceptible to the influence of mercuric nitrate than is the nitrating function. Tables III · V .

I.A. Nitration of Xylene.

Nitration is carried out with fuming nitric acid in the presence of either oleum or concentrated suphuric acid. Hence the mercury salt is first dissolved in the nitric awid and forms a fine suspension of the sulphate in the mixed acid. Its presence occasions no apparent difference in the behaviour of the reaction mixture while the compound is being added. There is no darkeing in colour and no tendency to great evolution of ~~gas~~ heat. The product isolated by pouring into water, is almost pure trinitro-o-xylene, the melting point of which is scarcely raised by recrystallisation from benzene.

In examining the effect of mercury on this reaction, involving complete nutration to the trinitro compound, the yield of which is normally low, the effect was tried both of increasing the quantity of the mercury salt, and of substituting in the presence of mercury concentrated sulphuric acid for oleum. It is obvious from the results, table I , that it is impossible to attribute to the mercury salt any constant effect on the course of the nitration, either in the presence or absence of oleum. Using five per cent of mercuric nitrate, the positive increase of the yield of nitro compound is never greater than 9'77 per cent, but this is an extreme value, and the effect on nitration if frequently negative. increase of mercuric nitrate to twenty per cent produces no constant effect, and the nagative effect is more pronounced.

Substitution of sulphuric acid fro oleum in those nitration mixtures containing mercury is without any apparent effect. But the fact that such substitution only rarely produces a lower yield of nitro compound indicates that the mercury salt in these cases is actually acting as a positive catalyst.

Estimation of oxalic acid shows that at the most only traces of this compound can be isolated. And this fact, together with the absence of any ~~affect~~ appreciable evolution of gaseous products either in the presence or absence of mercury is proof that there is no increase of oxidation as a consequence of the presence of mercury.

II. Nitration of Phenanthrene.

i. Using the method of Schmidt, (B. 12. 1154), in which the nitration is carried out by concentrated nitric acid in the presence of coarse sand, no difference in behaviour could be detected in parallel experiments, one of each pair of which contained 5 per cent of mercuric nitrate. There was no evolution of gas, and the respectve mixtures presented an entirely similar appearance, yielding in each case an impure product with identical melting points.

ii Nitrous Acid Method. Mercuric nitrate is incapable of promoting nitration of phenanthrene by this method, a theoretical yield of unchanged phenthrene being obtained in each case.

iii Trial was made of the method of Wieland, (B. 1921. 1770) by which phenanthrene in carbon tetrachloride is treated with absolute nitric acid at a temperature of -12 - -4°C. The matarial beomes very stringy and sticky during the final addition of nitric acid. A benzene extraction of this solid, (four to five extractions are necessary), deposits on standing crystals of a solid which on crystallisation from acetone gave the melting point of the nitro-ether obtined by Wieland. (v. p. 110) Addition of mercuric nitrate produces a favourable effect on this reaction and the yield of nitroether is increased by an amount varying from 8 - 12'8 per cent. Tables VI . At the temperature employed no evolution of gas could be observed.

III Nitration of Anthracene

III. Nitration of Anthracene.

In the nitration of anthracene by concentrated nitric acid in acetic acid, (B. 34. 321), a definitely catalytic effect of mercury is obtained, and the yield of nitrated product is diminished to an extent varying from seven to twenty three per cent according to the amount of mercury present. In this nitration, too, we have the first evidence that the effect of mercury can be cumulative. The full effect of the mercury salt here is, however, complex. Though the total weight of solid isolated is less in the presence of mercury, extraction with benzene, whereby any dinitro compound which may have been formed is dissolved, removes a large proportion of benzene soluble compound than does a similar extraction of a non-mercuriated nitration, showing that, as is commonly the case, the presence of mercury favours an increased nitration to the dinitro stage. Table VII . It will be seen that, while there is a decrease of mononitration there is an appreciable increase of dinitration.

IV. Nitration of Bromobenzene.

Of the various methods available for the nitration of brombenzene that of Coste and Parry, (B. 29. 788. 1896), gives the most satisfactory results. The compound is added to a well-cooled mixture of equal parts of concentrated nitric and sulphuric acids, in which mercuric nitrate, when present, is precipitated from its solution in the nitric acid as a fine suspension of the sulphate. After pouring into a large quantity of water, the yellow solid which separates, on crystallisation from fifty per cent methyl alcohol, yields almost pure p-nitrobrombenzene. A small further quantity of less pure para compound separates on standing, while on prolonged standing a quantity, representing from five to ten per cent of the original solid, of ortho compound separates. Throughout, the effect of small quantities of the mercury salt is negatve, and addition of five per cent of mercuric nitrate depresses the yield of crude nitro compound by an amount which varies considerably, but which is usually not less than 10%. But if the quantity of mercury salt be increased to ten per cent, and further to fifteen per cent, the yield of nitro compound may be increased to a quantity which is greater, (six per cent for 10%, and thirteen per cent for 15% of mercuric nitrate), than would be obtained in the absence of mercury. A similar effect had already been noticed by Rice, (ibid), in the nitration of phenol, though in this case the positive catalytic effect of the metal begins at a much lower concentration, i.e. at <0·5%. Estimation of the relative proportions of the ortho and para isomers shows that the effect brought about by the mercury salt is reflected in the weights both of ortho and of para compounds. It has not been possible to obtain a very accurate estimate of the relative quantities of the isomers, but as far as can be judged, the effect of mercury is slightly to increase the proportion of para compound at the expense of ortho.

VI. Nitration of Phenol.

In the nitration of phenol to ortho and para nitrophenol by a nitrating mixture of sodium nitrate and sulphuric acid the finely ground mercuric nitrate, when present, is first ground with the phenol which thus assumes a dark colour. This, partly in solution partly in suspension in a little alcohol, is added in the usual way to the nitrating mixture cooled in ice.

If we compare the yields of total nitrated product, ortho and para compounds, obtained in the absence of a catalyst and in the presence of ten per cent of mercuric nitrate respectively it is obvious that this quantity of mercury salt has no constant effect. In certain cases the total yield is increased, in others it is depressed. Increase of the concentration of the mercury salt to twenty and forty per cent respectively shows that the presence of twenty per cent of mercuric nitrate does bring about a marked increase of total nitration, varying from seventeen to forty per cent. The effect here also is not constant, but is always positive and never less than seventeen per cent. Further increase to forty per cent of mercury salt shows only a very slight and variable increase above that obtained for ten per cent of salt, i.e. increase of the concentration of mercuric nitrate above twenty per cent is a disadvantage and results in a depression of yield. Tables XV, XVI.

Analysis of the nitrated product shows, however, an interesting variation of the ortho/para ratio. This ratio, in the absence of mercury, the residue containing para compound being submitted throughout to three extractions for para compound, varies between the limits 0'8 / 1 and (with one exception) 3 / 1, the average value being 2'5 / 1. Addition of tenper cent of mercuric nitrate reduces this ratio to 1'58 / 1, the limits being 0;93 / 1 and 2;33 / 1. Further addition of mercury salt to twenty per cent scarcely affects this ratio, the average value of which becomes 1;65 / 1, and though forty per cent of mercuric nitrate again raises it slightly to 1'7/1 this effect is only apparent, for whereas the limits of value for this ratio for twenty per cent of marcury salt are 1'5/1 to 1'93/1, the variation in the presence of mercury, 40%, is only from 1'66/1 to 1'81/1. The effect of mercury in stabilising this ratio is noteworthy. The most striking effect of the catalyst on the whole nitration is however the appreciable increase of para constituent corresponding to an increase of total nitration. The average yield of ortho compound remains remarkably constsnt throughout v. table XV The yield of para constituent increases markedly ~~from~~ by the first addition of mercury nitrate, but is scarcely affected if the catalyst is increased to twenty per cent, though a slight further increase is noticeable when this is increased to forty per cent. Table XV This behaviour is reflected in the values of the ortho/para ratio which, reaching its highest value in the absence of mercury, is depressed to a minimum value by addition of ten per cent of mercuric nitrate. Each further addition of mercury salt slightly readjusts this ratio by a small increase in the amount of ortho constituent, but to no constant value, and to a value which is still appreciably belowe that reached in the absence of mercury.

VII. Nitration of Chlorophenol.

(Method of Faust and Saame. B. 1923. 238.) Dilute nitric acid is the medium of nitration here, as was fundamentally, though by means of aqueous sodium nitrate and sulphuric acid, in the nitration of phenol. The mercury salt, if ground with the phenol before mixing causes much darkening, and on adding to the reactikn mixture the whole tends to set to a black cake. This can be ground up and the mixture allowed to stand at room temperature for about four days. Results by this process seem to compare favourably with those obtained by a subsequent method, but this order of mixing was discontinued. Instead, the mercuric nitrate was dissolved with complete solution in the dilute nitric acid. Efficient stirring during admixture of the phenol prevents any caking. No rise of temperature above the normal temperature is observed by the admixture. The reaction mixture, after four days standing, is diluted with an equal volume of water, filtered, and the crude product subjected to dilute caustic soda treatment and subsequent steam distillation in the usual way; the 4-chloro-2-nitrophenol being vol-

-atile in steam, can thus be obtained pure. It is not possible to estimate with any accuracy the relative proportions of para compound, nor of any unchanged chlorophenol or of dinitrophenol which may be formed.

Both the effect of successive increases of mercuric nitrate, and of decrease of concentration of nitric acid on the relative proportions of crude nitrated product and of pure o-chlornitrophenol have been examined. Addition of ten per cent of mercuric nitrate has in general a positive effect on both the yield of crude and of pure ortho compound, though the results are not constant, and in two experiments a negative value was obtained. A marked increase of yield of both products is seen when the concentration of mercuric nitrate is increased to fifteen per cent, and these values are again slightly increased when twenty per cent of mercury salt is present. Increase of the concentration of the catalyst to forty per cent slightly decreases the yield, a decrease whcih is more marked if one hundred per cent of mercuric nitrate be present, though still well above the normal value in the absence of mercury. Tables 17-21.

The concentration of nitric acid was decreased slightly, both by using a less weight of nitric acid, and also by increasing the quantity of water added for the normal weight of nitric acid. A decrease of concentration of 1%, in the absence of mercury, dec-

-reases the yield of crude product, though a slight increased yield of of ortho compound is uniformly obtained. A further decrease to twenty three per cent nitric acid, and again to twenty one per cent, produces a uniform progressive decrease of yield of both crude and pure ortho compounds. Table 21. In the presence of ten per cent of mercuric nitrate there is a corresponding decrease of yield of both compounds as the concentration is progressively diminished, but it is noteowrthy that, with the exception of experiments containing tem per cent of mercury salt, the decrease in each case is considerably less when mercury is present than in its absence. Table 21 .

VIII. Nitration of o-Cresol.

Two mono nitro compounds of o-cresol can be prepared by nitration by fuming nitric acid in glacial acetic acid solution, (A.W.Hofmann and Miller. B. 14. 586. Raff. A. 224. 175), 6-nitro-orthocresol, m.p. 69'5°, and 4-nitro-o-cresol, m.p. 79 - 80°, the ortho compohnd being volatile in steam and therefore easily separable from the non-volatile para compound. But, in the presence of mercury, the course of the reaction becomes very difficult to control, admixture has to be carried out very mush more slowly, otherwise a violent reaction, with much darkeing and evolution of gas, occurs, mononitration becomes impossible. Experiments were therefore made to determine the effect of mercury on the yield of dinitro product, Using the same nitration mixture as for mononitrocresol, and allowing the temperature to rise somewhat, the dinitro compiund -4:6-dinitro-o-cresol, m.p. 86 - 87°, is produced in appreciable quantity.

The cresol is dissolved in glacial acetic acid, and cooled to -5°. The nitric acid, in which the mercuric nitrate when present is dissolved, mixed with glacial acetic acid, is added slowly with strong cooling, and continual stirring. The reaction product is isolated by pouring into water.

Addition of ten per cent of mercuric nitrate to a nitration mixture containing 1'5 parts of nitric acid produces a very slight increase in weight of crude product, but a more marked increase, averaging twenty per cent, of dinitrocresol. If the nitric acid is reduced to 1'3 parts, though the yield of crude product falls slightly, this is compensated for by the presence of ten per cent of mercury salt, and the yield of pure dinitro compound is increased by about fifteen per cent. The presence of mercury when further decrease of nitric acid is made to one part and to 0'75 parts respectively, still maintains the yield of pure dinitro compound slightly in excess of the normal yield in the absence of mercury, when 1 part of nitric acid is present, though the value falls below the normal value when the nitric acid is further reduced to 0'75 parts. If, however, the concentratuon of the mercury salt be in-

-creased to fifty per cent, there is again a rise in the yield of crdue and of pure dinitro compounds. Tables 22-24.

IX. Nitration of p-Cresol.

Method as for o-cresol. Similar conditions of nitration were used for p-cresol as for o-cresol, and here, too, the presence of mercury makes mononitration impracticable. The reaction was therefore examined for the effect of the addition of mercuric nitrate on the yield of dinitro product, 2 : 6-dinitro-p-cresol. Admixture was carried out at 0°, and the temperature allowed to rise slowly. The product isolated by pouring into water the reaction mixture which had been standing for some hours, was in all cases practically pure 2 : 6-dinitro-p-cresol, though a very characteristic effect of the mercury salt on this compound is an intense reddish-orange colour, quite different from the normal pale yellow colour of this compound obtained in the absence of mercury. It was found impossible entirely to remove this colour by crystallisation, and as the compound gave a sharp melting point for 2 : 6-dinitro-p-cresol it was ignored. Tables 26 .

A preliminary examination of the effect of mercury on this nitration showed that results were very variable, and it was difficult, therefore, to estimate at all accurately the real effect of the catalyst. As can be seen, table 26, there is, however, a definite variable increase of yield of dinitro compound occasioned

by the presence

by the presence of ten per cent of mercuric nitrate, an increase amounting in some cases to 26'7 per cent, but falling as low as 5'5 per cent in others. This effect is much more clearly shown if the proportion of nitric acid be reduced to 1'6 and 2'2 parts of nitric acid to one part of cresol. In the absence of mercury there is a marked fall in the yield of dinitro compound in such cases, amounting to about 12 per cent and 53 per cent respectively, a fall which the presence of ten per cent of mercuric nitrate corrects to within one per cent of the normal yield for 1'6 parts of nitric acid, and to within twenty seven per cent for 1'2 parts. Table 26

X. Nitration of m-Cresol.

Using the method of nitration by fuming nitric acid in glacial acetic acid already discussed for ~~all~~ ortho and para cresols, but carrying out the nitration at -15 - -5°, three products of nitration of m-cresol are produced in varying amounts, 2-nitro-m-cresol, volatile in steam, liquid, 6-nitro-m-cresol, volatile in steam, m.p. 56° and 4-nitro-m-cresol, non-volatile in steam, m.p. 129°. Isolation of these isomers becomes a matter of some difficulty owing to the fact that the liquid isomer as well as the solid 6-nitro-m-cresol is volatile in steam, and ethereal extraction of the aqueous distillate from a steam distillation of the nitration product leaves as a rule only a semi-solid of mixed composition; similar extraction of the aqueous residue gives a solid of impure melting point.

Addition of mercuric nitrate to such a mixture has the striking effect of diminishing the quantity of the liquid isomer and of increasing the proportion of the solid 6-nitro-m-cresol, thus providing yet another instance of modification of the normal ratio between isomers. Table 27 shows both the quantitative effect of mercury in such respect, when such can be estimated, as well as the effect on the character of the nitration in general.

XI. Nitration of Naphthol.

Nitration of naphthol to the final stage of trinitro-naphthol was carried out by the method of Diel, (B. 11. 1661), by which dinitronaphthol is treated in the cold with fuming nitric acid, (0'26 parts), and concentrated sulphuric acid, and allowed to stand for ten days, stirring continuously.

As ~~seems~~ ~~always to be~~ is the case when sulphuric acid is used, the mercury salt in such a mixture forms a suspension of the sulphate and the mixture must be kept continuously stirred to ensure complete admixture.

The solid product is isolated in the usual way by pouring into water, and any unchanged dinitrocompound is separated by rapid grinding with hot glacial acetic acid. Preliminary experiments showed that mercury produces a positive effect, increasing the yield of both crude nitration product as well as of pure trinitronaphthol.

That this catalytic effect might be sufficient to bring about a shortening of the usual, long time of standing, -ten days- seemed worthy of investigation, and experiments were therefore made in the presence of mercuric nitrate in which the time of stsnding was shortened to seven days. This proved unsuccessful, even twenty per cent of the mercury salt failing to bring the yield of ~~dini~~ trinitrocompound up to the normal value obtained without mercury.

There is no sign of oxidation either with mercury or without. No carbon dioxide can be detected, the total evolution of gas being very small, and the quantity of oxalic acid found in the sulphuric acid residue is too small to be estimated accurately. Increase of nitration produced by the presence of ten per cent of mercuric nitrate is observed up to twelve per cent on the crude nitration product, still containing unchanged dinitronaphthol, though, as might be expected, results vary considerably. Very much ~~less~~ more constant values are obtained if the relative weights of purified trinitronaphthol, freed from dinitronaphthol by acetic acid extraction, are compared. An average increase in weight of 12'3 per cent being obtained. The melting point of this product however, still indicates the presence of some unchanged dinitro-naphthol. A double crystallisation of this product from acetic acid shows a still greater increase, a relative increase of about

17 per cent being obtained, the melting point, 181 - 183°, showing now a high purity for trinitronaphthol. Tables 28 .

XII. Nitration of Benzoic Acid.

The use of potassium nitrate and concentrated sulphuric acid for the nitration of benzoic acid, by which the m-nitro acid separates as a solid, the ortho compound remaining in solution, is very suitable for an examination of the effect of mercury on the nitration, and on the ratio of the isomers formed. For, by comparison of the weights of the crude product and of the crystallised meta compound, the relative proportions of meta and of combined ortho and para compounds can be accurately estimated. The weight of crude solid, unchanged benzoic acid and meta nitro benzoic acid, isolated by pouring into water, is frequently, though not invariably, increased by the presence of mercury, but the ~~%~~ yield of pure m-nitrobenzoic avid isolated from this solid by removal of benzoic acid by steam distillation is invariable increased by the mercury salt. Table 31 . This increase is sufficient to allow of a reduction of the proportion bf potassium nitrate from two to one point eight parts, an increased yield of about eight per cent still being maintained. Table 31 .

XIII. Nitration of Salicylic Acid.

The effect of mercuric nitrate on the nitration of this acid affords an interesting comparison with benzoic acid by reason of the presence of the hydroxy group, which, as has been seen, has been of special significance in the susceptibility to catalytic influence of phenol nitrations.

In the method used, sodium nitrite and sulphuric acid, the mercury salt is dissolved in the water before admixture with the sodium nitrite and salicylic acid, and the concentrated sulphuric acid added slowly to this mixture with constant stirring, the temperature being kept below 20°. Provided the sukphuric acid is added to the mixture immediately after mixing with mercuric nitrate, no appreciable darkeing or evolution of nitrous fumes occurs, and the behaviour is scarcely different to a similar mixture containing no mercuric nitrate. But oxidation increases rapidly with standing if the addition of the sulphuric acid is delayed.

The nitration products of salicylic acid by this method are the 5-nitro and the 3-nitro acids, the latter being twice as soluble in water as the 5-nitro acid. Separation can, therefore, be effected by twice crystallisation of the crude product from boiling water. The addition of mercuric nitrate produces a very slight decrease of yield of crude product, amounting to about one per cent. Table 33 Actually in some experiments a similarly slight positive variation has been observed, v. experiments 4 & 10 . A greater difference is revealed if we examine the respective yields of pure 5-nitrosali-

-sylic acid, that obtained from mercuriated nitrations containing ten per cent mercuric nitrate showing an average decrease of 13'2 per cent. Obviously, here, the principal effect of mercury is to increase the formation of the 3-nitro isomer at the direct expense of the 5-nitro compound. Experiments in which the proportion of mercury salt is increased to twenty per cent show a tendency, though an irregular one, to maintain this, the decrease of 5-nitro acid falling in one experiment as low as 7'7 per cent, but rising to 20'6 per cent in another. Table 33 .

XXIV. Nitration of Cinnamic Acid.

Preliminary experiments were made to ascertain the nature of the nitration product in the presence of mercury.

A. The addition of fuming nitric acid to a mixture of cinnamic acid and mercuric nitrate caused, in spite of cooling, considerable oxidation, and on diluting with water no solid was obtained, showing complete oxidation. Oxalic acid can be isolated from the aqueous liquor.

B. Addition of fuming nitric acid to cinnamic acid dissolved in glacial acetic acid to which finely divided mercuric nitrate has been added causes much less oxidation and darkening, and crystals of nitrocinnamic acid are obtained on standing, and, more extensively, on diluting with water. Nitrous fumes and carbon dioxide are evolved if the addition of nitric acid is not carried out very slowly.

C. An attempt was made to nitrate further in the presence of mercury, the nitrocinnamic acid obtained by the above nitrations. A mixture of finely powdered mercuric nitrate and nitrocinnamic acid was suspended in glacial acetic acid, stirring continuously at ordinary temperature. Fuming nitric acid was added, and during the addition the solid completely dissolved. Further addition of nitric acid reprecipitated mercuric nitrate. There was no evidence of oxidation products, either oxalic acid or carbon dioxide, and there was no appreciable evolution of nitrous gases. One half of this liquid was poured into water. There was no immediate precipitation of solid, but some solid, which was found to be unchanged nitrocinnamic acid, separated on standing. The remaining half of the nitration mixture was heated at 70 - 80° for one hour. Carbon dioxide and nitrous fumes were evolved, and on pouring a portion into water no solid separated, though oxalic acid was found in the aqueous liquor. Addition of (a) alcohol and (b) petroleum ether to the remaining portions also failed to precipitate solid. It was assumed therefore, that complete oxidation had (therefore) occured Experiments were, therefore, made to determine the effect of mercury on the yield of nitrocinnamic acid by the normal method of nitration of cinnamic acid. O

One part of cinnamic acid plus five parts of nitric acid, (1'5) are co~~l~~oled and stirred vigorously while powdered cinnamic acid is added. On pouring into water or ice solid, which is mainly p-nitro-cinnamic acid, containing a small quantity of ortho acid, separates. The latter can be extracted by successive treatments with cold alcohol in which the para acid is insoluble. Table ~~4~~34 shows very clearly the effect on this nitration of adding mercury salt. There is a slight increase, amounting to never more than 6'5 per cent, of the yield of crude compound. A double extraction of this product with cold alcohol raises the melting point of the residue to 281 - 283°, (m.p. pure p-nitrocinnamic acid = 285°), but the wieght of para compound thus isolated in the mercuriated nitration is less, the decrease varying between five and ten per cent, than in a normal nitration. Evaporation of the combined alcohol extractions yields a small quantity of practically pure ortho compound, the proportion of which shows a very considerable increase, amounting in some cases to 125 per cent, in the mercuriated nitrations. Table 34.

A comparison of the effect of mercury on the nitration of the three acids, benzoic, salicylic and cinnamic, shows that salicylic acid, containing a hydroxy group, is exceptional in that mercury depresses nitration, oxidation of the acid being favoured at the direct expense of nitration. That the presence of the hydroxyl group does not in itself promote oxidation at the expense of nitr-

-ation is evident from the preceeding examination of the nitration of phenolic compounds, in which in every case mercury has a positive catalytic effect on nitration, and when there is an increase of oxidation, as with chlorophenol and phenol, it takes place simultaneously with nitration, i.e. at the expense of the compound reacting. The observed increase of nitration in the mercuriated nitration of benzoic and cinnamic acids eliminates the negative carboxyl group as of itself a factor for excessive oxidation. Comparison of the average values of percentage variation in yield of nitrated product, (v. table 35), shows an approximately equal variation in opposite senses for benzoic and salicylic acids. In other words, introduction into the benzoic avid molecule of a hydroxy group in the ortho position, not only neutralises the positive catalytic effect of mercury, but causes a depression from the normal value for nitration of benzoic acid to an extent equal to the increased nitration produced by mercury. When the carboxyl group is separated from the nucleus by a double bond, e.g. cinnamic acid, the influence of mercury is restricted, and though this is still favourable to nitration, the average increase in yield of nitrated product is only 4'34 per cent.

XV. Nitration of Benzaldehyde.

The addition of benzaldehyde to a mixture of nitric acid, 1'4, and concentrated sulphuric acid containing mercuric nitrate is apt to cause vigorous reaction unless the addition of the aldehyde is carried out slowly with cooling. The gaseous products of this reaction contain a considerable quantity of carbon dioxide, and nitrogen peroxide, and oxalic avid is invariably found in the solution in mercuriated nitrations. But the product~~s~~ o~~d~~f such nitration is practically pure m-nitrobenzoic acid, showing that the influence of the mercury salt is primararily to facilitate oxidation of the aldehyde group to carboxyl. As will be shown from an examination of other aldehydes, a readily oxidisable group as is -CHO cannot, in the medium of higher oxidation potential, which the presence of mercury entails, remain unoxidised. If, however, the relative weights of the products of mercuriated and non-mercuriated nitrations be compared, it is seen that a greater proportion of aldehyde undergoes nitration in the former than is the case in a normal nitration, providing further evidence of the thesis that nercury, as well as raising the oxidation potential of a nitric acid medium, is a positive catalyst of the nitrating function of the acid. This is, borne out in the results obtained in the mercuriated nitration of salicylic aldehyde and p-oxybenzaldehyde. Both these compounds under such conditions show increased nitration, amonting in some cases to as much as 40 per cent. Table 38 . But a comparison of tables 38 & 39 shows the great variability of results. Neither in the increase of toral nitration nor in the percentage difference of decreased nitroaldehyde formation is there any constant effect, and such seems to be the characteristic of reactions of nitric acid in which oxidation plays any marked part. Average values of such widely different results cannot be compared, but table 40 serves to illustrate the comparative order of effect, and to reveal the existence of a very marked difference between the three aldehydes. The introduction of a hydroxyl group in the ortho position raises the average values by 95'6 per cent, while a similar introduction in the para position increases it to 230'4 per cent, or a percentage increase of 68'8 in the change from ortho position to para.

Attempts were made to separate the ortho and para isomers, but neither method of separation, (by the sodium salt or by the bisulphite compound), gives results sufficiently accurate for them to be of any value in relative estimations of weights.

XIV. Nitration of Acetanilide.

Owing to the tendency to rapid evolution of heat when nitration with fuming nitric acid is carried out in the presence of mercury, the method of Notling and Collins, (B. 17. 262), by which acetanilide is suspended in four parts of concentrated sulphuric acid, and nitrated with a mixture of 0'59 parts of fuming nitric acid and 1'2 parts of concentrated sulphuric acid was used. The acetanilide was dissolved in a minimum quantity of hot acetic acid before addition of sulphuric acid, and the mercuric nitrate, when present, is added in a finely divided condition to the acetanilide which is kept constantly stirred. Considerable dark red colour developes in the solution containing mercury, though, on standing, both mixtures ultimately take on the same intensity of colour. On pouring the product into water the para compound separates as a solid, while the ortho compound can be extracted from the aqueous filtrate by extraction with chloroform. The yield of crude product shows a variable, (up to 15 per cent), increase in the presence of mercury, but the yield of ortho compound is variable, sometimes showing an increase, up to 50 per cent, sometimes a decrease of like amount. Consequently the ortho/para ratio, which in the normal nitration is constant between 0'09/1 and 0'18/1, shows wider limits of variability from 0'05/1 to 0'215/1. v. table 41 . It follows, therefore, that in the presence of mercury, while the total yield of ortho and para compounds and the yield of pure para compound shows an almost invariable increase, there is in some cases a raising of the ortho factor in the ortho/para ratio, in others a similar variation of the para factor. v. table. 41

XVII. Nitration of Methylacetanilide.

Nitration here is complete to the dinitro stage, and the influence of mercury was examined on the yield of dinitro compound and on the effect of varying addition of acid with inccreasing amounts of mercuric nitrate.

Though the yield of dinitro compound in a normal nitration is considerably below the theoretical yield, mercury is without ~~effect~~ appreciable effect on the yield, which in the most favourable experiments is only raised by four per cent. It seemed unlikely therefore that with a lower concentration of nitric acid, mercury would be able to maintain the yield at its normal value, and this was found to be the case. The more dilute acid occasiuns a decreased yield of dinitro compound in a normal nitration, and this can only very slightly be compensated for by addition of mercuric nitrate, the increase being, for small amounts of mercury salt, roughly dependent on the quantity of mercuric nitrate used, v. table 42. It is important to n~~i~~otice, however, that in the presence of fifteen per cent of mercury salt the low yield due to thirty per cent nitric acid is increased by an amount varying from 19 to 33 per cent.

A comparison of the effect of five per cent of mercuric nitrate in otherwise normal experiments with a similar effect in the nitration of acetanilide shows that, while the average value for the total percentage increase of nitration in the latter, as far as it can be estimated, is very low, (1'86%), the increase of para nitration corresponding almost exactly to the total increase of nitration in the nitration of methyl acetanilide.

XVIII. Nitration of Dimethylaniline.

The nitration of dimethylaniline by a "mixed acid" at a temperature below 5° gives, on pouring into water, the para compound as a yellow solid. On further dilution of the filtrate, the colour changes from yellow to deep red, and a separation of the meta isomer occurs In general two intermediate stages can be isolated as the filtrate is diluted, the solid separating during the addition of water being of an orange colour. The melting point of this solid shows it to be a mixture of para and meta isomers, consequently no accurate estimate of any change in the ratio of the two isomers, which may be initiated by the mercury salt, can be made, though it is of interest to compare the relative weights of pure para and meta compounds in the two cases. There is a definite increase of total nitration in the presence of mercuric nitrate, amounting to 4'6 per cent. The most marked effect is seen, however, in the effect of mercury on the formation of the para compound. The melting point of the crude para product in the presence of mercury is raised from 130 - 131° to 150 - 159°, representing almost pure paranitrodimethylaniline. So that not only is there an increased weight of crude product, but that product contains a much higher percentage of pure para compound. Table 43. On the other hand, the yield of meta compound shows a decrease, varying from 6 - 13 per cent. No change in melting point is observed here as a result of the presence of mercury.

Oxidation Products of Aromatic Nitrations.

In the nitrations of hydrocarbons and of halogen hydrocarbons examined, analysis of the amount of oxalic acid produced showed that this amount is in no case great. For example, ten grams of bromo benzene are only oxidised to an extent which is represented by 0'67 grams of oxalic acid. Mercuric nitrate, by raising the oxidising capacity of the system, may actually produce a lower yield of oxalic acid, as the oxidation is carried to the further stage of carbon dioxide, which is greater in the presence of mercury. But in the nitrations of hydrocarbons the proportions of both oxalic acid and carbon dioxide are, in general, greater in the presence of mercury than without. Tables 29

Of the three compounds bromobemzene, chlorobenzene and xylene, the latter showed the highest propotion of compound nitrated, and the lowest of compound oxidised. Table 29 . The percentage of compound undergoing oxidation then increases from xylene to chlorbenzene to bromobenzene, where, in the presence of mercury, its maximum value averages about 1 - 1'3 per cent, or nearly three times as much as occurs in normal non-mercuriated nitrations. A very striking difference becomes apparent when we compare the relative proportions of nitric acid undergoing oxidation in the nitration of xylene and bromobenzene respectively. In the latter, in a concen-

-trated nitric acid mixture, as much as 68 per cent, (no mercury), and 85 per cent, (mercury)m, disappears as oxides of nitrogen and nitrous acid, while in the nitration of zylene by a concentrated nitric acid-oleum or concentrated sulphuric acid mixture, this oxidation falls to 3 per cent, (no mercury), and 10 per cent, (mercury), a decrease adequately accounted for by the ssulphuric acid medium. Table IA . But, as is seen from the table , the total extent of oxidation of the compound is slight, and though mercury increases this to a small extent, it may be counterbalanced by the increase in nitration. When the catalytic effect on nitration is negative,as for bromobenzene, it might be expected that the increase in oxidation products would bear a direct relarion to the decrease in nitrated products. But this is not the case. The total amount of carbon dioxide and of oxalic acid estimated in the nitration of bromobenzene or of hydrocarbons containing mercuric nitrate never corresponds to the decrease in nitration, and is usually considerably below it. Tables IA + 29.

The most marked feature of the nitration of phenols is, in contrast to the nitration of hydrocarbons, the comparatively large proportion of accompanying oxidation. Phenol and p-chlorophenol, the nitration of which is carried out in dilute nitric acid media, undergo oxidation to an extent varying from 2'3 to 3;7 per cent Owing to the retention of nitric acid and nitrous acid by the sticky nitration product of chlorophenol it was found difficult to estimate residual nitric acid and nitrous acid in the nitration of this compound.

o-Cresol, which is nitrated in a "mixed acid" medium, undergoes still further oxidation, the extent of which is considerably increased by the presence of mercuric nitrate, v. table 25. Of all compounds examined in this respect o-cresol exhibits the most extensive oxidation of the organic compound. But the proportion of nitric acid undergoing reduction is considerably less, averaging 31 per cent, than was the case in phenol nitrations when as high a value as 79 per cent reduction is reached, a result which would be expected in the dilute medium. The total consumption of nitric acid in the two types of nitration is however approximately equal and nearly complete, averaging 93 - 98 per cent, the proportion of organic compound undergoing nitration being considerably higher for o-cresol than for phenol. Table 30

Estimations of the oxidation products of the nitration of acids and aldehydes shows that benzaldehyde and benzoic acid correspond very closely in the extent to which each is oxidised to carbon dioxide and oxalic acid, the value being low, and never exceeding 2 per cent. Both nitrations are carried out in concentrated sulphuric acid media, and the reduction of nitric acid in this proceeds to approximately the same extent in both, allowance being made for the increased reduction of acid by the aldehyde to the carboxylic acid, an oxidation which is particularly noticeable in the presence of mercury, v. table 37. Thus, while the percentage value of the reduction from benzoic acid averages from 26 - 33 per cent, it reaches in a non-mercuriated nitration of benzaldehyde 40 per cent, and in a mercuriated nitration, 51 per cent. On the other hand, the proportion of ~~benzene~~ benzaldehyde undergoing nitration is less than half the percentage nitration of the acid, and consequantly a considerably lower proportion of nitric acid is used up in this than in the former nitration.

The introduction of a hydroxyl group, v. table 37, markedly increases the amount of compound undergoing ~~nitration~~ oxidation, the value reached being about three times greater than for benzaldehyde. Corresponding to this is a more extensive reduction of nitric acid, partly accounted for by a greatly increased nitration.

A fact of considerable importance emerges from these results, namely that, though the total amount of nitric acid consumed in the various nitrations in every case reaches its greatest value in the presence of mercury, this increase is accounted for mainly by an increased nitration. In the nitration of phenol and o-cresol red--uction of nitric acid by reactions other than nitration of the organic compound is only very slightly increased by the presence of mercury, v. table 25. This, and the facts already discussed, forms a striking illustration of the catalytic effect of mercury on the functions of nitric acid, an effect which in no way favours oxidation at the expense of nitration.

Experimental.

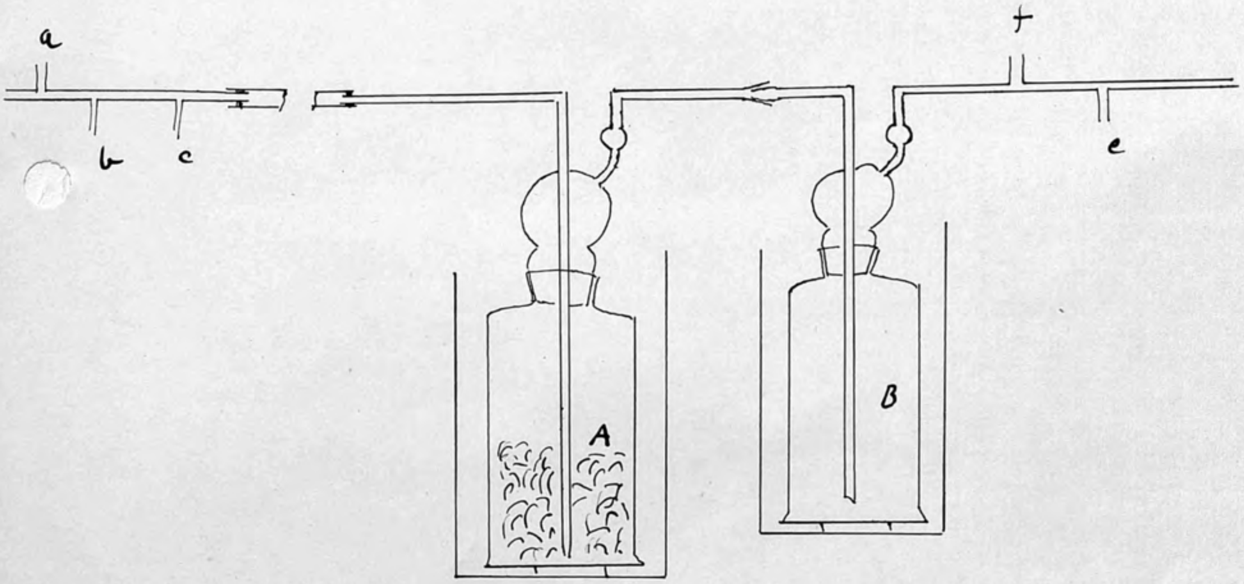
The Effect of Mercury Salts on Orientation in Aromatic Compounds.

The Action of Nitric Acid on Unsaturated Hydrocarbons.

The interactions of nitric acid and acetylene and of nitric acid and ethylene have been examined under varying conditions of concentration,oof temperature and in the presence of metallic salts. Acetylene and ethylene are absorbed with ease, the former much more readily than is ethylene, by absolute and more dilute nitric acid, or by mixtures of nitric acid and sulphuric acid. With dilution of the acid the rate of interaction, and hence of the readiness of absorption decreases, but ~~with~~ both are markedly susceptible to change of temperature, and to the presence of metallic salts, the latter modifying considerably not only the rate of reaction but the actual course of reaction. The products of interaction between the hydrocarbon and nitric acid are various, and the nature and proportion of these products is largely determined by the concentration of the acid, by temperature and by the presence of a catalyst and by concentrated sulphuric acid. The reaction is accompanied by a small developement of heat. Throughout the following experiments the temperature was kept at about 30°C.

Experimental:- The essential parts of the apparatus are shown in the accompanying figure, III. Acetylene and ethylene are absorbed so readily by sufficiently concentrated nitric acid at ordinary temperatures, that the Drechsel bubbler (A), in which the

Fig III



end of the inlet tube is somewhat constricted, serves as the reaction vessel; the bubbles of gas are broken by a layer of glass beads. This bubbler, which is nearly full, is immersed in a bath maintained at a constant temperature, usually 30°.

The second bubbler(B), which is placed in a cooling bath, contains sulphuric aid of 96 - 97 per cent; all the oxides of nitrogen coming from (A) are absorbed in (B). No nitrous or nitric oxides are found in the gas thus passed through sulphuric acid. Safety devices for meeting a developement of negative pressure or a sudden positive pressure are placed at a, b. and c. Samples of gas for analysis can be drawn off from the pipe line at e and f. (Orton and McKie. T. 1920. 117. 283),

Preparation of Materials

Acetylene: It was found most convenient to generate the acetylene in situ for each experiment. By using weighed quantities of calcium chloride, the acetylene yield of which, and purity of the acetylene was known from experiment, a fixed weight of acetylene could be introduced each time. It was necessary to devise some form of generator which would insure a slow and regular delivery of gas, and which in size did not add materially to the total capacity of the apparatus, and this was effected by the use of a small Erlenmeyer flask of 75 cc capacity, fitted with a very finely regulated water jet and gas delivery tube.

Purification of the acetylene was found unnecessary, and the gas, dried only, by passage through an adequate calcium chloride tube, was passed straight into the reaction vessel.

Ethylene. It was found impossible to estimate with any accuracy either the purity or quantity of the gas produced in situ either by the methods of Newth, by dropping alcohol into heated syrupy phosphoric acid, or by any of the ordinary methods for genarating ethylene. The methods was adopted, therefore, of introfucing from a gas holder ethylene of known purity and quantity. The most satisfactory method of preparation was found to be that devised by Sidgewick and Plant, (private communication), in which ethyl alcohol is vapourised in a long iron tube, heated to 280 - 300°, and packed with pumice stohe, previously soaked in syrupy phosphoric acid for twenty four hours. The alcohol is dropped into an adapter fitted into one end of the iron tube, at the rate of ten drops per minute. Ethylene is generated instantly, and is caused to pass through the tube by slight suction of the gas holder connected beyond a condenser and small receiver to the further end of the tube. It is obviously important that the whole apparatus be absolutely air-tight, and that a good alcohol seal be kept in the stem of the adapter. The rate at which the gas enters the holder can be regulated by the water valve of the gas holder at about one bubble per second, as indicated by a small bubler containing a little water, placed between the gas holder and the receiver. By this method ethylene of 97 - 99 per cent purity is readily obtained.

Nitric Acid. The nitric acid was prepared from a crude, fuming nitric acid (D^{15} 1'5), which sometimes contained much iodine as iodic acid, by distilling from an equal weight of sulphuric acid. The distillate had D^{15} 1'545; and the acid contained 2'2 per cent of nitrous acid as determined by permanganate. In all cases when an aqueous nitric acid was required this highly concentrated distilled acid was used and the amount of distilled water requisite for the particular dilution added. In such cases the water is placed first in the reaction vessel, and in order to prevent loss of nitrous acid by transference, metallic salts, when such are used, are intrdduced in a finely groudn condition into the reaction vessel containing the water, in which they dissolve completely. Absolute nitric acid dissolved very little metallic nitrate, which at the beginning of such experiment is in suspension, but dissolved later. In a nitric-sulphuric acid mixture the concentrated sulphuric acid precipitates the bulk of the salt as sulphate, which remains in suspension throughout the experiment. In a typical experiment 0'5 grams (0'33 per cent), of mercuric nitrate, (When used), is placed in the bubler A, then water, (75 cc when a 95 per cent acid is used), and finally the nitric acid, (138'6 grams, 90 cc). The quantity of nitric acid just given will dissolve

1'2 - 1'39 grams of mercuric nitrate at ordinary temperature. Into this mixture it is not advantageous to pass more than 4'5 - 4'6 litres of acetylene or 4'7 - 4'9 litres of ethylene. As the reaction proceeds the nitric acid is diluted; not only is the reaction then more tardy, and hence the absorption poorer, but oxidation, for acetylene, and hence evolution of carbon dioxide becomes more prominent. At the early stages of the reaction very little gas leaves A; later, oxides of nitrogen and carbon dioxide are evolved.

Products of the Reaction. The mechanism and products of reaction have been discussed in detail for each hydrocarbon, but there is a fundamental similarity of behaviour which can be indicated at this stage. Omitting the products of reduction of nitric acid, the reaction yields trinitromethane and certain other substances which can be converted into trinitromethane, carbon dioxide, (and traces of carbon monoxide), and oxalic acid; the latter may predominate in certain caess such as high or low concentration of acid or low temperature. Of the metals which have been tried as catalysts, mercury causes a marked increase of the proportion of trinitromethane and of carbon dioxide, to the exclusion, "or acetylene, of other products. Thus the reaction in the presence of mercury is simplified, and the hydrocarbon absorbed is represented quantitatively, for acetylene, by nitroform and carbon dioxide.

Analysis and Isolation of the Product. The product, after the passage of acetylene or ethylene, is of a deep red-brown colour, and contains considerable quantities of nitrous acid and oxides od nitrogen. Dilution with water causes a vigorous evolution of oxides of nitrogen, and the aqueous liquor is found to ~~be~~ contain as well as nitrogen oxide, dissolved nitroform, dinitromethane and frequently oxalic acid.

Nitroform. The product is diluted 1 to 10, and then the nitrous acid removed by ammonium nitrate, 20 grams to 100 cc of diluted product. The nitroform is then extracted by ether, preferable in a continuous apparatus. The ethereal extract is concentrated and added to alcoholic ammonia or alcoholic potassium hydroxide, when the salt crystallises out. From 100 grams of this product prepared under the best conditions, about 15 grams of the crude ammonium salt can be obtained.

Analysis of Nitroform, Nitrous and Nitric Acids. The estimation of nitrous acid cannot be made directly on the product, for other substances which reduce permanganate are present. Two procedures have been followed. The permangmnate titre of the product diluted 1 in 10 is determined; then either the nitrous acid is removed by aspiration or by boiling with ammonium nitrate, (Gailhat. J.Pharm.Chim. 1900 (vi), 12. 9; Gerlinger, Zeit.angew. Chem.1902. 14. 1250; they both use ammonium chloride). In the aspiration, it is not necessary to remove the whole of the nitrous acid, which is a very lengthy process. At a given temperature and with a given air current, the percentage loss of nitrous acid from the solution follows the well-known law, and is independent of the initial concentration. At 16°, with the rate of air current 0'1 litres per minute, trials with known solutions of nitrouc acid at various concentrations in aqueous nitric acid, and with known solutions of nitroform and nitrous acid in 7 - 8 per cent nitric acid, shew that 73'3 (72'8 - 73'9) per cent of nitrous acid disappear in one hour. After the partial removal of the nitrous acid by aspiration or the complete removal by ammonium nitrate, the residual permanganate titre is determined, whence the nitrous acid can be calculated. Determinations of the nitrous acid made by these two methods agree fairly well, but the method of aspiration is probably the more trustworthy. Nitroform can be titrated in aqueous solution by alkali hydroxide in the presence of phenolphthalein (Hantzsch and Rinckenburger. B. 1899. 32. 631). Recently E. Schmidt (B. 1919. 52. (B) 400) has described a method in which nitron is used as a precipitant. I have tested both these methods and found them rather less accurate than the estimation of nitroform by acid potassium permanganate, (McKie. T. 1920. 117. 646), a method which I have exhaustively tested and found accurate to within 0'3 per cent. The product contains, besides nitrous cid and nitroform. other substance (for example oxalic acid) which reduce permanganate. After removal of the nitrous acid, the nitroform may be extracted with ether and then titrated, or, preferably, distilled off and titrated.with permanganate.

The following is a typical analysis of the acetylene reaction: 2 - 5 cc of the "product" are added to 18 - 45 cc of N/2 - N-alkali hydroxide; 5 cc are then diluted with water, 10 - 15 cc, and 2 - 3 grams of ammonium nitrate added. The mixture is gently bolied for several minutes and then diluted to 100 cc, acidified with 5 - 10cc of 10 per cent sulphuric acid, and distilled until the distillate is colourless, (thirty minutes). The distillate may be collected in water or N/10-alkali; it is finally titrated with N/10-$KMnO_4$. One cc. of N/10-$KMnO_4$ is equivalent to 151/80.000 0.0019 grams of nitroform.

After destruction of nitrous acid and extraction of nitroform by ether, the residue still reduces permanganate. The reduction is but small under xonditions most favourable for the preparation of nitroform. Some, and sometimes most, of the reduction of the permanganate by the residue is to be attributed to oxalic acid. A rough estimate of the nitric acid in the product can be made by deducting from the total alkali titre the alkali titre equivalent to the permanganate titre of the diluted product. As this deduction does not amoubt to mbre than 10 per cent of the total alkali titre, a rough estimate of the nitric acid remaining is possible.

Analysis of Gaseseous Product. The gas coming from the bubbler (B) is collected over a neutral, saturated calcium chloride solution in a large vessel of known capacity; the last part of the gas in any experiment is measured in a graduated vessel. Both carbon dioxide and acetylene or ethyelen are less readily soluble in saturated calcium chloride than in other saline solutions; at 14°, carbon dioxide has a solubility of 0'1 in 1, and acetylene 0'08 in 1 by volume. The gas evolved during the heating of the product with sulphuric acid was collected in a similar manner. The liquid nearly filled the flask, which was ground on to a narrow condenser tube; this tube was carried on as a delivery tube for the evolved gas.

The gas consists in the main of carbon dioxide, with lesser quantities of hydrocarbon and traces of air. The acetylene or ethylene was absorbed by a 5 per cent solution of potassium bromide satureted with bromine; the absorption is somewhat slow towards the end, but complete. Carbon dioxide is estimated previously in the ordinary way. This procedure has been exhaustively tested on known mixtures of gases, in the course of these experiments, and found quite accurate.

Tetranitromethane. The product from the interaction of either acetylene or ethylene and nitric acid contains very little tetranitromethane, but both compounds can be made to yield tetranitro-

-methane in appreciable quantity by heating the undiluted product with phosphoric oxide, sulphuric acid or duming sulphuric acid. Whilst only some 4 - 5 per cent of the benzene nitrated can, by any of the recognised procedures, (Will. B. 1914. 47, 704) &c, be converted into tetranitromethane, it has been found that some 37 per cent of the acetylene and 20 per cent of the ethylene appears as this substance by this methdd under suitable conditions. It is important to notice that the total nitroform in the product does not account for the whole of the tetranitromethane thus isolated. About 15 per cent of the tetranitromethane is derived from substances which, v. p. 124, in the first stage are incompletely nitrated. It is obvious that the subsequent stage in a dehydrating medium brings about more extensive nitration than then the conversion of nitroform into tatranitromethane. Table 45 + 46

A satisfactory procedure, in which all the nitroform is converted into tetranitromethane and the maximum yield is obtained, is to mix the product from 90 cc of 100 per cent nitric acid with 190 - 380 grams of sulphuric acid or sulphuric acid containing 25 per cent of sulphur thioxide. The sulphuric acid is added to the product, and care is taken that the temperature does not rise. The mixture may be then directly distilled, but it is preferable to heat it, finally to 90 - 95°, under a reflux, until gas ceases to be evolved; this operation usually occupies about four hours.

For reasons given in the foregoing, it is important that the product be mixed with sulphuric acid as soon as possible after the passage of the hydrocarbon. That this mixture should then be kapt for some time before heating or distilling is immaterial.

On cooling, much of the tetranitromethane will appear as an oil, or even crystals; It may be collected by means of carbon tetrachloride or petroleum, but isolation by distillation is simples

The effect of certain variations in the procedure may be noted. The proportions of sulphuric acid may be reduced below the limits given above without producing any considerable diminution in the yield. The addition of 20 - 25 grams of nitric acid to the mixture of the product and sulphuric acid before heating leads to an improvement of the yield, especially if the conditions have otherwise been unfavourable; for instance if the temperature has been too low, or the nitric acid too dilute. Under optimum conditions such addition has, however, little effect. (Orton and McKie. T. 1920. 117. 283).

The Action of Nitric Acid on Acetylene.

Effect of varying concentration of acid. The absorption of acetylene by nitric acid of varying concentrations, from 70 - 100 per cent, and the effect of this variation on the ultimate products has been examined in detail. With progressive dilution of the acid the absorption of acetylene by a given quantity of acid stead-

-ily diminishes, the maximum absorption being obtained in 100 per cent nitric acid, v. table 47. Ifvthe tetranitromethane which can be isolated from the product, and which is a convenient measure to which nitroform and other antecedents are produced, be expressed as a percentage of this quantity of acetylene absorbed, this progressive decrease is not maintained. Both a high and a low concentration of acid are unfavourable to the nitration leading to the formation of tetranitromethane. The optimum concentration is about 95 - 97 per cent. Obviously in the interaction of nitric acid and acetylene the acid becomes diluted, and the yield will only be a maximum when a small quantity of acetylene is absorbed by this acid. The maximum yield of nitroform and tetranitromethane in one operation in the absence of a catalyst is obtained by the absorption of 2'7 - 2'9 litres of acetylene by 100 grams of 95 per cent acid. The yield of tetranitromethane is then 9 - 10 grams or 277 per cent of the acetylene abosrbed. (If two moles of tetranitromethane are formed from one of acetylene, "t.n.m." would amount to 1500 per cent in a quantitative yield, or, as is much more probable, v.p. 127, if one mole of acetylene yields one mole of tetranitromethane, 754 per cent).

Table 47.

Effect of Temperature. As the temperature of reaction is raised there is a progressive increase in the proportion of acetylene absorbed, a minimum absorption being obtained at a temperature of -3o

Table. 49

There is a marked increase of absorption between the temperatures 15 and 25°, the amount of acetylene absorbed at that temperature increasing very little as the temperature is raised to 40°, but at 50° this value falls slightly.

Corresponding to this change in the value of the acetylene absorbed there is a progressive increase in the percentage of tetranitromethane calculated on the acetylene absorbed, and at 50° this value reaches a maximum, though the actual weight of tetranitromethane is lower than is produced at 30°.

The carbon dioxide evolved when small quantities, 2 - 3 litres, of acetylene are being passed through is variable, though there is a tendency towards a maximum evolution at 30°. This variation is reflected in the ratio carbon dioxide/acetylene absorbed. But the passage of double this quantity of acetylene establishes for this ratio a ~~xxxx~~ regulaely increasing value. Tables 47 - 49.

Effect of the Presence of Metallic Salts. The addition of small quantities, 5 - 10 per cent, of the nitrates of platinum, silver, copper, uranium and mercury to the reaction mixture showed a very variable effect. Table 50. Mercury stands alone in effecting an inc rease both in the rate of and in the total amount of absorption of the hydrocarbon. Hence mercury markedly accelerates the rate in interaction. Concomitantly the yield of nitroform and of tetranitromethane is increased, and this yield, expressed as a percentage of the acetylene absorbed, is raised from 341 to 453. Copper, though depressing the total absorption, promotes a yield of tetranitromethane representing 371 per cent of the acetylene absorbed, slightly higher than the normal percentage in the absence of a metal, while the other three metals both depress the total absorption and the percentage yield of tetranitromethane. Consideration of the fate of the carbon in the acetylene absorbed shows that the carbon becoming tetranitromethane and that becoming carbon dioxide both reach their highest value in the presence of mercury, and together account for the whole of the acetylene absorbed. In that this means that all side reactions, other than direct nitration and oxidation, are eliminated, this is of considerable importance, v. p. 177 . The effect of copper is slightly to increase both the proportion of carbon becoming tetranitromethane and carbon dioxide, and hence correspondingly to reduce the proportion ~~becoming~~ used in side reactions. Uranium facilitates oxidation at the expense of al, other reactions, while platinum and silver both depress the extent of direct oxidation and nitration and facilitate side reactions. Table 50.

The proportion of mercuric nitrate used is important, and experimental investigation has shown that a maximum concentration of 0'33 per cent of the nitric acid has the most favourable effect in reducing side reactions, and in facilitating the formation of tetranitromethane. Table 52. Table 53 illustrates the optimum conditions, temperature, concentration &c under which mercury exerts its most favoarable effect. At a temperature of 30°, and in 95 per cent nitric acid, 0'33 per cent of mercuric nitrate promotes both the maximum absorption of acetylene and yield of tetranitromethane. Table 51 summarises the results of experiments carried out under these conditions.

It is interesting, and from the point of view of the mechanism of the reaction, (v. p. 124) important, to compare the relation between the amount of trinitromethane which can be estimated in the reaction mixture and the tetranitromethane which can be isolated from it by heating with concentrated sulphuric acid. In all cases the tetranitromethane isolated represents more, (50 per cent), than the equivalent amount of nitroform found in the mixture. Tables 45 and 46. If, however, the reaction mixture be stood for several days before admixture with the sulphuric acid for conversion to tetranitromethane, the amount of the latter which can then be isolated from it is considerably less than the normal quantity formed when admixture is not delayed, and represents scarcely more, - it may even be less- than the estimated amount of nitroform.

The Action of Nitric Acid on Ethylene.

Effect of Concentration of Nitric Acid. The absorption of ethylene by concentrated nitric is rather less ready than is the absorption of acetylene by corresponding concentrations of nitric acid. The most favourable concentration of acid, both in the presence and absence of mercury, seems to lie slightly below 95 per cent, Table 55, and for all subsequent investigations a concentration of 94 per cent nitric acid was used. The most obvious difference in the products of reaction of acetylene and of ethylene, as illustrated by tables 56 and 47, is the much smaller evolution of carbon dioxide in the latter reaction. The ratio of carbon dioxide /ethylene absorbed at a concentration of 95 per cent nitric acid is 0'4/1 for ethylene and 0'8/1 for acetylene, while for ~~22~~ 70 per cent nitric acid the respective ratios are ~~0'94/1 and 1'11/1.~~ 0¾98/1 and 1'09/1, showing a greater approximation. At a concentration of 90 per cent, the two ratios are nearly equal, however. In the presence of mercuric nitrate the discrepency is not so marked; 0'8 - 0'9/1 and 1'41 - 1'47/1 represent average values for this ratio for ethylene and acetylene respectively. The yield of tetranitromethane, expressed as a percentage of the hydrocarbon absorbed, in the ethylene reaction, never rises to, and is often much less, than the value obtained for acetylene, and no variation of experimental conditions has very markedly improved this. The maximum yield of tetranitromethane on the ethylene absorbed which has been obtained is 231'8 per cent, table 55, whereas, for the same concentration of nitric acid, 95 per cent, the reaction with

acetylene

acetylene yields tetranitromethane to the extent of 276'8 per cent. In the presence of 0'66 per cent of mercuric nitrate, and in 94 per cent nitric acid, this figure rises for ethylene, to 354'8 at 40°, and to 301'4 at 30°, the corresponding values for acetylene being 383 per cent for 0'66 per cent mercuric nitrate, and 453 - 552 per cent for 0'33 per cent metallic salt. Table 52. In all cases, therefore, the amount of carbon in the ethylene absorbed used up in side reactions is appreciable, and amounts to between 30 and 40 per cent, tables 57 and 57a. This can in part be accounted for by the formation of oxalic acid, which is usually present to a greater or less extent. Table 63 shows that 16 - 28 per cent of the carbon undergoes reaction in this way, and, once formed, experiment has shown that oxalic acid is not oxidised to carbon dioxide by nitric acid under the conditions of these experiments. Even so, 10 - 20 per cent of the carbon remains unaccounted for by recognisable products of the reaction.

Temperature. The optimum temperature is rather higher than for the corresponding acetylene reaction, and at 40° and 50° a higher yield of tetranitromethane is obtained than at 30°. At these temparatures, however, the yield is not as high as is realised for acetylene at 30°. Table 58.

Proportion of Mercuric Nitrate. A higher concentration of mercuric nitrate was required to bring about the maximum absorption and yield of tetranitromethane than was the case for acetylene, and 0'66 per cent was found to promote the best results. Table 57a. The readiness of absorption is increased, and the yield of tetranitromethane on the ethylene absorbed amount to 333 - 355 per cent. At the same time the proportion of carbon undergonig side reactions is reduced by a small amount.

It will be obvious from the tables that, under the optimum conditions, the ratio of carbon dioxide evolved/ethylene absorbed approaches 1/1, but only in exceptional cases exceeds it. At 30° this ration is slightly higher, 0'9/1, ~~than~~ in the absence of mercuric nitrate, showing that at this temperature the formation of carbon dioxide is proportionally less than it is at the higher temperatures 49 and 50°, where the ratio becomes 0'95 - 1'04/1.

<u>Isolation of β nitroethyl Alcohol</u>. This compound can be isolated from the reaction product of ethylene and nitric acid, both in the presence and absence of mercuric nitrate, by the following procedure:- The product is diluted with twice its bulk of water and extracted with ether after careful neutralisation with sodium carbonate. The ethereal extractes, washed and dried, are then submitted to vacuum fractional distillation. β -nitroethyl alcohol is obtained as a faintly yellow oil at 117 - 121° at a pressure of 30 - 35 mm. Careful estimation by weight of this substance, and comparison of the nitroform estimated in the fesidue from ethereal extraction by the usual procedure, shows that the amount of

nitroform is always in excess of the alcohol, the ratio of alcohol to nitroform being approximately 1/2'4. Table 59. The presence of mercuric nitrate seems to have little effect on this ratio, v. table 59. If, however, this estimation of the two compounds be carried out before the normal completion of the reaction a very marked difference in the value of this ratio is noticeable. The amount of β -nitroethyl alcohol, never a very constant quantity though the ratios show fair constancy, is not appreciably different, but the amount of nitroform which can be isolated is very considerably less. The ratio of the two substances when half and three quaeters of the normal quantity of ethylene had been passed through, varies from 1/1 to 1/1'5. The difference between these two stages is not appreciable. Two facts of considerable importance emerge from these facts. (1) Nitroform is produced subsequent to, and it would appear, at the expense of β -nitroethyl alcohol, and (2) The formation of nitroform takes place largely towards the end of the passage of the hydrocarbon. The significance of this is discussed more fully in another section, (v. p 122).

The experimental results indicate that in the main the reactions between acetylene and nitric acid and between ethylene and nitric acid follow fundamentally the same course. The principal reaction is one of simultaneous oxidation and nitration to carbon dioxide and trinitromethane, together with certain side reactions, ih part oxalic acid, which, under suitable conditions, can be entirely eliminated for acetylene, and appreciably reduced in amount for ethtlene. Temperature and concentration of the acid have relatively the same effect in both reactions, a tenperature slightly above leboratory temperature, and a concentration of 94 - 95 per cent of nitric acid providing the optimum conditions. In both reactions the presence of the catalyst, mercuric nitrate, markedly increases the rate of absorption and hence the readiness of interaction, and promotes a maximum yield of tetranitromethane.

The Effect of the Presence of Sulphuric Acid on the Interaction of Acetylene with Nitric Acid.

Known mixtures of concentrated nitric and sulphuric acids were treated with acetylene under the conditions used for normal experiments with nitric acid, (v. above), The first obvious effect of the admixture with sulphuric acid are (1) a marked increase in the percentage of acetylene absorbed by a given mixture and (11) a very considerable decrease in the amount of carbon dioxide evolved. The total volume of gas which can be collected is also vert much less, and analysis of the gaseous mixture failed to reveal the pre-

-sence of any other gas than carbon dioxide, acetylene (unabsorbed) and a trace of carbon monoxide. It is noteowrthy that the proportion of carbon dioxide to the total product is considerably less than is obtained either by the interaction of acetylene and nitric acid or by that of acetylene and sulphuric acid. The product, after the passage of 2 - 2½ liters of acetylene per 100 grams of "mixed acid", is slightly turbid and is quite colourless, in marked contrast to that obtained by the interaction with nitric avid alone, where the reduction products of nitric acid ~~mainly~~ produce a deep red-brown colour. On pouring onto ice, a neraly colourless solution, with no distinctive smell, is obtained. On making alkaline with sodium carbonate an intensely red-brown liqour, characteristic of ~~dinitro methane~~ the nitrolic acids. Warming with caustic alkali gives a copious evolution of ammonia, a reaction which is characteristic of the alkaline hydrolysis of these compounds. No nitroform nor other coloured nitro compounds are observed, nor can tetranitromethane be obtained from the product on further nitration, showing that all precursors of this substance are absent. As the proportion of sulphuric acid to nitric acid is increased, the percentage of acetylene absorbed increases up to a value given by a mixture of H_2SO_4/HNO_3 in the ratio of about 2/1, beyond which it falls off slightly. The evolution of carbon dioxide shows a slight graduual incrçease as the proportion of sulphuric acid is increased from

0'1/1 to 3/1. Some nitroform is formed when the ratio is as low as 0'1/1, but for all higher ratios examined no nitroform has been obtained. Tables60.

Effect of Dilution of Nitric Acid. Taking the ratio of supphuric avid to nitric acid as 1/1, experiments were made with concentrations of nitric acid of 75, 85, and 95 per cent. Dilution of the nitric acid causes no perceptible difference in the percentage of acetylene absorbed, but the proportion of carbon dioxide increases slightly with dilution. Table 61.

Effect of Catalysts. Of the three metals examined, uranium, platinum and mercury, when the ratio of sulphuric to nitric acids was 1/1, all cause decrease in the amount of acetylene absorbed. The effect of mercury here is sharply contrasted with its behaviour in acetylene-nitric acid mixtures. Platinum and mercury show about equal power in this respect; uranium depresses the absorption to about one half the extent obtained with these two metals. The amount of carbon dioxide is concomitantly slightly decreased. Table 62.

The probable course of the reaction which takes place in this medium is discussed fully, ps 142 et seq.

TABLE I.

NITRATION OF XYLOL.

10 grs Xylol.

(a) 5% Mercuric Nitrate Oleum.

Expt.	No Mercury Trinitro-Xylol	No Mercury Oxalic Acid	Mercury Trinitro-Xylol	Mercury Oxalic Acid	% Variation of yield of tri-nitro compound.
1.	16.3 gn	0 gn	16.5 gn	0 gn	+ 1.23
2.	16.0 gn	0.008 gn	15.8 gn	0.012 gn	- 1.25
3.	15.8 gn	0.111 gn	16.0 gn	0 gn	+ 1.26
4.	15.6 gn	0.02 gn	15.6 gn	0.014 gn	0
(b) 5% Mercuric Nitrate. Sulphuric Acid in mercuriated experiments					
5.	15.5 gn	0 gn	16.0 gn	0.013 gn	+ 3.22
6.	14.8 gn	0.018 gn	15.1 gn	0 gn	+ 2.02
7.	14.3 gn	0	15.7 gn	0.015 gn	+ 9.77
8.	(14.7 gn		11.9)		
9.	16.5 gn		14.4 gn		-12.7
10.	14.2 gn		14.2 gn		0
11.	15.3 gn		14.9 gn		- 2.6
12.	16.1 gn		16.3 gn		+ 1.24
13.	15.4 gn		15.9 gn		+ 3.24
14.	15.9 gn		15.7 gn		- 1.25
15.	14.9 gn		15.5 gn		+ 4.03
(c) 20% mercuric nitrate. Sulphuric Acid in mercuriated experiments.					
16.	15.8 gn		16.1 gn		+ 1.93
17.	15.1 gn		15.0 gn		- 0.66
18.	16.0 gn		15.9 gn		- 0.62
19.	15.7 gn		16.0 gn		+ 1.91

DISTRIBUTION OF NITRIC ACID

Table I. A

NITRIC ACID = 50 GRS

Expt.	Total nitrated product	Co2 grs	Oxalic acid	% Compound oxidised	% Compound nitrated.	Oxides of Nitrogen	Nitrous Acid	Nitrated product.	Remainder.	% Nitric Acid Reduced.	% Nitric Acid Used.
2 NoHg	16.0gn	0.0021	0.008 grs	0.034	70.47	0.015gn	1.45gn	12.55gn	35.98	2.93	28.04
Hg	15.8"	0.0027	0.012 "	0.044	69.6	0.027"	5.01 "	12.40"	32.56	10.07	34.88
3 NoHg	15.8grs	0.0015	0.111 "	0.038	69.6	0.018"	1.56 "	12.40"	36.02	3.15	27.96
Hg	16.0 "	0.002	0	0.006	70.47	0.03 "	5.14 "	12.55"	32.28	10.34	35.44

TABLE II.

NITRATION OF NAPHTHALENE.

			No Mercury.					Mercury.			
wt.cp.	Nitration mixture.	Wt HNO_3	M.n.n. crude.	m.p.	M.n.n. pure	other prod	% yield m.n.n.	m.n.n. crude.	m.p.	m.n.n. pure	other prod.	% yield m.n.n.
5 grs	Hno3 + H_2SO_4	5.2 grs	5.9	oil	3.5	4.5	30.4	6.5	semi solid	2.4	3.5	23.6
"	"	"	6.0	"	3.6	4.6	31.0	6.6	"	2.6	3.6	24.3
"	"	"	5.8	"		4.4	29.7	6.5	"		3.7	25.0
"	Hno_3(1.33)	46.5	8.0	55.5°	6.4	6.4	43.2	7.0	55°	6.0	6.0	40.5
"	"	"	7.6	"		6.2	41.9	6.9	"		6.1	41.2
"	"	"	7.8	"		6.2	41.9	6.7	"		6.0	40.5
"	"	"	7.6	55°		6.1	41.2	6.7	"		5.8	39.2

(L.n.n. - L. Nitronaphthalene)

DISTRIBUTION OF NITRIC ACID.

	Nitric Acid equivalent to				No Mercury.
Hno_3 used	L.n.n.	Total nit.prod.	Oxalic acid	Nitrous acid.	Total Hno_3 accounted for.
5.2 grs	1.64 gr	1.64 gr)	below	2.8 gn	4.44 gn
"	1.67 "	1.67 ")	1%	2.4 "	4.07 "
"	1.60 "	1.60 ")		3.0"	4.60 "
46.5	2.33 "	2.91 gr	"	36.2 "	39.11 "
	2.26 "	2.70 "	"	38.4 "	41.16 "
	2.26 "	2.84 "	"	35.9 "	38.74 "
	2.22 "	2.76 "	"	32.8 "	35.56 "
(b) 10% Mercuric Nitrate.					
5.2 "	1.27 "	1.27 "	"	3.4 "	4.67 gn
"	1.31 "	1.31 "	"	3.8 "	5.11 "
"	1.34 "	1.34 "	"	3.2 "	4.54 "
46.5	2.18 "	2.55 "	"	40.1 "	42.65 "
"	2.22 "	2.51 "	"	38.2 "	40.71 "
"	2.18 "	2.44 "	"	42.2 "	44.64 "
"	2.11 "	2.44 "	"	37.8 "	40.24 "

TABLE IV.

FIRST STAGE OF DINITRATION OF NAPHTHALENE.

			No Mercury		Mercury		
wt. Naphthalene	Nitration Mixture	wt Hno_3	Crude Prod.	m.p.	Crude Prod.	m.p.	% difference Prod by Mercury
5gn	Hno_3(1.54)	23.1gn	7.9 gn	150-155°	8.2 gn	150-155°	+3.8
"	"	"	9.8 "	"	8.3 "	"	-15.3
"	"	"	8.2 "	"	9.2 "	"	+12.2
"	"	"	7.8 "	"	8.3 "	"	+ 6.4
"	"	"	8.1 "	"	8.6 "	"	+ 6.1

TABLE V.

EFFECT OF INCREASE OF TEMPERATURE ON THE OXIDATION OF NAPHTHALENE IN THE PRESENCE OF MERCURY.

wt of Naphthalene	Temp. of Mixing	Co_2	Oxalic Acid	wt. of Naphthalene oxidised	Total Vol. Oxides of N.	Nitrous Acid.
5 grs	20°	0.167	0.621	4.4%	4.5cc N.T.P.	8.4 gn
"	20-30°	0.343	0.738	6.2%	10.8cc "	12.2 "
"	40-50°	0.681	1.026	9.8%	25.9 "	27.1 "

750° reaction becomes uncontrolable

TABLE VI.

NITRATION OF PHENANTHRENE.

Expt.	Nitration Mixture.	Wt of Phenanthrene	Wt of alcohol.-washed product.		% diff. prod. by Hg
			No. Hg	Hg.	
Schmidt's Method.					
1	Hno_3(1.55) + sand	5 gn	8.3 gn	8.5 gn	+ 2.4
2	"	"	8.1 gn	8.0 "	- 1.23
3	"	"	8.5 "	8.5 "	.0
4	"	"	8.2 "	8.3 "	+ 1.22
Nitrous air Method.					
5	H_2So_4 + Na No_2	10 gn	9.8	9.7	- 1.02
6	"	"	9.6	9.8	+ 2.08
7	"	"	9.6	9.6	.0
8	"	"	9.1	9.5	+ 4.39
Wieland's Method.					
9	Abs.Hno_3 in Chloroform	10 gn	7.6	8.6	13.1
10	"	"	7.2	7.9	9.7
11	"	"	7.5	8.1	8.0
12	"	"	7.1	8.0	12.8

TABLE VII

NITRATION OF ANTHRACENE.

(a) 10% Hg   Wt Anthracene = 5 grs.

	No Mercury			Mercury.				
Expt.	Wt of oxide prod.	Wt of pure prod.	Wt of dinitro c.p.	Wt of Oxide prod.	Wt of pure prod.	Wt of dinitro c.p.	% dec of oxide prod by Hg	% dec of pure mono-nitro. prod. by Hg.
1	6.8 gn	5.6 gr	1.2 grs	6.2 gn	4.9 gn	1.3 grs	- 8.8	12.5
2	7.1 "	6.0 "	1.1 "	6.3 "	4.4 "	1.9 "	-12.7	26.6
3	5.6 "	--	--	4.3 "	--	--	-11.2	--
4	6.6 "	5.8 "	0.8 "	6.1 "	4.5 "	1.6 "	- 7.5	22.4
5	6.2 "	5.4 "	0.8 "	5.8 "	4.1 "	1.7 "	- 6.4	24.0
6	6.2 "	5.3 "	0.9 "	5.7 "	4.0 "	1.7 "	- 8.0	24.5
7	6.0 "	5.1 "	0.9 "	5.4 "	3.8 "	1.6 "	-10.0	25. 5
(b)	20% Hg.							
8	6.2 "	5.2 "	1.0 "	5.1 "	3.5 "	1.6 "	-17.7	32.6
9	6.4 "	5.3 "	1.1 "	5.0 "	3.5 "	1.5 "	-22.0	33.9
10	6.6 "	5.7 "	0.9 "	5.1 "	3.6 "	1.5 "	-22.9	36.8

TABLE VIII.

NITRATION OF BROMOBENZENE.

Wt of Bromobenzene = 7 grs.

Wt of crude (Oxide) product.

Exp.	Nitration mixture.	NoHg	5%Hg	% dec.	10% Hg	% diff.	15% Hg	% diff
1	Hno_3-H_2So_4	8.0 gn	7.2	10	8.5	+6.25	9.1	+13.7
2	"	8.0 "	6.9	13.7	--			
3	"	7.5 "	5.6	25.3	7.0	-6.66	7.8	+ 3.99
4	"	8.0 "	7.7	3.7				
5	"	7.8 "	7.0	10.2	7.8	+0	8.0	+ 2.56
6	Hno_3(1.5)	8.8 "	8.0	9.07				
7	"	7.7 "	7.4	3.89				
8	"	6.6 "	6.3	4.54				

(The percentage difference of yield produced by mercury is calculated in each case on the normal yield in the absence of Mercury)

TABLE IX.

SHOWING EFFECT OF RECRYSTALLISATION.

		Crystalline No.Hg	Product Hg 5%	% decrease of pure product.
1	--	5.0 gn	4.3 grs	14.0
3		4.2 "	3.0 "	19.05
5		4.4 "	4.3 "	2.27
4		5.3 "	4.9 "	7.53

TABLE X.

Separation of Ortho and para isomers by successive extraction with methyl alcohol.

Expt	Crude product	Extraction. I	m.p.	II	m.p.	III	m.p.	IV	m.p.	V	m.p.	Total para	Total ortho.	Ortho para.
(i)														
1 NoHg	8.0 gm	4.4	125°	0.2	124°	0.5	125°	0.5	125°	0.6	40°	5.6	0.6	$\frac{1}{9.3}$
Hg	7.2 "	4.3	125°	0.7	119°	0.3	116°	0.4	125°	0.3	40°	5.7	0.3	$\frac{1}{19}$
(ii)														
2 NoHg	8.0 gm	5.3	125°	0.2	124°	0.2	124°	—	—	0.7	40°	5.7	0.7	$\frac{1}{8.1}$
Hg	6.9 "	4.9	125°	0.5	125°	0.2	124°	—	—	0.3	40°	5.6	0.3	$\frac{1}{18.6}$

TABLE XI.

OXIDATION OF BROMOBENZENE DURING NITRATION.

Nitric acid used - 21 grs Bromobenzene = 10 grs

Expt	Total nitrated product.	Nitric acid as								
		CO_2	Oxalic acid	HNO_2 + Oxides Nitrogen	Nitrated product	unused	Total HNO_3 consumed	% Oxidation	% nitration.	% Nitric acid reduced.
4 (NoHg	8.0 gm	0.012	0.047	16.41	2.49	2.1	18.9	0.49	62.2	68.6
(Hg	7.7	0.022	0.133	17.5	2.40	1.1	19.9	1.29	57.8	85.2
3 (NoHg	7.5	0.009	0.041	12.4	2.35	1.65	19.35	0.42	58.3	73.1
(Hg	5.6	0.025	0.093	15.	1.76	1.24	19.76	1.003	43.5	88.5

NITRATION OF CHLOROBENZENE.

Table XII

		10 grs of Chlorobenzene no mercury.			Mercury.			
Exp.	Nitration Mixture	Wt of crude para.cp.	Wt of pure para cp.	Wt of dinitro cp.	Wt of crude para cp.	Wt of pure para cp.	Wt of dinitro cp.	% decrease of para cp.
1	Hno$_3$(1.5)	7.2 grs	5.4 gn	1.8 gn	7.5 gn	5.0 gn	2.5 gn	7.41
2	"	7.1 "	5.1 "	2.0 "	7.6 "	4.8 "	2.8 "	5.88
3	"	7.5 "	5.2 "	2.3 "	7.5 "	4.9 "	2.6 "	5.77
4	"	7.3 "	5.4 "	1.9 "	7.8 "	5.0 "	2.8 "	7.41
5	"	7.6 "	5.5 "	2.1 "	8.0 "	5.2 "	2.8 "	5.45

TABLE XIII.

Simultaneous oxidation in one nitration of Chlorobenzene.

Nitric Acid = 30 grs

Chlorobenzene = 10 grs.

Expt.		Total nitrated product.	Co$_2$ grs	Oxalic Acid grs.	% Oxida- tion	Nitric Acid equivalent to		% nitric Acid reduced.
						Nitrous acid	Oxides of nitrogen	
2	No Hg	7.5 grs	0.018	0.056	0.31	14.46 gn	3.01 gn	58.2
	Hg	7.5 "	0.025	0.159	0.76	15.51 "	5.72 "	70.7
		7.6 "	0.021	0.047	0.28	14.01 "	2.94 "	56.5
		8.0 "	0.029	0.148	0.148	14.97 "	5.01 "	66.6

TABLE XIV.

SIMULTANEOUS OXIDATION IN THE NITRATION OF BROMOBENZENE AND OF CHLOROBENZENE.

10 grs of material taken for each experiment.

Expt.			Total Hydrocarbon oxidised.	Hno$_3$ equivalent to Hno$_2$ + oxides of nitrogen.
1	No.Hg	cl.benzene	0.31 grs	17.47 grs
		br.benzene	0.43 "	14.41 "
2	"	cl.benzene	0.28 "	16.95 "
		br.benzene	0.42 "	15.35 "
1	Hg	cl.benzene	0.76 "	21.23 "
		br.benzene	1.29 "	17.9 "
2	"	cl.benzene	0.72 "	19.98 "
		br.benzene	1.003 "	18.59 "

TABLE XV.

NITRATION OF PHENOL.

(a) 10% Mercury No Mercury.

Hno_3 = 22.8%
Phenol = 10 grs

Expt.	Total nitrated product	Ortho-	para-	ratio ortho para.	Total nitrated product	ortho-	para-	ratio ortho para	% increase of total nitration.
	(a) 10% Mercury				Mercury				
1	4.2 gn	3.4 gn	0.8 gn	(1/4.25)	4.0 gn	2.8 gn	1.2 gn	1/2.33	- 4.75%
2	5.0 "	2.2 "	2.8 "	1/0.78	5.4 "	2.6 "	2.8 "	1/0.93	8.0
3	5.0 "	3.5 "	1.5 "	1/2.3	3.1 "	2.6 "	0.5"	(1/3.7)	- 38.0
4	4.0 "	2.6 "	1.4 "	1/1.86	4.4 "	2.8 "	1.6 "	1/1.7	10.0
5	4.6 "	3.0 "	1.6 "	1/1.87	5.6 "	3.6 "	2.0 "	1/1.71	21.7
6	3.8 "	2.6 "	1.2 "	1/2.16	4.8 "	3.0 "	1.8 "	1/1.66	26. 3
7	4.0 "	3.0 "	1.0 "	1/3.0	5.0 "	3.2 "	1.8 "	1/1.78	25.0
8	—	2.6 "	—	—	—	3.0 "	—	—	—
Average values	4.37	2.86	1.47	1/1.98	4.86	2.94	1.86	1/1.68	
	(b) 20% Mercury.								
9	4.0 "	2.6 "	1.4 "	1/1.86	4.8 "	3.0 "	1.8 "	1/1.66	20
10	3.6 "	3.0 "	1.6 "	1/1.87	5.1 "	3.2 "	1.9 "	1/1.6	41.6
11	3.8 "	2.6 "	1.2 "	1/2.16	4.6 "	2.8 "	1.8 "	1/1.55	21.05
12	4.0 "	3.0 "	1.0 "	1/3.0	4.7 "	2.9 "	1.8 "	1/1.61	17.5
13	3.9 "	2.9 "	1.0 "	1/2.9	4.7 "	3.1 "	1.6 "	1/1.93	20.5
14	3.6 "	2.6 "	1.0 "	1/2.6	5.0 "	3.0 "	2.0 "	1/1.5	38.8
15	3.9 "	2.8 "	1.1 "	1/2.5	4.7 "	3.0 "	1.7 "	1/1.76	20.5
Average values.	4.1	2.8	1.3	1/2.22	4.8	2.9	1.8	1/1.66	
	(c) 40% Mercury.								
16	5.1 "	3.1 "	2.0 "	1/1.55	5.1 "	3.2 "	1.9 "	1/1.68	0%
17	4.4 "	2.8 "	1.6 "	1/1.75	4.8 "	3.0 "	1.8 "	1/1.66	9.1
18	5.0 "	3.0 "	2.0 "	1/1.5	5.1 "	3.2 "	1.9 "	1/1.68	2.0
19	5.2 "	3.4 "	1.8 "	1/1.89	4.5 "	2.9 "	1.6 "	1/1.81	-13.4
Average values.	4.9	3.07	1.85	1/1.67	4.87	3.07	1.8	1/1.70	

Table ~~XXV~~ XVI. B.

Nitration of Phenol.

Effect of Various Metallic Salts.

Metals added as nitrate.		10%.
	Nitric Acid	22'8%
	Phenol	10 grams.

Metal.	Total nitrated product grams.	ortho com- -pound grams.	para com- -pound grams.	ratio para / ortho	% increase of total nitration	HNO_3 as Nitrated product grams.	HNO_3 as Oxides of nitrogen HNO_2 grs.
Ag.	4'75	3'0	1'7	1/1'76	3'26	2'15	7'9
Cu.	5'0	2'9	1'6	1/1'81	8'69	2'26	7'4
Hg.	5'6	3'6	2'0	1/1'71	21'7	2'53	7'5
None.	4'6	1'6 3'0	1'6	1/1'87	—	2'08	7'7

Table XVI.C.

Effect of Iron Salts.

10% Ferric Nitrate.

Com- -pound nitrated.	Total nitrated product. No Fe.	Total nitrated product. Fe.	HNO_3 as oxides of N. etc. No Fe.	HNO_3 as oxides of N. etc. Fe.	% Decrease of Nitration.	% Increase of Oxidation.
Phenol.	4'6 grs.	2'4 grs.	7'7 grs.	9'5 grs.	47'91	295'8
o-Cresol.	7'2 ,,	5'1 ,,	2'34 ,,	5'7 ,,	29'2	143'6
Xylol.	16'3 ,,	12'8 ,,	1'46 ,,	7'2 ,,	20'0	393'1
Benzoic acid.	10'9 ,,	6'4 ,,	2'1 ,,	5'1 ,,	41'3	142'8

TABLE XVI.

COMPARATIVE AVERAGE VALUES.

	Ortho op	Para op	Total nitrated Product	Ratio Para/ortho
No Hg	2.8 gn	1.3 gn	4.1 gn	1/2.15
10% Hg	2.94 gn	1.86 gn	4.8 gn	1/1.58
20% Hg	2.98 gn	1.80 gn	4.78 gn	1/1.65
40% Hg	3.07 gn	1.80 gn	4.87 gn	1/1.70

TABLE XVII.

NITRATION OF P-CHLOROPHENOL

Mercuric Nitrate - 10%. P-chlorophenol = 5 gn. HNO_3 = 50 gn = 25.2%

	No Mercury		Mercury			
Expt.	Crude Product	Ortho Compound	Crude Product	Ortho Compound	% Variation of Crude Product	% Variation of Ortho Product
1.	6.3 gn	5.0 gn	6.5 gn	4.5 gn	+ 3.17	- 10
2.	6.1 gn	3.9 gn	6.0 gn	4.4 gn	- 1.64	+ 7.7
3.	6.4 gn	5.4 gn	7.2 gn	5.7 gn	+12.5	+ 5.54
4.	6.4 gn	5.1 gn	6.8 gn	5.7 gn	+ 6.25	+11.7
5.	6.1 gn	5.1 gn	6.2 gn	5.8 gn	+ 1.64	+13.7
6.	6.5 gn	5.4 gn	6.7 gn	5.9 gn	+ 3.1	+24.07
7.	6.0 gn	5.1 gn	5.9 gn	5.4 gn	- 1.66	+15.68
Average Values	6.257	5.16	6.47	5.34		

TABLE XVIII

(a)

DECREASE OF CONCENTRATION

10% Mercuric Nitrate HNO$_3$ - 50 gn - 24.2%

Expt.	No Mercury		Mercury		% decrease of crude product				% decrease of Ortho Compound			
	Crude Product	Ortho Compound	crude Product	Ortho Compound	No Hg	%	Hg	%	No Hg	%	Hg	%
Normal Average	6.26	5.0	6.47	5.34								
8	6.0 gn	5.5 gn	6.1 gn	5.6 gn	0.26 gn	4.15	0.37	5.96	0.5	10.0	0.26	4.86
9	5.9 "	5.2 "	6.2 "	5.6 "	0.36 "	5.74	0.27	4.17	0.2	4.0	0.26	4.86
10	5.9 "	5.3 "	5.9 "	5.3 "	0.36 "	5.74	0.57	8.81	0.3	6.0	+0.04	0.75
11	6.0 "	5.4 "	5.8 "	5.1 "	0.26 "	4.15	0.67	10.35	0.4	8.0	-0.24	4.49
12	6.1 "	5.4 "	6.0 "	5.2 "	0.16 "	2.56	0.47	7.26	0.4	8.0	-0.14	2.62
Average Values	5.98 "	5.36 "	6.0 "	5.36 "	0.28 "	4.47	0.47	7.31	0.36	7.2	0.06	

(b) 10% Mercuric Nitrate HNO$_3$ = 45 gn = 23.6%

Expt.	Crude Product	Ortho Compound	crude Product	Ortho Compound	No Hg	%	Hg	%	No Hg	%	Hg	%
13	5.4 gn	4.9 gn	5.8 gn	5.1 gn	0.86 gn	13.7	0.1	2.0	0.67	10.35	0.24	4.49
14	5.7 "	5.0 "	5.9 "	5.2 "	0.56 "	8.9	0	0	0.57	8.81	0.14	2.62
15	5.2 "	4.5 "	6.0 "	5.1 "	1.06 "	16.9	0.5	10.0	0.47	7.26	0.24	3.86
Average Values	5.43 "	4.8 "	5.9 "	5.13 "	0.82 "	13.1	0.3		0.52	8.8	0.20	3.86

(c) 10% Mercuric Nitrate HNO$_3$ = 40 gn = 21.9%

Expt.	Crude Product	Ortho Compound	crude Product	Ortho Compound	No Hg	%	Hg	%	No Hg	%	Hg	%
16	4.9 gn	4.0 gn	5.1 gn	4.2 gn	1.36 gn	21.7	1.0	20.0	1.37	21.1	1.14	21.3
17	4.8 "	4.1 "	5.2 "	4.6 "	1.46 "	23.3	0.9	18.0	1.27	19.6	0.74	13.8
18	5.1 "	4.3 "	5.4 "	4.9 "	1.16 "	18.5	0.7	14.0	1.07	16.5	0.44	8.2
Average Values	4.9 "	4.13 "	5.23 "	4.6 "	1.32 "	21.1	0.86	17.3	1.2	19.0	0.77	14.4

Table XIX

(a) MERCURIC NITRATE = 15% HNO_3 = 50gn - 25.2%

Expt.	No Mercury		Mercury					
	Crude product	Ortho compound	Crude product	Ortho compound	Variation of crude product		Variation of ortho compound	
19	6.2 gn	5.4 gn	7.0 gn	6.1 gn	+ 0.8 gn	12.89%	+ 0.7 gn	12.96%
20	6.3 "	5.2 "	6.9 "	5.9 "	0.6 "	9.51"	0.7 "	13.46"
21	6.1 "	5.1 "	7.0 "	6.1 "	0.9	"14.75	1.0 "	19.61"
	6.2 "	5.23 "	6.96"	5.96 "	0.76 "	12.38 "	0.8 "	15.32 "
(b)	MERCURIC NITRATE = 20%							
22	6.1 "	5.2 "	6.9 "	5.8. "	0.8 "	13.12"	0.6 "	11.54 "
23	6.0 "	5.3 "	7.2 "	5.4 "	1.2 "	20.0 "	1.1 "	20.75 "
(c)	MERCURIC NITRATE = 40%							
24	6.2 "	5.4 "	6.9 "	5.8 "	0.7 "	11.29"	0.4 "	7.41"
25	6.0 "	5.2 "	7.0 "	6.4 "	1.0 "	16.66"	1.2 "	23.1 "
26	5.9 "	4.9 "	6.8 "	6.0 "	0.9 "	15.25"	1.1 "	22.4 "
(d)	MERCURIC NITRATE = 100%							
27	6.4 "	5.2 "	6.8 "	5.7 "	0.4 "	6.25"	0.5 "	9.01"
28	6.1 "	5.0 "	6.5 "	5.4 "	0.4 "	6.55"	0.4 "	8.00"
29	6.2 "	5.2 "	6.9 "	5.7 "	0.7 "	11.29"	0.5 "	9.61"

Table XX

EFFECT OF MERCURY. AVERAGE VALUES

		Mercuric Nitrate				
	Normal	10%	15%	20%	40%	100%
Crude product	6.26	6.47	6.96	7.05	6.9	6.7
Ortho compound	5.0	5.34	5.96	6.1	6.1	5.6.

Table XXI

EFFECT OF CONCENTRATION OF NITRIC ACID.

AVERAGE VALUES.

NO MERCURIC NITRATE

	Nitric Acid			
	25.2%	24.2%	23.6%	21.9%
Crude product	6.26	5.98	5.43	4.9
Ortho compound	5.0	5.36	4.8	4.13

MERCURIC NITRATE - 10%

Crude product	6.47	6.0	5.9	5.23
Ortho compound	5.34	5.36	5.13	4.6.

TABLE XXII

NITRATION OF O-CRESOL

(a) Mercuric Nitrate = 10% Hno 3=1.5parts

5 grs. O-Cresol used throughout.

	Crude Product		Pure Dinitro Cresol		% increase	
Expt.	No Hg.	Hg.	No Hg.	Hg.	Crude	Dinitro
1	7grs.	6.7grs.	4.5grs.	5.7grs	-4.28	26.7
2	7.2grs	7.4"	4.7"	5.6"	+2.78	19.1
3	7.0"	7.3"	4.3"	5.1"	+4.28	18.6
4	6.8"	7.0"	4.5"	5.5"	+2.94	22.2
Average values	7.0"	7.1"	4.5"	5.38grs.		

(b) Mercuric Nitrate= 10% Hno 3 - 1.3parts

					No Hg.	Hg.	No Hg.	Hg.
5	6.8"	7.0"	4.7"	5.7 "	2.8%	1.4%	4.4%	5.9%
6	6.7"	7.1"	4.9"	5.4"	4.3"	0.0"	8.9"	3.7"
7	6.5"	6.9"	4.5"	5.1 "	7.1"	2.8"	0. "	5.2"
8	7.0"	7.4"	4.3"	5.0 "	0 "	4.2"	4.4"	7.0"
	6.75	7.1	4.6	5.3				

(c) Mercuric Nitrate= 10% Hno$_3$- 1part

9	6.0"	6.8"	4.1"	5.0 "	1.4%	4.2%	8.9%	7.0%
10	6.2"	6.9"	4.0"	5.1 "	1.1"	2.8"	11.1"	5.2"
11	5.5"	6.8"	4.2"	4.8"	2.1"	4.2"	6.6"	10.7"
	5.9"	6.83grs	4.1"	4.96grs.				

(d) Mercuric Nitrate - 10% Hno 3- 0.75parts.

12	5.1"	5.6"	4.0"	5.1 "	2.7"	3.2"	7.0"	5.2"
13	5.4"	5.9"	3.9"	4.4"	2.3"	2.7"	8.4"	18.2"
14	5.2"	5.8"	4.1"	4.7 "	2.6"	2.9"	5.6"	12.6"
	5.23	5.46	4.0	4.7 "				

TABLE XXIII.

(a) Mercuric Nitrate = 5% Hno3 = 1.3 parts

	Crude Product		Dinitro cp.		% increase of crude product		% increase of dinitro	
Expt	No Hg	Hg	No Hg.	Hg		%		%
15	6.7 grs	6.8 grs	4.9 grs	5.4 grs	0.1 grs	1.49	0.5 grs	10.1
16	6.4 "	6.6 "	4.8 "	5.0	0.2 "	3.12	0.2 "	4.2
	6.55	6.7	4.85 "	5.2 "				
(b)	Mercuric Nitrate = 20%				Hno3 = 0.75 parts			
17	5.0 "	5.2 "	4.1 "	4.4 "	0.2 "	4.0	0.3 "	7.3
18	5.2 "	5.5 "	4.0 "	4.6 "	0.3 "	5.7	0.6 "	15.0
19	5.2 "	5.6 "	4.2 "	4.5 "	0.4 "	7.7	0.3 "	7.1
	5.13	5.43	4.1	4.5				
(c)	Mercuric Nitrate = 50%				Hno3 = 0.75 parts			
20	5.1 "	6.2 "	4.0 "	5.0 "	0.9 "	14.5	1.0 "	25.0
21	5.0 "	6.4 "	4.1 "	5.4 "	1.4 "	21.8	1.3 "	31.7
22	5.4 "	6.1 "	4.3 "	5.5 "	0.7 "	11.5	1.2 "	27.9
	5.16 "	6.23 "	4.13 "	5.3				

TABLE XXIV

(a) Effect of Mercury Average Values

1.3 parts of Nitric Acid

	Normal	5%	10%	20%	50%
Crude Product	6.75	6.55	7.1		
Dinitro "	4.6	4.85	5.3		
0.75 parts of Nitric Acid					
Crude Product	5.23	-	5.46	5.43	6.23
Dinitro "	4.0	-	4.7	4.5	5.3

(b) Effect of reduction of Nitric acid Mercuric Nitrate = 10%

	1.5 parts Hno3 No Hg	Nitric Acid 1.5 parts	1.3 parts	1 part	0.75 parts
Crude Product	7.0	7.1.	6.75	6.83	5.46
Dinitro "	4.5	5.38	4.6	4.96	4.4

TABLE XXV

Simultaneous oxidation in the nitration of phenols.

	(a) Phenol		Nitric Acid = 12 gn				Dilute acid				
Expt.	Total Nitrated product. gn	CO$_2$ gn	Oxalic acid gn	% compound Oxidised	% compound nitrated	oxides of nitrogmn. gn	nitrous acid gn.	Nitrated product gn.	% nitric acid reduced	nitric acid remaining gn	% nitric acid consumed
6 No Hg	4.6	0.328	0.654	3.43	31.1	6.57	2.48	2.08	75.4	0.871	92.72
Hg	5.6	0.400	0.659	3.72	37.8	5.8	3.15	2.53	74.5	0.516	95.7
9 No Hg	4.0	0.351	0.591	3.3	27.0	6.73	2.67	1.81	78.3	0.792	93.44
Hg	5.0	0.432	0.528	3.37	33.8	5.76	3.54	2.26	77.0	0.438	96.35
5 No Hg	4.0	0.309	0.613	3.23	27.0	7.32	2.10	1.81	78.5	0.771	93.58
Hg	4.4	0.441	0.598	3.65	29.7	5.9	3.62	1.99	79.2	0.487	95.94
	(b) p-Chlorophenol		nitric acid = 50 gn								
3 No Hg	6.4	0.101	0.138	2.28		7.45					
Hg	7.2	0.147	0.146	2.8		8.21					
4 No Hg	6.4	0.095	0.129	2.14		7.93					
Hg	6.8	0.139	0.146	2.74		9.10					
	(c) O-Cresol		nitric acid = 7.5 gn								
2 No Hg	7.2	0.598	0.218	4.88	78.5	1.85	0.49	4.58	31.20	0.58	96.2
Hg	7.4	0.701	0.395	6.54	80.7	1.28	1.06	4.70	31.20	0.16	99.4
3 No Hg	7.0	0.601	0.221	4.92	76.3	1.69	0.57	4.45	30.13	0.79	95.9
Hg	7.3	0.739	0.392	6.76	79.6	1.17	1.42	4.64	34.53	0.27	99.1

TABLE XXVI.

NITRATION OF p.CRESOL

(a) Nitric Acid - 2 parts. Mercuric Nitrate - 10%. 10 gr p-cresol

Expt	wt of dinitro cp No Hg	wt of dinitro cp Hg	% increase of dinitro cp
21	5.6 grs	6.4 grs	14.3%
2	3.0 "	3.8 "	26.7
3	3.6 "	3.8 "	5.55
4	4.8 "	5.4 "	12.5
5	5.0 "	5.8 "	16.1
	3.84	4.15	
(a)	Nitroc Acid - 1.6 parts	Mercuric Nitrate - 10%	
6	3.4 "	3.6 "	5.88
7	3.4 "	4.0 "	17. 6
8	3.0 "	4.2 "	39. 9
9	2.8 "	4.0 "	42.8
	3.15 "	3.9	
(c)	Nitric Acid - 1.2 parts		
10	2.0 "	3.0 "	50.0
11	1.6 "	2.6 "	62.4

TABLE XXVII.

NITRATION OF M-CRESOL.

Mercuric Nitrate = 22%   7 gn m-cresol

Expt		Character of crude product	Residue from ether extract of steam distillate		Residue from ether extract of residue from steam distillation.	
1.	No Hg	Oil	Oil	3.3 grs	Oil	2.6 grs
	Hg	Oil	Semi-solid	6.0 grs	Semi-solid	2.5 grs
					m.p. after pressing on porous plate	100°
2.	No Hg	Oil	Oil	3.5 grs	Oil	2.4 grs
	Hg	Oil	Solid (m.p. = 45-50°)	5.4 grs	Semi-solid	2.7 grs m.p, 100°
3.	No Hg	Oil	Semi-solid	3.5 grs	Oil	2.1 grs
	Hg	Oil	Solid (m.p. = 50-52°)	5.7 grs	semi-solid	2.9 grs m.p. 100°
4.	No Hg	Oil	Oil	3.5 grs	Oil	2.5 grs
	Hg	Oil	Solid (m.p. 48-52°)	5.4 grs	Semi-solid	2.4 grs

Table XXVIII

NITRATION OF NAPHTHOL

L Naphthol - 5 gns

(a)

Expt.		10 Days No Mercury	10 Days 10% Mercuric Nitrate.	% Increase	7 Days 10% Mercuric Nitrate.
1	A	5.2 gn	5.3 gn	1.92	4.7 gn
	B	3.7 "	4.2 "	13.5	3.5 "
2	A	5.1 "	5.3 "	3.92	4.6 "
	B	3.5 "	3.9 "	11.4	3.0 "
3	A	5.2 "	5.4 "	3.84	4.9 "
	B	3.7 "	4.2 "	13.5	4.0 "
	C	2.8 "	3.1 "	10.7	2.9 "
4	A	5.3 "	5.7 "	7.53	5.5 "
	B	3.9 "	4.1 "	5.12	4.2 "
	C	2.7 "	3.2 "	18.50	3.0 "

(A= crude product. B = pure α nitronaphthol once crystallised.
C = " " " twice crystallised.)

(b) Time = 10 days.

Expt.	Crude Product No Hg.	Crude Product Hg.	% Increase.	Once crystallised prod. No Hg.	Once crystallised prod. Hg.	% Increase.	Twice crystallised product. No Hg	Twice crystallised product. Hg	% Increase.
5	5.0 gn	5.6 gn	12.0	3.7 gn	4.2 gn	13.4	2.9 gn	3.4 gn	17.2
6	5.2 "	5.8 "	11.5	3.9 "	4.4 "	12.8	3.0 "	3.6 "	20.0
7	5.1 "	5.5 "	7.8	3.7 "	4.3 "	16.2	2.8 "	3.3 "	17.8

TABLE XXIX.

COMPARATIVE VALUES OF THE EFFECT OF MERCURY IN THE NITRATION OF HYDROCARBONS and Halogen Compounds

10% Mercuric Nitrate. Average Values.

Hydrocarbon	% variation of yield	% Oxidation.	% Nitration No. Hg.	% Nitration Hg.	% Nitric acid reduced.
xylol	+ 4.1	(.006) (.044)	70	74	10
Naphthalene	- 3.4	--	116.8	100.6	51.9
			(calculated for mono-nitro)		
Anthracene	- 22.6	--	100	90.2	--
Phenanthrene.	+ 10.9	--	60	64.8	--
			(Wieland's method)		
Bromobenzene	- 9.0	11.4	87.1	78.1	18.2
Chlorobenzene	+ 1.0	7.4	48.1	49.8	21.1

Table XXX

COMPARATIVE VALUES OF THE EFFECT OF MERCURY IN THE NITRATION OF PHENOLS.

Mercuric Nitrate = 10%   Average Values

henol	% Variation of yield	% Oxidation	% Nitration No Hg	% Nitration Hg	% Nitric acid reduced
Phenol					
10% Hg	Ortho) 5.0 Para)43.0 Total)17.0	3.6	28.3	33.7	77.4
20% Hg	Ortho) 6.4 Para)38.4 Total)16.5				
40% Hg	Ortho) 9.6 Para)38.4 Total)18.7				
Chlorophenol					
Ortho	10% Hg 9.7		73.9	79.0	–
"	20% Hg 16.1			90.26	–
O-cresol	21.6	6.6	77.4	80.1	32.8
P-cresol	14.9	–	20.94	22.63	–
Napthol	12.8	–	56.9	58.05	

TABLE XXXI

NITRATION OF BENZOIC ACID

(a) Potassium nitrate = 2 parts
Sulphuric Acid = 3 parts

Benzoic acid = 10 gn
Mercuric Nitrate - 10%

Expt.	crude product No Hg	Hg	m-nitro-acid No Hg	Hg	% increase of m-nitro-acid
1 (½)	7.5 gn	7.0 gn	5.8 gn	6.3 gn	8.6%
2 (½)	5.6 "	7.0 "	5.0 "	6.4 "	14.0%
3	12.4 "	14.8 "	10.9 "	12.3 "	12.8%
4	12.2 "	14.9 "	11.1 "	13.2 "	18.4%
5	14.8 "	14.2 "	11.4 "	12.7 "	11.4%
6	14.0 "	14.1 "	11.1 "	12.5 "	12.6%
7	13.8 "	14.0 "	11.5 "	13.7 "	19.1%

(b) Potassium nitrate - 1.8 parts
Sulphuric Acid = 3 parts

8	12.6 gn	12.4 gn	11.0 gn	11.8 gn	7.3%
9	12.2 gn	12.5 gn	11.1 gn	12.0 gn	8.1%
10	12.4 gn	12.3 gn	11.3 gn	11.5 gn	1.76%

TABLE XXXII

DISTRIBUTION OF NITRIC ACID.

10 gn KNO_3 equivalent to 6.3 gn HNO_3

Expt.	Total nitrated product gn.	CO_2 gn	Oxalic acid gn.	% benzoic acid nitrated	% benzoic acid oxidised	% nitric acid reduced	Nitric Acid euivalent to nitrated product gn.	oxides of nitrogen gn	Nitrous Acid	Re-mainder	% nitri acid used
3.											
No Hg	10.9	0.157	0.151	79.66	1.20	33.65	4.11	0.06	2.06	0.07	99.01
Hg	12.3	0.170	0.101	89.86	1.06	26.03	4.64	0.07	1.57	0.02	99.72
4.											
No Hg	11.1	0.148	0.217	81.1	1.70	32.55	4.19	0.06	1.99	0.06	99.14
Hg	13.2	0.167	0.146	96.45	1.17	20.80	4.98	0.07	1.24	0.01	99.81

TABLE XXXIII

NITRATION OF SALICYLIC ACID.

(a) Mercuric Nitrate = 10% Salicylic Acid = 10 grs

Expt.	Crude Product No Hg	Crude Product Hg	% decrease of Crude product	Twice crystallised 5-nitro-salicylic acid No Hg	m.p.	Twice crystallised 5-nitro-salicylic acid Hg	m.p.	% decrease of 5-nitro salicylic acid
1.	9.5 gn	9.6 gn	1.04%	6.8 gn	220°	5.8 gn	221°	14.7%
2.	9.4 gn	9.4 gn	0	6.7 gn	219°	6.0 gn	218°	10.4%
3.	9.7 gn	9.5 gn	2.1%	6.9 gn	221°	6.1 gn	220°	11.6%
4.	9.5 gn	9.6 gn	+1.04%	6.7 gn	220°	5.9 gn	219°	11.9%
5.	9.4 gn	9.3 gn	1.06%	6.5 gn	221°	5.7 gn	221°	12.3%
6.	9.8 gn	9.2 gn	6.1%	7.6 gn	188°	6.0 gn	208°	21.0%
7.	9.7 gn	9.4 gn	3.1%	6.6 gn	220°	5.9 gn	220°	10.6%

(b) Mercuric Nitrate = 20%

Expt.	Crude Product No Hg	Crude Product Hg	% decrease of Crude product	Twice crystallised 5-nitro-salicylic acid No Hg	m.p.	Twice crystallised 5-nitro-salicylic acid Hg	m.p.	% decrease of 5-nitro salicylic acid
8.	9.5 gn	9.6 gn	1.05%	6.5 gn	218°	6.0 gn	219°	7.7%
9.	9.4 gn	9.3 gn	1.06%	6.6 gn	220°	5.8 gn	220°	12.1%
10.	9.4 gn	9.5 gn	+1.06%	6.3 gn	220°	5.0 gn	220°	20.6%

Table XXXIV

NITRATION OF CINNAMIC ACID

MERCURIC NITRATE - 10%. CINNAMIC ACID - 5 GN.

Expt.	Crude product		% Increase of crude product	Para-cinnamic acid		% Decrease of p-acid	Ortho-cinnamic acid		% Increase of o-acid	Ratio ortho/para	
Expt	No Hg	Hg		No Hg	Hg		No Hg	Hg		No Hg	Hg
1	4.5 gn	4.7gn	4.4%	3.8gn	3.4gn	10.5%	0.5gn	0.9gn	80.0%	$\frac{1}{7.6}$	$\frac{1}{3.77}$
2	4.3 "	4.4 "	2.3"	3.7 "	3.5"	5.4"	0.4"	0.6"	50.0"	$\frac{1}{9.2}$	$\frac{1}{5.\ 9.}$
3	4.5 "	4.7 "	4.4"	3.8 "	3.6"	5.2"	0.5"	0.8"	59.9"	$\frac{1}{7.6}$	$\frac{1}{4.\ 5}$
4	4.6 "	4.9 "	6.5"	3.7 "	3.5"	5.4"	0.45"	0.8"	77.8"	$\frac{1}{8.2}$	$\frac{1}{4.\ 3}$
5.	4.8 "	5.0 "	4.1"	3.6 "	3.6"	0.	0.4"	0.9"	125%	$\frac{1}{9.0}$	$\frac{1}{4.\ 0.}$

Table XXXV

COMPARATIVE VALUES OF THE EFFECT OF MERCURIC NITRATE IN THE NITRATION OF BENZOIC, SALICYLIC AND CINNAMIC ACIDS

Average Values

	Benzoic	Cinnamic	Salicylic Acid.
Percentage Variation	- 13.8%	-4.34%	- 13.2%

TABLE XXXVI.

NITRATION OF BENZALDEHYDE.

(a) Mercuric Nitrate - 10% Benzaldehyde = 10 grs.

Nitric Acid = 50 grs.

Expt	Wt of e nitro benzine	Wt of Nitro-benzoic acid with Mercury	Wt of Nitro-aldehyde equivalent to nitro Acid	% increase of Nitration.
1.	4.7 grs	5.7 grs	5.15 grs	9.6%
2.	4.0 grs	4.7 grs	4.24 grs	6.0%
(b) Nitric Acid = 45 grs				
3.	3.8 grs	4.2 grs	3.8 grs	0 %
4.	4.8 grs	5.8 grs	5.2 grs	8.3%
5.	8.3 grs	9.0 grs	8.13 grs	-2.0%

double quantities.

TABLE XXXVII.

DISTRIBUTION OF NITRIC ACID.

(a) Benzaldehyde. Nitric Acid - 50 grs.

Expt.	Total nitrated product.	Co_2 grs.	Oxalic acid grs.	% aldehyde oxidised	%aldehyde nitrated.	% nitric acid reduced.	Nitrated product grs.	Oxides of nitrogen grs.	nitrous acid gr	remainder grs	% nitric acid consumed.
1 NoHg	4.7	0.197	0.173	1.27	30	39.6	1.96	5.41	14.42	28.21	43.5
Hg	5.15	0.218	0.171	1.32	(approx) 33	51.23	2.15	7.77	17.84	22.24	55.5
(b) p - oxybenzaldehyde.				Nitric acid =		7.59	grs.				
3.NoHg	5.5	0.281	0.187	3.67	80.37	55.98	2.07	2.54	1.66	6.27	83.6
Hg	6.5	0.324	0.176	3.93	94.97	63.71	2.45	3.07	1.71	2.23	96.4
4 NoHg	5.4	0.276	0.195	3.69	78.91	57.4	2.04	2.79	1.51	6.34	84.5
Hg	6.6	0.314	0.184	3.91	96.42	62.3	2.49	2.87	1.80	7.16	95.4

Table XXXVIII

NITRATION OF P-OXY-BENZALDEHYDE

MERCURIC NITRATE - 10%. P-OXY-BENZALDEHYDE - 5 GN

	Total Nitrated product		% In Crease of Nitration.	Total Nitroaldehyde		% decrease of Nitroaldehyde	Nitro Acid		% increase of Acid formation
Expt.	No Hg.	Hg		No Hg.	Hg.		No Hg.	Hg.	
1.	5.0 gn	7.0 gn	40%	2.5 gn	2.0gn	- 20 %	3.0 gn	3.5 gn	16. 6%
2.	5.2 "	6.8 "	30.7"	2.5 "	2.1 "	- 16 "	2.6 "	3.5 "	21. 8"
3.	5.4 "	6.6 "	22.2"	2.1 "	2.0 "	- 4.7"	3.2 "	4.4 "	37. 0"
4.	5.5 "	6.5 "	18.1"	2.3 "	2.1 "	- 8.7"	3.1 "	4.3 "	38. 7
5.	5.3 "	6.2 "	16.9"	3.5 "	3.0 "	- 14.3"			
6.	5.6 "	6.1 "	8.9"	3.6 "	2.7 "	- 25. "			

Table XXXIX

NITRATION OF SALICYLALDEHYDE

MERCURIC NITRATE - 10%. SALICYLALDEHYDE - 5 GN

1.	3.0 gn	3.5 gn	16.6%						
2.	4.1 "	4.6 "	12.2"	2.9 gn	2.6gn	- 11.8%	1.2 gn	2.0 gn	66. 7%
3.	5.1 "	5.2 "	1.96"	1.8 "	1.7 "	- 5.5"	3.3 "	3.5 "	6. 05"
4.	4.9 "	5.2 "	6.1"	2.2 "	2.4 "	+ 9.1"	2.7 "	2.8 "	3. 8"
5.	5.4 "	4.6 "	-14.8"						
6.	4.0 "	4.8 "	20.0"						
7.	4.5 "	4.8 "	6.6"	2.4 "	2.0 "	- 16.6"	2.1 "	2.8 "	33. 3"
8.	5.0 "	6.0 "	20.0"	1.0"	1.1 "	+ 10 "	4.0 "	4.9 "	22. 5"

Table XL

COMPARATIVE VALUES OF THE EFFECT OF MERCURIC NITRATE IN THE NITRATION OF BENZALDEHYDE, P-OXY-BENZALDEHYDE AND SALICYLALDEHYDE.

Average Values.

	Benzaldehyde	P-oxy-benzaldehyde	Salicylaldehyde
% Variation	6.9 %	22. 8 %	13. 5%

TABLE XLI.

NITRATION OF ACETANILIDE.

10% Mercuric Nitration.
Expts 1-8 5 grs Acetanilide: Expts. 9-14 10 grs Acetanilide

Expt.	Para-compound No Hg	Para-compound Hg	% increase of Para Compound	Ortho-compound No Hg	Ortho-compound Hg	% increase of ortho Compound	Ratio No Hg	Orth/para Hg
1.	4.8 gn	5.4 gn	12.5%					
2.	4.6 gn	5.3 gn	15.2%	1.0 gn	1.5 gn	50%	.22/1	.28/1
3.	4.7 gn	5.2 gn	10.6%					
4.	4.9 gn	5.1 gn	4.1%	0.9 gn	1.1 gn	22.2%	.18/1	.215/1
5.	5.2 gn	5.2 gn	0	0.9 gn	1.1 gn	22.2%	.17/1	.21/1
6.	5.7 gn	5.7 gn	0	0.5 gn	0.3 gn	-40.0%	.09/1	.05/1
7.	5.5 gn	5.8 gn	5.4%	0.7 gn	0.5 gn	-28.6%	.13/1	.08/1
8.	5.3 gn	5.4 gn	1.9%	0.6 gn	0.4 gn	-33.3%	.11/1	.07/1
9.	10.0 gn	10.3 gn	3.0%gn	1.1 gn	1.3 gn	18.2%	.11/1	.12/1
10.	9.8 gn	9.4 gn	-4.1%	1.0 gn	1.2 gn	20.0%	.102/1	.13/1
11.	10.0 gn	10.1 gn	-1.0%	1.1 gn	1.1 gn	0	.11/1	.11/1
12.	9.7 gn	9.7 gn	0	0.9 gn	0.8 gn	-11.1%	.09/1	.08/1
13.	9.6 gn	9.8 gn	2.1%	1.0 gn	0.9 gn	-10.0%	.104/1	.09/1
14.	9.7 gn	10.0 gn	3.1%	0.9 gn	1.2 gn	33.3%	.093/1	.12/1

NITRATION OF METHYLACCTANILIDE

Expt	Weight of crude No Hg.	Product Hg.	% Variation of Yield.
(a)	40% Nitric Acid		5% Mercuric Nitrate
1	3.1 gn.	3.2 gn.	3.2%
2	2.8 "	2.9 "	3.5%
3	10.4 "	10.8 "	4.0%
(b)	30% Nitric Acid		5% Mercuric Nitrate.
4	1.6 "	1.6 "	0
5	2.7 "	2.7 "	0
6	2.6 "	2.5 "	-3.8
(c)	30% Nitric Acid		10% Mercuric Nitrate.
7	2.9 "	3.1 "	6.8%
8	2.8 "	3.0 "	7.1
9	2.7 "	3.1 "	14.5
10	2.8 "	2.9 "	3.6
(d)	30% Nitric Acid		15% Mercuric Nitrate
11	2.5 "	3.1 "	24.0%
12	2.4 "	3.2 "	33.3
13	2.6 "	3.1 "	19.2
(e)	40% Nitric Acid		10% Mercuric Nitrate
14	6.5 "	6.5 "	0 %
15	6.4 "	6.6 "	3.1 "
16	6.6 "	6.6 "	0 "
17	6.4 "	6.5 "	1.5 "

NITRATION OF DIMETHYLANILINE.

Mercuric nitrate = 1%   nitric acid = 19.3 gm (1.4)

	wt. of crude product		m.p. of crude product		% variation of yield	Colours of crude product.	
Expt.	No Hg	Hg	No Hg	Hg			
1. i	2.0 gn	2.5 gn	132°	158°		yellow	para cp
ii	0.5 gn	1.8 gn	150°	114°		orange	impure
iii	1.3 gn	1.5 gn	122°	121°		"	
iv	10.8 gn	9.8 gn	55-57°	56°		red	meta cp
Total -	14.6 gn	15.6 gn	.		6.8%		
2. i	1.9 gn	2.8 gn	130°	158°		yellow	
ii	0.6 gn	1.7 gn	130°	120°		orange	
iii	1.4 gn	1.5 gn	120°	120°		"	
iv	10.9 gn	9.4 gn	56°	56°		red	
Total =	14.8 gn	15.4 gn			4.07%		
3. i	2.1 gn	2.3 gn	131°	158°			
ii	0.7 gn	1.7 gn	152°	118°			
iii	1.0 gn	1.7 gn	120°	120°			
iv	10.7 gn	9.7 gn	55-56°	55-57°			
Total =	14.5 gn	15.4 gn			6.2%		
4. i	1.8 gn	2.5 gn	135°	159°			
ii	0.9 gn	1.4 gn	151°	119°			
iii	0.9 gn	1.2 gn	121°	118°			
iv	10.5 gn	9.9 gn	56°	56-57°			
Total =	14.1 gn	15.0 gn			6.3%		

Table XLIV

(b) To show the Relative Variation of yields of para- and meta-compounds and of total nitration produced of mercuric nitrate

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	% increase of pure para-compound	% decrease of pure meta-compound	% increase of total nitration.
<u>Expt</u>			
1	25·0%	9·25%	6·84%
2	47·3"	13·7 "	4·05"
3	9·5"	9·3"	6·20"
4	38.8"	5·7"	6·38"

ACETYLENE. Table XLV.

Relation between Nitroform estimated and Tetranitromethane isolated.

Experiment.			Time of standing prior to mixing.	"T.N.M." isolated.	Nitroform estimated, expressed as"T.N.M."	Nitric acid equivalent to no_2 in mixture.
136 A	95% Hno_3	$7^{0}=30^{0}$, Hg	0 hrs	20 grs	11 grs	9.1 grs
B	"	"	4 days		11.3 "	11.4 "
134 A	"	"	0	18.2 "	15.6 "	9.2 "
B	"	"	4 days	11.0 "	10.3 "	17.8 "
137 A	"	"	0	21.0 "	14.4 "	11.9 "
B	"	"	5 days	———	11.7 "	13.3 "
C	"	"	7 "	15.7 "	9.5 "	16.5 "
132	"	"	21 "	10.5 "	13.3 "	4.9 "
138	100% "	" "	0	22.0 "	16.0 "	9.5 "
133	95% "	$7^{0}=14^{0}$, No HgO		3.4 "	2.8 "	8.5 "
135	100% "	" "	0	1.97 "	2.2 "	15.2 "

(In expts. 133 and 135 half the quantity only of Acetylene was introduced)

ACETYLENE.

HNO_3 = 138.6 gn

Experiment	Nitroform	T.n.m. ≡ Nitroform	T.n.m. isolated	% Nitroform of T.n.m. isolated	HNO_3 left in RM calc. by Eq. Nos I & II	HNO_3 in RM by analysis	HNO_3 in trap	Total HNO_3 in RM by analysis	HNO_2
133 S 14° 95% No Hg	2.18 gn	2.83 gn	3.4 gn	84.7%	127.7	113.9	3.4 gn	117 gn	8.5
135 S 14° 100% No Hg	1.72 gn	2.2 gn	1.97 gn		132	108			15.2
132 D 30° 95% Hg≡ .33%									
A (stood 3 weeks)	10.27 gn	13.29 gn	10.64			87.12	16 gn	103 gn	2.6)
B (" " " plus 24 hours)	11. gn	14.28 gn							2.9)
134 " " "									
A No standing	11.99) gn	15.6 gn	18.18 gn	85.2%	57.3	82.8			9.2)
As 132 double speed	)								)
B Stood 7 days	13.16)	17.1 gn	16.6 gn						17.8)
136 A No standing	8.4) gn	10.7 gn	20	53.5%					8.9)
As 132	)								)
B Stood 4 days	10)	11.33 gn	No T.n.m. on direct distillation						11.3)

ACETYLENE TABLE XLVII

VARYING CONCENTRATIONS OF NITRIC ACID.

	C_2H_2 absorbed by 100 grams of nitric acid Litres	Co_2 evolved per 100 grams of nitric acid Litres	Co_2/C_2H_2 by volume	"7.N.M." as percentage of C_2H_2 absorbed	
(a) 100% Hno_3					
Expt 32	1.610	0.306	0.19/1	75.5	
36	1.640	0.373	0.238/1	124.0	
101	5.051	7.633	1.5/1	390.0	(double acetylene)
(b) 97.5% Hno_3					
33	1.516	0.503	0.283/1	163.0	
77	4.58	4.706	1.051	238.7	(double C_2H_2)
80	4.46	5.190	1.23/1	213.0	(treble C_2H_2)
(c).95% Hno_3					
69	1.795	1.444	0.80/1	238	
34	1.59	0.842	0.61/1	314	
39	1.679	0.478	0.33/1	244.5	
40	2.855	2.288	0.94/1	278.7	(double C2H2)
45	2.784	1.396	0.49/1	117.9	..
47	3.026	1.069	0.706/1	264.3	..
52	2.855	2.227	0.77/1	209.5	..
53	2.902	2.262	0.78/1	276.8	..
54 (undistilled acid)	1.970	1.268	0.64/1	165.0	..
55 A 11hrs heating for "7.N.M."	2.884	2.219	0.79/1	273	..
B 2½ hrs heating + fresh nitric	..	..	..	270	..

TABLE XLVIII

VARYING CONCENTRATION OF NITRIC ACID

(a)

Experiment	Percentage of Nitric Acid	C_2H_2 absorbed by 100 grams of nitric acid Litres	"T.n.m." as percentage of C_2H_2 absorbed	CO_2/C_2H_2 Volume
32	100.0	1.610	75.5	0.19/1
33	97.5	1.516	163.0	0.283/1
69	95.0	1.795	238.0	
67	90.0	1.097	160.0	0.80/1
49	85.0	0.546	158.0	1.11/1
131	70.0	0.401	60.0	1.09/1

(b) Double quantities of Acetylene

101	100.0	5.051	390
97	97.5	4.385	429.6
53	95.0	2.902	276.8
49	85.0	0.757	166.0

ACETYLENE

TABLE XLIX

VARYING TEMPERATURE

(a) Volume of acetylene = 2,300 cc

Expt.	7°	Percentage Nitric Acid	C_2H_2 absorbed by 100 grams Nitric Acid Litres	CO_2 evolved per 100 grams of Nitric Acid Litres	CO_2/C_2H_2 by volume	"7.n.m" as percentage of C_2H_2 absorbed
61	-3	95	1.20	0.54	0.45/1	104
14	15	95	1.296	1.04	0.8/1	238
82	25	95	2.055	2.087	1.01/1	257.8
68	30	95	2.008	1.308	0.65/1	340
83	30	95	2.066	2.169	1.05/1	330.9
71	40	95	2.076	1.530	0.736/1	412
75	50	95	1.667	1.873	1.12/1	472.4

(b) Volume of acetylene = 4,600 cc

53	15°	95	2.902	2.263	0.78/1	276.8
81	30	95	3.728	4.10	1.09/1	424.0
72	30	95	3.358	3.73	1.11/1	428.0
76	50	95	3.232	3.688	1.14/1	440.0
79	50	95	2.972	4.210	1.41/1	493.5

ACCTYLENE.

THE EFFECT OF THE PRESENCE OF METALLIC SALTS.

Temperature = 30°

Expt	Metal	$C_2 H_2$ Absorbed by 100 grams of Nitric Acid Litres	CO_2 evolved per 100 grams of Nitric Acid Litres.	"T.n.m." as percentage of $C_2 H_2$	Percentage of C in $C_2 H_2$ becoming T.n.m.	Percentage of C. in C_2H_2 becoming CO2.	Percentage of C. in C_2H_2 becoming other substance
18	Pt	2.68	2.25	203.	13.5	41.3	44.7
19	Ag	2.73	2.20	221	14.7	49.3	36.0
20	Ur	2.60	3.32	222	14.9	63.6	21.5
21	CU	2.55	2.64	371	24.2	51.5	24.3
22	Hg	3.02	4.38	453	29.18	70.81	0.0
23	None	2.81	2.72	341	22.6	49.0	28.4

ACETYLENE

TABLE LI

EFFECT OF THE PRESENCE OF METALLIC SALTS.

(a) Mercury 95% Nitric Acid. Temperature = 30°

Expt.	C_2H_2 absorbed by 100 grams of nitric acid Litres	CO_2 evolved per 100 grams of nitric acid Litres	CO_2/C_2H_2 by volume	"7.n.m." as percentage of C_2H_2 absorbed	Percentage of carbon in C_2H_2 becoming	
					"7.n.m."	CO_2
84	2.178	3.077	1.41/1	523.5	34.87	70.58
88	2.124	3.110	1.46/1	524.1	34.73	71.61
90	2.215	2.698	1.21/1	457.6	30.35	60.61
98	1.763	2.591	1.47/1	528.0	34.83	73.19
123	2.157	2.224	1.03/1	549.0	36.52	51.34
	DOUBLE ACETYLENE					
112	4.252	5.295	1.24/1	364	24.13	61.97
114	4.178	5.630	1.35/1	408	28.03	71.24
70	4.320	5.907	1.36/1	319.1	21.13	68.05
87	4.240	6.093	1.43/1	383.	25.43	71.5
89	4.192	6.065	1.44/1	453	30.02	72.01
92	4.196	5.314	1.26/1	431.1	28.65	63.16
94	4.145	5.947	1.43/1	461	30.59	71.4
100	3.550	5.033	1.41/1	422	28.0	71.42

TABLE LII

THE PROPORTION OF MERCURIC NITRATE.

Nitric Acid = 95%

Experiment	$HG(no_3)2$ as percentage	C_2H_2 absorbed by 100 grams of nitric acid Litres	CO_2 evolved per 100 grams of nitric acid Litres	"7.n.m." as percentage of C_2H_2	Percentage of C in C_2H_2 becoming "7.n.m"	Percentage of C in C_2H_2 becoming CO_2	Percentage of C in C_2H_2 becoming other substances
24	0.66	3.06	4.39	383	25.4	71.5	3.1
25	0.33	3.02	4.38	453	29.2	70.8	0.0
26	0.33	1.55	1.62	552	37.1	62.7	0.2
27	0.28	3.16	4.34	429	28.5	68.2	3.3
2	0.165	3.03	3.83	431	28.6	63.1	8.2
29	0.0	2.81	2.72	341	22.6	49.0	28.4

In experiment 27 the concentration of nitric acid was 97.5%

TABLE LIII

ACETYLENE

(a) Mercuric Nitrate = 0.66 per cent   Temperature = 15°

Expt.	Percentage of Nitric Acid	C_2H_2 absorbed by 100 grams of nitric acid. Litres	CO_2 evolved per 100 grams of nitric acid Litres	CO_2/C_2H_2 by volume	"T.n.m." as percentage of C_2H_2 absorbed	other substances as a percentage
11	90	1.490	2.27	1.52/1	204	9.82

(b) Temperature varied

7°

12 -3	95	1.20	0.54	0.394/1	104	61.0
13 15	95	1.296	1.04	0.8/1	238	44.0
14 30	95	1.49	1.566	1.05/1	331	25.4

(c) Mercuric nitrate = 0.3 - 0.66 per cent. Temperature 30°

15	95	1.571	2.22	1.41/1	523	0.0
16	100	3.456	4.87	1.4/1	410	2.4
17	70	0.581	1.1	1.91/1	47	1.9

TABLE LIV

ACETYLENE.

To Show the effect of Mercuric Nitrate under Optimum Conditions.

Mercuric Nitrate = 0.33 per cent

Temperature = 30°

Expt.	Percentage of nitric Acid	C_2H_2 absorbed by 100 grams of nitric acid Litres	Nitroform grams.	CO_2 evolved per 100 gms of nitric acid Litres	"T.n.m." as a percentage of C_2H_2	Percentage of carbon in Acetylene becoming		
						"T.n.m."	CO_2	Other substances
30	95.0	3.068	10.3	4.38	436	28.94	71.04	0.0
31	97.5	3.163	10.5	4.34	430	28.8	68.5	2.3
32	100.0	3.456	11.0	4.87	410	27.6	70.5	2.4
33	100.0	2.883	9.9	4.07	448	29.73	70.3	0.0

TABLE LV.

VARYING CONCENTRATION OF NITRIC ACID.

(a)

Expt.	Percentage of Nitric Acid.	C_2H_4 absorbed by 100 grams of Nitric Acid litres.	"T.n.m." as percentage of C_2H_4 absorbed	$\frac{CO_2}{C_2H_4}$ Volume.
151	100·0	1·502	25·1	0·28/1
152	97·5	1·374	38·4	0·3 /1
146	95·0	1·484	43·5	0·4 /1
148	90·0	1·646	110·2	0·84/1
162	70·0	0·398	29·4	0·98/1

(b) Double quantities of Ethylene.

Expt.	Percentage of Nitric Acid.	C_2H_4 absorbed by 100 grams of Nitric Acid litres.	"T.n.m." as percentage of C_2H_4 absorbed	$\frac{CO_2}{C_2H_4}$ Volume.
153	100·0	2·146	98·4	0·41/1
154	97·5	3·100	116·2	0·43/1
140	95·0	2·980	231·8	0·62/1
149	90·0	2·763	164·2	0·81/1

TABLE LVI

Varying Concentrations of Nitric Acid.

(a) 90% Hno$_3$

Exps.		C_2H_4 absorbed by 100 grams of Nitric Acid Litres	CO_2 evolved per 100 grams of Nitric Acid Litres	$\frac{CO_2}{C_2H_4}$ Vol.	"Tnm" as percentage of C_2H_4 absorbed
146		1·484	0·608	0·41/1	43·5
147		1·549	0·548	0·35/1	73·1
150		1·397	0·641	0·46/1	56·4
155	double)	2.980	0.210	0.07/1	198.1
	quantities)				
156	of C_2H_4)	2.846	0.451	0.16/1	201.4

(b) 95% Hno$_3$

Exps.		C_2H_4 absorbed by 100 grams of Nitric Acid Litres	CO_2 evolved per 100 grams of Nitric Acid Litres	$\frac{CO_2}{C_2H_4}$ Vol.	"Tnm" as percentage of C_2H_4 absorbed
148		1·646	1·382	0·84/1	110·2
157		1·842	1·654	0·89/1	118·4
158		1·800	1·594	0·88/1	99·4
164	double)	3·014	2·746	0·91/1	173·4
169	quantities)	3·158	2·699	0·85/1	194·2
170	of C_2H_4)	2·764	2·504	0·90/1	204·3
149	)	2·763	2·238	0·81/1	164·2

TABLE LVII

EFFECT OF MERCURIC NITRATE.

Mercuric nitrate = 0.66 per cent

Temperature = 30°
Nitric Acid = 95%

Expt.	C_2H_4 absorbed by 100 grams of nitric acid Litres	CO_2 evolved per 100 gms of Nitric Acid Litres	CO_2/C_2H_4 by Volume	"T.n.m." as a percentage of C_2H_4	Percentage of carbon in Ethylene becoming.		
					"T.n.m."	CO_2	Other substances or uncombined
142	2.125	1.869	0.88/1	301.4	21.53	44.0	34.47
143	2.601	1.613	0.62/1	297.9	21.28	31.0	47.72
144	3.044	2.453	0.806/1	332.9	23.78	40.3	35.92
145	3.152	2.679	0.85/1	354.8	25.34	42.5	32.16
147*	4.818	3.011	0.625/1	456.1	32.58	31.2	36.22

* Temperature rose during experiment.

ETHYLENE. TABLE ______

THE PROPORTION OF MERCURIC NITRATE.

Temperature = 30° Nitric acid = 95%

Expt.	$Hg(NO_3)_2$ as percentage	C_2H_4 absorbed by 100 grams of Nitric Acid Litres.	CO_2 evolved per 100 grams of Nitric Acid Litres	CO_2/C_2H_4 by volume	"T.n.m." as a percentage of C_2H_4	Percentage of carbon in Ethylene becoming		
						"T.n.m."	CO_2	Other substances or uncombined
145	0.66	3.152	2.679	0.85/1	354.8	25.34	42.5	32.16
144	0.66	3.044	2.453	0.806/1	332.9	23.78	40.3	35.92
176	0.28	2.798	1.878	0.67/1	272.3	19.46	38.4	42.14
177	0.33	2.846	2.005	0.705/1	333.4	23.32	40.14	36.04
175	0.33	2.900	1.930	0.665/1	300.4	21.46	37.98	40.56
170	0	2.764	2.504	0.90/1	204.3	15.74	51.04	33.22

ETHYLENE

TABLE LVIII

VARYING TEMPERATURE

Mercuric Nitrate = 0.66% Nitric Acid = 95%

Expt.	7°	C_2H_4 absorbed by 100 grams of Nitric Acid Litres	CO_2 evolved per 100 gms of Nitric Acid Litres	CO_2/C_2H_4 by volume	"T.n.m." as percentage of C_2H_4	Percentage of carbon in Ethylene becoming		
						"T.n.m."	CO_2	Other substances or uncombined
144	30	3.044	2.453	0.806/1	332.9	23.78	40.3	35.92
145	30	3.152	2.679	0.85/1	354.8	25.34	42.5	32.16
181	40	4.568	4.340	0.95/1	364.4	26.03	54.38	19.59
184	40	4.720	4.667	0.99/1	382.9	27.35	56.66	15.99
186	50	4.991	5.190	1.04/1	398.7	28.48	59.54	11.98
188	60	Reaction too vigorous to give comparative results.						

TABLE LIX

RELATION BETWEEN $_{B}$NITROETHYL ALCOHOL ISOLATED AND NITROFORM ESTIMATED.

Experiment	$_{B}$Nitroethyl alcohol gram.	Nitroform grams.	Ratio Nitro-alcohol / Nitroform
190 95% Hno_3 No Hg	1.98	4.6	1 : 2.17
191 .. .. Hg	4.59	11.4	1 : 2.48
192 90% Hno_3 No Hg	1.12	2.8	1 : 2.5
193 .. .. Hg	4.10	8.9	1 : 2.17

(1 gram B nitro eZl alcohol is equivalent to 1.659 grs nitroform.)

Experiment	$_{B}$Nitroethyl alcohol gram.	Nitroform grams.	Ratio Nitro-alcohol / Nitroform
194 95% Hno_3 No Hg (½ C_2H_4 passed in)	1.36	1.9	1 : 1.40
195 95% Hno_3 No Hg (¾ C_2H_4 passed in)	2.98	3.01	1 : 1.01
196 95% Hno_3 Hg (½ C_2H_4 passed in)	3.38	5.14	1 : 1.52
197 95% Hno_3 Hg (¾ C_2H_4 passed in)	1.38	7.98	1 : 1.38

ACETYLENE

TABLE LX

Varying concentrations of Sulphuric Acid.

95% Nitric Acid.

H_2SO_4/HNO_3	C_2H_2 absorbed litres	CO_2 evolved litres	CO_2/C_2H_2	"T - n -m"
0.0:1	1.296	1.04	0.25:1	248.0%
0.11:1	1.336	0.395	0.25:1	148.5"
0.5:1	1.41	0.137	0.09:1	0 "
1.0:1	1.88	0.098	0.05:1	0 "
2.6:1	1.774	0.17	0.1:1	0 "
3.0:1	3.42	0.144	0.04:1	0 "

Varying concentrations of Nitric Acid.

TABLE LXI

$H_2SO_4/HNO_3 = 1/1$

% HNO_3			
75	1.848	0.126	0.058:1
85	1.896	0.109	0.057:1
95	1.88	0.098	0.052:1

THE EFFECT OF CATLYSTS.

95% Nitric Acid.

H^2SO^4/HNO^3	,**Metal**	C^2H2 absorbed Litres	C^2H^2 % absorbed	CO^2 evolved Litres	CO^2/C^2H^2
1 : 1	Ur	1·858	62·1	0·176	0·947 : 1
1 : 1	Pr	1·724	57·0	0·140	0·0812: 1
1 : 1	Hg	1·692	55·7	0·138	0·0816: 1
1 : 1	None	1·88	71·6	0·098	0·052 : 1

RELATION BETWEEN OXALIC ACID AND HYDROCARBON ABSORBED.

(a) Acetylene.

% Nitric Acid	hydrocarbon absorbed Litres	CO_2 evolved Litres	CO_2 Hydrocarbon	Oxalic Acid grams.	CO_2 Oxalic Acid by wt.	Percentage Carbon becoming			carbon unaccounted for
						CO_2.	T.n.m.	Oxalic Acid	
95	3·792	3·212	1·14/1	2·357	$\frac{3\cdot69}{1}$	42·15	17·42	15·29	25·14
95	2·81	2·72	0·96/1	—	0	49·0	22·6	—	28·4
95	3·91	—	—	4·246	–	—	—	26·76	—

(b) Ethylene.

95	3·044	2·746	0·806/1	1.997	$\frac{2\cdot73}{1}$	40·3	23·78	16·30	19·62
95	3·152	2·099	0·85/1	2·774	$\frac{1\cdot93}{1}$	42·5	25·34	21·61	10·55
90	1·484	0·008	0·41/1	1·710	$\frac{0\cdot71}{1}$	20·49	29·8	28·34	21·37

Table 1

VARIATION OF ORIENTATION.

Chlorobenzene   ortho compound by difference only.

Chlorobenzene = 10grs.   Concentrated Nitric Acid.

	No Mercury			Mercury		
Exprp	para compound grams	ortho compound grams	ratio p/o	para compound grams	ortho compound grams	ratio p/o
1	5·4	1·8	3:1	5·1	2·4	2·1:1
2	5·1	2·0	2·5:1	4·8	2·8	1·7:1
3	5·2	2·3	2·2:1	4·9	2·6	1·8:1
4	5·4	1·9	3·0:1	5·1	2·7	1·8:1
5	5·5	2·1	2·6:1	5·2	2·8	1·8:1

average ratio= 2·66:1

para compound decreased 30·8%

total nitration increased 4·7%

Bromobezene. concentrated nitric-sulphuric acid medium   no variation of the ortho : para : ratio ;

ACETANILIDE

TABLE II

Medium - concentrated - Nitric - Sulphuric - Acetic acids.

	No Mercury			Mercury		
Experiment	Ortho compound grams	Para compound grams	ratio o-/p	Ortho compound grams	Para compound grams	ratio o/p
1	0.9	5.2	1:5.7	1.1	5.2	1:4.7
2	0.5	5.7	1:11.4	0.3	5.7	1:19
3	0.7	5.5	1:7.8	0.5	5.8	1:11.6
4	0.6	5.3	1:8.9	0.4	5.4	1:13
5	1.1	10.0	1:9.0	1.3	10.0	1:7
6	1.0	9.8	1:9.8	1.2	9.4	1:7
7	1.1	10.0	1:9.0	1.1	10.1	1:10
8	0.9	9.7	1:10.0	0.8	9.7	1:12
9	1.0	9.9	1:9.9	0.9	9.8	1:11
10	0.9	9.7	1:10.7	1.2	10.0	1:8

No definite or constant increase of either ortho or para compound.

SALICYLIC ACID

Table III.

Medium - Sodium nitrite and
sulphuric acid.

Para compound by difference only

(a) 10% mercuric nitrate

	No Mercury			Mercury.		
Experi-ment	Ortho Compound gram	Para Compound gram	O/p	Ortho Compound gram	Para compound gram	O/p
1	6.7	2.7	2.4:1	6.0	3.4	1.7:1
2	6.9	2.8	2.4:1	6.1	3.4	1.7:1
3	6.7	2.8	2.3:1	5.9	3.7	1.6:1
4	6.5	2.9	2.2:1	5.7	3.6	1.6:1
5	6.6	3.1	2.1:1	5.9	3.5	1.7:1
(b) 20% mercuric nitrate						
6	6.5	3.0	2.1:1	6.0	3.6	1.6:1
7	6.6	2.8	2.3:1	5.8	3.5	1.6:1
8	6.3	3.1	2.1:1	6.0	3.5	1.7:1

Para compound increased 28%

No change in total nitration.

TABLE IV

CINNANNIC ACID.

Medium. Absolute nitric Acid.

Mercuric nitrate = 10%

Experiment	Para/ortho No Mercury	Para/ortho Mercuric
1.	7.6 : 1	3.77 : 1
2.	9.6 : 1	4.37 : 1
3.	7.6 : 1	4.5 : 1
4.	7.4 : 1	4.37 : 1
5.	9.0 : 1	4.0 : 1

Increase
(Triercasc) of ortho compound = 48%

No change in total nitration.

TABLE V

PHENOL

Medium - aqueous sodium nitrate and sulphuric acid

Experiment	Ratio Ortho/para No Mercury	Ratio Ortho/para 10% $Hg(NO_3)_2$	Ratio Ortho/para 20% $Hg(NO_3)_2$	Ratio Ortho/para 40% $Hg(NO_3)_2$
1.	2.16 : 1	1.84 : 1	1.58 : 1	
2.	3.0 : 1	1.77 : 1	1.8 : 1	
3.	2.9 : 1	1.62 : 1	2.0 : 1	
4.	2.6 : 1	1.6 : 1	1.95 : 1	
5.	2.33 : 1	1.8 : 1	1.8 : 1	
		1.5 : 1		1.7 : 1
		1.69 : 1		1.7 : 1
		1.5 : 1		1.7 : 1
		1.8 : 1		1.8 : 1

Average decrease of ortho

Compound For 10% $Hg(NO_3)_2$ = 34%

" 20% " = 30%

" 40% " = 34%