THREE STEREOCHEMICAL PROBLEMS.

DECLARATION.

I hereby declare that the following thesis has been composed by myself and contains a record of work done by me. When I have had to deal with work done by others, due reference has been made to them in every case. One passage has been taken from a paper published jointly with a collaborator, and it may be advisable to mention that the paper from which the passage was taken was composed by me.

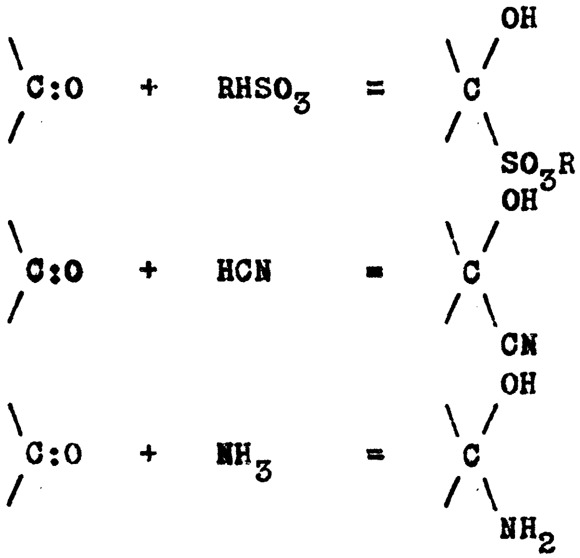
A. W. Stewart

PART I.

STERIC HINDRANCE IN KETONIC REACTIONS.

In 1904 it occurred to me that an interesting example of steric hindrance was that found in the case of the addition of sodium bisulphite to the carbonyl group of ketones. It is well known that, while acetone easily combines with bisulphites, neither acetophenone nor pinacoline will yield a bisulphite compound. A research in this branch of the subject seemed to promise results, for it would be easy to observe the effect produced by the introduction of methyl groups into the molecule of acetone; and as the homologues of acetone are all easily procured, a complete series of changes could be studied.

On referring to the literature of the subject, I was unable to find any papers dealing with the point from the practical side; though Angeli (Atti R. Accad. Lincei, 1895,5.84) had pointed out the resemblance between the addition reactions of bisulphites, hydrocyanic acid and ammonia to carbonyl compounds:



$$>C{:}O + RHSO_3 = >C(OH)(SO_3R)$$

$$>C{:}O + HCN = >C(OH)(CN)$$

$$>C{:}O + NH_3 = >C(OH)(NH_2)$$

and had suggested that these reactions were influenced by the nature of the radicals attached to the carbonyl group.

I have since found that P.Petrenko-Kritschenko (J.pr.Chem., |ii|,61,431; 62,315; Ber.,34,1699) had done some work in this branch of stereochemistry; but as his object was different from mine, I had not traced his papers. My work was thus done without reference to his; although we arrived at similar results in the cases of several compounds. Petrenko-Kritschenko has for a considerable time devoted himself to the study of the configuration of carbon chains; and he has used some cases of steric hindrance in support of his views.

In the first instance, my object was to estimate, as accurately as possible, the effect of replacing the hydrogen atoms of acetone in turn by methyl groups, using the amount of bisulphite compound formed in a given time as a measure of the reactive power of the carbonyl radical in each case. Now since the solubilities of the bisulphite compounds of various ketones are different, it is evident that the estimation of the amount of bisulphite compound formed should preferably be carried out in the solution, without isolating the addition product: and this necessarily implies the adoption of some titration method. A reference to the literature showed that Ripper (Monatsh.,21, 1079) had devised a method for the estimation of formaldehyde which depended upon the formation of a bisulphite addition product. He found that the $-SO_3Na$ group in the bisulphite compound was not oxidised by a solution of iodine; so thatthe amount of bisulphite compound formed in any case could be estimated from the difference between the titration values of two solutions; one of pure bisulphite, the other containing an equal quantity of bisulphite mixed with the aldehyde.

I applied this method in the case of the ketonic bisulphite compounds, but found that it had certain defedts: the chief one atising from the presence in the solution of hydriodic acid produced during the titration; as this acid, if left free, tends to break up the bisulphite compound, thus rendering the end-point uncertain. With a view to avoiding this, titration of the excess of the bisulphite with standard alkali was tried, but it was found that the final slight excess of alkali present was sufficient to break up the bisulphite compound as rapidly as the hydriodic acid had done. This method was therefore abandoned. Attempts were then made to utilise sodium bicarbonate to neutralise the excess of hydriodic acid in Ripper's method; and solutions of strengths deduced from the equations below were tried:

$$NaHSO_3 + 3\ NaHCO_3 + I_2 = Na_2SO_4 + 2\ NaI + 2\ H_2O + 3\ CO$$

$$NaHSO_3 + 2\ NaHCO_3 + I_2 = NaHSO_4 + 2NaI + H_2O + 2CO_2$$

The results were useless, however, so a retuen was made to Ripper's method.

In the first experiments, alcoholic solutions of the ketones were used, but it was found that owing to the action of alcohol upon the starch-iodine blue these did not give the best results. Purely aqueous solutions could not be used, owing to the insolubility of certain ketones in water; so that a compromise had to be made. It was found best to use as a solvent water to which 20% of alcohol had been added, and to make M/12 solutions of the ketones. By this method all the common ketones could be brought into solution, with the exception of acetophenone.

In the early trials which I made, I chose an arbitrary time limit and estimated the percentage of bisulphite compound which was formed during a given number of minutes. The results were not at all satisfactory, and I had some difficulty in arriving at a good method of estimating the velocity of the reaction.

The factors which enter into the problem are: the temperature of the solution, the decomposition of the bisulphite compound after its formation, and the action of the hydriodic acid generated during the titration. The first factor was disposed of by working at a constant temperature. The tendency of the hydriodic acid to break up the bisulphite compound was, as far as possible, minimised by rapid titration. By constant practice, I was able to combine this and the personal equation into a comparatively constant factor. The question of the decomposition of the bisulphite compound was more difficult to treat from the experimental side; and I was finally forced to do a series of titrations at frequent intervals and then draw curves which indicate approximately the rate at which addition is going on at different times. I should like to point out that Petrenko-Kritschenko has throughout adhered to the arbitrary time limit method; and I do not consider that his results represent the reaction velocity with any degree of accuracy.

The details of the method finally adopted were as follows. Fifty c.c. of an M/12 solution of the ketone to be investigated, prepared as described, were shaken in a flask with fifty c.c. of M/12 aqueous sodium bisulphite. The mixture was then allowed to remain, corked, in a vessel of ice and water. Every ten minutes, ten c.c. were withdrawn and titrated, being kept surrounded with ice-water during the operation. The iodine solution used was of such a strength that 14-15 c.c. were required to oxidise 5 c.c. of the bisulphite solution. The relative strengths of the two solutions were determined at the beginning and end of each series of titrations. The results obtained by this method were apparently accurate to within one per cent. after the mixture had been standing for an hour.

It seemed desirable to find some method by means of which the general correctness of the results thus obtained could be controlled; and for this purpose I measured the velocity of oxime formation in the case of certain ketones whose velocity constants I had already found in the case of bisulphite addition. I tried to measure the rate of semicarbazone formation, and of the addition of hydrocyanic acid to the carbonyl group;but unfortunately in neither case was I able to obtain concordant results.

In the case of the oximes, several methods were tried before a suitable one was found, the one finally adopted being a modification of Meyeringh's method (Ber.,10,1940) for the estimation of hydroxylamine. The details of the method are as follows. The ketone solution was made up in the same way as in the case of the bisulphite compounds, the same concentration, M/12, being used. Fifty c.c. of the ketone solution were mixed with an equal volume of M/12 hydroxylamine sulphate solution, and the mixture was left in an ice-bath. Every ten minutes, ten c.c. were withdrawn, to which were added twenty c.c. of N/5 iodine solution and twenty c.c. of N/5 disodium hydrogen phosphate solution. The whole was placed in a water bath for one minute, an the excess of iodine then remaining was titrated with sodium thiosulphate solution in the usual way. The rationale of the method is as follows. The ketone, in forming an oxime, uses up a certain quantity of hydroxylamine; the remaining hydroxylamine is decomposed by warming with the iodine solution, and the hydriodic acid thus produced is taken up by the sodium phosphate before it affects the oxime; the amount of iodine left unchanged is then estimated by means of the sodium thiosulphate titration, and from it the amount of hydroxylamine employed in oxime formation can be deduced. The results obtained by this method also are concordant to within one per cent.; but the method fails when applied to aldehydes, owing to their ready oxidation, and also in the case of compounds containing the group $-CO-CH_2-CO-$ whose methylene hydrogen atoms react with iodine on warming.

The results obtained by both methods are given in the tables below:

BISULPHITE COMPOUNDS.

% bisulphite comp. formed in	10	20	30	40	50	60	70 minute
Acetaldehyde	85.2	86.6	88.0	88.7	88.7	88.7	88.7
Acetylacetone	47.1	54.2	60.5	64.0	67.6	70.0	71.8
Acetoacetic ester	37.4	47.0	56.0	60.0	64.0	67.6	67.6
Acetone	28.5	39.7	47.0	53.6	55.9	56.2	58.9
Methyl ethyl ketone	14.5	22.5	25.1	29.1	32.4	36.4	38.4
Methyl propyl ketone	8.5	11.0	14.8	18.4	19.6	23.4	25.5
Laevulinic ester	7.2	10.0	14.0	15.0	16.5	19.4	21.6
Methyl isopropyl ketone	4.2	5.4	7.5	9.4	11.6	12.3	13.0
Pinacoline	4.2	5.6	5.6	5.6	5.6	5.6	5.6
Acetone dicarboxylic ester	40.2	55.3	61.0	64.5	68.5	71.2	73.0
Diacetylacetone	14.6	17.8	21.3	23.9	26.3	27.8	--
Acetonylacetone	5.7	8.8	11.5	14.6	16.6	19.5	--
Maltose	2.6	2.9	3.1	--	--	--	--
Glucose	5.2	5.2	5.2	--	--	--	--
Lactose	7.7	8.4	9.0	--	--	--	--

Potassium β-camphorsulphonate gave a constant value of 3.5%. Unsuccessful attempts were made to prove the existence of addition products in the case of epichlorhydrin, carbamide, acetamide, formamide, allyl alcohol and cinnamic ester. Dimethyl pyrone gave traces of some additive compound, but concordant results were not obtained.

OXIME FORMATION.

% Oxime formed in	10	20	30	40 min.
Acetone	45.1	49.7	50.0	50.1
Methyl ethyl ketone	36.6	39.2	39.2	39.2
Methyl propyl ketone	34.7	37.3	39.9	41.2
Methyl isopropyl ketone	31.4	31.5	32.0	32.0
Laevulinic ester	26.1	30.0	33.9	35.0
Acetonylacetone	19.0	30.0	35.0	39.0
Pinacoline	12.9	17.0	24.5	24.5

The velocity constants calculated on the first ten minutes from the above figures are as follows:

	$NaHSO_3$	NH_2OH
Acetaldehyde	0.5755	---
Acetone	0.04027	0.08215
Methyl ethyl ketone	0.01696	0.05773
Methyl propyl ketone	0.00929	0.05314
Methyl isopropyl ketone	0.00458	0.04577
Pinacoline	0.00438	0.01481
Acetylacetone	0.08902	---
Acetonylacetone	0.00604	0.02346
Diacetylacetone	0.01710	---
Laevulinic ester	0.00776	0.03582
Acetoacetic ester	0.05974	---
Acetone dicarboxylic ester	0.06722	---
Glucose	0.00549	---

Now whenwe examine these numbers, several deductions may be drawn. In the first place, the effect of replacing a hydrogen atom by a methyl radical is well marked; a steady decrease in the amount of bisulphite compound formed in a given time follows the successive replacement of the hydrogen atoms by methyl groups. This can be seen by comparing the following figures, which show the percentage of bisulphite compound and oxime formed by various ketones in ten minutes, as well as the velocity constants calculated from these data.

	$NaHSO_3$		NH_2OH	
	%	K	%	K
$CH_3.CO.H$	85.2	0.57550	—	—
$CH_3.CO.CH_3$	28.5	0.04027	45.1	0.08215
$CH_3.CO.CH_2.CH_3$	14.5	0.01696	36.6	0.05773
$CH_3.CO.CH(CH_3)_2$	4.2	0.00438	31.4	0.04577
$CH_3.CO.C(CH_3)_3$	4.2	0.00438	12.9	0.01481

In the case of the bisulphite compounds, the difference between methyl isopropyl ketone and pinacoline is so slight that it lies within the limits of experimental error.

I have already pointed out that the gross amount of bisulphite compound formed after a fixed time is of but little value in determining the reactivity of a given carbonyl group; as can be seen from the figures given in the large table, equilibrium is established after very different intervals of time in the cases of different ketones. For example, the figures below show approximately the number of minutes which elapse before equilibrium is established in various cases:

$CH_3.CO.H$	40 minutes
$CH_3.CO.C(CH_3)_3$	20 ,,
$CH_3.CO.CH_2.COOEt$	60 ,,

This is in agreement with the results obtained by Menschutkin in his various researches on the influence of carbon chains upon reaction velocities.

From the theory of steric hindrance, I had been led to expect that compounds containing a chain of carbon atoms of equal length would have approximately the same additive power, at least when the carbonyl group in each case lay in a similar position in the chain. This view proved to be quite erroneous, however; and as it was on this discovery that my later work was founded, it is necessary to give some details on the point in question.

If we consider the compounds methyl ethyl ketone and acetoacetic ester, it is evident that both of them contain a chain of four carbon atoms directly united to each other. Acetoacetic ester, of course, contains six carbon atoms in all, but only four of these are in the main chain, the others being united to the rest of the molecule by the intermediation of an oxygen atom. If we write down the formulae of ~~the intermediate~~ these two compounds for the purpose of comparison:

$$CH_3.CO.CH_2.CO.OC_2H_5$$

$$CH_3.CO.CH_2.CH_3$$

it is evident that since the part $CH_3.CO.CH_2-$ of both molecules is the same, any difference in steric hindrance must be attributed to the difference in size between the remaining parts of the molecule; that is, between the sizes of the groups $-CH_3$ and $-COOC_2H_5$. From Traube's results in his calculations of atomic volumes we should expect to find that the $-COOC_2H_5$ group had a greater xxxxx hindering effect than the methyl radical; and we should therefore anticipate that the addition velocity of acetoacetic ester would be less than that of methyl ethyl ketone. An examination of the experimental results shows that this anticipation was not justified:

	K
Methyl ethyl ketone	0.01696
Acetoacetic ester	0.05974

The velocity constant of acetic ester, instead of being lower than that of methyl ethyl ketone, is actually more than three times as high.

It is now advisable to compare the velocity constants of three other ketones, each of which contains a chain of five carbon atoms, viz., methyl propyl ketone, laevulinic ester and acetone dicarboxylic ester:

	K
$CH_3.CO.CH_2.CH_2.CH_3$	0.00929
$CH_3.CO.CH_2.CH_2.COOC_2H_5$	0.00776
$COOC_2H_5.CH_2.CO.CH_2.COOC_2H_5$	0.06722

From an examination of these figures, a new fact comes to light. The $-COOEt$ group xxxxxf in itself appears to have no great influence upon the reactivity of the carbonyl radical; for the rate of addition is lower in the case of laevulinic ester than in the corresponding methyl propyl ketone: but when the $-COOEt$ group is placed in the β-position to the carbonyl radical it exercises a very strong influence upon the reactive power of the latter. This increase in reactivity may be gauged by a comparison of the following figures:

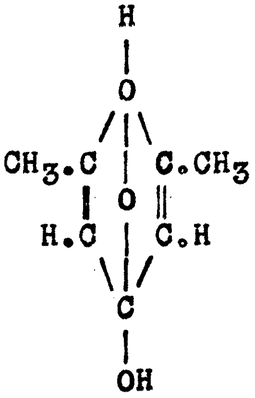
	K
$CH_3.CO.CH_3$	0.04027
$CH_3.CO.CH_2.COOEt$	0.05974
$COOEt.CH_2.CO.CH_2.COOEt$	0.06722

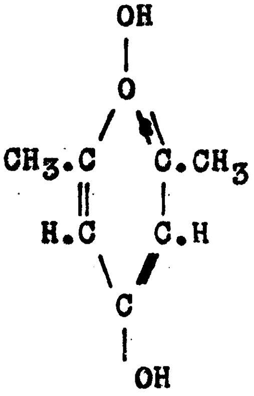
It seemed possible, though hardly probable, that this increase in the amount of bisulphite compound formed was really due in these cases to an addition of bisulphite to the -COOEt group itself, in a similar manner to the addition of sodium ethylate which was observed by von Pechmann (Ber., 31,503). The behaviour of laevulinic ester cast doubt upon the probability of the hypothesis but for the sake of certainty I made some experiments with ethyl acetate in order to see if any addition of bisulphite to its -COOEt group could be detected. No trace of any such addition could be found.

Now the exceptional reactivity of the carbonyl group when in the β-position to the group -COOEt is analogous to the lability of the hydrogen atoms in a methylene group which is placed between two carbonyl radicals, as in acetoacetic ester, or malonic ester. We are therefore dealing in this instance with a particular case of a general problem; and any explanation which may be put forward for the reactivity of the carbonyl group should also throw light upon the ease with which the methylene hydrogen atoms in malonic and similar esters are replaced by sodium. This point will be dealt with later in this section. There is, however, one case to which attention must be drawn here, viz., that of diacetylacetone. As can be seen from the velocity constants, each carbonyl group of that substance has a reactivity which does not differ to any extent from that of the carbonyl radical in methyl ethyl ketone:

	K
$CH_3.CO.CH_2.CO.CH_2.CO.CH_3$	0.01710
$CH_3.CO.CH_2.CH_3$	0.01696

Except by making some very doubtful assumptions, this cannot be explained on any steric hypothesis, and we are therefore driven to find a chemical explanation. The best seems to be to adopt Collie's formula for diacetylacetone: (Trans. [illegible]





In the presence of bisulphite, this may be supposed to change slowly into the open chain ketonic form; so that the rate of bisulphite compound formation is really a measure of this rate of change, and not of the rate of addition of bisulphite to the carbonyl groups.

This explanation involves the abandonment of the purely steric view; but this can be justified in other cases. For instance, glucose under the same conditions has a very low velocity constant

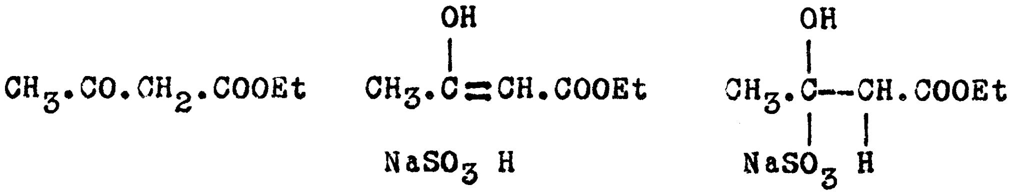
$$K = 0.00549$$

The influence at work here cannot be a purely steric one, but must be attributed to the accumulation of hydroxyl groups in the chain.

In addition to the compounds mentioned, I studied also several others, but as they have no particular bearing upon the problem dealt with in this section, it is needless to give the results here. In many cases I was unable to make estimations owing to the insolubility of the ketonic substances.

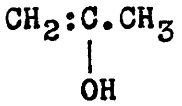
From the results which have already been summarised, it is apparent that the ketones dealt with may be divided into two classes: first, those whose reactivity is in agreement with the steric hindrance hypothesis; and, secondly, those which, judged by this standard, are abnormal. In the first class are those ketones derived from acetone by the substitution of methyl groups for hydrogen atoms; while the second class includes those ketones which have a -COOEt group in the -position to the carbonyl radical. Now the phenomenon of tautomerism is known to be specially marked in substances belonging to this latter class; so that we are faced by the apparent paradox that when a compound exists altogether in the true ketonic form it has less reactivity than when part of it exists in the ketonic and part in the enolic condition. In other words, a ketone shows its ketonic properties best when it exists in the enolic form.

It seemed possible that the abnormal rate of addition in the case of compounds containing the grouping $-CO-CH_2-CO-$ might be due to the following mechanism. In the first place, the enolic form of the ketone might be produced, and the bisulphite molecule might then attach itself to the double bond. In the case of acetoacetic ester, this would be represented by the following formulae:



$$CH_3.CO.CH_2.COOEt \qquad CH_3.\underset{NaSO_3}{\overset{OH}{\overset{|}{C}}}{=}\underset{H}{C}H.COOEt \qquad CH_3.\underset{\underset{NaSO_3}{|}}{\overset{OH}{\overset{|}{C}}}\text{--}\underset{\underset{H}{|}}{C}H.COOEt$$

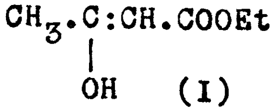
Ordinary ketones might be supposed to act in a similar way; but since they are less tautomeric than compounds containing the group $-CO.CH_2.CO-$, their activity would be less. For instance, acetone would form the enolic compound:



$$CH_2{:}\underset{\underset{OH}{|}}{C}.CH_3 \quad .$$

Now if this view were correct, then unsaturated compounds such as allyl alcohol should have the faculty of uniting with bisulphites almost as readily as ketones do. To test this, I examined the behaviour of allyl alcohol and cinnamic ester; but in neither case was there any measurable addition. It seems improbable, therefore, that the addition reaction is brought about in the manner shown above.

We must now consider the bearing of tautomerism upon the origin of the reactivity of the carbonyl group from another point of view. If we examine the process of tautomerism, we shall find that it is merely the change of a compound of the type (I) into one of the type (II), and vice versa.

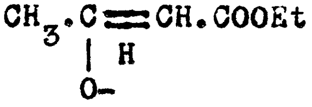


$CH_3.C(OH):CH.COOEt$ (I)

$CH_3.CO.CH_2.COOEt$

(II)

Now this change implies that the hydrogen atom is loosened from the oxygen atom and transferred to the adjacent carbon atom. And just at the instant when the hydrogen atom breaks free from the oxygen atom, the latter will have a valency free which next moment would be used to form the double bond of the carbonyl group. In other words, the stage between (I) and (II) may be roughly represented by the formula below:



$CH_3.C(O-)(H)=CH.COOEt$

(III)

At this instant, if there be in the neighbourhood of the carbonyl group a molecule capable of reacting with it, the reaction is more likely to take place then than at any other time; for the oxygen atom in (III) would have properties very closely approximating to those of a nascent atom, and it would therefore be much more reactive than the normal oxygen atom. The reactivity of any carbonyl group would thus be proportional to the frequency with which it became "nascent".

In order to make any further progress in this branch of the subject, it was imperative to have a measure of the amount of tautomerism in a given ketonic compound, which could be utilised independently of the results arrived at by means of my previous methods; so that a comparison could be made between the degree of tautomerism and the reactivity of the carbonyl radical. Such a measure of tautomerism could only be useful if it were made by a physical method, as chemical methods would lead to a mere repetition of the work I had already done. Now, at this time, Mr. Baly and Dr. Deschhhad just completed an investigation of the absorption spectra of certain enol-keto tautomers, the results of which, in so far as they concern my work, may be summarised here.

Baly and Desch (Trans. 85. 1039; 87, 766) were able to show that while both the enolic and ketonic forms of tautomeric substances gave only general absorption, an equilibrium mixture of the two gave an absorption band in the ultra-violet region of the substance's spectrum. The persistence of this band was a measure of the tautomerism of the substance under the given conditions. This, then, gave the required measure of the tautomerism; and at this point, in order to give completeness to my investigation, I joined forces with Mr. Baly. Together (Stewart and Baly, Trans. 89. 489) we examined the spectra of a very considerable number of ketonic substances, with the results which will now be described.

The method employed by us differed in no respect from that devised by Hartley; but instead of limiting ourselves to absorption in the ultra-violet region of the spectrum, we examined the visible region as well. In the curves appended to this paper, the figures on the right hand side of the diagram represent the relative thicknesses of solution whose absorptive power was measured; the unit being one millimetre of a N/10,000 solution. The figures on the left hand side are the logarithms of the corresponding numbers on the right hand side. The numbers at the top of the diagram give the frequencies.

Baly and Desch had confined their work to compounds containing the group $-CO-CH_2-CO-$, but it appeared probable that a relation between reactivity and tautomerism might exist in the case of the simple mono-ketones of the type R-CO-R'. The spectra of several of these were therfore examined, and in every case we found a band which had not been observed before. Not only so, but the persistence of this band was proportional to the reactivity of the ketone's carbonyl group which had been measured by me some time previously. This will be made clear at once from a comparison between the curves in Figure 1, and the following numbers, which give the percentage of oxime formed by these ketones in twenty minutes.

	% Oxime
Acetone	49.7
Methyl ethyl ketone	39.2
Methyl propyl ketone	37.3
Methyl isopropyl ketone	31.5
Pinacoline	17.0

A relation is thus established between the absorption spectra of these ketones and their reactive capacity: ~~xixaxxtkx~~ and since the absorption bands in the spectra of the mono-ketones occur in the same region of the spectrum as those of the di-ketonic compounds examined by Baly and Desch, it seems not unwarrantable to attribute them to a similar process. The reactivity of the carbonyl group in acetone may therfore be ascribed to the transition of the compound fa from the enolic to the ketonic form. Baly and Desch, however, have suggested that it is not necessary to assume that an actual change from one form to the other is going on continually: it is enough to suppose that some sort of intra-atomic strain is set up, which, if carried to its end, would finally lead to this vibration of a hydrogen atom.

Lapworth (Trans. 85.32) was able to prove that the action of halogens upon acetone was preceded by the formation of the enolic form of the ketone; and he found that this reaction was most readily carried out under conditions which favoured the establishment of equilibrium between the two tautomeric forms of the ketone. (Cf. Trans. 81.1503; 83.1121) His results are therefore in close agreement with the theory set forth above.

Again, the hydrogen atom affected by the enol-keto change must also be extremely reactive if this theory be correct; and here also the facts are in agreement with the new views. For example, the reactivity of the carbonyl group in acetoacetic ester is greater than that of acetone, and the readiness with which the hydrogen atoms of the methylene group in acetoacetic ester are replaced by halogens far exceeds the ease of substitution in the case of acetone. The close relation between the reactivities of the carbonyl group and the hydrogen atom associated with it certainly tend to strengthen the argument in favour of the view that tautomerism and reactivity are closely connected phenomena.

In the course of my work, I had shown that both acetylacetone and benzoylacetone react slowly with phenylhydrazine. It was therefore to be expected that they would be tautomeric substances and that their spectra would show shallow absorption bands. These spectra had already been examined by Baly and Desch (Trans. 87.760) who stated that they were pure ketonic compounds. Since these two data were not in agreement, Mr.Baly and I examined the spectra of the two compounds,using solutions of greater concentrations than had been employed before; and in our plates we detected a rapid extension of the spectrum at one point (See III and IV in Figure 2) which extension corresponds to a very shallow absorption band. My work, therefore, had acted as a control upon the spectroscopic experiments: and the close agreement between the results deduced from the measurement of reaction velocities and the absorption spectra seems to strengthen still more the probability of the correctness of the work.

A further test was applied as follows. It is a well known fact that the speed of a reaction is influenced by the solvent in which it is carried out; and Petrenko-Kritschenko (J.Russ. Phys.Chem.Soc.,1903,35,404) has examined the matter quantitatively in the case of phenylhydrazone formation. He found that the more unsaturated the solvent was, the slower the reaction proceeded. In order to check this, we examined the spectra of acetone and acetoacetic ester. A comparison of curves (I) and (III) in Figure 1 will show at once the effect which the solvent exerts upon the tautomeric prodess. In the case of acetoacetic ester, the curve of di-ethyl acetoacetic ester is given as a comparison. (See (I) and (II) in Figure 2) In this case also, the action of the unsaturated solvent water is much greater than that of the saturated alcohol.

It might be objected that as the band in acetone is well marked, while the acetoacetic ester spectrum shows a mere extension, and no true band, therefore the reactivity of acetone should be greater than that of acetoacetic ester. In reply, it is only necessary to point out that the two bands occur at different dilutions; and a band which appears at N/1000 obviously represents a more powerful vibration than one whose influence is exhausted at N/10.

Up to this point, all the evidence favoured the view that tautomeric change in the group $-CH_2.CO-$ lay behind the reactivity of the carbonyl group in ketonic compounds; but since further evidence was desirable, we resolved to ascertain the reactivity of the carbonyl radical in the cases of acetone, acetoacetic ester, acetone dicarboxylic ester and pyruvic ester. A new method was employed, which it was hoped would yield rather more accurate results than my previous ones. Fifty c.c. of a M/20 solution of potassium bisulphite were cooled to zero and mixed with an equal volume of a 50% alcoholic M/10 solution of the given ketone, which had been cooled to zero. The liquid was immersed in a freezing mixture and kept at a temperature of -10°C. Ten c.c. were withdrawn every five minutes and titrated with iodine. The results are given in the following table:-

	5	10	15 min.	K
Acetone	5	7	9	0.000105
Acetoacetic ester	12	18	24	0.000272
Acetone dicarboxylic ester	30	36	42	0.000857
Pyruvic ester	52	64	76	0.002666

The figures give the percentages of bisulphite compound which were formed, and the constant K is calculated on the first five minutes. In spite of the precautions taken, the results are probably not quite accurate; but the differences between the numbers themselves are very much greater than any experimental error under the conditions employed.

An examination of the numbers shows that the introduction of a -COOEt group into acetone increases the additive capacity of the carbonyl group; the introduction of two -COOEt groups still further enhances the reactivity of the carbonyl; but the most striking effect is produced when, as in the case of pyruvic ester, the carbonyl and carboxyl radicals are brought into juxtaposition in the chain.

Now, in the case of pyruvic ester, although the compound sometimes reacts in the enolic form, it is most improbable that the change from the enolic to the ketonic form and vice versa is going on at a rate at all comparable to that at which it is occurring in acetoacetic ester or acetone dicarboxylic ester, so that it is not likely that the exceptional additive capacity of the carbonyl group in pyruvic ester is due to this kind of tautomerism.

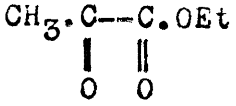
In order to settle the question, we examined the spectrum of pyruvic ester, with the following result. (See II in Figure 2) The absorption spectrum contains a band of considerable persistence whose head lies at 3500. This band, (which for the sake of convenience in reference we may call the "pyruvic band"), might be supposed to originate in either of two ways: it might be due to tautomeric change in the group $CH_3.CO-$, as was found in acetone and other simple ketones; or it might be caused by some interaction between the groups of the radical $-CO.COOEt$. Now if the first hypothesis were true, since the process would be the same as in the simple ketones, the band might be expected to occur in approximately the same place in the spectrum, (allowing for the difference in weight of the groups involved); but as a matter of fact the band in acetone has its head at 4200, nearly seven hundred units away from that of pyruvic ~~xxxd~~ the band. Since the heads of the bands in the homologues of acetone do not appear to diverge more than a hundred and fifty units from a mean position, it appears reasonable to conclude that the pyruvic band is not due to the same cause which produces the bands in the simpler ketones.

We are therefore thrown back upon the assumption that the pyruvic band owes its origin to some change which is continually going on in the -CO.COOEt part of the molecule. We may neglect the idea that the carbonyl group alone suffices to produce this band, for then we should find it in acetone; we may also rule out of account the -COOEt group, as the spectrum of ethyl acetate shows no such absorption. Evidently, therefore, the two parts -CO- and -COOEt are needed to cause the appearance of the band. The question at once arises, is the ethoxy radical necessary for the production of the absorption, or could this be brought about by the juxtaposition of two ordinary carbonyl groups, -CO.CO- ?

The simplest means of putting the matter to the test seemed to be to examine the spectrum of diacetyl, which contained the required grouping, but in which the -OEt radical did not occur. We photographed the spectrum of diacetyl, and found , as we expected, that it contained ~~the~~ an absorption band almost in the same place as that found in the pyruvic ester spectrum. (Figure 3) It is obvious, therefore, that the group CH_3.CO.CO. is sufficient to produce the band.

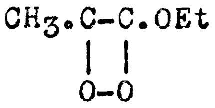
I have already mentioned that Baly and Desch concluded that though the bands occurring in the spectra of tautomeric compounds were *produced* by intra-atomic vibrations, they were *caused* by the alteration of linkage due to the change from the ketonic to the enolic form and vice versa. If we apply this idea to the present case, we should expect to find a somewhat similar state of affairs; and we should further expect to find a "nascent carbonyl group" being formed, as we have to account for the exceptinal reactivity of the carbonyl radical in pyruvic ester. The only possible way in which these two requirements can be expressed in formulae is to suppose that pyruvic ester exists in two forms like acetoacetic ester. The two forms would be represented as below, but I wish to point out that these formulae are not supposed to have any static existence: they are to be understood merely as representations of two extreme phases of a vibration:

(I)



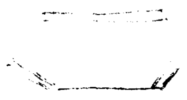
$$\mathrm{CH_3.\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}.OEt}$$

(II)



$$\begin{array}{l}\mathrm{CH_3.C-C.OEt}\\ \qquad\ \ |\quad |\\ \qquad\ \mathrm{O-O}\end{array}$$

An illustration will perhaps serve to make the meaning clearer. In the Kekulé vibration formula for benzene, it is assumed that the two forms:



do not represent different compounds, but merely phases in the vibration of 1,2-dichlorobenzene. The two forms of pyruvic ester are supposed to be analogous to the two benzene phases. Further, since the change of (II) into (I) would produce a "nascent carbonyl radical" the reactivity of pyruvic ester also finds its explanation in this hypothesis.

At this point, it may be well to summarise the conclusions which can be drawn from the work described in the foregoing pages.

(1) The reactivity of any carbonyl group is not inherent in the group itself, but is produced by the action

of neighbouring atoms which render the group "nascent".

(2) Such action may take the form of tautomerism or of a modification of tautomerism such as Laar originally postulated, in which there is no actual transfer of the hydrogen atom from one atom to the other.

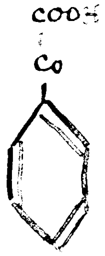
(3) The action may also take the form of a play of forces between two adjacent carbonyl groups.

(4) The reactivity of a given carbonyl group may be approximately estimated from the persistence of a certain band in the absorption spectrum of the ketone containing it.

(5) The reactivity of the hydrogen atoms in the group $-CH_2-CO-$ depends upon the "nascency" of the carbonyl group; consequently in the group $-CO-CH_2-CO-$, it is to be expected that the hydrogen atoms would be more active than in acetone, owing to their being adjacent to <u>two</u> carbonyl groups instead of one.

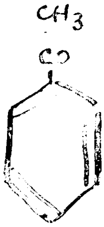
(6) The theory put forward in the foregoing pages is superior to the ordinarily accepted hypothesis of steric hindrance, as it is able to explain all hindrances in carbonyl group reactions, including several cases which are anomalous from the steric point of view. For instance, the compound (I) forms an oxime easily, while (II) does not do so, although the methyl radical is probably much

smaller than the carboxyl group. This cannot be explained by steric hindrance, but it is simply a parallel case to that observed by myself in the case of acetone and pyruvic ester.



(I)

Forms oxime



(II)

Forms no oxime

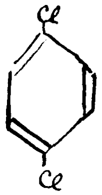
PART II.

STERIC HINDRANCE IN THE SUBSTITUTED QUINONES.

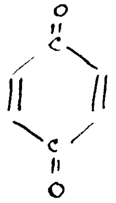
It is well known that a close relation exists between the para-positions of a benzene ring; and it therefore seems not improbable that a "pyruvic band" might be found in the absorption spectrum of quinone, owing to some interaction of the carbonyl groups in the para-position to each other. The spectrum of quinone had already been examined by Hartley, Dobbie and Lauder (Brit. Assoc. Report, **1903, 126**) but they had confined themselves to the ultraviolet part of the spectrum, and had attributed the yellow colour of quinone to general absorption in the visible region. We re-examined the spectrum, and found, as we anticipated, that the yellow colour was due to a band in the visible region, its head lying at about 2200. (See Figure 4). It is evident that in quinone a change similar to that in diacetyl is going on. In other words, quinone must be continually passing from one phase to another in such a way as to give rise to a "nascent carbonyl group".

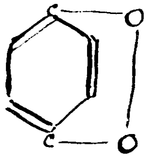
At this point it may be well to recall the chemical evidence which bears upon this question. When quinone is treated with hydroxylamine, it gives rise to a dioxime which has the formula:

If, on the other hand, quinone be subjected to the action of phosphorus pentachloride, it yields para-dichloro-benzene:



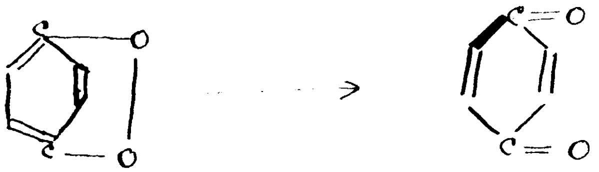
In the one case, then, there is a true carbonyl group reaction, while in the other action the oxygen behaves as if it were part of a hydroxyl radical. To explain this, it is often assumed that quinone exists in two forms:

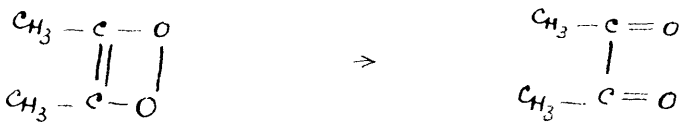

(I)

(II)


from the first of which the dioxime is produced, while the second yields dichloro-benzene.

Now, when we examine the process by which (I) is derived from (II), we shall find that a "nascent carbonyl group" is produced at each of the two para-positions; so that the case is similar to that of diacetyl:





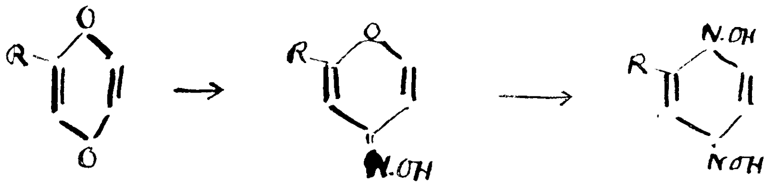
In the case of quinone, there cannot be supposed to be any enol-keto tautomerism going on; in fact, the spectrum shows that this process is not occurring to any measurable extent, for there is hardly a trace of a band at frequency 4000 in the ultra-violet.

At this point, the interests of Mr.Baly and myself diverged to a certain extent; as he was attracted by the possibility of explaining the colour of yellow compounds by means of the "nascent carbonyl group" hypothesis; while I was more concerned with the purely chemical side of the question. We continued to work in common, but it is unnecessary to deal with the colour theory in this place.

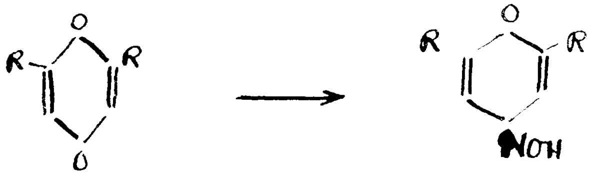
It appeared to me, that since we had been able ~~to~~ in the case of the simple ketones, to provide an hypothesis alternative to that of steric hindrance, it might be possible to extend our work to the case of the substitution products of quinone.

Kehrmann (Ber.,21,3315; J.pr.Chem.39,399; 40,257) has shown that when the hydrogen atoms of quinone are replaced one at a time by methyl radicals or halogen atoms, a distinct change takes place in the reactivity of the carbonyl groups in the compounds. His conclusions, which are based upon a very considerable amount of research, are as follows:-

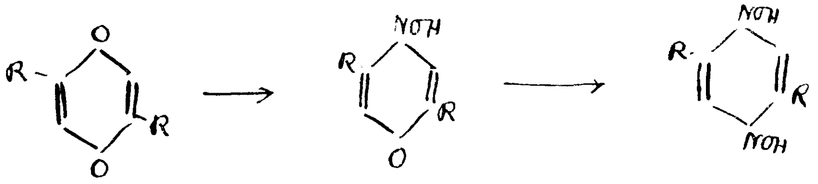
I. Mono-substituted quinones, when treated with hydroxylamine, first form a monoxime, the carbonyl group in the ortho-position to the substituent being unattacked. On further treatment, this monoxime yields a dioxime:



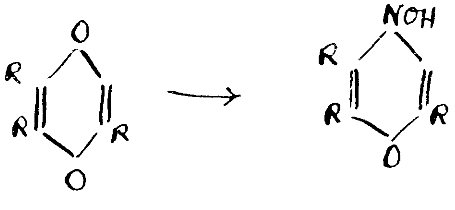
II. Di-substituted quinones, when both substituents are in the ortho-position to the same carbonyl group, yield only monoximes:



III. Di-substituted quinones, when the substituents are in the para-position to one another, give mono- and di-oximes, but only with some difficulty:



IV. Tri-substituted quinones give only monoximes, that carbonyl group being attacked which has only one ortho-substituent:



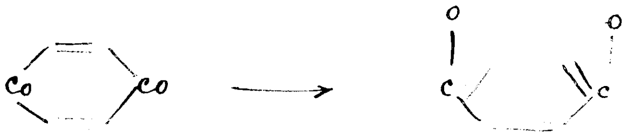
V. Tetra-substituted quinones give no oximes.

Up to the present time, it has been usual to attribute the phenomena observed by Kehrmann to the influence of steric hindrance. It was supposed that the chief cause of the non-reactivity of the carbonyl groups was to be found in the occupation of the space around them by the vibrations of the substituents in the ortho-position; this being considered sufficient to prevent the approach of any hydroxylamine molecules. It seemed to me that an extension of the theory of the "nascent carbonyl group" might lead to a better explanation of Kehrmann's results; and it was therefore decided to investigate the point. (Stewart and Baly, Trans. 89. 618).

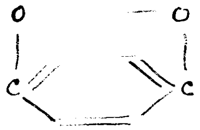
In the first place, we considered the advisability of estimating for ourselves the exact reactivity of the carbonyl groups in quinone; but we abandoned this idea for two reasons. First, I had already endeavoured to make exact measurements in the case of quinone, and had been forced to give up the task owing to the ease with which the substance is affected by reagents. Second, a study of Kehrmann's results seemed to indicate that the differences in the reactivity of quinones were much more marked than those observed among the simple ketones; so that Kehrmann's own observations would suffice for our purpose.

We therefore examined the absorption spectra of the following quinones: benzoquinone, toluquinone, p-xyloquinone, thymoquinone, chloro-benzoquinone, dichloro-benzoquinone, trichloro-benzoquinone, trichloro-toluquinone, bromo-benzoquinone, dichloro-thymoquinone, and dibromo-thymoquinone, with results which must now be described.

It should be pointed out that the reactivity of the carbonyl groups in quinone is closely related to the persistence of the "pyruvic band" which has its head at 2200; the deeper this band is, the more reactive the carbonyl groups appear to be. That is to say, the more frequently the process



is going on, the more reactive the carbonyl groups are. But if the quinone molecule exists for a considerable time in the form:



it will have a distinctly benzenoid structure, and will ne less reactive than if it were continually undergoing iso-dynamic change. We can form an estimate of the amount of the compound which actually exists in the benzenoid form at any given moment by means of the spectroscope. Benzenoid compounds show a series of well marked bands lying in the neighbourhood of 4000. If, therefore, the particular quinone we are dealing with exists to any extent in the benzenoid form, we should expect to find traces of these benzene bands in its spectrum; and, further, since the "pyruvic band" is due to those molecules which are changing from quinonoid to benzenoid structure, it will be less marked in the inverse ratio to the increase of the benzene band. That is to say, the reactivity of the quinone carbonyl groups is inversely proportional to the persistence of the benzenoid band in the spectrum of the quinone. We must now examine the actual results which were obtained.

In the first place we may deal with those quinones in which hydrogen atoms have been replaced by alkyl radicals. It is usual to measure the persistence of a given band by calculating the length of dilution over which it extends. This has been done in the case of quinone, (Figure 4), toluquinone (Figure 5), and thymoquinone (Figure 6), with the results given below. The figures for p-xyloquinone, (Figure 7), are very slightly different from those for toluquinone, and they have therefore been omitted.

	Quinone	Toluquinone	Thymoquinone
Band begins at.....	78.4	21.0	13.8
,, ends ,, ...	10.0	10.5	7.2
Change of dilution over which the pyruvic band persists:	85.8%	50.0%	47.8%

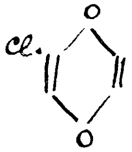
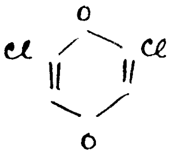
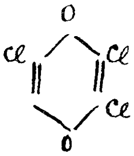
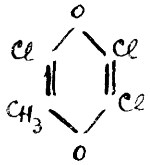
From these figures it is evident that the entrance of alkyl groups into the quinone nucleus has had the effect of reducing the persistence of the "pyruvic band" to a considerable degree. But this is not the only alteration noticeable in the spectra as we pass from the parent substance to higher homologues; for inspection of the curves shows that while the "pyruvic band" diminishes, a benzenoid band having its head at 3900 appears and increases in persistency.

We may deduce from this that substitution in the quinone series has the effect of altering the internal stability of the molecule in some way which renders the benzenoid vibration more frequent than it is in the molecule of simple quinone. And since the reactivity of the quinone carbonyl groups is closely connected with the quinonoid vibration, we should expect to find less reactivity in the case of the substituted quinones. This had already been shown experimentally by Kehrmann.

Most of Kehrmann's work was carried out upon the halogen substitution products of quinone, so it became necessary for us to examine the spectra of several bodies of this class. The results were even more striking than in the case of the alkyl derivatives.

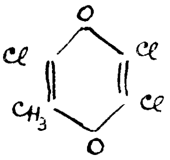
An examination of the curves shows that when one hydrogen atom of the quinone nucleus is replaced by a chlorine atom (Figure 8) the "pyruvic band" becomes merely a slanting line lying between 2000 and 2600. When two chlorine atoms are introduced in the ortho-position to one carbonyl group, as in 2,6-dichloroquinone (Figure 9), the line representing the "pyruvic band" approaches more nearly to the general curve. In trichloro-quinone, (Figure 10) and trichloro-toluquinone (Figure 11), there is no measurable "pyruvic band."

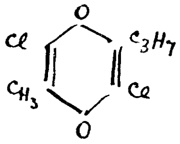
But at the same time as the "pyruvic band" diminishes, the benzenoid band in the spectra of these compounds steadily increases, as the following figures show:

				
Band begins at	17.4	57.5	63.0	87.1
,, ends ,,	10.0	15.8	14.5	10.0
Dilution change	42.0%	55.0%	77.0%	88.0%

The results which we obtained from the remaining compounds, bromo-quinone, dibromo-thymoquinone, and dichloro-thymoquinone confirmed our previous ones, so that it is not necessary to deal with the two former in detail. With regard to dichloro-thymoquinone, (Figure 12), however, it is interesting to compare its spectrum with that of trichloro-toluquinone (Figure 11). When the two formulae:

(I)





(II)

are examined, it will be seen that (II) is obtained from (I) by the replacement of a chlorine atom by a propyl group. This exchange of a halogen atom for an alkyl group produces a decrease in the persistence of the benzenoid band in the spectrum, as is shown by the following figures:

	Trichloro-toluquinone	Dichloro-thymoquinone
Band begins at	87.1	66.1
,, ends ,,	10.0	12.0
Change of dilution	88.0%	82.0%

This decrease in the persistence of the benzenoid band is quite in accordance with Kehrmann's observations. He found that a halogen substituent has a much greater hindering effect than that shown by an alkyl group in the same position.

We must now consider the effect which substitution exerts upon the carbonyl group in the quinone series. It is evident that there are three factors which must be taken into consideration:

(1) Steric hindrance produced by the action of the substituents.

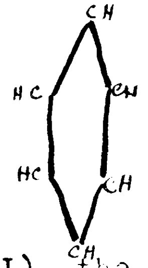
(2) The distortion of the benzene ring consequent on the unequal distribution of weight in the nucleus which substitution produces.

(3) The possibility of the formation of a "nascent carbonyl group".

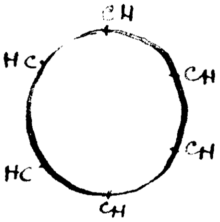
With regard to the first of these, it may be said that up to the present, there has been no reliable method by which we can estimate the purely steric factor in the problem. It is probably not negligible, but it has not yet been proved to be an essential element in the problem.

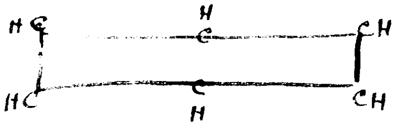
In order to make clear the bearing of the second factor, it is necessary to recall a theory of the benzene ring which was suggested by Mr. Baly and embodied in a paper which was published by us in conjunction with the late Mr. W.H. Edwards. A full account of this theory is given on pp.523-9 of Volume 89 of the Chemical Society's Transactions. For the present purpose, however, it will be sufficient to say that the benzene ring is supposed to be in a state of vibration similar to that of an elastic ring which has just been struck. Three principal phases in the motion are all that we need concern ourselves with: they are shown below.

I

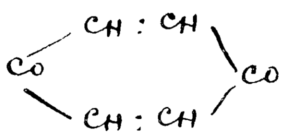


II

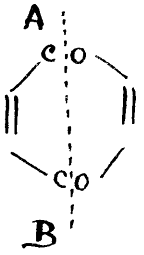




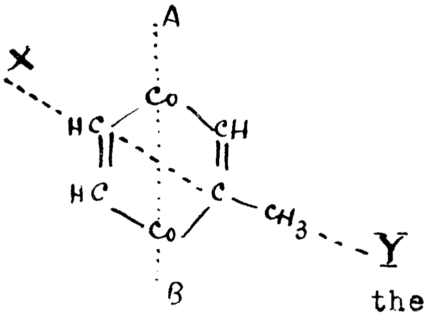
In (I), the ring is compressed along one axis and extended along another; in (II), it has recovered its symmetrical form and is just about to pass over into the shape (III) in which the axis of compression of (I) becomes an axis of extension. Now when we load the ring unsymmetrically, this vibration is complicated by the weight of the substituents. From the evidence given in the foregoing pages, it becomes a fair deduction that in the unsaturated ring system:-



there are two mutually antagonistic forces at work: the process which produces the "pyruvic band", and the tendency of the system to return to the most stable arrangement, viz., the benzenoid form. The first process consists of some interaction of the two carbonyl groups; and in order that this process may continue, the compound must exist in the quinonoid form. Undoubtedly the chief vibrations of such a compound would be parallel to the line of symmetry of the molecule, that is, the line AB:-



If the vibrations were not in this direction, it would hardly be possible for any interaction between the carbonyl groups to take place, as they would approach each other only at very infrequent intervals. Now if we alter the centre of gravity of the system by introducing new groups instead of hydrogen atoms, the conditions of stability of the system are completely altered. For instance, if a single methyl radical be introduced, we should expect to find the molecule vibrating along the new line of symmetry XY:-



In this case, the interaction between the carbonyl groups would not attain the same intensity as in the preceding instance, since the vibration of the molecule would not tend to produce with sufficient frequency the conditions necessary for that interaction. But as soon as the carbonyl groups cease to act upon one another, the tendency of the system is to rearrange itself into the more stable benzenoid form in which the "pyruvic band" is not produced. The effect of substitution is thus two-fold. In the first place, it prevents the frequent interaction of the two carbonyl radicals;

and in the second place it encourages the transition of the substance into the benzenoid configuration.

These factors, however, are probably of less importance than the third, viz., the possibility of a "nascent carbonyl group" being formed. It has already been shown in the foregoing pages that when the hydrogen atom of the group :CH-CO- is replaced by a methyl radical, the tendency to form a "nascent carbonyl group" is checked, and the reactivity of the carbonyl group in $:C(CH_3)-CO-$ is much less than in the parent substance. It has also been shown that the "nascent carbonyl group" may be formed by a process analogous to tautomerism, in which there is no actual transfer of the hydrogen atom from the carbon to the oxygen, but merely a mutual action between the oxygen and hydrogen, which action, if continued, would end in tautomeric change. If we apply the same reasoning to the carbonyl group in quinone, we find that in quinone itself we have the grouping :CH-CO-CH: where there are two hydrogen atoms to interact with the oxygen atom. In toluquinone, one of these is replaced by a methyl radical, $:CH-CO-C(CH_3):$, so that the possibility of interaction is greatly decreased.

Summarising what has already been said, we may conclude that the effect of substitution upon quinones is as follows:-

(1) It tends to diminish the interaction between the oxygen atoms and the neighbouring hydrogen atoms which gives rise to "nascent carbonyl groups".

(2) It loads the ring unevenly, and thus tends to produce the benzenoid in preference to the quinonoid

PART III.

THE RELATION BETWEEN ABSORPTION SPECTRA AND OPTICAL ROTATORY POWER.

Since carrying out the research described in the foregoing section, Mr.Baly and I have ceased to work together. As he has been good enough to lend me his spectroscope, I have been able to make the following investigation which I hope to publish shortly.

Up to the present time, no attempt seems to have been made to correlate the spectra of active substances and their rotatory powers. A research on these lines appeared to promise results; especially in the case of racemic and active substances, for it seemed possible that it might lead to a method of determining whether or not a true racemic compound were present in solution. I therefore decided to investigate this branch of the subject.

It is well known that the state of saturation of a carbon compound is closely connected with its rotatory power. Walden (Zeit.physikal.Chem.,20,569) has made a detailed study of the point; and has shown that in general it may be said that unsaturation produces a rise in rotatory power. As his results were sufficient for my purpose, it was unecessary for me to determine the rotations of any substances; I had only to examine the spectra of those which Walden had already measured.

The first question which presented itself was the effect of substituting double and triple bonds for a single linkage. It has been shown by Walden that when the single bond is converted into a double one by the loss of two hydrogen atoms, the molecular rotatory power of the substance was increased. When the double bond was changed to a triple one, by a further loss of two hydrogen atoms, the result was very different; for, instead of rising again, the molecular rotatory power diminished, though it did not fall so low as that of the single bond compound. Walden's figures for the amyl esters of hydrocinnamic, cinnamic and phenylpropiolic acids are as follows:-

	$|M|_D$
$C_6H_5.CH_2.CH_2.COOC_5H_{11}$	+ 4.98
$C_6H_5.CH:CH.COOC_5H_{11}$	+16.36
$C_6H_5.C{\equiv}C.COOC_5H_{11}$	+12.05

It is evident that since the alcohol is the same in each case, the difference in rotatory power is due to the change in the acidic radical; and it will suffice if we consider the spectra of the three acids. The absorption curves of these are shown in Figure 13.

In the work which Mr. Baly and I did together, we were concerned entirely with absorption bands in the spectra of substances; and naturally I examined the three spectra of the cinnamic series in the hopw of finding some relation between the absorption bands and the rotatory power. No such relation seems to exist. If we consider the persistence of the absorption bands in the three spectra, we find that the cinnamic acid band has the greatest persistence, then comes the hydrocinnamic band, and finally the band of phenyl-propiolic acid, which is so shallow that it appears as a mere extension of the spectrum at one point. This is not the order in which the rotations lie. Again, it might be supposed that the frequencies at which the heads of the bands are found might be in some way connected with the rotatory power. But this also is not the case; for the heads of the hydrocinnamic acid bands lie between 3700 and 3900; that of cinnamic acid at 3600; and that of phenyl-propiolic acid is probably situated at a frequency of 3900.

I therefore abandoned the idea that the absorption bands were connected with the rotatory power, and endeavoured to find other peculiarites in the spectra.

Now if we leave absorption bands out of account, the only way in which substances can differ from one another in spectra is in their general absorptive power. We must therefore examine the three spectra with regard to the general absorption shown by each substance above the bands.

If we take the abscissa 26 as a convenient standard, we find that it is cut by the three curves in the following order: cinnamic acid, phenyl-propiolic acid, and hydrocinnamic acid. In other words, the general absorptive powers of the three substances are related to one another in the same order as their molecular rotations. The points at which the three curves cut the abscissa are shown in the following table:-

Cinnamic acid	3100
Phenyl-propiolic acid	3[illegible]00
Hydrocinnamic acid	3700

There appears to be no close numerical connection between these numbers and the rotatory powers; but it should be borne in mind that such a numerical connection may exist at higher concentrations than that used (N/100).

It seeemed not improbable that the agreement in the foregoing case was accidental; and in order to see whether the rule was of more general application, I examined the spectra of several other acids.

As I had already dealt with a series of aromatic mono-basic acids, the next compounds which I chose were aliphatic ones. Walden in his paper gives the rotations of the amyl esters of normal butyric and crotonic acids as follows:

	$\|M\|_D$
$CH_3.CH_2.CH_2.COOC_5H_{11}$	+ 4.43
$CH_3.CH:CH.COOC_5H_{11}$	+ 6.62

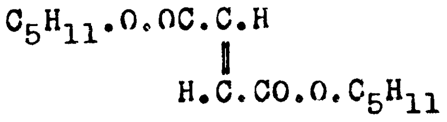
The absorption curves of the two acids are shown in Figure 14.

It is evident that here the same relation holds as in the case of the other series, for crotonic acid, whose ester has the greatest rotation, shows the greatest general absorption.

It must be pointed out that there is no relation between the two series, as series; for while crotonic acid has a greater molecular rotation than hydrocinnamic acid, its absorptive power at the same concentration is less. The rule of "greater rotation, greater absorption," then, can be applied only in the case of compounds which contain chains of the same number of carbon atoms.

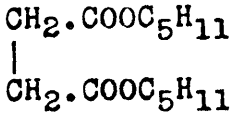
Having dealt with two series of mono-basic acids, it seemed advisable to investigate the case of some di-basic ones. It will suffice for the present to give the results obtained with succinic and fumaric acids, whose curves are shown in Figure 15. The following figures are given by Walden:-

$|M|_D$



$$\begin{array}{l} C_5H_{11}.O.OC.C.H \\ \qquad\qquad\quad \| \\ \qquad\qquad H.C.CO.O.C_5H_{11} \end{array}$$

+15.17



$$\begin{array}{l} CH_2.COOC_5H_{11} \\ | \\ CH_2.COOC_5H_{11} \end{array}$$

+ 9.71

Here again it is apparent that the same rule holds, for the absorptive power of the unsaturated acid is very much greater than that of the saturated acid.

It only remained to try two tri-basic acids. The molecular rotations of the amyl esters of tricarballylic and aconitic acids have been determined by Walden:-

$$\begin{array}{ll} CH_2.COOC_5H_{11} & \quad |M|_D \\ | & \\ CH.COOC_5H_{11} & \quad +15.48 \\ | & \\ CH_2.COOC_5H_{11} & \end{array}$$

$$\begin{array}{ll} CH.COOC_5H_{11} & \\ \| & \\ C.COOC_5H_{11} & \quad +23.66 \\ | & \\ CH_2.COOC_5H_{11} & \end{array}$$

The absorption curves which are shown in Figure 16 indicate that in this case also the rule holds good.

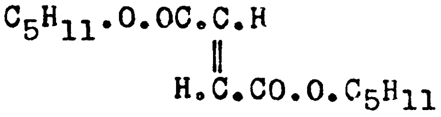
Since the rule stands the test in all these widely differing classes of compounds, it seems not unwarranted to suppose that it is of general application.

The next question which attracted my attention was the possibility that the same rule might apply in a slightly altered form to the case of stereo-isomeric acids.

Walden in another paper (Zeit.physikal.Chem.20.377) has proved that the amyl esters of various stereo-isomeric acids in the ethylene series have different rotaory powers according as the maleinoid or fumaroid acid is used. In general, there appears to be a difference of about four degrees between the molecular rotations of the two forms, the fumaroid form having the greater rotatory power. It appeared to me that if this were the case I should be able to detect a difference in the spectra of the stereo-isomeric acids; and I therefore examined several.

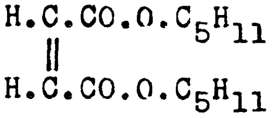
In the first place, we may consider the case of maleic and fumaric acids. The figures given by Walden for the amyl esters of these are as follows:-

$|M|_D$



$$\begin{array}{l} C_5H_{11}.O.OC.C.H \\ \qquad\qquad \| \\ \qquad\qquad H.C.CO.O.C_5H_{11} \end{array}$$

+15.17



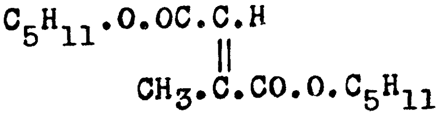
$$\begin{array}{l} H.C.CO.O.C_5H_{11} \\ \quad \| \\ H.C.CO.O.C_5H_{11} \end{array}$$

+11.82

It can be seen from the curves given in Figure 15, that the rule of "greater absorption, greater rotation" holds in this case also, for the absorption curve of fumaric acid lies at a slightly lower frequency than that of maleic acid.

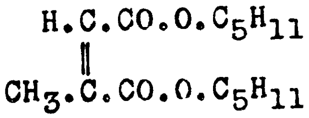
Figure 17 shows the absorption curves of mesaconic and citraconic acids. Since mesaconic acid shows the greater absorption, it is to be expected that its amyl ester will have the higher rotatory power of the two. This is actually the case, as Walden's figures show:-

$|M|_D$



$$\begin{array}{l} C_5H_{11}.O.OC.C.H \\ \qquad\qquad \| \\ \qquad CH_3.C.CO.O.C_5H_{11} \end{array}$$

+16.01



$$\begin{array}{l} \quad H.C.CO.O.C_5H_{11} \\ \qquad \| \\ CH_3.C.CO.O.C_5H_{11} \end{array}$$

+11.17

In the cases which have been described, a comparison has been drawn between substances in which the atoms in the chain are linked together in the same manner in each isomer; but

At this point it may be well to indicate the results obtained when unsaturation occurs at a different point in the chain. For this purpose it will be sufficient to quote the case of itaconic acid, which can be compared with the isomeric mesaconic and citraconic acids. The molecular rotation of itaconic diamyl ester has been found by Walden to be $|M|_D = + 13.42$ We might expect to find that the absorptive power of the acid lay between those of mesaconic and citraconic acids, but in point of fact it shows less absorption than either. (Figure 17). We must therefore extend what has already been laid down with regard to unsaturation, and state the case in the following manner:-

> " If the spectra of a saturated and a corresponding unsaturated acid be compared, the acid whose amyl ester has the greater rotatory power will show the greater absorptive power; the same holds in the case of two stereo-isomeric acids of the ethylene series; but it does not hold for structurally isomeric substances."

When we examine the molecular rotatory powers of the amyl esters of homologous aliphatic acids, it is well known that a steady rise is shown as we go up the series, e.g.

	$|M|_D$
Amyl formate	+ 2.33
Amyl acetate	3.29
Amyl propionate	3.99
Amyl butyrate	4.25

These figures were found by Guye and Chavanne (Compt.rend.120.452) (Bull.soc.chim.|3| 15.275). It is therefore to be expected that the acids would show a similar steady increase in general absorption; but the difference in the spectra would be very slight, and might even be unmeasurable in many cases. Measurements are unnecessary in this case, however, as it is a well known fact that an increase in the molecular weight of a molecule tends to increase its general absorption.

The last branch of the subject which I have studied up to the present includes the spectra of optical antipodes and of the corresponding racemic compounds. It appeared to me that if I made up normal solutions of dextro- and laevo-tartaric acid, photographed their spectra through given thickness of solution, mixed the solutions in equal quantity, and then photographed the mixed solution through the same thicknesses as in the case of the active isomers, I should find a difference between the two absorption spectra; for in the case of the mixture the number of molecules present in a given thickness of solution will be only half that in the solution of an active isomer. This is, of course, due to the fact that when equal volumes of two *normal* solutions of the dextro- and laevo-isomer are mixed, the result is a semi-normal solution of racemic acid (if the racemic acid exists in solution).

I made up aqueous solutions of dextro- and laevo-tartaric acid; and compared their absorption spectra, which proved to be identical. On mixing the solutions, I found that the resulting racemic compound had a *greater* absorption than either active isomer. I checked this result by using synthetic racemic acid instead of the mixture of dextro- and laevo-forms, and found the same result. The curves are shown in Figure 18.

An examination of the curves brings to light two points of interest. In the first place, just above the abscissa 58 there is a considerable part of the spectrum of the racemic acid which shows very faint transmission of light. It is shaded in the figure. No such transmission is to be found in the spectra of the active isomers. When the form of this shaded part is examined, it seems evident that it is really the heads of two absorption bands in the racemic acid spectrum. I endeavoured to use solutions of a higher concentration in order to photograph the rest of the band, but owing to the comparatively low solubility of racemic acid I was unable to get sufficiently strong solutions for the purpose. On account of the arrangement of Mr.Baly's spectroscope, I was unable to use greater lengths of solution; so I have been unable to plot the curve further than is shown in the figure.

The second point of interest lies in the fact that at low concentrations (N/10) the spectra of racemic and active tartaric acids are identical. This is in agreement with the evidence derived from the work of Raoult (Zeit.physikal.Chem.1,186), Ostwald (J.pr.Chem.|2| 32.341) and Marchlewski (Ber.25,1556); for it is well known that if a 14% aqueous solution of racemic acid be made up, 13.9% breaks down into active tartaric acid, and this decomposition is even more marked in dilute solutions. From this it is apparent that the curve which I have drawn cannot represent the true absorption spectrum of racemic acid, though it is probably as near to it as can be found.

The following conclusions may be deduced from this part of y work:-

(1) Within certain well defined limits, a close relation exists between the molecular rotatory powers of two substances and their absorption spectra.

(2) The loss of two hydrogen atoms from a compound, (by which a single bond is replaced by a double one), produces an increase in absorptive power as well as a rise in rotatory power.

(3) The loss of four hydrogen atoms, (by which a single bond is changed to a triple one), also produces an increased absorption, though it has not such a great effect as the change from the single to the double bond. The same is true for the rotatory power.

(4) In the case of stereo-isomeric substances, the compound having the greater molecular rotation also has the greater absorption.

(5) The same rule does <u>not</u> hold in the case of structure isomers, at least not in the unsaturated series.

(6) In homologous series, the compound having the greatest molecular rotation will have the greatest absorptive power. I have not yet proved this experimentally, but as it is a deduction from well established data, it is safe to assume that it is true.

(7) The spectra of two optical antipodes are identical.

(8) The spectrum of a racemic compound shows greater absorption than the spectra of the antipodes from which it is formed.

The following applications of this work are interesting:-

I. In certain cases the configuration of ethylenic acids has not been determined, owing to experimental difficulties. The spectra of the two isomers would at once show which was which, as the fumaroid form would have the greater absorptive power of the two. (The molecular rotatory power might also be used, though I never saw this suggested.)

II. There is still a conflict of evidence in the questionof the existence of racemic compounds in the liquid state. By means of the spectroscope it will be a simple matter to examine doubtful cases.

THE RELATION BETWEEN ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION. PART I. THE CHEMICAL REACTIVITY OF THE CARBONYL GROUP.

BY

ALFRED WALTER STEWART (Carnegie Research Fellow)

AND

EDWARD CHARLES CYRIL BALY.

From the Transactions of the Chemical Society, 1906. Vol. 89.

LIV.—*The Relation between Absorption Spectra and Chemical Constitution. Part I. The Chemical Reactivity of the Carbonyl Group.*

By ALFRED WALTER STEWART (Carnegie Research Fellow) and EDWARD CHARLES CYRIL BALY.

IT has been shown by many different workers that certain reactions which can be carried out easily with parent substances are much more difficult to bring about when derivatives of these compounds are used. The work of Menschutkin on the esterification of aliphatic acids and the analogous researches of Victor Meyer and Sudborough on the aromatic acids are examples of what is meant.

From the standpoint of stereochemistry, it has been usual to attribute the effects in question to a variation in the amount of free space around the reactive groups of the molecule, since it is obvious that the substitution of a larger for a smaller radicle in the vicinity of the reactive part of the molecule will decrease the possibility of new reagents coming in contact with the active radicle. It may be granted that, if atoms have any volume at all, these premises are correct; but it is not yet proved that the effects attributable to this cause play any very considerable part in the reactions in question. It seems more probable that the free paths of the atoms in their intramolecular vibrations are so large in comparison with the size of the atoms themselves that this heaping up of substituents in the vicinity of the reactive group will have no very marked effect. For the present, however, the hypothesis of steric hindrance forms a convenient mechanical explanation of the non-reactivity of certain compounds.

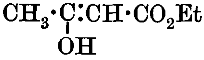
Stewart (Trans., 1905, **87**, 185; *Proc.*, **21**, 78) has shown that when a hydrogen atom near the carbonyl group of a ketone is replaced by a methyl radicle, the result is a decrease in the additive capacity of the carbonyl group. This is what might have been anticipated from the hypothesis of steric hindrance, since the volume of the methyl radicle must be greater than that of a hydrogen atom. A contradiction between theory and practice is to be found in the case where, instead of a methyl radicle, a $-CO_2Et$ group is introduced into the molecule. In the case of the latter group, it is found that instead of decreasing the velocity of addition of sodium hydrogen sulphite, as its bulk might lead one to predict, it has the contrary effect, for some of those ketones which contain a carboxyl group are much more reactive than the corresponding simple ketone, and consequently still more active than the methyl-substituted ketone. The numbers found for acetone, methyl ethyl ketone, and ethyl acetoacetate show this clearly:

	10	20	30	40 minutes.	
Ethyl acetoacetate	37·4	47·0	56·0	60·0 per cent.	bisulphite compound formed
Acetone	28·5	39·7	47·0	53·6 ,,	
Methyl ethyl ketone	14·5	22·5	25·1	29·1 ,,	

60·0 per cent. } bisulphite
53·6 ,, } compound
29·1 ,, } formed

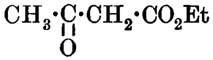
It is thus evident that some new influence which tends to mask or modify the steric hindrance due to the more voluminous group.

The carboxyl group, however, is not in itself sufficient to produce this increased reactivity of the carbonyl radicle, as the rate of addition of sodium hydrogen sulphite to ethyl lævulate was found to be slightly lower than that found in the case of methyl propyl ketone, which contains a carbon chain of the same length, and a like result was observed in the case of the diketone, acetonylacetone. On the other hand, ethyl acetonedicarboxylate has an additive capacity even greater than that of ethyl acetoacetate. Acetone shows very little sign of tautomeric change, whilst, on the contrary, ethyl acetoacetate and ethyl acetonedicarboxylate are tautomeric compounds. Thus, here again theory and practice appear to be opposed to one another: the true carbonyl compound having much less reactive power than the semi-enolised substance. It occurred to us that in this fact was to be found the key of the problem, and the exceptionally great reactivity of the carbonyl group in tautomeric compounds was due to the actual process of tautomeric change. Ethyl acetoacetate, under ordinary conditions, exists as an equilibrium mixture of the two substances (I) and (II), and the conversion of the first into the second and *vice versâ* is going on continuously.



$CH_3\cdot\underset{|}{\overset{}{C}}(OH)\colon CH\cdot CO_2Et$

I.



$CH_3\cdot\underset{\Vert}{C}(O)\cdot CH_2\cdot CO_2Et$

II.

Now, when a molecule of (I) changes into a molecule of (II), the result is the formation of a carbonyl group from a hydroxyl group. From analogy with the behaviour of atoms in the nascent state, we must suppose that this "nascent carbonyl group" is endowed with a much greater reactivity than that possessed by the ordinary non-nascent carbonyl radicle. This activity, however, need not be occasioned purely by the actual wandering of the hydrogen atom from the oxygen to the carbon: it may be due to some finer play of forces within the molecule which manifests itself in the production of the characteristic absorption band in the β-diketone spectrum. The condition into which the hydrogen atom is thrown as a result of this play of forces may be termed a condition of "potential tautomerism," and in it the hydrogen atom will possess a reactive power more or less analogous to that acquired by an atom as a consequence of the ionisation process (Baly and Desch, Trans., 1905, **87**, 766). Evidence of the probability of this hypothesis will be adduced later; for the present it will be sufficient to call attention to the conception of the "nascent carbonyl group."

If we now apply this idea to several cases which have hitherto been classed under the head of steric hindrance, it will be found that they can be satisfactorily explained. Taking the cases of the ketones which have already been dealt with by one of us (Stewart, *loc. cit.*), a marked decrease in reactivity of the carbonyl group is shown when the hydrogen atoms of acetone are successively replaced by methyl radicles.

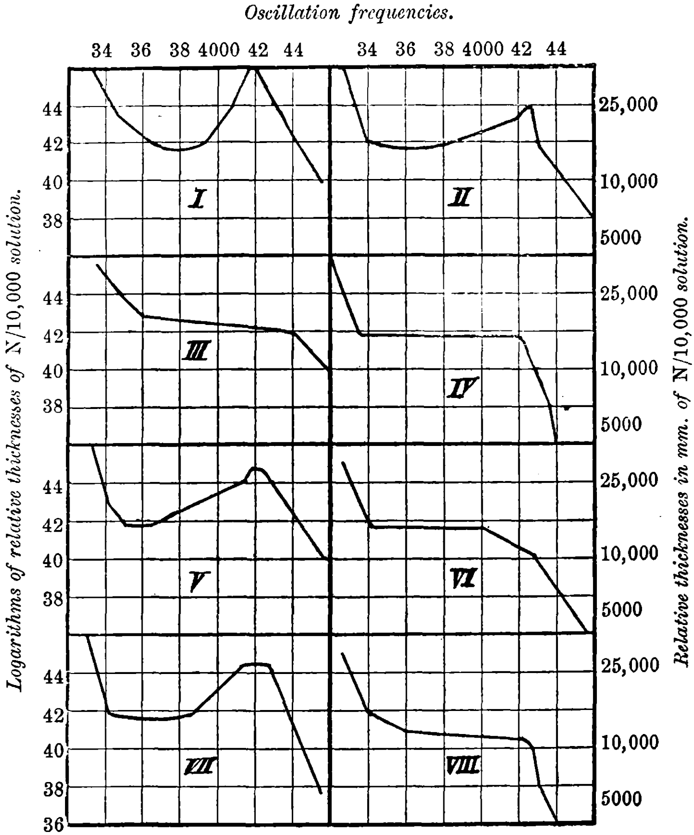
In the course of their investigations of the spectra of derivatives of ethyl acetoacetate, Baly and Desch (Trans., 1904, **85**, 1039) proved that the change from the enolic into the ketonic form produced an absorption band in the ultra-violet region of the spectrum, and they also showed that this band was not due merely to the shifting of a hydrogen atom, but was rather to be considered as the result of some intra-atomic change. In the hope of finding some analogous process in the simple ketones, we examined the spectra of several, and we found that a similar absorption band exists there as well. We further noticed that the persistence of this band decreases *proportionately to the diminution in the reactivity of the carbonyl group in the ketone.*

For instance, the following numbers show the percentages of oxime formed by various ketones in twenty minutes, and on comparing these amounts with the curves of the absorption spectra shown in Fig. 1, the relation between the two will be apparent.

	Oxime.		Oxime.
Acetone	49·7 per cent.	Methyl *iso*propyl ketone	31·5 per cent.
Methyl ethyl ketone ...	39·2 ,,	Pinacolin	17·0 ,,
,, propyl ,, ...	37·3 ,,		

Lapworth (Trans., 1904, **85**, 32) showed that the action of halogens on acetone was preceded by the production of the enolic form of the ketone, and he found, further, that the presence of acids hastened the reaction. Now, he had already shown (Trans., 1902, **81**, 1503, and 1903, **83**, 1121) that the presence of acids brings about a rapid attainment of equilibrium between the tautomeric forms of carbonyl compounds: or, in other words, the addition of acid has a tendency to produce a "nascent carbonyl group." Hence, in the case of acetone itself, not only is there direct spectroscopic evidence in favour of tautomeric change, but the chemical evidence at our disposal is also favourable. Instead of attributing Lapworth's results to the actual formation of the enolic form and an immediate addition of halogen, we prefer to look at them from another point of view. It is obvious that if we consider the change of the group $-\mathrm{CH{:}CH(O\overset{*}{H})}-$ into $-\mathrm{CH\overset{*}{H}{\cdot}CO}-$, the hydrogen atom marked with an asterisk must become "pseudo-nascent" in the process of change. It would therefore be peculiarly liable to chemical action, and would be easily replaced by halogens. The very great ease with which the methylene hydrogen atoms in acetylacetone are replaceable by halogens lends further support to our hypothesis.

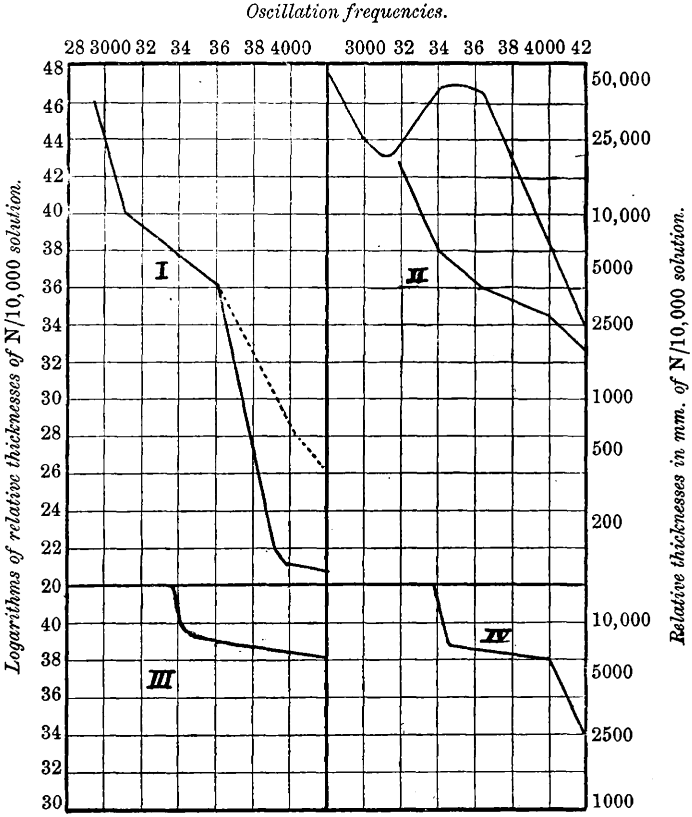
FIG. 1.



I. *Acetone in alcohol.*
II. *Methyl* iso*propyl ketone.*
III. *Acetone in water.*
IV. *Pinacoline.*
V. *Methyl ethyl ketone.*
VI. *Methyl hexyl ketone.*
VII. *Methyl propyl ketone*
VIII. *Methyl nonyl ketone.*

In their second paper (Trans., 1905, **87**, 760), Baly and Desch stated that acetonylacetone and ethyl lævulate were pure ketonic substances; but on examining their spectra at greater concentrations than were previously employed we have been able to detect at one point a rapid extension of the spectrum, which corresponds to a very

FIG. 2.



I. *Ethyl acetoacetate in alcohol* (full curve).
Ethyl acetoacetate in water (dotted curve).
III. *Ethyl lævulate.*

II. *Ethyl pyruvate.*
Ethyl diethylacetoacetate.
IV. *Acetonylacetone.*

shallow absorption band (see Fig. 2). The shallowness of the band indicates that the tautomerism in these two compounds is very weak, which agrees well with what has been found with regard to the reactivities of their carbonyl groups. The close agreement between theory and practice in these cases is very noteworthy.

Now, Petrenko-Kritschenko has shown (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 404) that the speed of phenylhydrazone formation is greatly influenced by the nature of the solvent in which the reaction is carried out. It appeared probable to us that this might be due to the influence of the solvent on the tautomerism process, and to test the matter we examined the spectra of acetone and ethyl acetoacetate in aqueous solution, using as a control in the latter case the spectrum of an alcoholic solution of ethyl diethylacetoacetate, which is much less tautomeric than the parent substance. From the curves for acetone in alcoholic and in aqueous solution (Fig. 1), it will be seen that the influence of water is very marked, the band in the latter case being much shallower than in the former. The three curves shown in Fig. 2 give the absorption spectra of the ethyl acetoacetate series and it is obvious from them that the water has reduced the tautomerism very considerably. It is probable that the greater the unsaturation of the solvent, the less reactivity will be shown by the carbonyl group of the dissolved ketone.

The evidence from simple ketones being so far favourable, we must now examine the case of ketones containing a carbethoxyl group. If tautomeric change alone were the cause of the reactivity of the carbonyl radicle, compounds containing the group $-CO\cdot CH_2\cdot CO-$ should be more reactive than those which do not contain it, and the reactivity of the carbonyl group in ethyl pyruvate should not be at all abnormal, since the grouping in question does not occur in it; if, however, the reactivity were found to be great, we hoped that some light might be thrown on the problem by a study of the spectrum exhibited by the compound.

We therefore decided to compare the rates of addition of potassium hydrogen sulphite to acetone, ethyl acetoacetate, ethyl acetonedicarboxylate and ethyl pyruvate. At first, experiments were made to find out how rapidly the "bisulphite compound" was decomposed by water, and it was observed that a considerable dissociation occurred, even at zero. Error is thus introduced into the problem, and all that could be done was to reduce this error to a minimum. Since the inverse change increases in the direct ratio to the amount of "bisulphite compound" formed, it is evident that the aim of the experiments must be to estimate the amounts of compound formed before equilibrium is established. Secondly, since the surplus sulphite is destroyed in the course of the estimation, thus bringing about a disturbance in the state of equilibrium of the solution, it is advisable to reduce the relative quantity of potassium hydrogen sulphite as much as possible. Thirdly, no harm could follow from keeping down the temperature, as this would act as a retarding agent on the direct and inverse reactions, while facilitating the measurement of differences in the rates of formation. With these facts in view, the following method of estimation was devised. Fifty c.c. of a $M/20$ solution of potassium hydrogen sulphite were cooled to zero and mixed with an equal volume of a 50 per cent. alcoholic $M/10$ solution of the ketone, which had also been cooled to zero. The liquid was immersed in a freezing mixture and maintained at a temperature of $-10°$. Ten c.c. were withdrawn every five minutes and titrated with iodine. The results obtained by this method are given in the table below :

	5	10	15 minutes.	
Acetone	5	7	42	Percentage of bisulphite compound formed.
Ethyl acetoacetate	12	18	76	
Ethyl acetonedicarboxylate .	30	36	42	
Ethyl pyruvate	52	64	76	

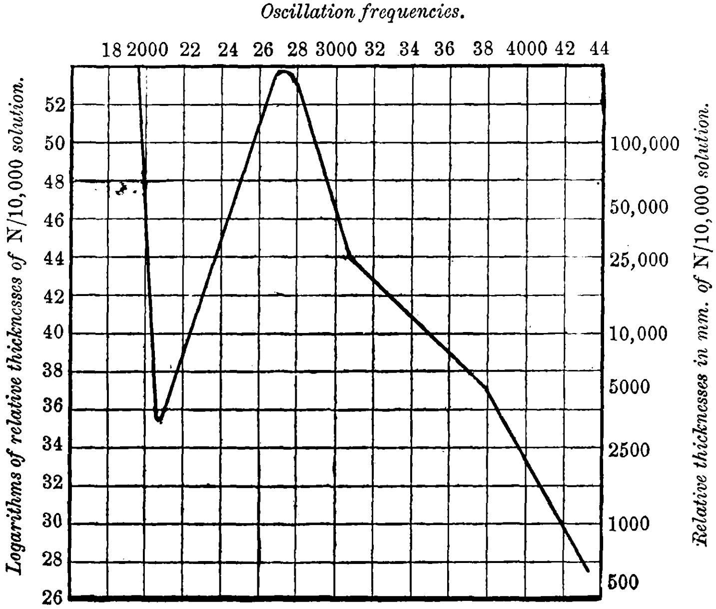
In spite of the precautions taken, these numbers are probably not quite accurate, owing to various causes which cannot be controlled, but the differences between the numbers themselves are very much larger than any possible experimental error under the conditions employed.

An examination of the numbers shows that the introduction of a carbethoxyl group into acetone increases the additive capacity of the carbonyl group; the introduction of two carbethoxyl groups still further enhances the reactivity of the carbonyl, but the most striking effect is produced when, as in the case of ethyl pyruvate, the carbonyl and carboxyl groups are brought into juxtaposition in the chain. Now, in the case of ethyl pyruvate, although the compound sometimes reacts in the enolic form, it is most improbable that the change from the enolic to the ketonic form and *vice versâ* is going on at a rate at all comparable to that at which it is occurring in ethyl acetoacetate or ethyl acetonedicarboxylate, so that it is not likely that the exceptional additive capacity of the carbonyl group in ethyl pyruvate is due to this kind of tautomerism.

We thought it advisable to examine the spectrum of ethyl pyruvate in the hope that some light might thus be thrown on the problem of the activity of the carbonyl group. We found that ethyl pyruvate gives an absorption band which lies much nearer the red end of the spectrum than the band given by ethyl acetoacetate (Fig. 2). The origin of the band in the ethyl pyruvate spectrum might be looked for in two phenomena: either in the keto-enol change of the group $CH_3\cdot CO-$ or in the interaction of the carbonyl and carboxyl groups of the radicle $-CO\cdot CO_2Et$. The first explanation is impossible, since if the band were produced by a similar state of intra-atomic vibration in both instances, it would occur in nearly the same place in the spectrum, whilst actually the new band has its head at 3100, while that of the tautomeric β-diketones lies at 3700 ; and, further, since the molecule of ethyl pyruvate is lighter than that of ethyl acetoacetate, we should expect to find the band in the latter case nearer to the red end of the spectrum than in the former, whilst the reverse of this is observed.

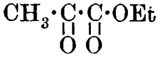
In order to make certain that the band in question was actually produced by the proximity of the two true carbonyl groups in the chain, that is, that it was not due to the $-\overset{\bullet\bullet}{C}\cdot OEt$ residue of the carboxylate radicle, we examined the spectra of several diketones and found a similar absorption band in all of them, though in them it was situated nearer the red end of the spectrum. For example, in the case of camphorquinone (see Fig. 3) it will be seen that a band is shown of very long persistence, with its head at 2070. The results in the case of the other α-diketones were similar, but as their consideration is reserved for the next paper it is needless to discuss them here.

FIG. 3.



Camphorquinone.

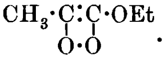
It was thus proved that the band in question was due to the two carbonyl groups in the α-position to one another. It has already been pointed out that Baly and Desch concluded that, although the absorption band was produced by intra-atomic vibration, it was caused by the change of linking brought about by the oscillation of the hydrogen during the change from the ketonic to the enolic form. From analogy, we should expect to find a somewhat similar state of things in the present case. Now the only possible way in which such a change of linking can be supposed to occur in ethyl pyruvate is by imagining that, like ethyl acetoacetate, it occurs in two forms :



$$\begin{array}{l}CH_3\cdot C\cdot C\cdot OEt\\ \qquad\;\; \|\;\;\, \|\\ \qquad\;\; O\;\, O\end{array}$$

I

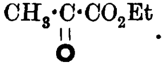
and



$$\begin{array}{l}CH_3\cdot C\colon C\cdot OEt\\ \qquad\;\; |\;\;\;\, |\\ \qquad\;\; O\cdot O\end{array}.$$

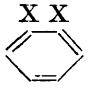
II.

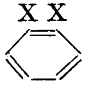
It is very hard to indicate exactly what is meant by the aid of the usual structural formulæ, as they only indicate a static condition of the molecule, whilst what we wish to suggest is essentially a dynamic state. We wish to make it perfectly clear that we do not suppose that these two forms actually exist, but, owing to the defect of ordinary structural formulæ, it is impossible to write them otherwise if the usual symbols be employed. We would prefer to indicate the presence of a "nascent carbonyl group" by printing the oxygen symbol in heavy type, thus:



$$\begin{array}{l}CH_3\cdot C\cdot CO_2Et\\ \qquad\;\; \|\\ \qquad\;\; \mathbf{O}\end{array}.$$

Our conception can best be comprehended if it be clearly borne in mind that the two formulæ are not intended to represent actual compounds, but merely two phases of the same compound, just as the two formulæ





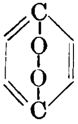
represent the same substance in two different phases of vibration. This idea is not new, having been first suggested by Kekulé in 1865, and afterwards extended by Collie (Trans., 1897, **71**, 1013). If this conception of phases be understood, it will be apparent that the change of linking is continually going on, and that this change will affect the intra-atomic relations of the molecule very much in the same way as they are affected by the phenomena of tautomerism.

At the same time, it should be noticed that the change of linking from (II) to (I) would produce what we have already defined as a "nascent carbonyl group," which would have great reactivity. Thus we are led to conclude that substances which show these peculiar absorption bands will in general be more active chemically than other compounds which do not exhibit such selective absorption.

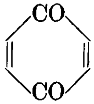
The idea which we have put forward cannot be considered as part of the theory of tautomerism, as, owing to its associations, the name tautomerism will always suggest the wandering of a hydrogen atom.

It is unfortunate that the name "desmotropism" has already been employed to denote tautomerism, as it seems well fitted to describe the phenomenon with which we have dealt. We therefore wish to propose the word *Isorropesis* (ἰσορροπία : equipoise) to describe the process.

The arguments in favour of this theory appeared to us to warrant its application to other classes of compounds, and we proceeded to make a further series of investigations, some of which will be dealt with in a later paper. For the present, *p*-benzoquinone is the only compound which need be described. The known close relation to one another in which the two para-positions in a benzene stand seemed to lend probability to the idea that a band somewhat similar to those observed in compounds containing the group –CO·CO– might be found in the spectra of the para-quinones. Our anticipations were again justified, as the *p*-benzoquinone spectrum has a band almost identical with that of camphorquinone, its head being at 2150 (see Fig. 5 in following paper). Now it is known that *p*-benzoquinone can exist in two forms, for both of which chemical evidence has been adduced :



I.



II.

The chief points in favour of the first formula are: the reduction of *p*-benzoquinone yields quinol, a benzenoid derivative ; the action of phosphorus pentachloride produces a *p*-dichlorobenzene ; the oxidising power of benzoquinone, in which it resembles a peroxide. The second formula is supported by the following facts : its reactions with hydroxylamine and phenylhydrazine prove that the quinone carbonyl group resembles that in an aliphatic ketone ; quinone takes up two and four atoms of chlorine or bromine as if it were a tetrahydrobenzene derivative.

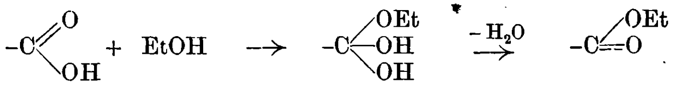
Chemical evidence being favourable to both formulæ, it appears not unwarrantable to assume that in this case also the absorption band is caused by the "making and breaking" of contact between the two oxygen atoms. Thus it may be concluded that the actual wandering of a hydrogen atom is not necessary for the production of these absorption bands. Again, since the result of this "making and breaking" would be the production of two nascent carbonyl groups, an explanation is thus given of the great chemical activity of the carbonyl radicles in benzoquinone.

It appears to us that our results throw much light on those reactions which are supposed to be influenced by steric hindrance, for if the tautomerism or isorropesis of any carbonyl group can be influenced by substitution, all the results will be produced which are often attributed to purely spacial relations. We intend to investigate the question more fully later, and at present need only mention one or two instances.

The action of phosphorus pentachloride on ethyl acetonedicarboxylate produces ethyl monochloroglutaconate. Now, if the tautomerism of the carbonyl group be reduced by substituting alkyl groups for hydrogen atoms in the methylene radicles, the reaction should be more difficult to bring about. Petrenko-Kritschenko (*Annalen*, 1896, **289**, 52) has found that this is actually the case, tri-alkylated derivatives giving very small yields, and no reaction at all being found when tetra-alkylated substances are employed.

Petrenko-Kritschenko and Ephrussi (*Annalen*, 1896, **289**, 59) have shown that substitution produces an analogous effect on hydrazone formation, neither the dimethyl nor diethyl derivatives of ethyl acetonedicarboxylate giving a hydrazone, although the parent substance easily yields one. This might be attributed to purely steric causes, but V. Meyer (*Ber.*, 1896, **29**, 836) has shown that space relations have less effect than purely chemical ones, since, although acetylmesitylene gives no oxime, yet when the more bulky $-CO_2Et$ group is substituted for a hydrogen atom an oxime is easily formed, as in the case of ethyl mesitylglyoxylate. Somewhat similar effects can be found in the difficulty of hydrazone formation in the case of the substituted phloroglucinols (Herzig and Zeisel, *Ber.*, 1888, **21**, 3493).

We have not yet investigated the case of the esterification of substituted acids, although here also the evidence points to the fact that when tautomerism is reduced the esterification constant is lowered. If V. Meyer's view of the esterification process be accepted, it will be seen that the chief factor in the problem is the additive capacity of the carbonyl group, which, according to our view, depends greatly on tautomerism effects.



I. II. III.

According as the carbonyl group in I is more or less reactive, the yield of II will be greater or less, and hence the esterification process will be more or less rapid.

The question of the bromination or chlorination of fatty acids also throws some light on the point. Here, owing to the proximity of a carbonyl group, the hydrogen atoms attached to the α-carbon atom will be in the condition which we have termed "potential tautomerism," and will therefore be much more reactive than the other hydrogen atoms of the compound. The halogen therefore attacks them first.

We should also like to point out that if our conclusions are accepted they involve the rejection of the deductions drawn by Petrenko-Kritschenko (*J. pr. Chem.*, 1900, [ii], **61**, 431; 1900, **62**, 315; *Ber.*, 1901, **34**, 1699, 1702; *Annalen*, 1905, **341**, 150) from his measurements of the reactivity of open chain and cyclic ketones He assumed that if open chain compounds had a more or less cyclic configuration in space, their carbon atoms would exert the same degree of steric hindrance as those in the corresponding closed chain compound. Hence, if the steric hindrance were different in open and in closed chain compounds, the two substances would have different configurations.

Petrenko-Kritschenko, starting from the above assumption, proceeded to measure the effect of allowing certain open chain and cyclic ketones to react for one hour with potassium hydrogen sulphite, hydroxylamine, and phenylhydrazine, and he found, as he had predicted, that the quantities of product formed by cyclic ketones in that time were greater than those formed by aliphatic ketones. His results are undoubtedly correct and valuable, although it would have been better to measure the rates of formation of the product rather than merely to estimate its gross amount after an arbitrary time had elapsed; but we venture to point out that the deductions which he draws from his results are not so trustworthy. Tautomerism is much more marked in the case of cyclic compounds than in aliphatic substances, and hence the cyclic carbonyl compound is much more reactive than the fatty one. Consequently, a cyclic ketone might be expected to show much greater activity than an open chain one, quite apart from any purely steric considerations. It seems to us that too much reliance should not be laid on deductions from ketonic reactions as to the space formulæ of carbon chains. Professor Petrenko-Kritschenko has approached the subject from other less debatable standpoints.

All the substances employed in this investigation were obtained in the greatest possible state of purity. As a general rule, *N*/10 solutions in alcohol were made up and the iron spectrum photographed through 35, 30, 25, 20, 17, 15, 12, 10, 8, 6, 5, and 4 mm. This was repeated for the same lengths of *N*/100, *N*/1000, and, if necessary, *N*/10,000 solutions. The curves shown were obtained by plotting the limits of absorption against the logarithms of the relative thicknesses of a *N*/10,000 solution.

Conclusions.

(1) The reactivity of any carbonyl group is not inherent in the group itself, but is produced by the action of neighbouring atoms which render the carbonyl group "nascent."

(2) Such action may take the form of tautomerism or of a modification of tautomerism which does not require the actual transfer of a hydrogen atom from one atom to another, but merely some intra-atomic disturbance in the system $-CH_2{\cdot}CO-$.

(3) The action may also take the form of the process which we have termed isorropesis, in which no actual wandering of atoms occurs, but in which a finer play of forces between two carbonyl groups is involved.

(4) Many cases which are at present accounted for on the hypothesis of steric hindrances can be better accounted for either by tautomerism or isorropesis, and some cases which are in direct contradiction to the steric theory can also be explained. It is therefore claimed that the hypothesis of the "nascent carbonyl group" accounts more satisfactorily for the facts, and is preferable to explanations based on the idea of steric hindrance.

(5) When the possibility of the formation of a nascent carbonyl is excluded, the usual ketonic reactions are not observed. The carbonyl group may then be considered an "inactive" carbonyl group in contradistinction to a "nascent" one.

In conclusion, we wish to express our thanks to the Chemical Society for a grant towards the expenses of this research, to Professor Collie and Dr. Smiles for the great interest they have taken in the work, and to Mr. W. B. Tuck, B.Sc., for assistance during the course of the investigation.

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THE RELATION BETWEEN ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION. PART II. THE α-DIKETONES AND QUINONES

BY

EDWARD CHARLES CYRIL BALY

AND

ALFRED WALTER STEWART (Carnegie Research Fellow).

From the Transactions of the Chemical Society, 1906. Vol. 89.

LV.—*The Relation between Absorption Spectra and Chemical Constitution. Part II. The α-Diketones and Quinones.*

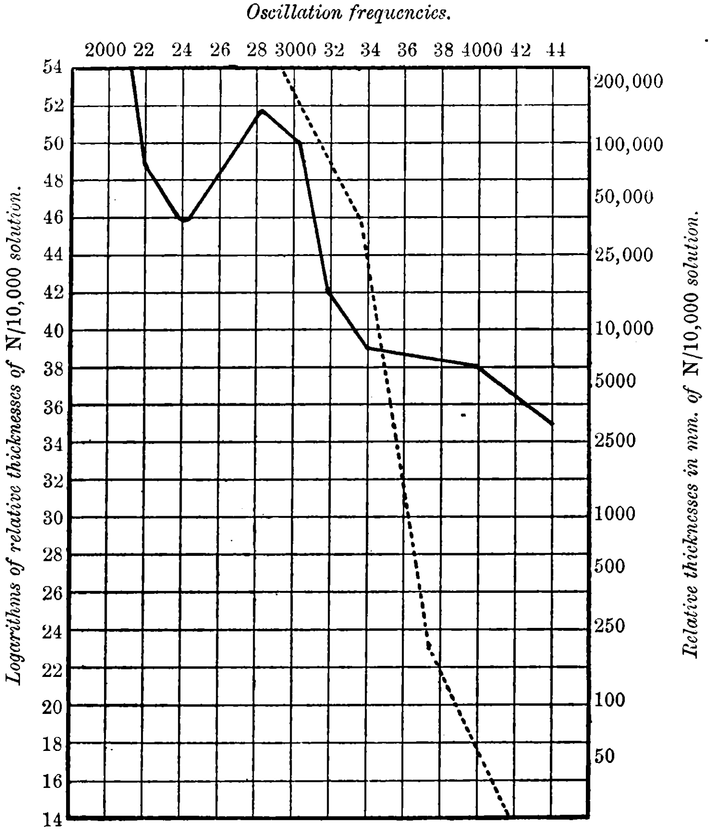
By Edward Charles Cyril Baly and Alfred Walter Stewart
(Carnegie Research Fellow).

In the preceding paper, the absorption spectrum of ethyl pyruvate was described, and it was shown how an absorption band with its head at an oscillation frequency of 3100 is developed at from 50 to 23 mm. of a $N/10$ solution. The position of this band and the concentration at which it appears are entirely different from those occurring with the keto-enol tautomeric process (Baly and Desch, Trans., 1904, **85**, 1039, and 1905, **87**, 760), and it was suspected that the new band has its origin in the juxtaposition of the two carbonyl groups because of the exceptional activity of the ketonic group in this compound. That this supposition was entirely justified we proved by observing the absorption spectrum of camphorquinone, in which there are two true ketonic groups in juxtaposition. As was described in the last paper, the new band is strongly exhibited in the case of this substance, showing that the presence of two carbonyl groups adjacent to one another gives rise to a new type of oscillation which causes the absorption of light of a much greater wave-length than that absorbed by the process of keto-enol tautomerism. For this new type of oscillation we have proposed the name "isorropesis," and in the present paper we propose to treat of the phenomenon of isorropesis and show how it is the origin of the colour of the α-diketones and quinones.

Now we have also examined the absorption spectrum of diacetyl, the absorption curve of which is shown in Fig. 1; it will be seen that here, too, is present the same absorption band as in the case of camphorquinone. The frequency of the head of the band is a little greater than in the case of camphorquinone, owing to the fact that the molecular weight of diacetyl is considerably less than that of camphorquinone.

The absorption spectra of many β-diketones have already been described (Baly and Desch, *loc. cit.*), and in every case the absorption bands lie in the extreme ultra-violet, and their origin has been traced to the phenomenon of the labile hydrogen or metallic atom. The frequency of these bands is of a mean value of 3800, although they naturally tend to shift towards the longer wave-lengths when the total mass of the molecule is increased. Since the position of this band is far down in the ultra-violet, the compounds showing a simple keto-enol tautomerism are not visibly coloured; in the compounds such as the α-diketones just described, the oscillation or isorropesis between the residual affinities on the oxygen atoms of the carbonyl groups results in the absorption of light of a mean wave-length of 4200 Ångström units, which is situated in the blue region of the spectrum.

FIG. 1.



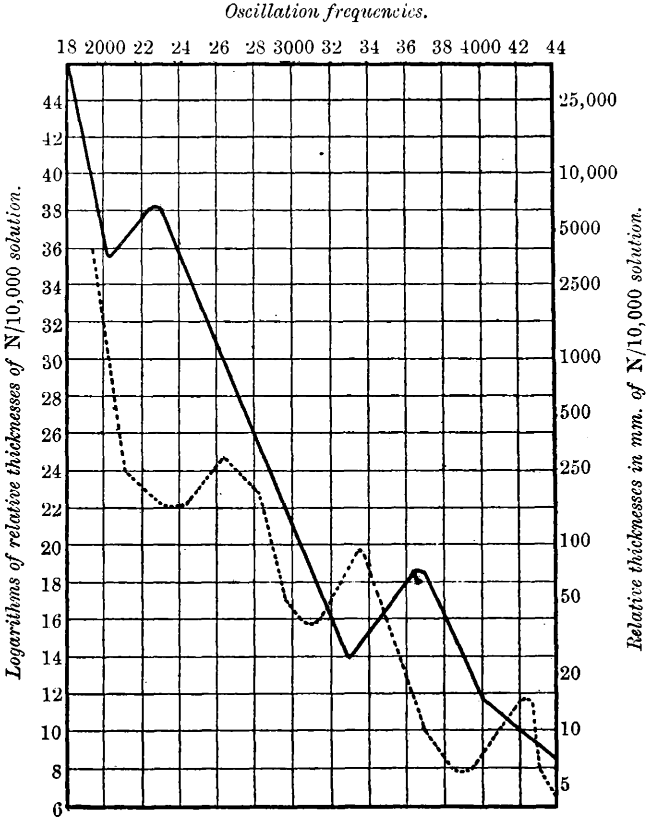
Diacetyl (full curve).
Diacetyldioxime (dotted curve).

These substances are, therefore, strongly yellow, ***their colour being due to the isorropesis between the carbonyl oxygen atoms in juxtaposition.***

We have extended our observations to include other compounds, containing two true carbonyl groups in juxtaposition. For example, we have measured the absorption of acenaphthenequinone and phenanthraquinone; in the spectra of both these substances (Fig. 2), the new absorption band is exhibited, so that here again the isorropesis between the two oxygen atoms is the origin of the yellow colour.

Isatin is a further example of this type of substance, and, as shown by Hartley and Dobbie (Trans., 1899, **75**, 640), its absorption spectrum exhibits a similar band with head at a frequency of 2400, which again

FIG. 2.

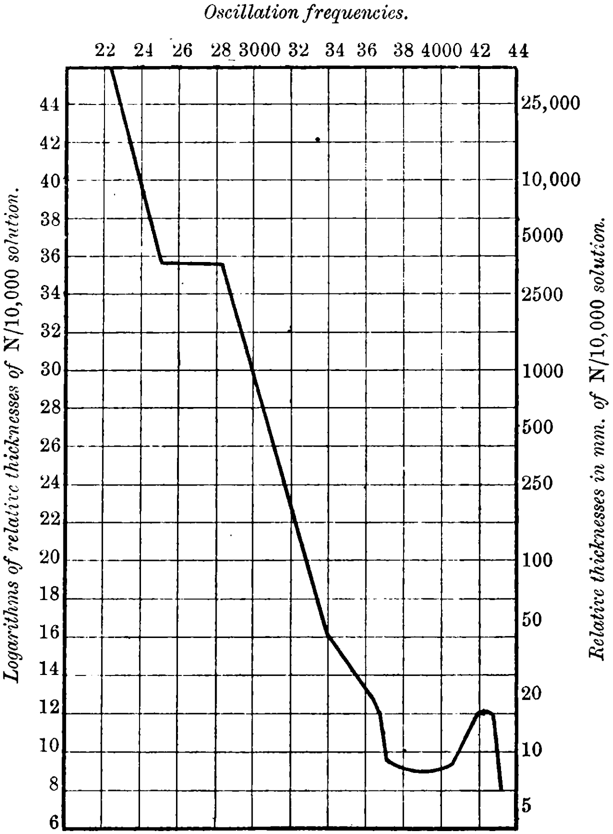


Acenaphthenequinone (full curve).
Phenanthraquinone (dotted curve).

shows the connection between the two adjacent carbonyl groups and colour.

Another very interesting case of an α-diketone is that of benzil, the absorption curve of which is shown in Fig. 3. Now it was shown in a previous paper, dealing with the absorption spectra of certain monosubstituted derivatives of benzene (Baly and Collie, Trans., 1905, **87**, 1331), that the residual affinity of the oxygen atom in acetophenone modified the absorption spectrum of benzene in a very marked manner. All the absorption bands belonging to benzene have entirely disappeared, showing that the ordinary benzenoid tautomerism has been stopped. This is doubtless owing to the attraction between the residual affinity of the oxygen of the carbonyl group and the atoms of the ring.

FIG. 3.

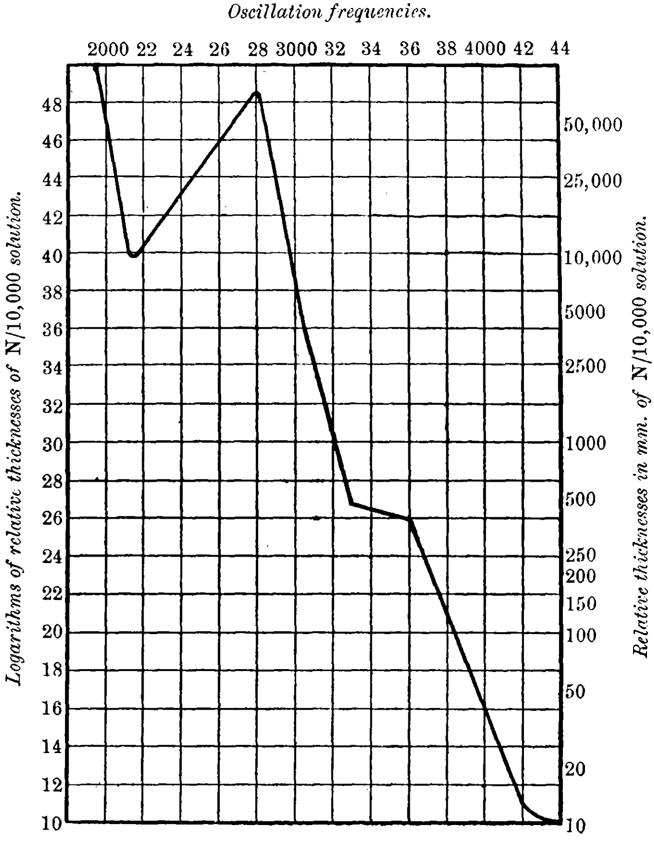


Benzil.

This undoubtedly accounts for the fact that the carbonyl group of acetophenone is unusually inactive towards sodium bisulphite, &c., because the residual affinity of this group is almost entirely occupied with and fixed by the residual affinity of the benzene ring, with the result that the group does not easily exist in the nascent state necessary to the formation of additive compounds. It might be expected, therefore, in the case of benzil, that the residual affinities of the two carbonyl groups would each be occupied and fixed by the adjacent phenyl group, and that therefore no isorropesis between the residual affinities would occur. On reference to the absorption curve of this substance, Fig. 3, it will be seen that in the region of least concentration there is an absorption band with head at a frequency of 3900. This band occupies the region of the benzene bands, and its presence in the spectrum of benzil supports the view that the benzenoid tautomerism is undoubtedly present to a certain extent. For this reason, therefore, we may conclude that the residual affinities of the two carbonyl groups are not entirely fixed, and that a small amount of isorropesis between these groups is possible. It is evident that this conclusion is justified from an inspection of the upper portion of the absorption curve of benzil, where a shallow band with head at a frequency of 2650 appears. The existence of this band shows that isorropesis is taking place, and its shallowness proves that it is only present to a small degree (compare Baly and Desch, Trans., 1905, **87**, 766). It may be noted that the yellow colour of benzil is not very pronounced, and readily disappears on dilution. The measurements of the additive capacity of the benzil carbonyl groups made by Petrenko-Kritschenko agree very closely with our hypothesis.

The most striking application of this principle is in the case of quinones, for in these compounds we have a type resembling in some respects an α-diketone, and in these compounds, too, the new absorption band is exhibited showing the undoubted existence of the process of isorropesis between the quinonoid oxygen atoms. As regards the absorption spectrum of *p*-benzoquinone itself, this was observed by Hartley, Dobbie, and Lauder (*Brit. Assoc. Report*, 1903, 126) with an aqueous solution, when they found the presence of two bands with heads at the frequencies of 3400 and 4050. The authors conclude that the yellow colour of *p*-benzoquinone is only due to the presence of general absorption, since both the absorption bands are in the ultra-violet. Now it is evident that water is an unsatisfactory solvent for organic compounds the absorption spectra of which are to be observed; in every case, we are investigating the influence or the properties of residual affinity, and the use of such solvents as water, which possess strong residual affinity of their own, is clearly inadvisable except in special circumstances (compare previous paper, p. 494). The absorption spectrum of *p*-benzoquinone in alcoholic solution is entirely different from that observed by Hartley, Dobbie, and Lauder for the aqueous solution. The absorption curve is reproduced in Fig. 4 and shows only one band, with its head at a frequency of 2100. This band is almost identical with the absorption band shown by camphorquinone, and, as stated in the preceding paper, is undoubtedly caused by the isorropesis between the two oxygen atoms in the para-position, exactly in the same way as between those of the α-diketones. Further, it is evident that the new absorption band of *p*-benzoquinone in the visible region of the spectrum (wave-length 480$\mu\mu$) is the true origin of the colour of this substance; or, in other words, the colour of *p*-benzoquinone is due to the isorropesis between the two oxygens in the para-position.

FIG. 4.

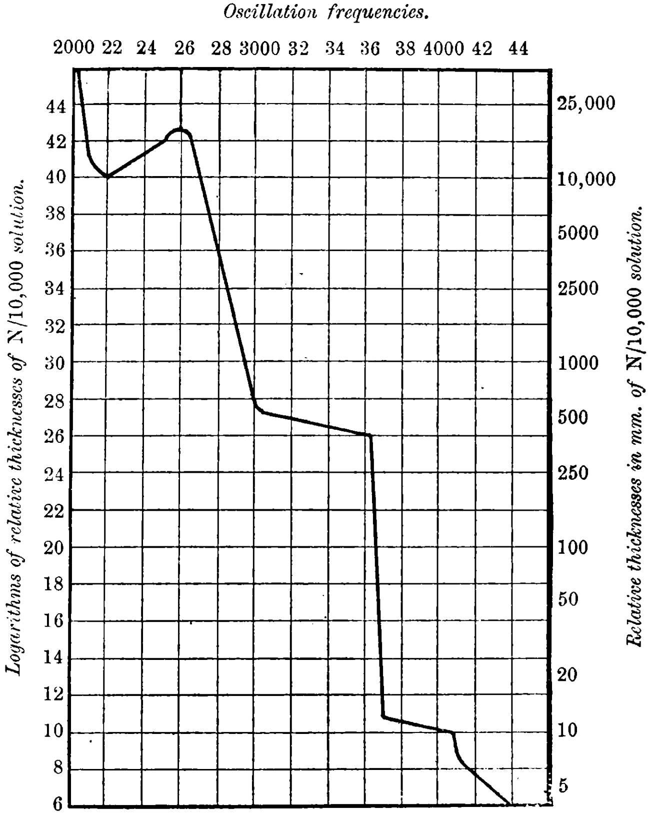


Quinone.

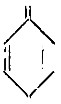
We have also investigated the absorption spectra of the following quinones: toluquinone, *p*-xyloquinone, thymoquinone, α-naphthaquinone, and anthraquinone, and find that the same band is present in each case. The absorption curves are reproduced in Figs. 5, 6, 7, and 8 respectively, and, as can be seen, show the presence of the new band. The process of isorropesis exists in the case of these quinones just as in quinone itself, and, indeed, is the origin of the colour of these compounds.

The importance of these results as regards Armstrong's theory of colour is manifest; they would seem to supply the key to his generalisations, and at the same time to explain the colours of many substances which are difficult of interpretation by Armstrong's quinonoid linking alone. Armstrong, in stating that colour was due to the quinonoid linking,

FIG. 5.

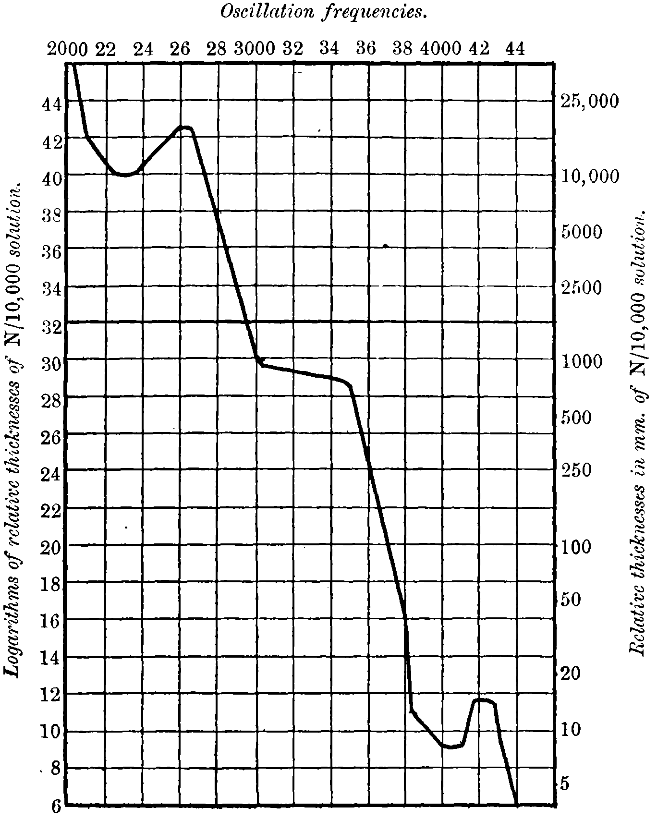


Toluquinone.



was, of course, perfectly correct, but this formula gives us no reason why colour is produced. There is no esoteric value in any of the linkings of the formula as light-absorbing centres; the results given in this paper, however, show that when the quinonoid form exists, a new type of oscillation is set up between the atoms in the para-position, the period of which is equivalent to that of light waves in the visible blue region of the spectrum; such a quinonoid linking therefore produces a yellow colour.

Fig. 6.

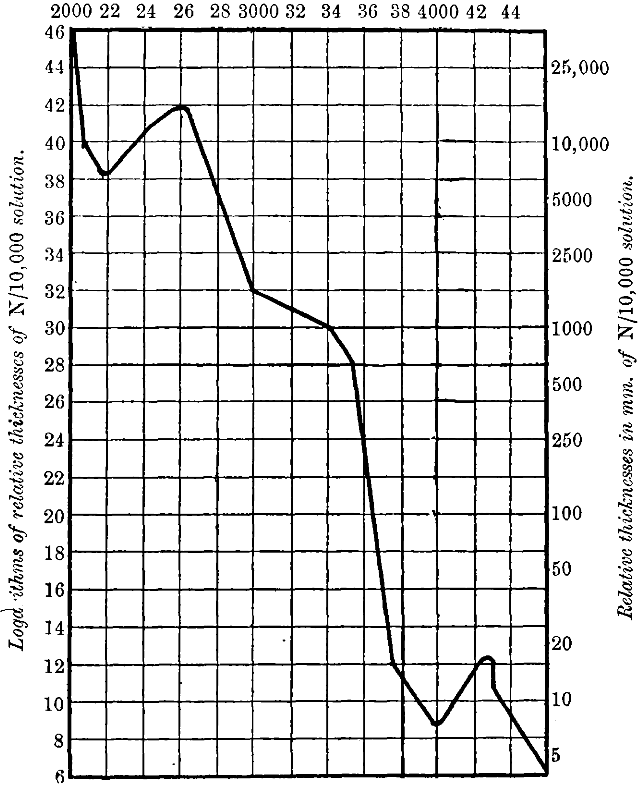


p-*Xyloquinone.*

The results given above show that the process of isorropesis is common to α-diketones and quinones, so that they may be thus generalised: when two ketonic groups are adjacent to one another in the same molecule, the compound will be coloured owing to the existence of a new type of oscillation which is set up between the two residual affinities of the oxygen atoms. There is little doubt that this generalisation can be extended to include many other types of residual affinity than that of the ketonic oxygen, and we are at present engaged on a series of investigations in this direction which we hope to communicate to the Society. In the next paper we deal with compounds of the quinone type with one or both atoms of oxygen replaced by nitrogen, and it is shown that the same type of oscillation occurs in these compounds as in the quinones and α-diketones.

FIG. 7.

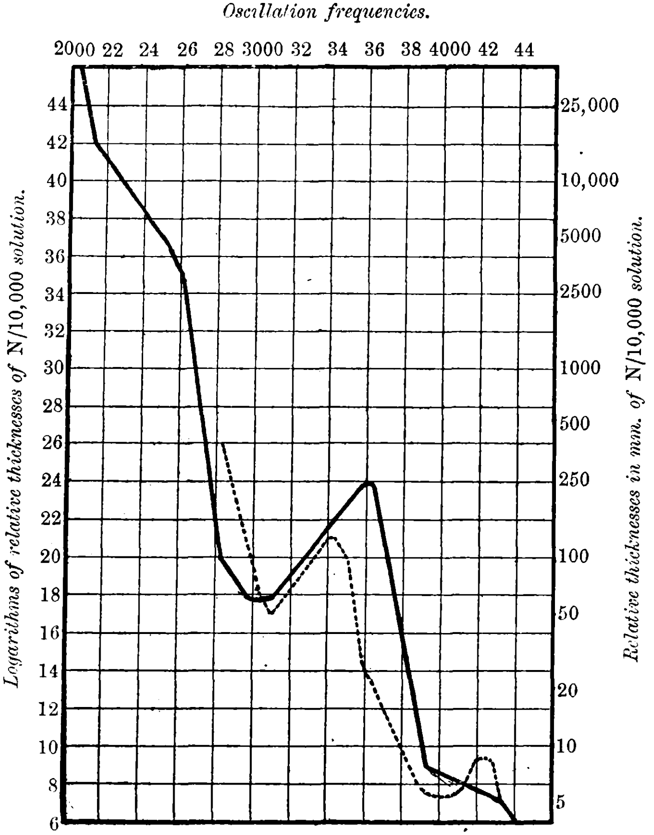
Oscillation frequencies.



Thymoquinone.

In considering the whole question of colour of compounds which may be raised at this point, there is little doubt that the new principle may be extended to include every case; that is to say that isorropesis can take place between any atoms possessing residual affinity. It must be remembered, however, that in order for the new oscillation to take place, it is absolutely necessary for some exciting or disturbing influence to be present. For example, let us take the group –CO·CO– of the α-diketones; each oxygen atom possesses a definite amount of residual affinity, and it is evident that no oscillation can arise between the atoms unless one or both residual affinities are disturbed. Now, in diacetyl, $CH_3·CO·CO·CH_3$, this influence is furnished by the hydrogens of the methyl groups. In this compound there is an attraction exerted on the hydrogen atoms by the oxygen atoms with the result that the residual affinities on the two oxygen atoms tend to be altered,

FIG. 8.



α-*Naphthaquinone* (full curve).
Anthraquinone (dotted curve).

This was discussed at length in the preceding paper. Now we have direct evidence of this potential tautomerism in the absorption curve of diacetyl (see Fig. 1), for, as can be seen, the curve shows a sudden extension at the ordinate 38. This extension undoubtedly means the incipient formation of an absorption band which occupies the position of the band due to the tautomerism of a labile hydrogen (Baly and Desch, *loc. cit.*). Clearly, therefore, the residual affinities of the two oxygen atoms are being slightly disturbed, and it is owing to this disturbance that the new oscillation or isorropesis takes place. We may now understand why the dioxime of diacetyl is colourless, for in this compound we have apparently the condition for colour, and yet only general absorption is indicated. The residual affinity of the nitrogen atoms exerts no attraction on the hydrogen atoms of the methyl groups and therefore is not disturbed in any way ; thus no isorropesis is set up, and the compound is colourless. The absorption curve of diacetyldioxime is shown in Fig. 1. Perhaps the process may be looked at from another point of view ; diacetyl consists of two $CH_3{\cdot}CO$ groups, both of which are potential colour systems, using the word colour in its broadest sense as being the property of any compound which shows an absorption band, whether in the ultra-violet or the visible region. When two or more of these systems are present and mutually dependent, then the new process of oscillation or isorropesis is set up between the two systems. The proviso of mutual dependence is inserted of necessity to account for the new oscillation being started; two perfectly independent vibrating systems will not combine to give a new note, they must be connected or interdependent to some extent.

It may be pointed out here that these results show that a difference of colour cannot be taken as an argument in favour of a necessary fundamental difference in constitution. Many compounds can and do exist with all the conditions for isorropesis, and yet there is lacking the influence to disturb the equilibrium between the residual affinities and so the compounds are colourless. Other compounds agreeing in every essential detail of constitution are strongly coloured simply owing to their having the disturbing influence present. All assumptions, therefore, that two compounds must have essential differences in constitution if one is coloured and the other white are untrustworthy.

It is very noteworthy that the wave-length of the light absorbed by the process of isorropesis is about the same as that emitted by the simpler fluorescent substances ($\lambda = 4800$ to $\lambda = 4000$). It may be that there is an intimate connection between fluorescence and isorropesis, and that the former is only a manifestation of the latter. The existence of an absorption band in the spectrum only means that a free period exists within the molecule capable of being excited when the light falls upon it. This is true in the case of isorropesis, the free period being established by the oscillation between the residual affinities. If now the oscillation between the residual affinities were not only able to establish the free period, but also to excite it, then we should have the phenomenon of fluorescence. There is nothing inherently improbable in this idea. In both cases, colour and fluorescence, a free period is produced by the isorropesis; in the former case, the free period is excited by the incident light, and we have absorption; in the latter case, the free period is excited by the isorropesis, and we have emission. An important fact bearing on the connection between isorropesis and fluorescence has recently been recorded by Nichols and Merritt (*Physical Review*, 1904, **18**, 447); these authors have observed that, when the fluorescence of fluorescein and certain other substances is excited by a beam of ultra-violet light, a distinct absorption occurs of light of the same wave-length as that emitted by the substance when fluorescent.

Every possible precaution was taken to obtain the substances in a state of the greatest possible purity, and the absorption curves shown in the figures were drawn by plotting the limits of absorption against the logarithms of the relative thicknesses of a $M/10,000$ solution.

Conclusions.

The following conclusions may be drawn from our experiments

(1) When two true ketonic groups are in juxtaposition in the molecule, an oscillation or isorropesis occurs between the residual affinities of the oxygen atoms, which results in the absorption of light in the visible region of the spectrum. These substances are therefore coloured.

(2) This isorropesis also occurs between the residual affinities of the oxygen atoms in the quinones, and is the origin of the yellow colour of these substances.

(3) In order to start the oscillation, it is necessary that some influence should be present to disturb the residual affinities on the oxygen atoms.

(4) Subject to the proviso referred to in (3), there is no doubt that this principle may be extended, and that the phenomenon of visible colour is due to the oscillation between the residual affinities on atoms or groups of atoms in juxtaposition.

(5) Any assumption that two compounds must be fundamentally different in constitution if one is coloured and the other white is quite untrustworthy.

(6) It is possible that colour and fluorescence are evidences of the same phenomenon—isorropesis. In the former case, the isorropesis provides the mechanism, and incident light actuates it; in the latter case, the isorropesis both provides and actuates the mechanism.

Our thanks are due to Mr. W. B. Tuck, B.Sc., for much valued assistance during the carrying out of the experiments. We are again indebted to Professor Collie for the great interest he has taken in this work, and also to the Chemical Society for a grant in aid of this investigation.

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THE RELATION BETWEEN ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION. PART IV. THE REACTIVITY OF THE SUBSTITUTED QUINONES.

BY

ALFRED WALTER STEWART (CARNEGIE RESEARCH FELLOW)

AND

EDWARD CHARLES CYRIL BALY.

From the Transactions of the Chemical Society, 1906. Vol. 89.

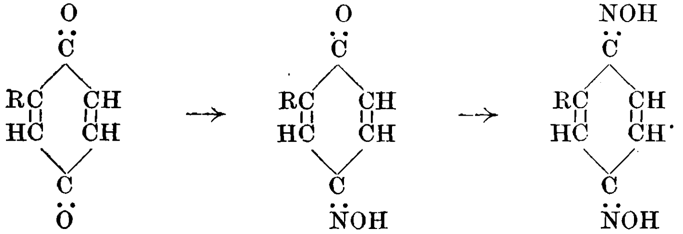
LXVIII.—*The Relation between Absorption Spectra and Chemical Constitution. Part IV. The Reactivity of the Substituted Quinones.*

By ALFRED WALTER STEWART (Carnegie Research Fellow) and EDWARD CHARLES CYRIL BALY.

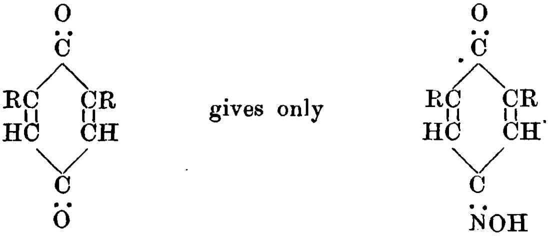
IN our previous papers, we have shown the effect of substitution on the absorption spectra of ketonic compounds, and in the case of some ketones we have been able to prove that the persistence of a certain absorption band in their spectra is proportional to the reactivity of their carbonyl groups. From a consideration of our results, we were enabled to put forward a chemical explanation which covered all the phenomena hitherto attributed to steric hindrance. The present paper contains an account of similar researches in the quinone series.

Kehrmann (*Ber.*, 1888, **21**, 3315; *J. pr. Chem.*, 1889, **39**, 399; **40**, 257) has shown that when the hydrogen atoms of *p*-benzoquinone are replaced one at a time by methyl radicles or by halogen atoms, a distinct change takes place in the reactivity of the carbonyl groups in the compounds. Although he made no accurate measurements, his results are quite sufficient for the present purpose. His conclusions, which are based on the examination of many substituted quinones, may be summarised as follows:

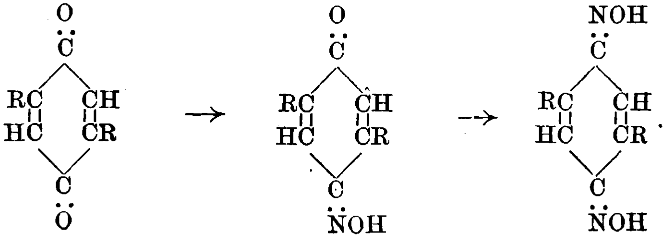
(1) Monosubstituted quinones, when treated with hydroxylamine, first form a monoxime, the carbonyl group in the ortho-position to the substituent being left unattacked. On further treatment, this monoxime yields a dioxime:



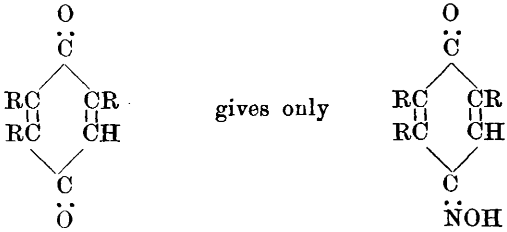
(2) Disubstituted quinones, when both substituents are in the ortho-position to the same carbonyl group, yield only monoximes:



(3) Disubstituted quinones, when the substituents are in the para-position to one another, give mono- and di-oximes, but only with some difficulty:



(4) Trisubstituted quinones give only monoximes, that carbonyl group being attacked which has only one ortho-substituent:



(5) Tetrasubstituted quinones give no oximes.

Up to the present time, it has been usual to attribute the phenomena observed by Kehrmann to the influence of steric hindrance. It was supposed that the chief cause of the non-reactivity of the carbonyl groups was to be found in the occupation of the space around them by the vibrations of the substituents in the ortho-position, this being supposed to be sufficient to prevent the approach of any hydroxylamine molecules. This rough and ready mechanical idea has been very useful, as it gave an easily comprehensible explanation of most of the phenomena of hindrance which occur in chemical reactions. It appeared to us, however, that other causes might lie at the root of the matter, and we began to examine the absorption spectra of a series of substitution products of quinone, hoping to find some more probable explanation for the phenomena which Kehrmann indicated.

Having already proved the connection between the persistence of the isorropic absorption band and the reactivity of the carbonyl groups in certain open-chain ketones, we endeavoured to find out whether the same rule holds good in the case of the quinone carbonyl groups. Our results show that it is valid, as can be seen by examining the curves of benzoquinone, toluquinone, and thymoquinone which we have already published (Baly and Stewart, this vol., pp. 507—510).

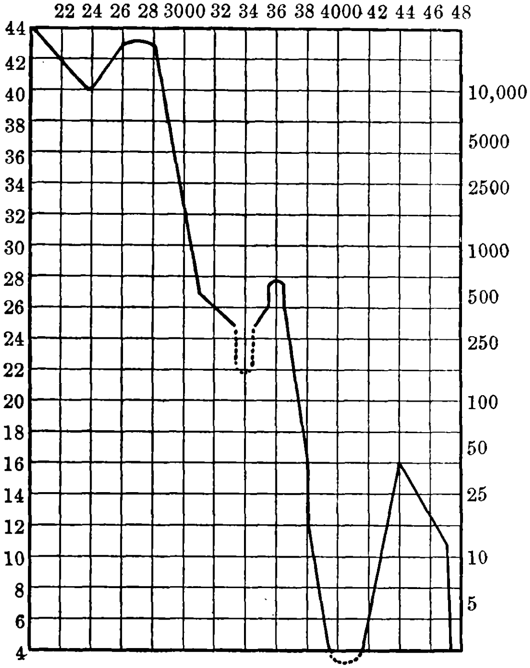
The measurements of the persistence of the absorption band in each case are as follows:

	Benzoquinone.	Toluquinone.	Thymoquinone.
Absorption band begins at	72·4	21·0	13·8
,, ,, ends at...........	10·0	10·5	7·2
Change of dilution over which absorption band persists	85·8	50·0	47·8 per cent.

It is evident that the effect of the substitution has been to diminish the persistence of the isorropic band to a considerable degree. But at the same time as its persistence decreases, a new band appears and increases. Benzoquinone in alcoholic solution shows no trace of a benzenoid structure, so far as spectroscopic evidence can be adduced, for it shows no sign in its spectrum of any of the absorption bands which are characteristic of benzene. But already in the spectrum of toluquinone a very shallow band makes its appearance at 3900, and in *p*-xyloquinone this band deepens and becomes recognisable as that of a benzenoid compound.

The spectrum of benzoquinone in alcohol differs to a great extent from its spectrum in aqueous solution. The curve of its absorption spectrum in alcoholic solution has been published by us (Stewart and Baly, this vol., p. 507), whilst that of an aqueous solution has been published by Hartley, Dobbie, and Lauder (*Brit. Assoc. Report,* 1902, 99). As these authors did not mention the presence of the isorropic band in benzoquinone, we repeated the examination of an aqueous solution at higher concentrations and found the isorropic band. We give the complete curve in Fig. 1. The effect of the solvent is very marked in this instance. Apparently an additive product is formed; the isorropic band shrinks, and a benzenoid band makes its appearance at 4000. Thus there are three bands in the absorption spectrum of benzoquinone in aqueous solution.

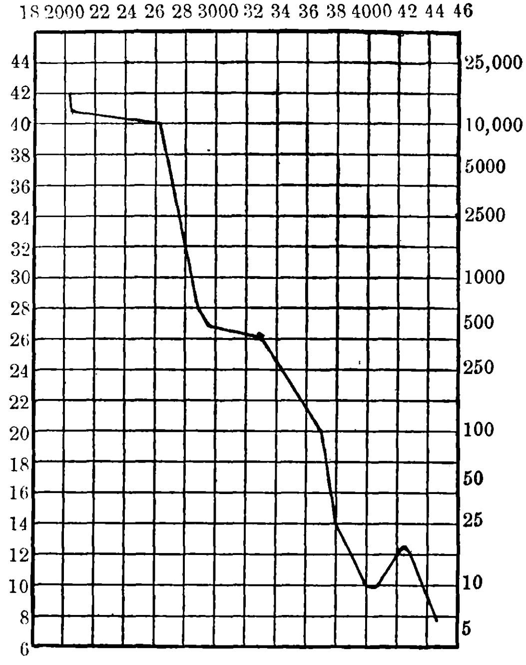
FIG. 1.



Benzoquinone in water.

The second point which we wish to mention is the fact that the middle band of the three, the head of which lies at 3400, occurs in the spectrum of an alcoholic solution of benzoquinone, but in that case it appears merely as an extension of the spectrum and not as a true band. The action of the solvent water extends the band considerably. We find that the same band occurs in the spectra of the substituted quinones, hydroquinone, and quinhydrone. We intend at a later date to investigate this point more fully, as it appears likely to throw light on the intramolecular vibration of the quinone system.

FIG. 2.

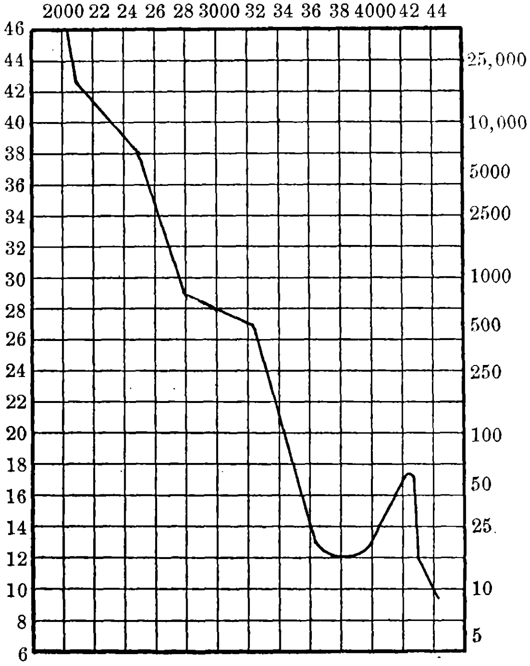


Chlorobenzoquinone.

As most of Kehrmann's investigations were carried out on halogen-substituted quinones, the spectra of several of these compounds were examined. The results obtained confirm what has already been said with regard to the effect of substitution. In chlorobenzoquinone (Fig. 2), the isorropic band becomes merely a slanting line lying between 2000 and 2600; in 2 : 6-dichlorobenzoquinone (Fig. 3), the line representing the isorropic band approaches more nearly to the general curve, while in trichlorobenzoquinone (Fig. 4) and trichlorotoluquinone (Fig. 5) there is no measurable isorropic band. At the same time as the isorropic band diminishes, the benzenoid band increases steadily, as can be seen from the following figures :

	Chloro-benzoquinone.	2:6-Di-chloro-benzoquinone.	Trichloro-benzoquinone.	Trichloro-toluquinone.
Absorption band begins at	17·4	57·5	63·0	87·1
,, ,, ends at	10·0	15·8	14·5	10·0
Change of dilution over which the absorption band persists	42·0	55·0	77·0	88·0 per cent.

FIG. 3

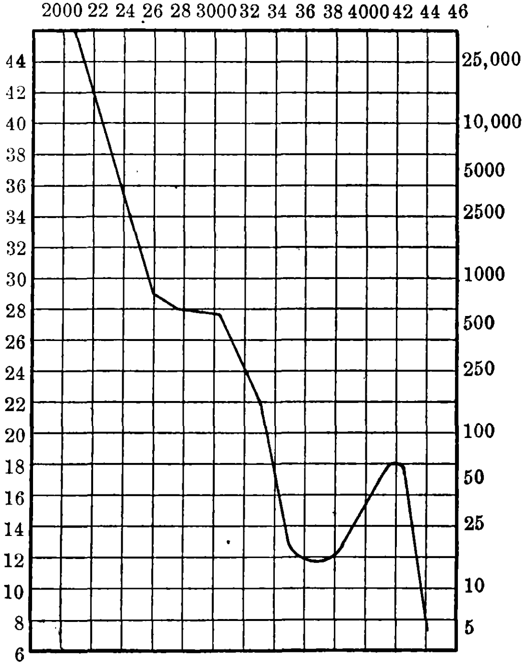


Dichlorobenzoquinone.

Three substances remain to be described. When the curve of bromobenzoquinone (Fig. 6) is compared with the corresponding chlorobenzoquinone, a distinct difference is noticeable between the two. In the former, *both* the isorropic and the benzenoid bands appear to be less marked than in the chlorine compound. This can easily be explained. Bromine is more unsaturated than chlorine, and it has been shown by Baly and Collie (Trans., 1905, 87, 1332) that the introduction of an unsaturated group into the benzene nucleus tends to merge the benzene absorption bands into one another and interfere with them to a great extent. The effect of introducing bromine into the benzene nucleus is well shown by the absorption spectrum of bromobenzene (Fig. 6), where the seven distinct absorption bands of the benzene spectrum are completely obliterated. The relatively weaker effect of the chlorine atom may be seen by comparing Fig. 6 with the curves of chlorobenzene given by Baly and Collie (*loc. cit.*).

With regard to the second compound, dichlorothymoquinone (Fig. 7), it is interesting to compare it with trichlorotoluquinone (Fig. 5), from which it may be derived by the substitution of a propyl group for a chlorine atom. This exchange of an alkyl group for a halogen atom produces a decrease in the persistence of the benzenoid band of the compound, as is shown by the following numbers:

FIG. 4.

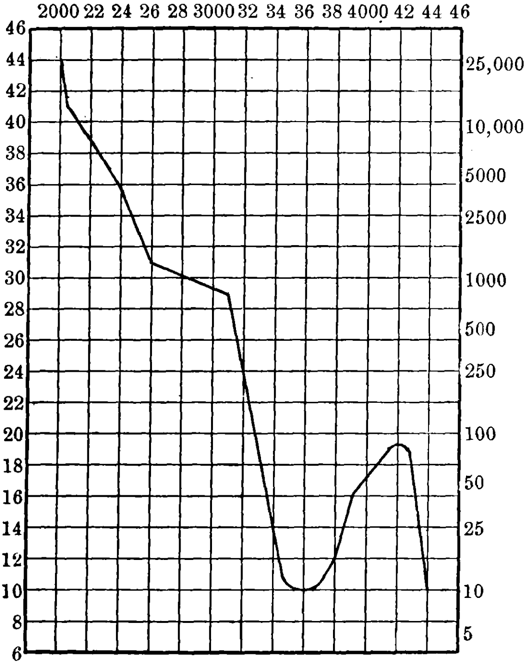


Trichlorobenzoquinone.

	Trichloro-toluquinone.	Dichloro-thymoquinone.
Absorption band begins at	87·1	66·1
,, ,, ends at	10·0	12·0
Change of dilution over which absorption band persists	88·0	82 0 per cent

This decrease in the persistence of the benzenoid band corresponds to the respective influences of the two substituents on the reactivity of the carbonyl group, as observed by Kehrmann, who found that the introduction of a halogen atom had a greater effect than that of an alkyl group. The same difference may be noticed, and is even more strongly marked, in the cases of toluquinone (Baly and Stewart, this vol., p. 508) and chlorobenzoquinone (Fig. 2). The isorropic band which is clearly marked in the toluquinone spectrum, is almost extinguished when the chlorine atom is substituted for the methyl group, whilst the same exchange extends the benzenoid band from a straight line into a well-marked band.

FIG. 5.



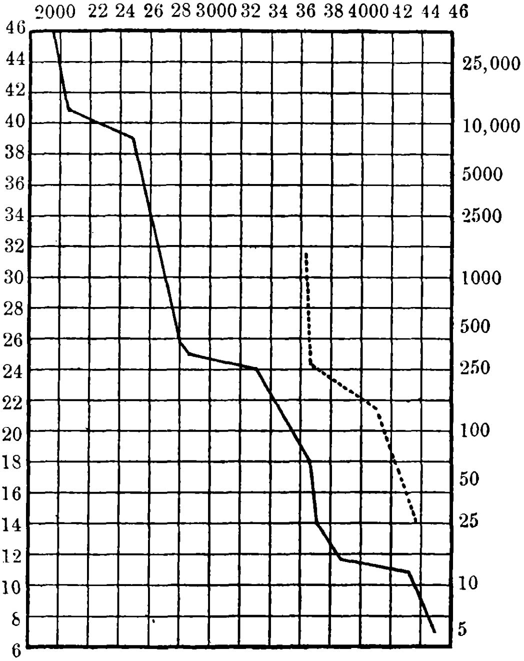
Trichlorotoluquinone.

The third compound, dibromothymoquinone (Fig. 8), when compared with dichlorothymoquinone (Fig. 7), shows the more marked influence exerted by the bromine atoms in comparison with the chlorine substituents.

	Dichloro-thymoquinone.	Dibromo-thymoquinone.
Absorption band begins at	66·1	109·6
,, ,, ends at	12·0	15·9
Change of dilution over which absorption band persists	82·0	85·0 per cent.

It is obvious that the successive substitution of the hydrogen atoms in the quinone nucleus has produced a change in the whole system of the substance. Benzoquinone itself probably exists in the true quinonoid form, but during the course of the substitution it becomes more and more benzenoid in character. What form it eventually takes cannot be determined. It is not improbable that its vibrations approximate more or less closely to those implied in the ordinary peroxide formula for benzoquinone, but no definite conclusion can be drawn at present. What is evident is that the process of isorropesis is being gradually diminished, and from this we may infer that less and less of the compound is vibrating in the quinonoid form.

FIG. 6.



Bromobenzoquinone (full curve).
Bromobenzene (dotted curve).

In considering the question of the effect which substitution exerts on the quinone carbonyl group, several factors must be taken into account.

(1) Steric hindrance produced by the vibration of the substituents.

(2) The distortion of the benzene ring consequent on the un-

equal distribution of weight in the nucleus which substitution produces.

(3) The possibility of the formation of a nascent carbonyl group.

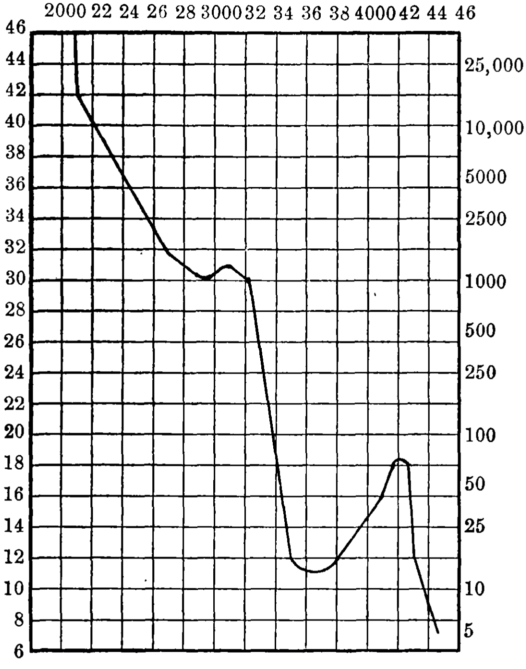
With regard to the first of these factors, we have already in our previous paper (Stewart and Baly, *loc. cit.*) shown that it need not be assumed to enter into the matter—at least to any measurable extent.

The question of the distortion of the benzene ring owing to its being unequally loaded is of more importance. From the evidence which we have published, it seems a fair deduction that in the unsaturated ring system,

$CO\langle{}^{CH=CH}_{CH=CH}\rangle CO$

there are two forces at work, which are mutually antagonistic: the isorropic process and the tendency which the system will have to return to the most stable grouping, namely, the benzenoid form. The isorropic process consists of some vibration between the two carbonyl groups, and in order that this process may continue, the compound must exist in the quinonoid form. Undoubtedly, the principal vibrations of the atoms of such a compound

FIG. 7.



Dichlorothymoquinone.

would be parallel to the line of symmetry of the molecule, that is, along the line *AB*:

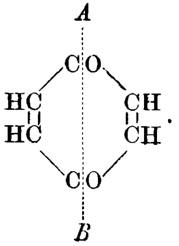
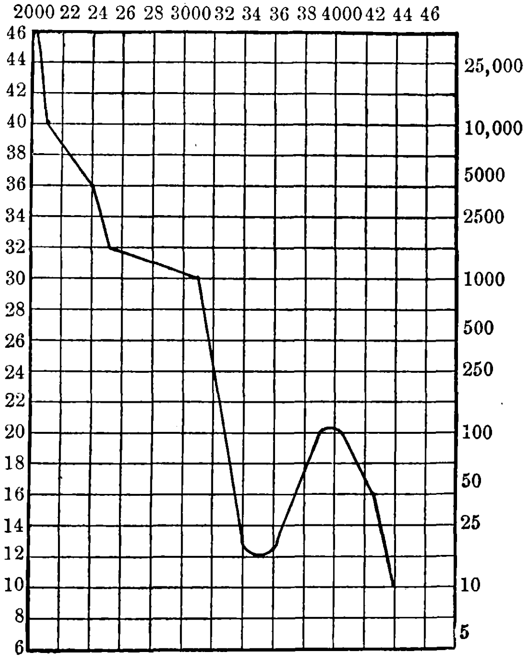
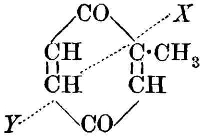


FIG. 8.



Dibromothymoquinone.

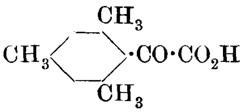
If the vibrations were not in this direction, it would hardly be possible for any isorropic process to take place. If one now supposes that the centre of gravity of the system is altered by the replacement of hydrogen atoms by methyl groups, the conditions of stability in the system are completely altered. For instance, if one introduces a single methyl radicle, one would expect that the molecule would vibrate along the new line of symmetry *XY*;

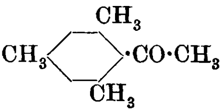


In this case, the isorropic process would not attain the same intensity as in the preceding instance, since the vibration of the molecule would not tend to produce sufficiently frequently the conditions necessary for its existence. But as soon as the isorropic process is diminished, the tendency of the compound will be to assume the most stable benzenoid structure, so that the effect of substitution will be twofold, first, in preventing the isorropesis, and, second, in thus encouraging the formation of the benzenoid type of compound in preference to the quinonoid.

The last of the three factors, namely, the possibility of a nascent carbonyl group being formed in the compound, is probably the determining factor in the problem, although it is to a great extent controlled by the vibratory motions of the ring. We have already shown in our first paper (Stewart and Baly, *loc. cit.*) that when the hydrogen atom of the group $=CH\cdot CO-$ is replaced by a methyl radicle, the tendency to form a nascent carbonyl group is checked, and the reactivity of the carbonyl group in $=C(CH_3)\cdot CO-$ is much less than in the parent substance. We have also shown that the nascent carbonyl group may be formed by a process analogous to tautomerism (potential tautomerism) in which there is no actual transfer of the hydrogen from the carbon to the oxygen, but merely a mutual action between the two atoms, oxygen and hydrogen, which action, if continued, would end in tautomeric change. If one applies the same reasoning to the case of the quinone carbonyl group, one finds that in quinone itself one has the grouping $=CH\cdot CO\cdot CH=$, where two hydrogen atoms could take part in the process of potential tautomerism. In toluquinone, one of these is replaced by methyl, $=CH\cdot CO\cdot C(CH_3)=$, so that the possibility of potential tautomerism is greatly decreased. This alone would suffice to explain the hindering effect of an ortho-substituent, but another and probably more powerful cause exists as well. We pointed out in our second paper (Baly and Stewart, this vol., p. 511) that the isorropic process in diacetyl was not an independent action, but was brought into action by the potential tautomerism in the $CH_3\cdot CO-$ groups. That is to say, if one could destroy this starting mechanism one would prevent the isorropesis and therefore the formation of a nascent carbonyl group in the substance. Now, in the case of toluquinone, half the starting mechanism of the group $=CH\cdot CO\cdot CH=$ has been destroyed by the substitution of a methyl group for one of the hydrogen atoms. This has a marked effect on the isorropic process, as the curves show. When a second substituent is introduced, as in the case of dichlorobenzoquinone, the isorropic process almost ceases, and the second carbonyl group reacts chiefly on account of the potential tautomerism which is still possible.

It appears to us that this purely chemical explanation of these phenomena is more probable than one which depends on an idea of mechanical shocks and collisions between atoms. Such collisions may certainly influence the reaction, but do so, in all probability, only to an immeasurably slight extent. The conception of steric hindrance has never satisfactorily explained several very important cases, such as the ease with which the compound (I) forms an oxime, in contradistinction to the difficulty found in the case of (II), although the methyl radicle is probably much smaller than the carboxyl group :


(I.)


(II.)

The hypothesis which we have put forward in the course of our work on this subject seems much more satisfactory, since it is capable of explaining not only all that the steric hindrance hypothesis can explain, but also those exceptions which cannot be elucidated by any idea of steric hindrance.

To avoid the possibility of misconception, we wish to call attention to the following fact. It is evident that the process of isorropesis is decreased by substitution, but the compounds still remain yellow (although on dilution their colour disappears much more rapidly than is the case with benzoquinone), even when no isorropic band is shown in our curves. There is, however, no contradiction between our present and our previous work. In the photographs which we have taken, the limits of the isorropic band are not always clearly marked, especially in the case of the more highly substituted quinones. In order to avoid inaccuracies due to brighter lines in the spectra, we have smoothed the curves, and in the course of the smoothing the very faintly marked isorropic band has in some cases been practically obliterated. Although this does not matter very much from the point of view of the present paper, we think it advisable to call attention to the fact that our present work in no way invalidates our previous papers.

Conclusions.

The effect of substitution on quinones is as follows:

(1) It tends to diminish the possibility of potential tautomerism and thus indirectly renders isorropesis less frequent.

(2) By unevenly loading the ring, it produces in benzoquinone a greater tendency to assume the benzenoid form; thus, in another way, diminishing the possibility of isorropesis taking place.

(3) Halogen substituents have more effect on the isorropic process than methyl groups owing to their unsaturated character, which affects the vibrations of the ring.

In conclusion, we wish again to thank Professor Collie for the great interest he has taken in the research during its progress.

The Spectroscopic Laboratory,
University College, London.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

THE RELATION BETWEEN ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION. PART III. THE NITROANILINES AND THE NITROPHENOLS.

BY

EDWARD CHARLES CYRIL BALY,

WALTER HENRY EDWARDS,

AND

ALFRED WALTER STEWART (CARNEGIE RESEARCH FELLOW).

From the Transactions of the Chemical Society, 1906. Vol. 89

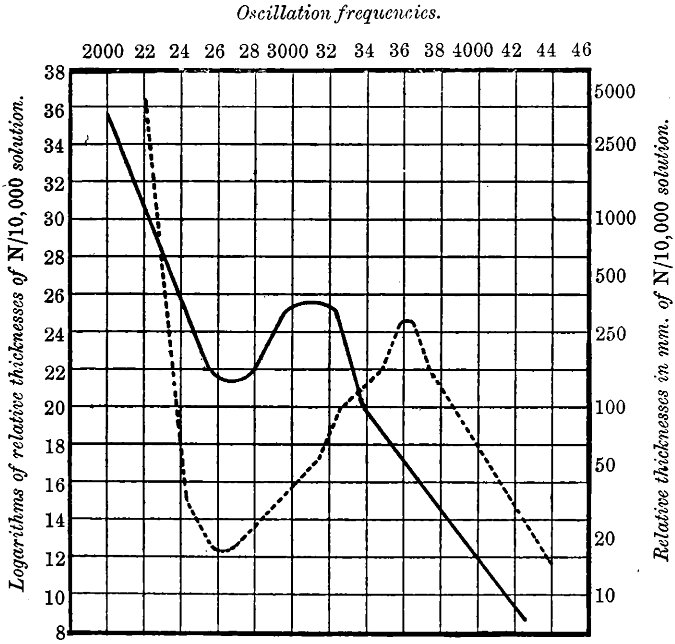
LVI.—*The Relation between Absorption Spectra and Chemical Constitution. Part III. The Nitroanilines and the Nitrophenols.*

By Edward Charles Cyril Baly, Walter Henry Edwards, and Alfred Walter Stewart (Carnegie Research Fellow).

In the preceding paper, dealing with the absorption spectra of the quinones and α-diketones, it was shown that the colour of these compounds is due to an absorption band in the visible blue region produced by a new type of oscillation which occurs when two ketonic groups are in juxtaposition within the same molecule. To this process we have given the name isorropesis, and we have shown that the yellow colour of the aromatic quinones is also due to this process taking place between oxygen atoms in the para-position. In the present paper, the nitroanilines and nitrophenols are discussed, and it is shown how the process of isorropesis is present between the residual affinities of two nitrogen atoms in the one case and of an oxygen and a nitrogen atom in the other.

The spectra of the nitroanilines were examined originally by Hartley and Huntington; we, however, reproduce the curves in Fig. 1 of the meta- and para-compounds (from measurements of our own plates), because the Hartley and Huntington curves are inconvenient for comparison with our curves. It will be noticed that the persistence of the absorption bands is much less in the meta-compound than in the case of the ortho- and para-compounds. There is, however, no possibility of doubt that the absorption band is due to the meta-compound itself, and not to a small quantity of a highly coloured impurity. This can readily be understood from a comparison of the persistences of the ortho- and meta- and the para-compounds; the persistence of the band with the meta-compound is roughly one-third what it is with two isomerides; that is to say, if the colour were due to an impurity present to the amount of 1 per cent., this impurity would necessarily have a colouring power and an absorption band with a persistence more than thirty times that of the *o*- and *p*-nitroanilines. This is manifestly absurd, as the absorption bands given by the most intensely coloured substances do not show a persistence which in any way approaches this amount. Now we have examined the absorption spectra of solutions of the nitroanilines in hydrochloric acid. These solutions are quite colourless, provided that the concentration of the acid be sufficient. It is very important in view of what follows that whilst the ortho- and para-compounds have to be dissolved in concentrated acid, the meta-compound requires far less to decolorise its solution. The absorption curve of *p*-nitroaniline dissolved in hydrochloric acid is shown in Fig. 2, from which it can be seen that there is no absorption band; the curves of the ortho- and meta-isomerides are very similar.

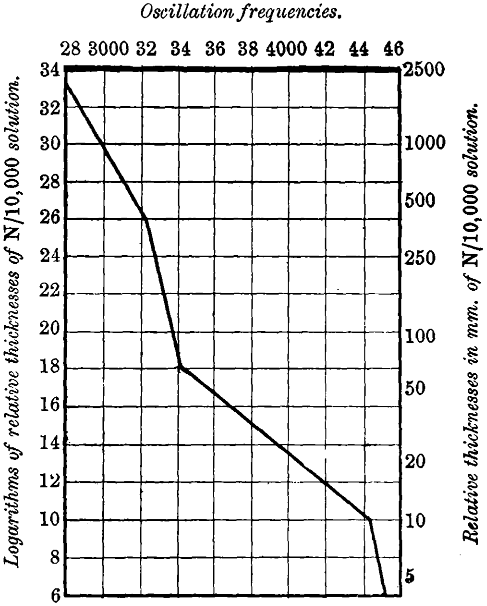
FIG. 1.



m-*Nitroaniline* (full curve).
p-*Nitroaniline* (dotted curve).

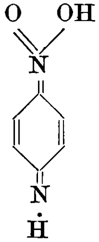
From a comparison of the spectra of aniline and its hydrochloride and the monoalkylated benzenes, it has been shown (Baly and Collie, Trans., 1905, 87, 1331) that in the hydrochloride the $-NH_2HCl$ group behaves in almost exactly the same way as a single alkyl group; that is to say, the very striking effect of the residual affinity of the $-NH_2$ group in aniline has entirely disappeared. It was also shown in the same paper that the effect of the nitro-group is to block almost entirely the tautomerism of the benzene ring, thereby introducing a fixed state of strain, with the result that strong general absorption is evidenced. Probably this effect arises from the attraction exerted by the unsaturated oxygen atoms on the atoms in the ring. Arguing from these facts, there is little doubt but that the structure of the nitroanilines in acid solution is that of the true hydrochloride, thus: $C_6H_4(NO_2)NH_2,HCl$.

FIG. 2.

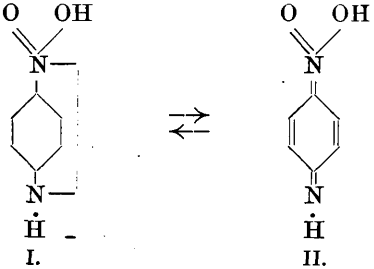


p-*Nitroaniline in* HCl.

When, however, the free substances are examined in alcoholic solution, the absorption curves (see Fig. 1) show the presence of a similar absorption band to that present in the quinones and α-diketones. We may therefore conclude at once that the substances have changed into the quinonoid form and that the process of isorropesis is taking place in exactly the same way as in the quinones. The residual affinity of the oxygen atoms of the nitro-group exerts an attraction on the hydrogen atoms of the amino-group, so that the compounds pass over to the quinonoid form :

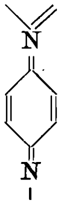


The two nitrogen atoms then occupy the position of the oxygen atoms of *p*-benzoquinone and function in the same way. As in the case of *p*-benzoquinone, this may be expressed graphically by saying that it is possible for the molecule to exist in two phases :

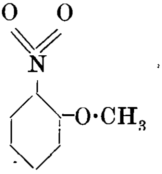


I. II.

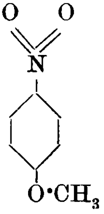
Just as in the case of diacetyl and ethyl pyruvate quoted in the preceding papers, the formula (I) represents in all probability only an extreme phase, and therefore we are not justified in attributing this static formula to the nitroanilines. There is no doubt that the residual affinities of the nitrogen atoms as expressed by the formula



are being disturbed by the motions of the benzene nucleus, and that therefore isorropesis is set up between them. Such a process cannot, of course, be represented by any static chemical formula, and that given above (I) is only intended to represent a condition which the isorropesis may tend to bring about. It is not improbable that the possibility of writing both types of formula for a substance may be used as a test of the possibility of isorropesis. The nitrophenols and nitrosophenol are very similar to the nitroanilines. The absorption curves of *o*- and *p*-nitroanisoles are shown in Fig. 3, and undoubtedly represent the molecular vibration curves of the formulæ



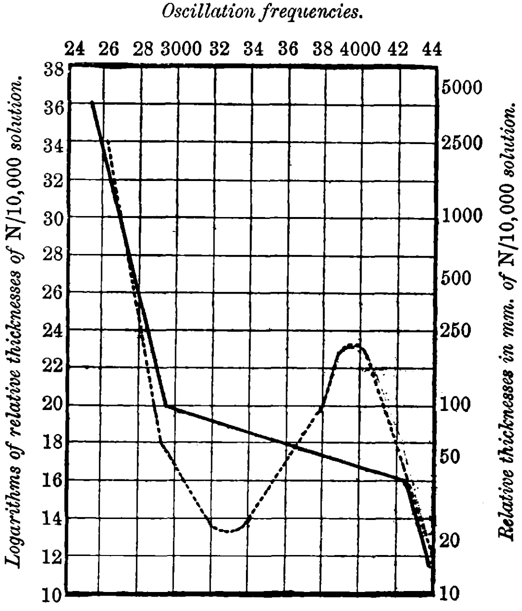
and



respectively.

Neither of these curves is altered in any way by the addition of sodium ethoxide to the solutions of the nitroanisoles. The absorption

FIG. 3.



o-*Nitroanisole* (full curve).
p-*Nitroanisole* (dotted curve).

curves of *o*- and *p*-nitrophenols have already been described by Hartley and Huntington (*loc. cit.*); we have reproduced them plotted on logarithmic scale in order to compare them with the curves of the analogous substances. The absorption curve of *p*-nitrophenol in neutral alcoholic solution is shown in Fig. 5 by the full curve and is identical with that of *p*-nitroanisole; we have no hesitation, therefore, in saying that *p*-nitrophenol in neutral alcoholic solution has the formula

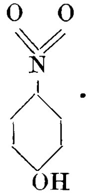
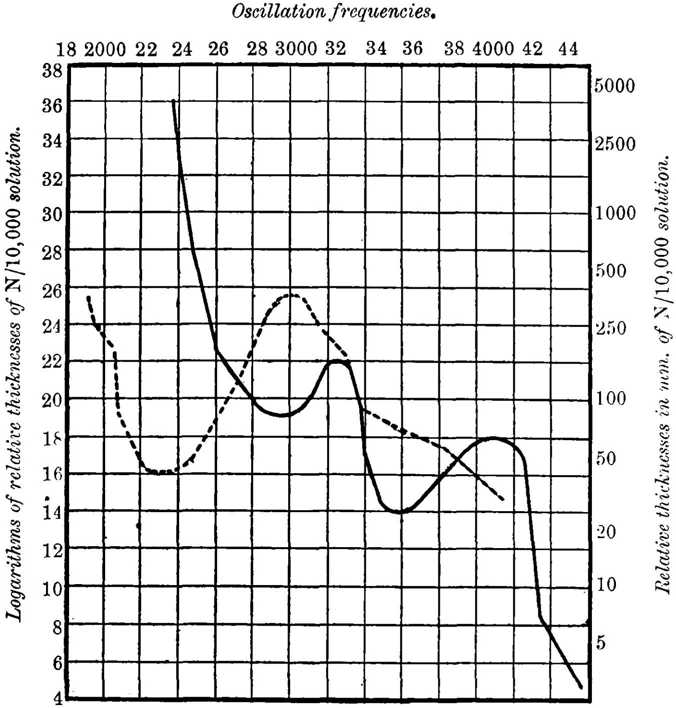
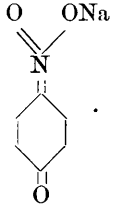


FIG. 4.



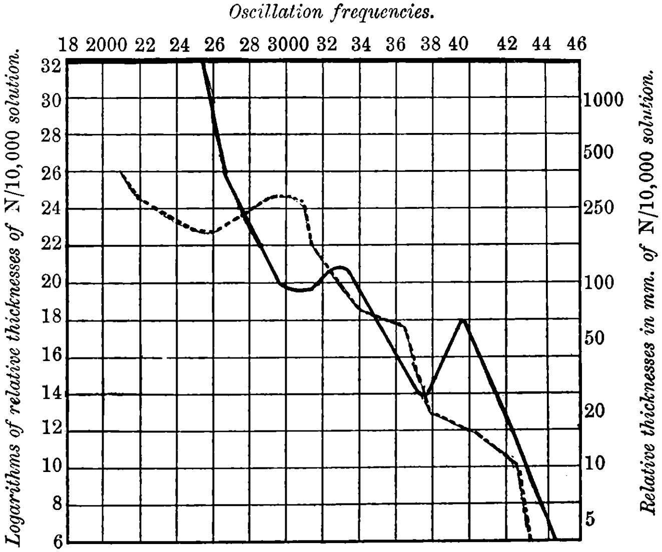
o-*Nitrophenol in neutral solution* (full curve).
o-*Nitrophenol in alkaline solution* (dotted curve).

On the addition of sodium ethoxide and the formation of the sodium salt, the absorption spectrum entirely alters, and is shown by the dotted curve in Fig. 6. A similar band has now appeared in the visible region to that in the nitroanilines, and therefore we may conclude that the residual affinity of the oxygen atoms of the nitro-group exerts insufficient attraction for the hydrogen of the free nitrophenol to cause the formation of the quinonoid form, but that when the hydrogen is replaced by the more electro-positive sodium atom, then the attraction of the oxygen atoms is sufficient to bring the sodium over, with the formation of the quinonoid form :



Very much the same is the case of *o*-nitrophenol, the absorption curves of which are shown in Fig. 4 in neutral (full curve) and alkaline (dotted curve) solution respectively.

FIG. 5.



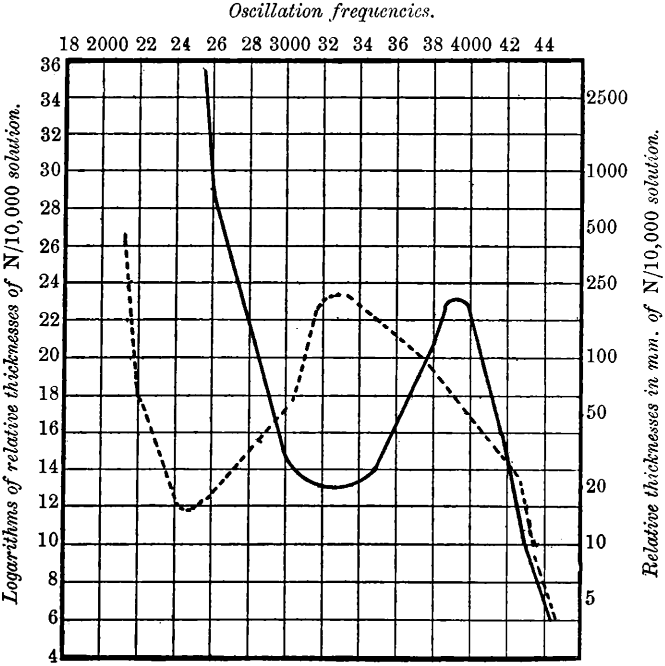
m-*Nitrophenol in neutral solution* (full curve).
m-*Nitrophenol in alkaline solution* (dotted curve).

In the case of *m*-nitrophenol, the absorption curves of which in neutral and alkaline solution are shown in Fig. 5 by the full and dotted curves respectively, the free substance in all probability exists in the ordinary phenolic form, whilst in alkaline solution the presence of the isorropesis band shows that the quinonoid form is undoubtedly present.

As the band is shallow, however, it is evident that but a small quantity of this form is possible. That this band is due to the quinonoid form of the *m*-nitrophenol itself and not to the presence of a small quantity of a highly coloured impurity is evident from a comparison of the persistence of the band with those of the ortho- and para-isomerides and with those of any of the colouring matters.

We have also studied the absorption spectrum of *p*-nitrosophenol, and the absorption curves of this substance are shown in Fig. 7, the full curve being that of the compound in neutral alcoholic solution and the dotted curve being that obtained when the solution is rendered alkaline with sodium ethoxide. The absorption of *p*-nitrosophenol in neutral solution has already been observed by Hartley, Dobbie, and Lauder (*loc. cit.*) and differs considerably from ours; these authors find two bands whilst we find only one. The principal band observed by Hartley, Dobbie, and Lauder agrees in position with ours. It will be seen that this curve is sufficiently similar to that of nitrosobenzene (Fig. 7, dot and dash curve) to

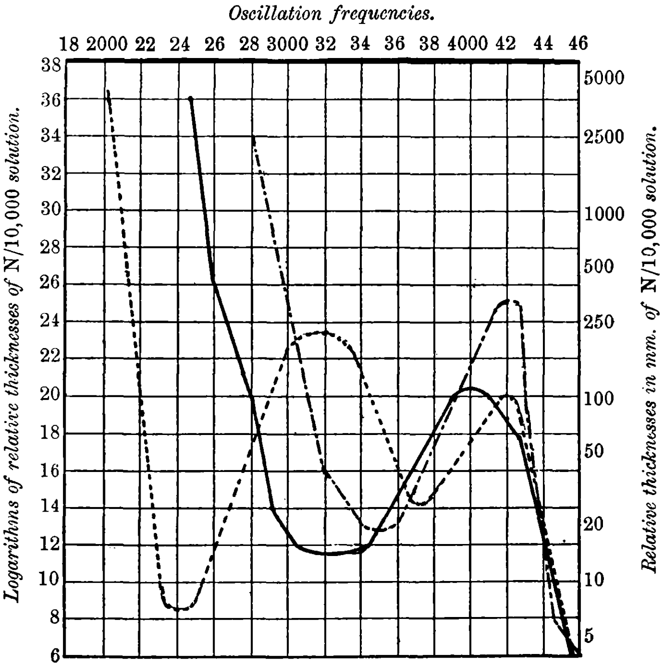
FIG. 6.



p-*Nitrophenol in neutral solution* (full curve).
p-*Nitrophenol in alkaline solution* (dotted curve).

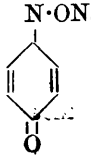
justify the conclusion that the free substance has the true nitrosophenol formula. The case is absolutely different when alkali has been added (Fig. 7, dotted curve), and the presence of the band in the visible region is evidence of isorropesis and the necessary existence of the quinonemonoxime form. When in the free state, the residual affinity of the oxygen of the nitroso-group is not sufficient to attract the hydrogen atom away from the hydroxyl group; when,

FIG. 7.



p-*Nitrosophenol in neutral solution* (full curve).
p-*Nitrosophenol in alkaline solution* (dotted curve).
Nitrosobenzene (dot and dash curve).

however, this hydrogen atom has been replaced by sodium, the attraction of the nitroso-oxygen is powerful enough to bring the sodium away from the phenolic oxygen, with the result that the following compound is produced:

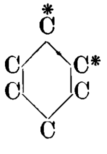


From these results we may conclude that the three nitroanilines in neutral solution and the three nitrophenols and nitrosophenol in alkaline solution exist in the quinonoid form and that a process of isorropesis is taking place between the residual affinities of the two nitrogen atoms in the nitroanilines and the nitrogen and oxygen atoms in the nitrophenols and in nitrosophenol, with the result that an absorption band is formed in the visible region and the compounds are coloured.

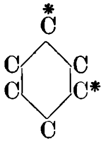
The cases of *m*-nitroaniline and *m*-nitrophenol require separate consideration, for their absorption spectra show that while the absorption bands are slightly nearer the shorter wave-lengths than in the case of the ortho- and para-compounds, yet there is no doubt that the absorption bands are due to the meta-compounds themselves, and tha their structure and the resulting isorropesis must be quite analogous to that occurring in the ortho- and para-compounds. It would thus appear necessary to accept the existence of meta-quinones. Now it is not necessary to insist upon the static existence of a meta-quinonoid linking, and, indeed, the spectroscopic evidence is against this, because in both *m*-nitroaniline and *m*-nitrophenol the persistence of the absorption band is much less than in the ortho- and para-compounds, and therefore there is not so much of the quinonoid form present with the meta-compound. No doubt in the ortho- and para-compounds the whole are in the quinonoid form because, in the case of the nitrophenols, no further change is produced after the addition of one equivalent of sodium ethoxide. An increase in the amount of the ethoxide does not increase the amount of quinonoid form; it can be concluded that the quinonoid and phenolic forms are not in a state of dynamic equilibrium, and that the whole of the molecules are quinonoid in structure. On the other hand, the meta-compound is not wholly quinonoid. We can only assume therefore, that as no change is produced by a further addition of sodium ethoxide, there is some restraining influence acting against the formation of the quinonoid form.

The space formula proposed by Collie (Trans., 1897, 71, 1013) had the advantage of representing the benzene molecule as a system of atoms in a state of continual vibration, and by this means it was possible to express all the various formulæ which had then been put forward as phases of one formula. We consider that this idea of a system in motion is extremely important, and we wish to emphasise its value by certain considerations which will now be dealt with; but at the same time it is evident that vibrations of the atoms not expressly described in Collie's original paper must be introduced in order to bring the theory into line with the spectroscopic and chemical evidence now at our disposal. These new motions will now be described.

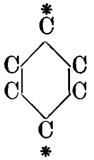
Now it has been shown (Baly and Collie, *loc. cit.*) that benzene shows seven very similar and closely-situated absorption bands, and it was pointed out that the formation of these can be accounted for by assuming that each band is due to a separate making and breaking of linking between the carbon atoms of the ring. There are seven such makings and breakings possible, as can be seen from the following figures, the asterisks being attached to those atoms which are changing their linking:



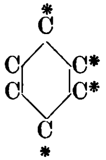
(1.)



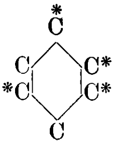
(2.)



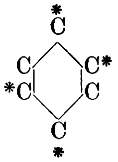
(3.)



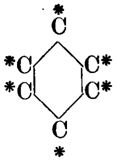
(4.)



(5.)



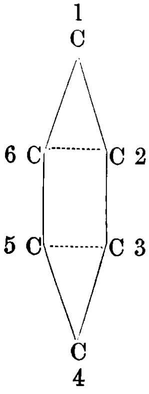
(6.)



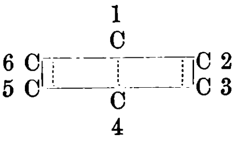
(7.)

It will be seen that in case (2) a single meta-linking is being formed or broken; this throws some light on the possibility of the existence of meta-quinones.

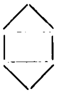
Now in order to bring the seven phases into existence, it is necessary to assume the displacement of the carbon atoms of the ring, and we can do this in the simplest way possible, that is to say, by the ordinary vibration as is accepted by any elastic ring. Thus we may say that the benzene ring is pulsating between the two displaced forms *a* and *b*.

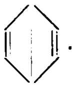


a.



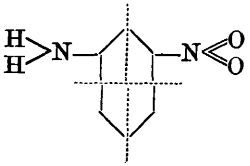
b.

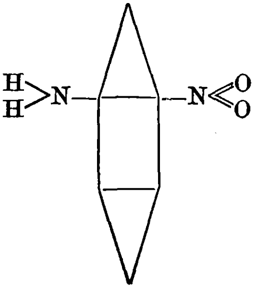

a′.


b′.

Each carbon has residual affinity, and consequently in the condition represented in *a*, when the atoms 2 and 6 and the atoms 3 and 5 are brought close together, these residual affinities will produce linkings as shown by the dotted lines. The atoms 1 and 4, however, are far removed from one another and from the other atoms, and are therefore unsaturated. On the other hand, when the ring has passed into the other phase *b*, then the three atoms 2, 1, and 6 come very close to the three atoms 3, 4, and 5 respectively, and linking may be considered to be formed between these pairs of atoms. The linkings existing in phases *a* and *b* are shown for greater convenience on the ordinary hexagons in *a′* and *b′*. As the ring is pulsating between the forms *a* and *b*, many of the seven phases of linking change described above will be obtained. For example, let us consider the ring to have reached the form *b*; as it starts opening, the first break will occur between the atoms 1 and 4, followed by the breaking of the two ortho-linkings 2 : 3 and 5 : 6. When the ring passes through the half-way stage, that is, the circular form, then we shall have the centric formula, with the result that phase No. 7 is produced. We can in this way account for phases 1, 2, 3, 6, and 7; Nos. 4 and 5 can readily be understood if the motions described above are slightly interfered with by collisions between adjacent molecules. In the above it was assumed that the displacement takes place so that the atoms 1 and 4 are at the ends of the ellipse in the form *a*, but in general the displacement can take place along any of the three possible axes

This scheme of displacement of the benzene ring renders it perfectly possible for meta-quinones to have a transitory existence; let us take *m*-nitroaniline:

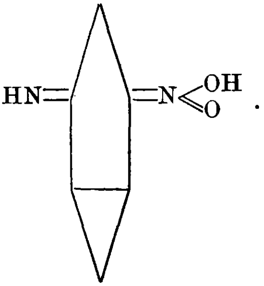




a.

and let the displacement take place along the dotted lines, when we shall obtain phase *a*. When in the form *a*, then the meta-quinone form can exist, thus:

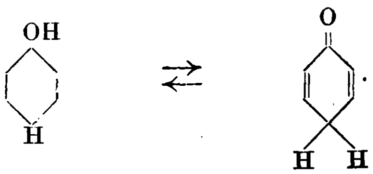
It must be remembered that this meta-quinone can only exist when the displacement occurs along the dotted lines shown on p. 525. It is not, therefore, necessary to conceive of the static existence of a meta-quinone, but it is clearly possible for such a linking to exist during part of the motions of the ring.



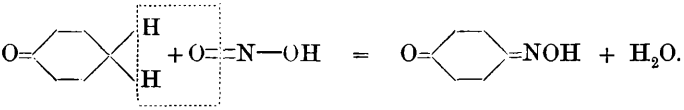
The results obtained with *m*-nitroaniline and with *m*-nitrophenol in alkaline solution show that only a portion of the substance exists in the quinonoid form. Doubtless the persistence of the absorption bands compared with those of the ortho- and para-compounds will give a measure of the relative number of molecules possessing the quinonoid form, that is to say, the number of molecules vibrating or pulsating in the special way described above. Inasmuch as a special form of vibration is necessary in order that the meta-quinone may exist, we may say that in this fact is to be found the undoubted restraining influence against the formation of the meta-quinone referred to above. In this way we may account for the much greater ease with which *m*-nitroaniline is decolorised by hydrochloric acid. On these grounds, therefore, we conclude that all three of the nitroanilines and the three nitrophenols in alkaline solution exist in the quinonoid form, and that isorropesis then occurs between the two nitrogen atoms or the nitrogen and oxygen atoms, with the result that an absorption band is formed in the visible region and the substance is coloured.

It may be pointed out that the pulsation of the benzene ring is able to explain very satisfactorily many of the characteristic reactions and properties of benzene and its derivatives. Four of the most striking may be very briefly indicated :

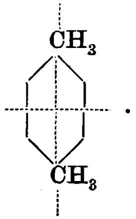
1. It is at once apparent that the carbon atoms in the para-position came very near to one another during the vibration, so that the wandering of atoms or groups of atoms from one carbon atom to that in the para-position is easy of explanation. Furthermore, it has been shown that phenol is a labile substance possessing keto-enol tautomerism (Baly and Ewbank, Trans., 1905, 87, 134). On account of the near approach of the para-carbon atoms, we should expect the phenolic hydrogen to wander to the para-position, thus:



The action of nitrous acid on phenol is then easily understood, thus:

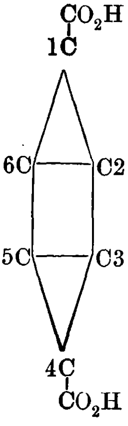


2. The absorption spectra of the disubstituted benzenes show that the para-compound is always more symmetrical than the two isomerides; that is to say, the internal motions of the benzene ring are less disturbed by the para- than by either the ortho- or meta-substitution (Baly and Ewbank, Trans., 1905, **87**, 1355). This fact is clearly accounted for by the theory of a pulsating ring, because it is evident that in a compound such as *p*-xylene the vibration will take place very readily along the dotted axes shown in *a*:



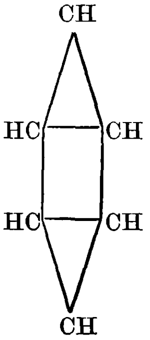
In the ortho- and meta-compounds the unsymmetrical loading of the ring will to a great extent militate against the vibration of the ring. Further, the meta-substitution will disturb the vibration more than the ortho-substitution.

3. The reduction of the phthalic acids is equally easy of explanation. In terephthalic acid, the vibration is less disturbed than in the case of the ortho- and meta-isomerides. Terephthalic acid must therefore exist to a considerable extent in the phase represented by the following formula. In this phase, the carbon atoms 1 and 4, being far removed from the other atoms of the ring, are unsaturated, with the result that they will each take up a hydrogen atom with ease, with the formation of $\Delta^{2:5}$-dihydroterephthalic acid. Similarly, the reduction of phthalic acid, although with greater difficulty, to $\Delta^{3:5}$-dihydrophthalic acid is explained. Lastly, in the case of *iso*phthalic acid, the motions are very greatly interfered with by the meta-substitution, so that it is doubtful if any of the carbon atoms in the ring reach the unsaturated position readily; *iso*phthalic acid is only reduced with difficulty by nascent hydrogen (Perkin and Pickles, Trans., 1905, **87**, 293), and tetrahydro-acids only are produced.

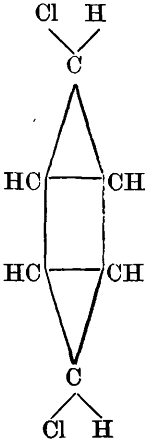


4. In the chlorination of benzene, the formation of the *p*-dichloro-compound, to the exclusion of the ortho-

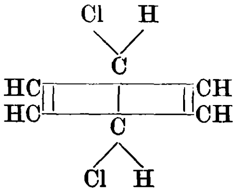
isomeride, is explained. When the benzene ring exists in phase *a*, the two carbon atoms at the end of the ellipse are unsaturated and take up chlorine, giving the compound shown in *b*. When the opposite



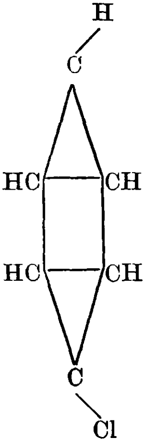
a.



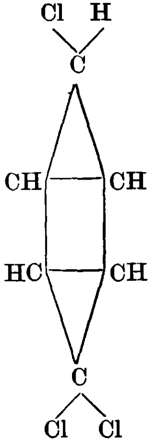
b.



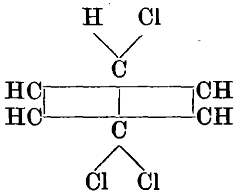
c.



d.



e.



f.

extreme is reached, as in *c*, a molecule of hydrogen chloride is split off, giving chlorobenzene. This, on reaching the first position, as in *d*, again takes up two atoms of chlorine, as in *e*; this additive compound, on reaching the form shown in *f*, again loses a molecule of hydrogen chloride and gives *p*-dichlorobenzene. It will be seen that by these motions of the ring there is no opportunity of the ortho-compound being formed, and in actual experiment none is produced.

Many other examples might be quoted in which the reactions of benzene and its compounds can be at once explained by this conception of the pulsation of the ring. For example, it has been shown (Baly and Collie, Trans., 1905, **87**, 1332) that in nitrobenzene the tautomerism of benzene on the motions of the ring has been stopped, doubtless owing to the attraction of the residual affinities of the oxygens of the NO_2 group. In the chloronitrobenzenes, therefore, there is little or no benzenoid motion, and thus these compounds approximate to the fatty type. It can be thus understood how the chlorine is replaced by hydroxyl on heating with sodium hydroxide.

A strong point in favour of this theory is its simplicity. The motion described is the simplest possible, and is the form of vibration adopted by any elastic ring, as, for example, a bell when struck.

The compounds the absorption spectra of which are described in this paper were all most carefully recrystallised and were undoubtedly pure. The *p*-nitrosophenol and nitrosobenzene were prepared with the greatest care; it is difficult to account for the difference in our observations of the absorption of the *p*-nitrosophenol and those recorded by Hartley, Dobbie, and Lauder.

Conclusions.

The following conclusions may be drawn from these observations:

1. The three nitroanilines in neutral solution and the three nitrophenols and *p*-nitrosophenol in alkaline solution exist in the quinonoid form.
2. The process of isorropesis then exists between the two nitrogen atoms in the case of the nitroanilines and between the nitrogen and oxygen atoms in the case of the nitrophenols and *p*-nitrosophenol. This process is the origin of the colour of these substances.
3. It is necessary to assume the transitory existence of a meta-quinonoid linking to account for the phenomena observed with *m*-nitroaniline and *m*-nitrophenol.
4. Many of the physical properties of benzene are explained by considering that the ring is elastic and undergoes the same vibrations as are suffered by any elastic ring.
5. The meta-quinone linking is possible during one phase of this displacement of the benzene ring.
6. This simple vibration of the benzene ring accounts for very many of the characteristic reactions and properties of benzene and its compounds—for example, the preparation of *p*-nitrosophenol by the action of nitrous acid on phenol, the production of only the *p*-dichloro-compound in the chlorination of benzene, the reduction of the phthalic acids, and also the absorption spectra of the three isomerides in the case of the disubstituted benzenes.

We have again to thank Professor Collie for the great interest he has taken in these experiments and to express our indebtedness to the Chemical Society for a grant in aid of the work.

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THE ADDITION OF SODIUM HYDROGEN SULPHITE TO KETONIC COMPOUNDS.

BY

ALFRED WALTER STEWART, B.Sc., 1851 Exhibition Scholar
of the University of Glasgow.

From the Transactions of the Chemical Society, 1905. Vol. 87

XXII.—*The Addition of Sodium Hydrogen Sulphite to Ketonic Compounds.*

By ALFRED WALTER STEWART, B.Sc., 1851 Exhibition Scholar of the University of Glasgow.

BEILSTEIN, in his *Handbuch* (3rd Edition, vol. I., 999), states that pinacoline forms no additive product with sodium hydrogen sulphite. This statement, together with the current idea that bisulphite compounds are formed only with those ketones which contain an acetyl group, suggested that the hindrance to the formation of a pinacoline bisulphite compound was of a stereochemical character, analogous to that detected by Victor Meyer in his work on the rates of esterification of the aromatic acids. In the literature of the bisulphite compounds, the only reference found was a paper by Angeli (*Atti R. Accad. Lincei*, 1896, **5**, 84), in which he suggested that steric hindrance played a part in the reactions involving the addition of metallic hydrogen sulphites, hydrocyanic acid, and ammonia to carbonyl groups. Angeli appears to have contented himself with this theoretical observation, at least so far as the bisulphite compounds are concerned; and apparently no attempt has been made up to the present to treat the matter by a quantitative method.

The following research was carried out in order to estimate the relative amounts of bisulphite compound formed with different ketones and with a view to ascertaining the hindering effect produced by various groups.

Although no work had been done on the ketonic bisulphite compounds, Ripper (*Monatsh.*, 1900, **21**, 1079) had devised a method for the estimation of aldehydes which depended on the formation of a bisulphite additive product. He found that as the SO_3Na group in the bisulphite compound was not oxidised by iodine solution; the amount formed could be estimated from the difference between the titration values of two solutions: one of pure sodium hydrogen sulphite, the other containing this salt and the aldehyde.

The great difficulty encountered in this method arises from the presence in the solution of hydriodic acid generated by the reaction. This acid, if left free, tends to break up the bisulphite compound, and thus gives an uncertain end-point.

With a view to avoiding this, several other solutions were prepared, among which three only need be mentioned. First, *N*/20 caustic soda was used to titrate the sodium hydrogen sulphite, but the final slight excess of the alkali present decomposed the double compound even more rapidly than the hydriodic acid had done. The other two solutions were the result of an attempt to make the reaction follow the lines of the equations:

$$NaHSO_3 + 3NaHCO_3 + I_2 = Na_2SO_4 + 2NaI + 2H_2O + 3CO_2;$$
$$NaHSO_3 + 2NaHCO_3 + I_2 = NaHSO_4 + 2NaI + H_2O + 2CO_2$$

Iodine and sodium hydrogen carbonate were made up in a solution of the strength required by each equation, in the hope that, the free hydriodic acid being eliminated as soon as it was formed, the end-point would be unaffected. The results, however, were useless.

There being no other method available, a return was made to the titration with iodine solution. At first, alcoholic solutions of the ketones were used, but finally it was found best to make up an *N*/10 aqueous solution of the ketone, and then dilute to *N*/12 with alcohol. This mixture dissolved most of the common ketones, methyl hexyl ketone and acetophenone only being excluded.

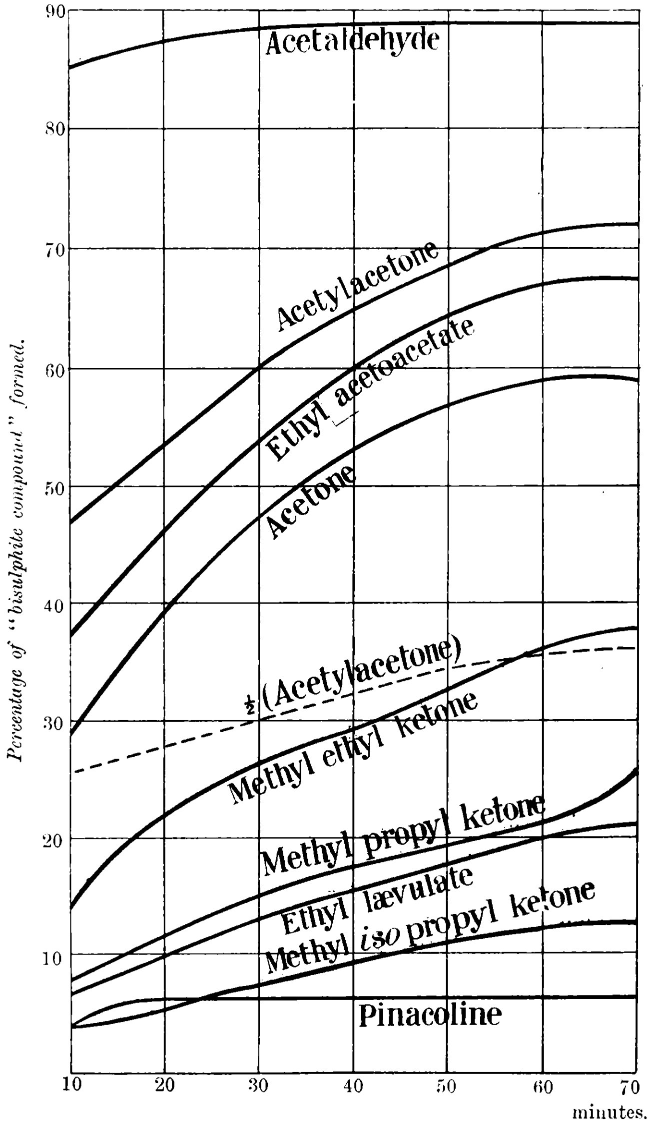
The results were apparently accurate to within one per cent. after allowing equal quantities of ketone and *N*/12 hydrogen sulphite solution to remain together for an hour at the ordinary temperature.

It did not seem desirable to choose an arbitrary time limit, and in the end titrations were done at regular intervals; a period of five minutes was first chosen, but this was not found so satisfactory as the ten-minute interval which was finally adopted. At first the method did not give concordant results, but the failure was traced to variations of temperature. After this, all operations were carried out at 0°, which kept the temperature constant, and also reduced the speed of the reaction.

The details of the method finally adopted were as follows: 50 c.c. of *N*/12 ketone solution, prepared as described, were shaken in a flask with 50 c.c. of *N*/12 aqueous sodium hydrogen sulphite, and then allowed to remain, corked, in a vessel of ice and water. Every ten minutes, 10 c.c. of the liquid were taken out and titrated, being kept surrounded by ice-water during the operation. The iodine solution used was of such a strength that 14—15 c.c. were required to oxidise 5 c.c. of the hydrogen sulphite solution. The relative strengths of the two solutions were determined at the beginning and end of each series of titrations. The results obtained are shown in the following table:

	Percentage of bisulphite compound formed in						
	10	20	30	40	50	60	70 minutes.
Acetaldehyde	85·2	86·6	88·0	88·7	88·7	88·7	88·7
Acetylacetone	47·1	54·2	60·5	64·0	67·6	70·0	71·8
Ethyl acetoacetate	37·4	47·0	56·0	60·0	64·0	67·6	67·6
Acetone	28·5	39·7	47·0	53·6	55·9	56·2	58·9
Methyl ethyl ketone	14·5	22·5	25·1	29·1	32·4	36·4	38·4
Methyl propyl ketone	8·5	11·0	14·8	18·4	19·6	23·4	25·5
Ethyl lævulate	7·2	10·0	14·0	15·0	16·5	19·4	21·6
Methyl *iso*propyl ketone	4·2	5·4	7·5	9·4	11·6	12·3	13·0
Pinacoline	4·2	5·6	5·6	5·6	5·6	5·6	5·6

The following curves give the same results graphically.



Acetylacetone contains two carbonyl groups therefore the amount of bisulphite compound formed by each group is half the amount shown in the table. This is represented in the curves by the dotted line.

From an examination of the foregoing numbers, the effect of replacing a hydrogen atom by a methyl group is easily seen. If we consider acetaldehyde, acetone, methyl ethyl ketone, methyl *iso*propyl ketone, and pinacoline, and take the percentage of bisulphite compound formed after 40 minutes, we find the following result:

	Per cent.		Per cent.
$CH_3CO{\cdot}H$	88·7	$CH_3CO{\cdot}CH(CH_3)_2$ ...	9·4
$CH_3CO{\cdot}CH_3$	53·6	$CH_3CO{\cdot}C(CH_3)_3$	5·6
$CH_3CO{\cdot}CH_2{\cdot}CH_3$	29·1		

Another point of interest is that both acetaldehyde and pinacoline appear to reach their end-points within the first 40 minutes, whilst the other compounds, intermediate on the scale, do not reach their equilibrium until after 70 minutes.

A curious result is obtained by comparing the values of those compounds containing carbon chains of the same length. For example, ethyl acetoacetate and methyl ethyl ketone each contain a chain of four carbon atoms; ethyl lævulate and methyl propyl ketone have a chain of five. Taking, as before, the percentage of bisulphite compound formed after 40 minutes, we get:

	Per cent.		Per cent.
Ethyl acetoacetate ...	60·0	Methyl propyl ketone.	18·4
Methyl ethyl ketone ..	29·1	Ethyl lævulate	15·0

The carboxyl group seems to have no hindering effect, but rather accelerates the action, since ethyl acetoacetate forms more bisulphite compound than acetone, and much more than methyl ethyl ketone where the CO_2Et group is replaced by methyl. This relation does not hold good in the case of ethyl lævulate, for in this case, when compared with methyl propyl ketone, the ester forms less of the double compound. It seems as if the carbonyl and carboxyl groups had some action on each other's properties when near to one another, and that this is weakened when two carbon atoms are placed between them.

This communication has been limited to those compounds which contain the group $CH_3{\cdot}COR$, but the investigation will subsequently be extended to other ketonic and nitrogen compounds, both with open and closed chains.

In conclusion, the author desires to thank Professor Collie and Dr. Smiles for valuable suggestions made by them during the course of this research.

UNIVERSITY COLLEGE,
LONDON.

R. CLAY AND SONS, LTD., BREAD ST. HILL E.C., AND BUNGAY, SUFFOLK.

THE VELOCITY OF OXIME FORMATION IN CERTAIN KETONES.

BY

ALFRED WALTER STEWART, B.Sc., 1851 Exhibition Scholar
of the University of Glasgow.

From the Transactions of the Chemical Society, 1905. Vol. 87.

LI.—*The Velocity of Oxime Formation in Certain Ketones.*

By Alfred Walter Stewart, B.Sc., 1851 Exhibition Scholar of the University of Glasgow.

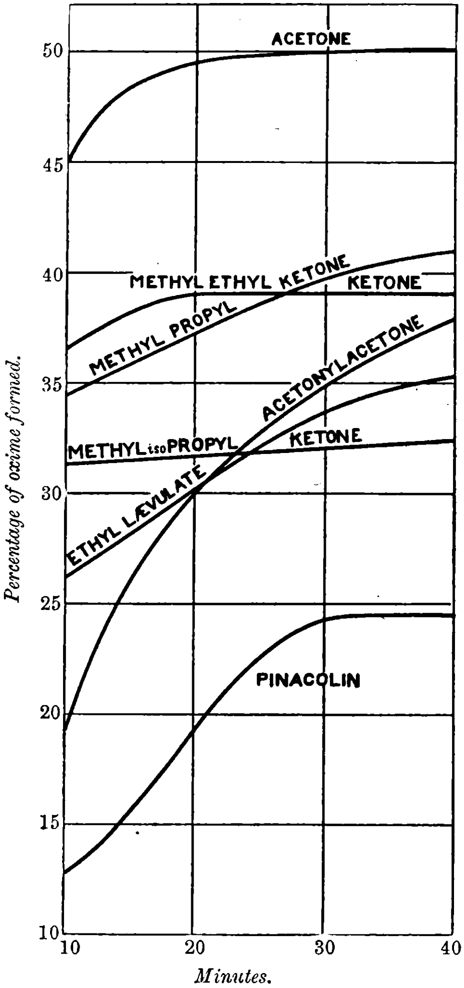
The hindering influence produced by the introduction of various groups into ketonic compounds has been already studied by the author in the case of the additive products formed with sodium hydrogen sulphite (Trans., 1905, **87**, 185), and it seemed desirable to apply a somewhat similar method to the case of oxime formation, with the view of finding whether steric hindrance was actually the chief factor in the problem. If the rates of formation of the oximes of various ketones showed the same relations to each other as those found in the case of the "bisulphite" compounds, the probability that steric hindrance played a great part in the reaction would be increased, since chemically the reactions are quite different in character.

The simplest method of estimating the percentage of oxime formed in a given case seemed to be to determine the amounts of free hydroxylamine present in a solution both before and after the reaction has lasted for a fixed interval of time.

Several series of experiments were carried out before a satisfactory process was discovered. At first an indirect method was tried: a fixed excess of ferric sulphate was boiled with the oxime solution in an atmosphere of carbon dioxide, and the amount of ferrous sulphate thus formed was estimated by titration with potassium permanganate. This did not give concordant results, nor did direct titration of the unchanged hydroxylamine, either with Fehling's solution or with a solution of potassium nitrite.

In the end the following mode of estimation, adapted from a method of estimating hydroxylamine described by Meyeringh (*Ber.*, 1877, **10**, 1940), was found to be the best. In order to obtain results comparable with those already found in the case of the "bisulphite" compounds, $N/10$ aqueous solutions of the ketones were diluted with alcohol to $N/12$. Fifty c.c. of the ketone solution were mixed with an equal volume of $N/12$ hydroxylamine sulphate solution, and the mixture was left in ice. Every ten minutes, 10 c.c. were withdrawn, to which were added 20 c.c. of $N/5$ iodine solution and 20 c.c. of $N/5$ disodium hydrogen phosphate solution; the whole was placed on a water-bath for one minute, and the excess of iodine remaining was then titrated with sodium thiosulphate in the usual way.

The rationale of the method is as follows. The ketone, in forming an oxime, uses up a certain quantity of hydroxylamine; the remaining hydroxylamine is decomposed by warming with the iodine solution, and the hydriodic acid thus produced is taken up by the sodium phosphate before it affects the oxime; the amount of iodine left unchanged is then estimated by means of the thiosulphate titration, and from it the amount of hydroxylamine employed in oxime formation can be deduced. This method was found to be sufficiently accurate, the results being concordant to within one per cent., which is sufficiently close for the purpose in view. It fails, however, when employed with aldehydes, owing to their ready oxidation; and also in the case of compounds containing the group $-CO{\cdot}CH_2{\cdot}CO-$ which react with iodine on warming.



The results obtained are shown in the table and curves. In the case of acetonylacetone, twice the usual quantity of the hydroxylamine solution was used, and the results given show the percentage of oxime formed at each carbonyl group.

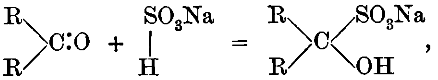
	10	20	30	40 minutes.	
Acetone	45·1	49·7	50·0	50·1	percentage of oxime
Methyl ethyl ketone ...	36·6	39·2	39·2	39·2	,, ,,
,, propyl ,, ...	34·7	37·3	39·9	41·2	,, ,,
,, *iso*propyl ketone	31·4	31·5	32·0	32·0	,, ,,
Ethyl lævulate	26·1	30·0	33·9	35·0	,, ,,
Acetonylacetone	19·0	30·0	35·0	39·0	,, ,,
Pinacolin	12·9	17·0	24·5	24·5	,, :

On the whole, the foregoing results appear to support those already obtained as to the influence of the methyl group when it is substituted for a hydrogen atom near the carbonyl group. During the first ten minutes of all the reactions, the only divergence from the relations determined in the case of the "bisulphite" compounds is to be found with ethyl lævulate, the velocity of the "bisulphite" reaction of which lay between those of methyl propyl and methyl *iso*propyl ketones, whilst in the foregoing table it has a lower rate of reaction than methyl *iso*propyl ketone. Apart from this instance, the same influences appear to govern the courses of both reactions. If the percentages of oxime formed by acetone, methyl ethyl ketone, methyl *iso*propyl ketone, and pinacolin at the end of twenty minutes are considered, the following numbers are obtained:

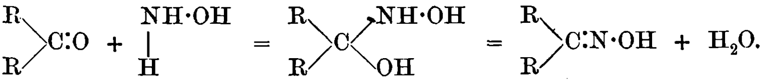
$CH_3{\cdot}CO{\cdot}CH_3$	49·7 per cent.	$CH_3{\cdot}CO{\cdot}CH(CH_3)_2$......	31·5 per cent.
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3$......	39·2 "	$CH_3{\cdot}CO{\cdot}C(CH_3)_3$	17·0 "

It will be noticed that the velocity of the reaction in the case of methyl ethyl ketone appears to undergo retardation after twenty minutes, causing the percentage of oxime generated at the end of a forty-minute period to fall below that produced in the case of methyl *iso*propyl ketone.

The reaction of oxime formation appears to be, on the whole, more rapid than the addition of sodium hydrogen sulphite to the carbonyl group; a state of equilibrium is reached more speedily. This is to be expected when we take into account the nature of the reaction and the relative masses of the groups involved. In the case of the "bisulphite" compounds it is merely a question of adding on a bulky group:



whereas in the second instance a smaller group enters, and water is immediately eliminated:



The oximes appear to be better suited than the "bisulphite" compounds for estimations of the velocity of formation of additive compounds of ketones, when many methyl groups lie in the neighbourhood of the carbonyl. The oxime method has also a great advantage over the other, since in the titration of the "bisulphite" compounds a slow inverse action takes place, which does not occur in the case of the hydroxylamine estimation. This method might conceivably be useful in confirming the constitutions of cyclic carbonyl compounds containing many methyl groups.

In conclusion, the author wishes to thank Professor Collie and Dr. Smiles for assistance given during the above research.

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THE ORIGIN OF COLOR

E. C. C. BALY AND A. W. STEWART

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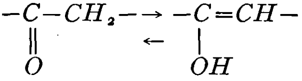
VOLUME XXIV OCTOBER 1906 NUMBER 3

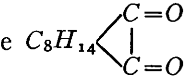
THE ORIGIN OF COLOR. I

By E. C. C. BALY and A. W. STEWART[1]

In the previous paper it was shown how the presence of two carbonyl groups in juxtaposition gives rise to the appearance of an absorption band in the spectrum very much nearer to the red than that which is produced by the process known as enol-keto tautomerism,[2] or a reversible equilibrium such as



$$\underset{\displaystyle O}{\underset{\|}{-C}}-CH_2- \overset{\longrightarrow}{\underset{\longleftarrow}{}} \underset{\displaystyle OH}{\underset{|}{-C}}=CH-$$

In the case of pyruvic ester $CH_3CO\ COOEt$, in which it was first discovered, the absorption band is situated at a frequency of 3100, while the band due to enol-keto tautomerism is always very near to 3800. Now, in pyruvic ester there is only one true carbonyl group, for it is well known that the $-CO-$ group of a carboxyl radicle is not endowed with all the properties usually appertaining to this group. In order to investigate this process more fully, we have examined the absorption spectra of a series of compounds which contain two true carbonyl groups in juxtaposition, and we then found that the new absorption band is still nearer to the red than in the case of pyruvic ester. Camphorquinone  was dealt with in the pre-

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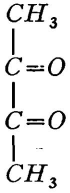
[1] Carnegie Research Fellow.

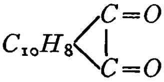
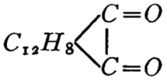
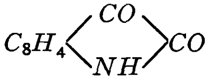
[2] Baly and Desch, *Astrophysical Journal*, 23, 110, 1906.

vious paper where its absorption curve was given; a very persistent absorption band is exhibited with its head at a frequency of 2100. The simplest compound of this type is of course diacetyl



$$\begin{array}{l} CH_3 \\ | \\ C=O \\ | \\ C=O \\ | \\ CH_3 \end{array}$$

and the absorption curve of this substance is shown in Fig. 1, where the new absorption band appears at a frequency of 2400. Since these two compounds, camphorquinone and diacetyl, show absorption bands in the visible blue (λ=4760 and 4170 t.-m. respectively), they are naturally colored yellow, and clearly therefore the process which produces these absorption bands is the origin of color in the case of these compounds.

In the previous paper we showed that the origin of the new absorption band is to be found in some form of oscillation between the residual affinities of the oxygen atoms of the carbonyl groups, and for this oscillation we proposed the name *isorropesis*. Before dealing with the theoretical aspect, we may say that we have extended our observations to include many other compounds containing two carbonyl groups in juxtaposition, and in every case we find the new absorption band present. For example, the absorption curves of acenaphthenequinone  $C_{10}H_8\left\langle\begin{array}{l} C=O \\ | \\ C=O \end{array}\right.$ and phenanthraquinone  $C_{12}H_8\left\langle\begin{array}{l} C=O \\ | \\ C=O \end{array}\right.$ are shown in Fig. 2; isatin, whose spectrum has already been recorded by Hartley and Dobbie,[1] is another case in point and shows the same absorption band with head at a frequency of 2400. The formula of isatin  $C_8H_4\left\langle\begin{array}{c} CO \\ \\ NH \end{array}\right\rangle CO$ at once explains the appearance of the band, as there are present two carbonyl groups in juxtaposition.

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[1] *Chem. Soc. Trans.*, 75, 640, 1899.

Another very interesting case of an α-diketone is that of benzil, $C_6H_5.CO.CO.C_6H_5$, the absorption-curve of which is shown in Fig. 3. It is well known that the oscillating double linking of the benzene ring, or the benzenoid tautomerism, produces absorption bands which have about the same frequency as the absorption band due to enol-keto tautomerism. In the case of benzene itself there

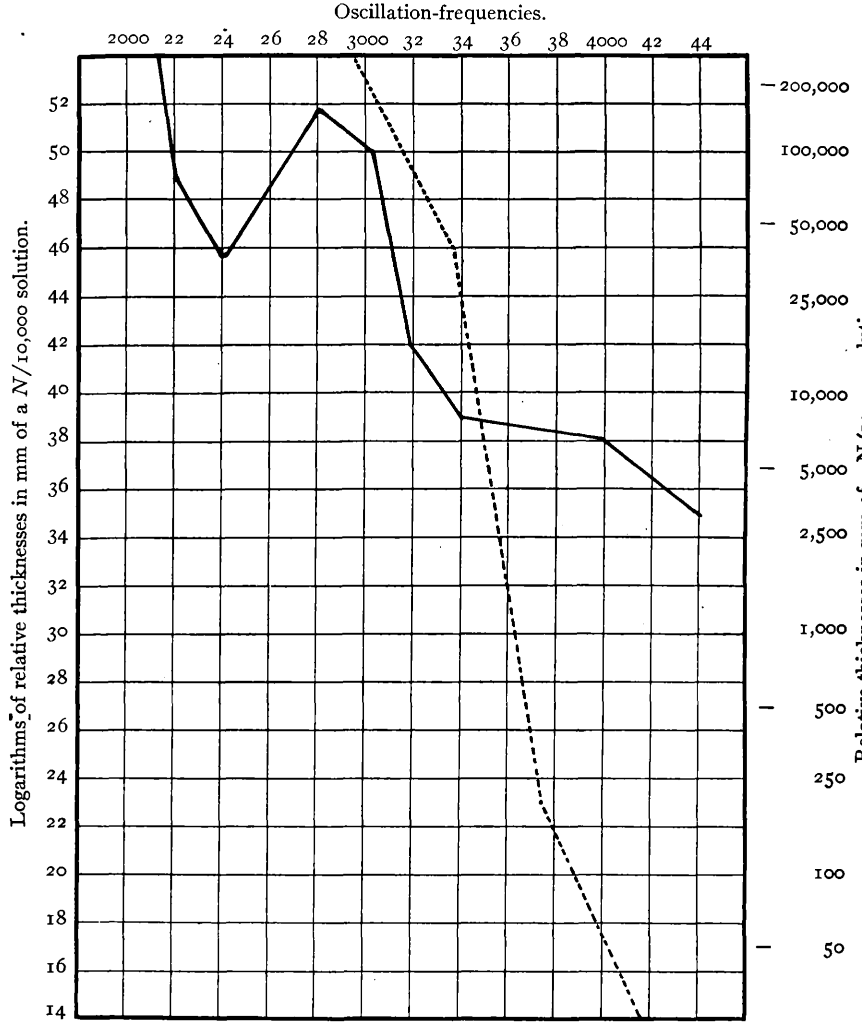

FIG. 1.—Diacetyl (full curve): Diacetyl dioxime (dotted curve).

are seven narrow absorption bands[1] with heads at frequencies of 3725, 3765, 3830, 3915, 4025, 4110, and 4200. These absorption bands are considerably modified by substituting different groups for the hydrogen atoms, especially if the substituent groups possess

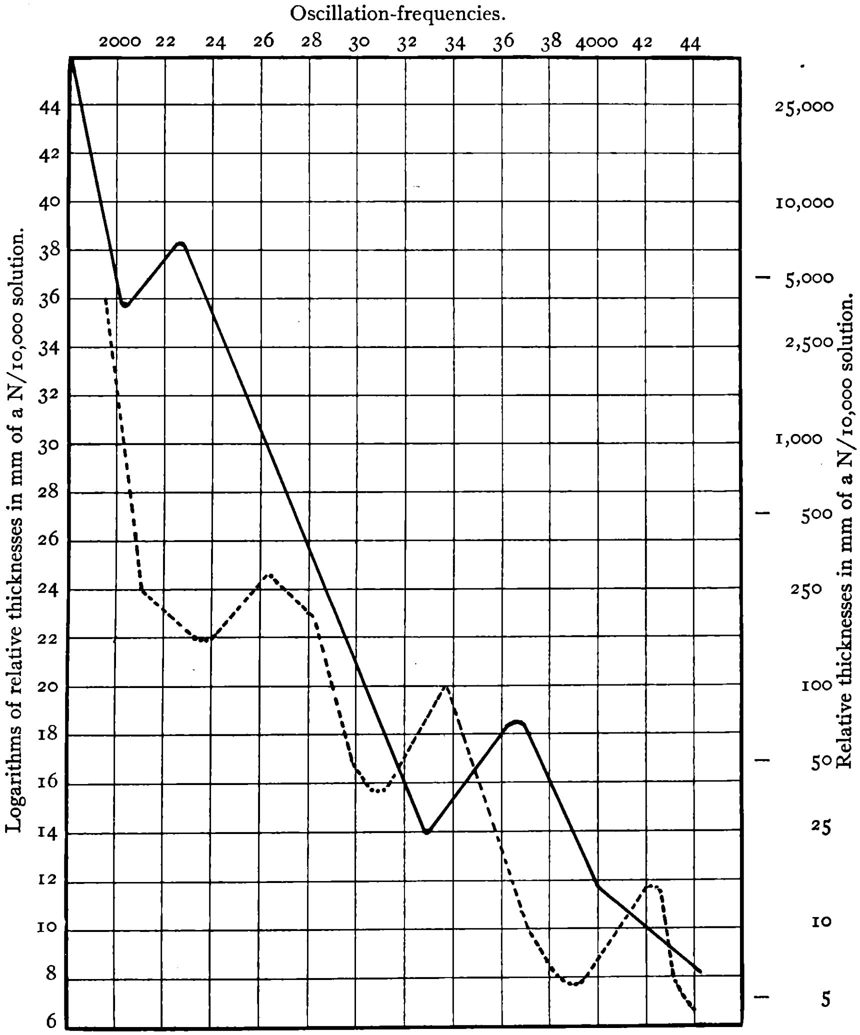

FIG. 2.—Acenaphthenequinone (full curve).
Phenanthraquinone (dotted curve).

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[1] Baly and Collie, *Ibid.*, **87**, 1332, 1905.

residual affinity. Thus acetophenone, $C_6H_5.CO.CH_3$, in which one hydrogen of benzene has been replaced by the acetyl group $—CO.CH_3$, shows an absorption very different from that of benzene.

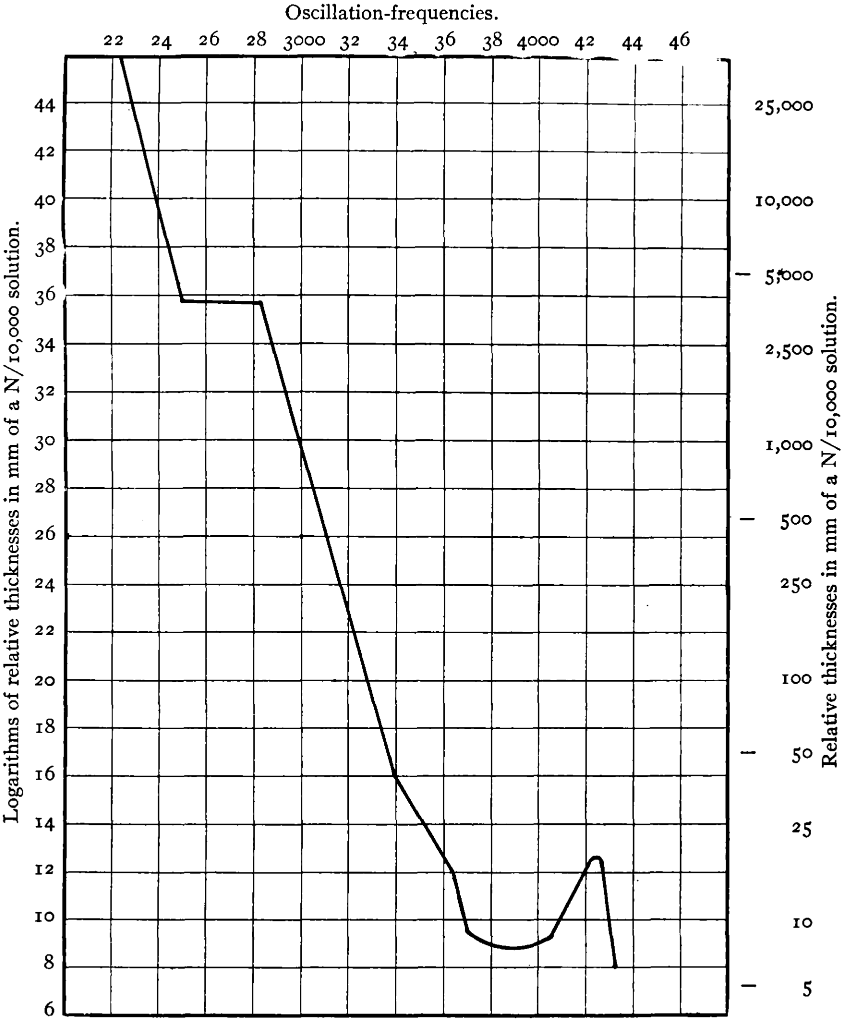
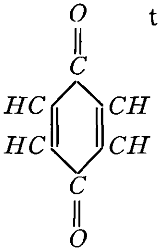
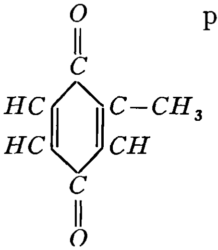
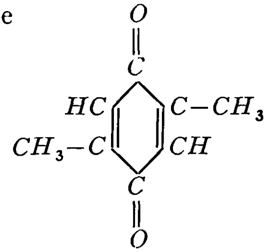
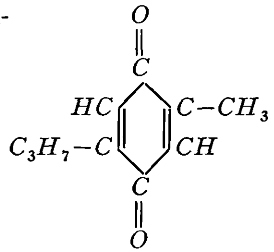
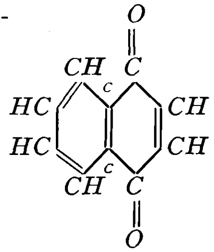
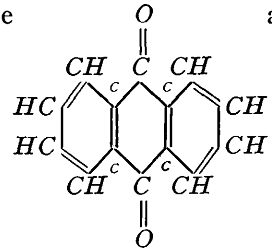
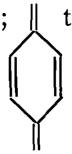
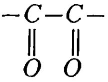


FIG. 3.—Benzil.

All the characteristic absorption due to the benzene ring has disappeared, owing no doubt to the fact that the residual affinity of the benzene ring has been fixed by the attraction between the carbonyl group and the atoms of the ring. This accounts for the fact that the carbonyl group of acetophenone is unusually inactive toward sodium bisulphite, etc., because the group does not readily pass into the nascent state necessary to the formation of additive compounds. It might be expected, therefore, that in benzil the residual affinities of the two carbonyl groups would each be occupied with and fixed by the adjacent benzene nucleus, and that therefore no isorropesis would occur. In reference, however, to the absorption-curve of this substance (Fig. 3) it will be seen that in the region of least concentration there is an absorption band with head at a frequency of 3900. The presence of this band argues that the benzenoid tautomerism is undoubtedly present to a small extent. For this reason we may conclude that the residual affinities of the carbonyl groups are not entirely fixed, and that a small amount of isorropesis between them is possible. It is evident that this conclusion is justified from an inspection of the upper portion of the absorption-curve of benzil, where a shallow band with head at a frequency of 2650 appears. The existence of this band shows that isorropesis is taking place, and its shallowness proves that it is present to a small extent only. It may be noticed that the yellow color of benzil is not very pronounced, and readily disappears in dilution. The measurements of the additive capacity of the benzil carbonyl groups made by Petrenko-Kritschenko agree very closely with the above observation.

There is thus little doubt that the color of the compounds, diacetyl, camphorquinone, acenaphthenequinone, phenanthraquinone, isatin, and benzil is due to the two carbonyl groups in juxtaposition, since this configuration gives rise to a new type of oscillation or isorropesis between the residual affinities upon the two adjacent oxygen atoms. The most striking application of this principle is in the case of the true benzenoid quinones, for in these compounds, which are all strongly colored, we have a type of compound resembling an α-diketone, and in these compounds, too, the new absorption band is exhibited showing the undoubted existence of the process of isorropesis between the quinonoid oxygen atoms. Quinone itself was dealt with in the preceding paper and its absorption-curve there reproduced. It may, however, be again emphasized that all the chemical evidence supports the view that the two para positions in the benzene ring are very close together, and that we should therefore expect the two $=CO$ groups of quinone  to have the same properties as those of an α-diketone. We have also examined the absorption spectra of toluquinone  para xyloquinone  thymoquinone  α naphthoquinone  and anthraquinone  and find that the same absorption band is present in each case. The absorption-curves of the two first compounds are reproduced in Figs. 4 and 5; the remaining compounds show very similar curves. There is no doubt therefore that the process of isorropesis exists in the quinones and is the origin of color of these compounds.

Now, Armstrong has developed a theory of color in which he attributes this property to the quinonoid linking;  the importance of these results in relation to his theory is manifest. They would seem to supply the key to his generalizations and at the same time to explain the colors of many substances which are difficult of interpretation by Armstrong's theory alone. Armstrong's theory gives no explanation of why color is produced by the quinonoid linking; there is no esoteric value in any of the linkings of the formula as light-absorbing centers. The results we have given, however, show that when the quinonoid configuration exists, isorropesis is set up between the residual affinities of the groups in the para position, with the result that an absorption band is developed in the visible region of the spectrum, producing a yellow or orange color.

In considering the whole question of color, there is no doubt that the new principle may be extended to include every case; that is to say, that isorropesis may occur between any adjacent atoms possessing residual affinity. It must be remembered, however, that in order for the new oscillation to take place, it is absolutely necessary for some exciting or disturbing influence to be present. For example, in the group  $-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$ of the α-diketones, each oxygen atom possesses a definite amount of residual affinity, and it is evident that no oscillation can arise between these atoms unless one or both residual affinities are disturbed. Now, in diacetyl, $CH_3-CO-CO-CH_3$, this influence is furnished by the hydrogen atoms of the methyl groups. There is an attraction between the hydrogen and oxygen atoms, with the result that the residual affinities on the latter tend to be altered. We have direct evidence of this potential enol-keto tautomerism in the absorption-curve of diacetyl (Fig. 1), for the curve shows a sudden extension at the ordinate 38. This extension undoubtedly means the incipient formation of an absorption band which occupies the position of the band due to the tautomerism of a labile hydrogen atom.[1] Clearly therefore the residual affinities of the two oxygen atoms are being slightly disturbed, and it is owing to this disturbance that the new oscillation or isorropesis takes place. We may now understand why diacetyl-dioxime is colorless

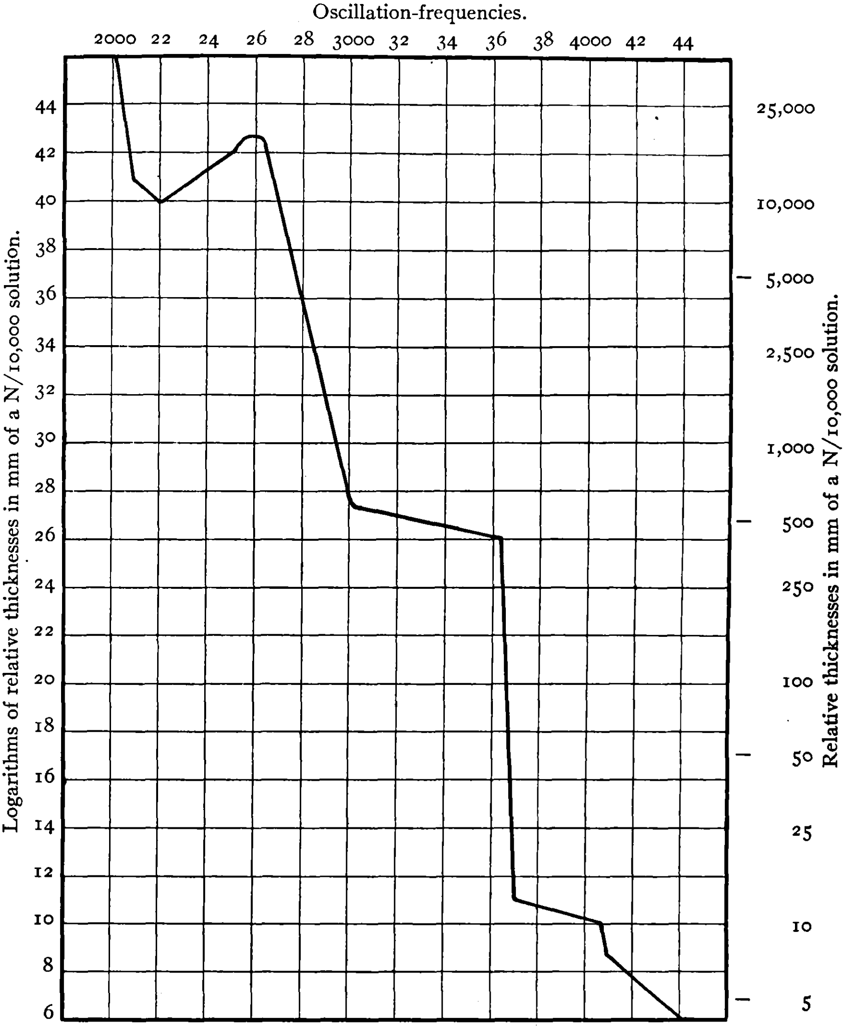


FIG. 4.—Toluquinone.

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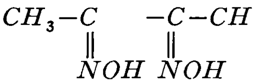
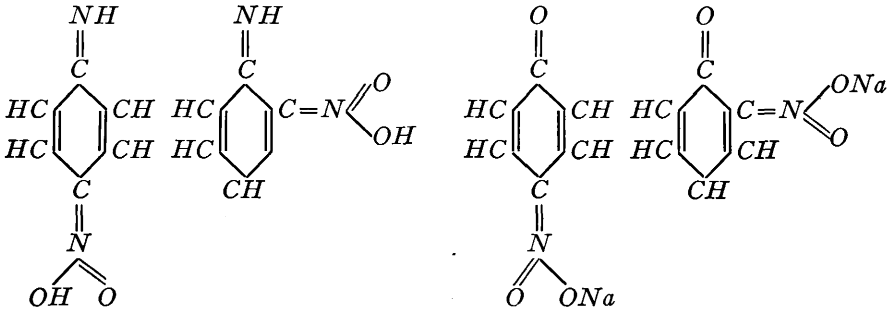
[1] Baly and Desch, *loc. cit.*



$CH_3-\underset{\underset{NOH}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3$, for in this compound we have apparently the condition for color, and yet only general absorption is exhibited. The residual affinity of the nitrogen atoms exerts no attraction on the hydrogen atoms of the methyl groups, and therefore is not disturbed in any way. No isorropesis therefore is set up and the compound is colorless. The absorption-curve of diacetyl-dioxime is shown in Fig. 1. It follows from this that all assumptions that two compounds must have essential differences in constitution if one is colored and the other white are untrustworthy.

It is evident that, if our generalizations upon color are correct—namely, that isorropesis occurs between the residual affinities of unsaturated atoms in juxtaposition, there is a large field for investigation among compounds of the quinonoid type in which the oxygen atoms of quinone are replaced by other unsaturated atoms. It should be noticed that in the quinones the necessary disturbing influence is provided by the tautomerism of the benzene ring, and that we are not entirely dependent upon the near presence of hydrogen atoms.[1] We have investigated the nitroanilines and the nitrophenols, in which unsaturated nitrogen atoms are present.[2] The color of the former and of the latter in alkaline solution has been accounted for by Armstrong on the assumption that they exist in the quinonoid form thus



para- ortho-
nitroaniline

para- ortho-
nitrophenol (sodium salt)

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[1] Stewart and Baly, *Chem. Soc. Trans.*, **89**, 618, 1906.

[2] Baly, Edwards and Stewart, *Ibid.*, **89**, 514, 1906.

Considerable difficulty was met with by Armstrong in the case of the meta compounds, because it is impossible to imagine the static

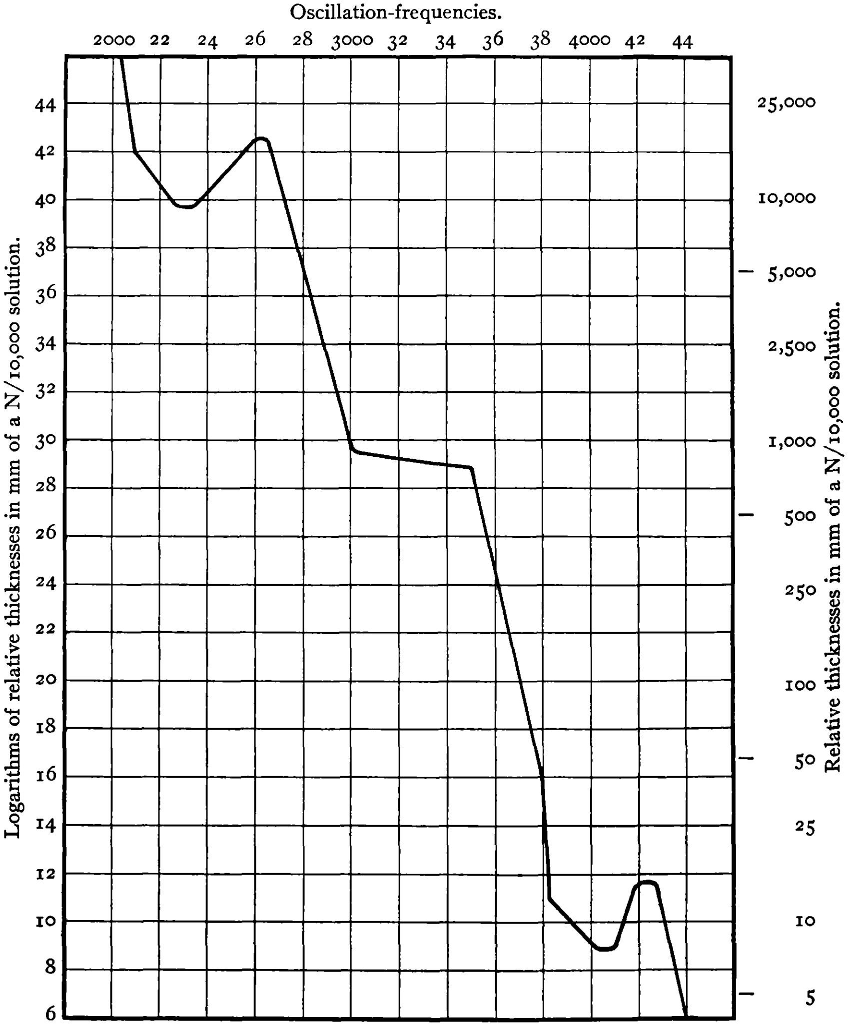
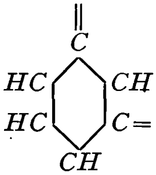
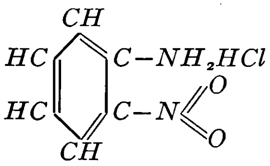


FIG. 5.—Para-xyloquinone.

existence of a linking of this type, as can readily be seen from the formula, there being no satisfactory way of linking the four remaining carbon atoms of the ring,



In Fig. 6 are reproduced the curves of meta- and paranitroaniline, and they show the presence of the absorption band due to isorropesis; this band has, however, much less persistence in the case of the meta compound. The absorption of the ortho compound is practically identical with that of the para derivative. Now, these substances all give colorless solutions in the presence of strong hydrochloric acid; the absorption of these solutions is the same in each case and is exemplified by the curve in Fig. 7. There is no doubt from this that in the presence of hydrochloric acid the compounds possess the structure of the true hydrochloride, e. g.:



and that in neutral solution they possess the quinonoid form as given above. Isorropesis therefore occurs in these compounds between two unsaturated nitrogen atoms. Similarly, it has been proved that isorropesis occurs between the unsaturated nitrogen and oxygen atoms in the quinonoid forms of the nitrophenols. In these latter compounds, as in the case of the nitroanilines, the isorropesis is very much less in the meta than in the ortho and para isomers, showing that the metaquinonoid form undoubtedly exists, but only to a small extent. It is evident, therefore, that some restraining influence is at work against the formation of the meta-quinone. It was stated above that the static existence of a meta-quinone is impossible, but we have in these compounds undoubted evidence of the meta-quinone existing in proportionately small amounts; we may conclude, therefore, that this form has not a static but only a transitory existence. This may be explained as follows.

The space-formula proposed by Collie[1] has the advantage of representing the benzene molecule as a system of atoms in a state of continual vibration, and by this means it was possible to express all the various formulae which had then been put forward as phases

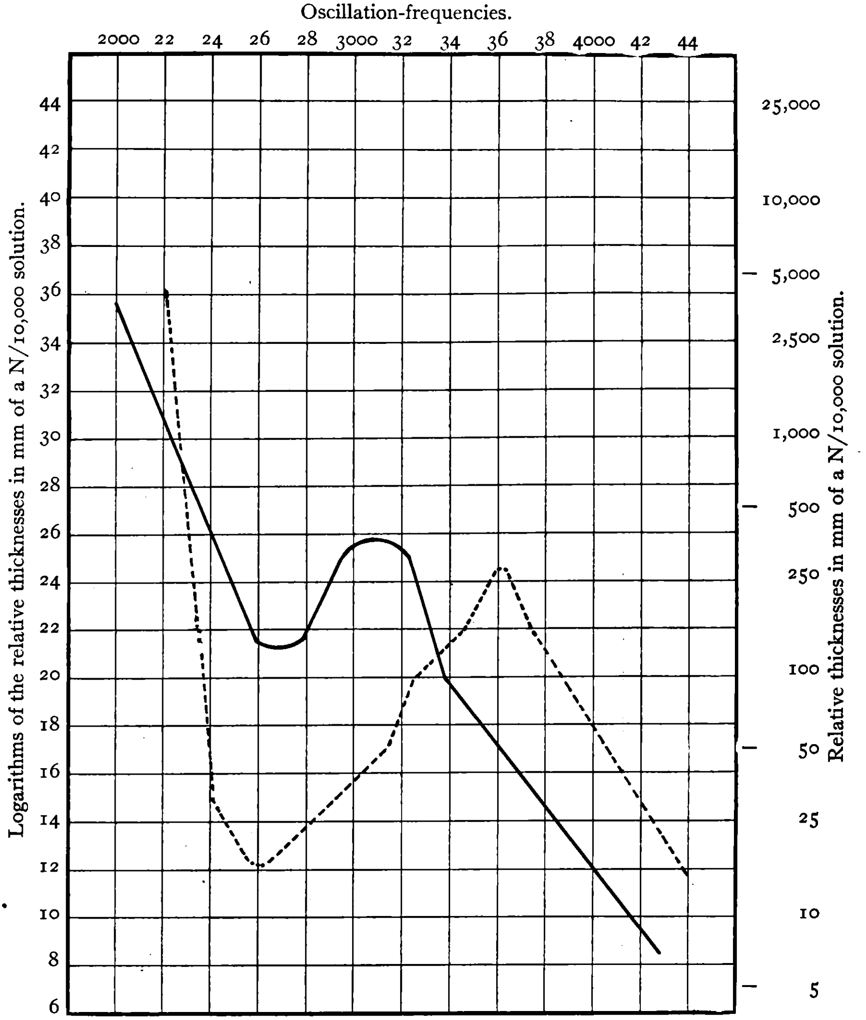


FIG. 6.—Meta-nitroaniline (full curve); Para-nitroaniline (dotted curve).

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[1] *Chem. Soc. Trans.*, 71, 1013, 1897.

of one formula. We consider that this idea of a system in motion is extremely important, but at the same time it is evident that vibrations of the atoms not expressly described in Collie's original paper must be introduced in order to bring the theory into line with the spectroscopic and chemical evidence now at our disposal. It has been shown[1] that benzene gives seven very similar and closely situ-

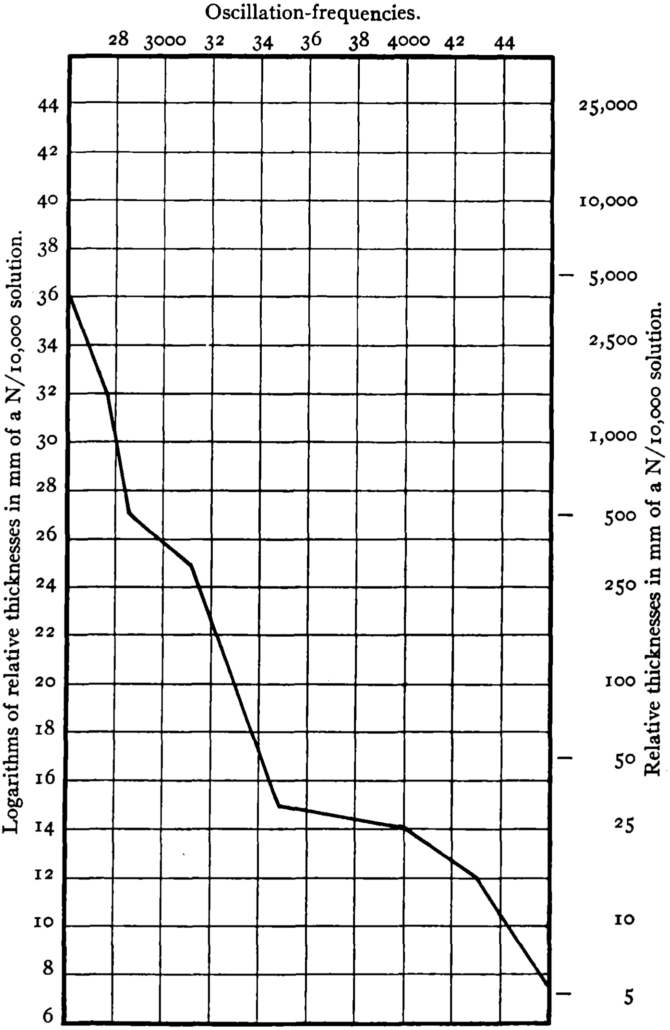

FIG. 7.—Ortho-nitroaniline in hydrochloric acid.

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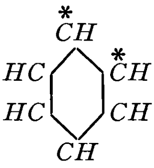
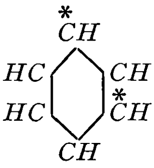
[1] Baly and Collie, *loc. cit.*

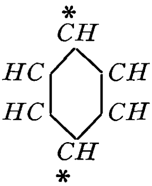
ated absorption bands, and it was pointed out that the formation of these can be accounted for by assuming that each band is due to a separate make-and-break of linking between the carbon atoms of the ring. There are seven such makes and breaks possible, as can be seen from the following figures, the asterisks being attached to those atoms which are changing their linking:



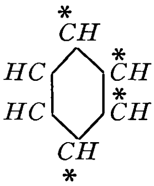
(1)



(2)



(3)



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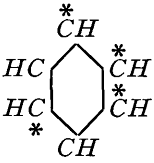

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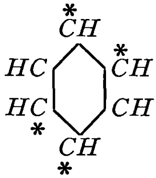
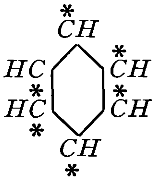


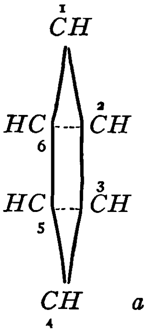
(6)



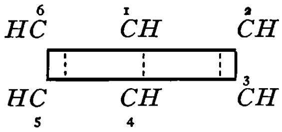
(7)

It will be seen that in case (2) a single meta-linking is being formed or broken; this throws some light on the possibility of the existence of meta-quinones.

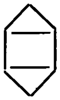
Now, in order to bring the seven phases into existence, it is necessary to assume the displacement of the carbon atoms of the ring, and we can do this in the simplest way possible—that is to say, by the ordinary vibration as is accepted by any elastic ring. Thus we may say that the benzene ring is pulsating between the two displaced forms *a* and *b*



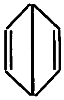
a



b



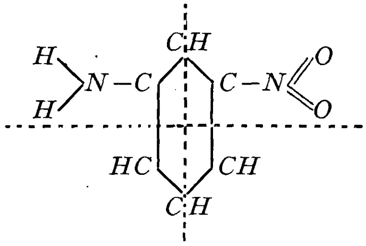
a′

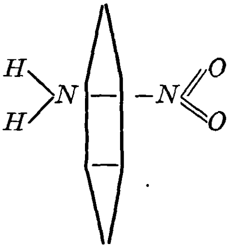


b′

Each carbon atom possesses residual affinity, and consequently in the condition represented in *a*, when the atoms 2 and 6 and the atoms 3 and 5 are brought close together, these residual affinities will produce linkings as shown by the dotted lines. The atoms 1 and 4, however, are far removed from one another and from the other atoms, and are therefore unsaturated. On the other hand, when the ring has passed into the other phase *b*, then the three atoms 2, 1, and 6 come very close to the three atoms 3, 4, and 5 respectively, and linking may be considered to be formed between these pairs of atoms. The linkings existing in phases *a* and *b* are shown for greater convenience on the ordinary hexagons in *a′* and *b′*. As the ring is pulsating between the forms *a* and *b*, many of the seven phases of linking-change described above will be obtained. For example, let us consider the ring to have reached the form *b;* as it starts opening, the first break will occur between the atoms 1 and 4, giving phase No. 3. This will be followed by the breaking of the two ortho-linkings 2:3 and 5:6, giving phases Nos. 3 and 6. When the ring passes through the half-way stage—that is, the circular form—then we shall have the centric formula, with the result that phase No. 7 is produced. We can in this way account for phases 1, 2, 3, 6, and 7; Nos. 4 and 5 can readily be understood if the motions described above are slightly interfered with by collisions between adjacent molecules. In the above it was assumed that the displacement takes place so that atoms 1 and 4 are at the ends of the ellipse in the form *a*, but in general the displacement will take place along any of the three possible axes.

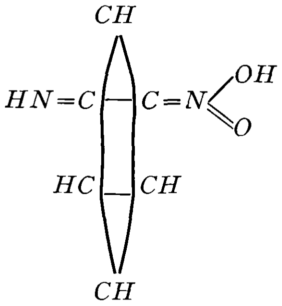
This scheme of displacement of the benzene ring renders it perfectly possible for meta-quinones to have a transitory existence. Let us take meta-nitroaniline,





a

and let the displacement take place along the dotted axes, when we shall obtain phase *a*. When in the form *a*, then the metaquinone can exist thus:



It must be remembered that this meta-quinone can exist only when the displacement occurs in the way shown. It is not therefore necessary to conceive the static existence of a metaquinone, but it is clearly possible for such a linking to exist during part of the motions of the ring.

It has been stated above that meta-nitroaniline and that meta-nitrophenol in alkaline solution exist only partly in the quinonoid form. Inasmuch as a special form of vibration is necessary in order that the meta-quinone may exist, we may say that in this fact is to be found the undoubted restraining influence against the formation of the meta-quinone referred to above.

This pulsation of the benzene ring explains very satisfactorily many of the characteristic physical and chemical properties of benzene and its derivatives. The explanation of the chemical properties need not be detailed here,[1] but one most striking result observed in the absorption spectra of disubstituted benzene derivatives[2] is readily accounted for. In these compounds the para isomer is always more symmetrical than the ortho and meta isomers; that is to say, the internal motions of the benzene ring are less disturbed by the para- than by either the ortho- or meta-substitution. This fact is clearly explained by the theory of the pulsating ring, because it is evident that in a compound such as para-xylene the vibration will take place very readily along the dotted axes shown in the figure

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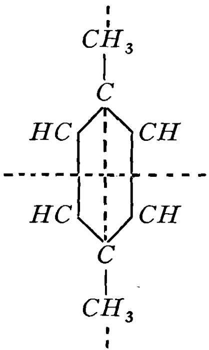
[1] *Cf.* Baly, Edwards, and Stewart, *loc. cit.*

[2] Baly and Ewbank, *Chem. Soc. Trans.*, 87, 1355, 1905.



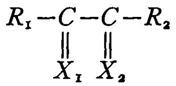
para-xylene

In the ortho-and meta-compounds the unsymmetrical loading of the ring will to a great extent militate against the vibration of the ring, with the result that the ring is distorted and the several absorption bands become confused.

Again, this theory of pulsation readily explains the well-known fact that the two para positions are very close together.

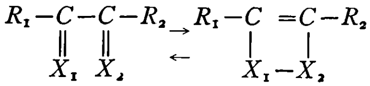
A strong point in favor of this hypothesis is its simplicity. The motion described is the simplest possible, and is the form of vibration adopted by any elastic ring—as, for example, a bell when struck.

These results leave no doubt that when two carbonyl groups are adjacent to one another in a molecule, a new free period of vibration is established; and, further, that when both the groups are true carbonyl as distinct from carboxyl carbonyl groups, the frequency of the new free period is situated in the visible region so that the substance is colored. In general, our results go to prove that the new free period or isorropesis is caused by the existence of the linking:

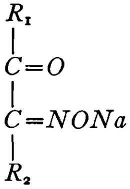


$$R_1-\underset{\underset{X_1}{\|}}{C}-\underset{\underset{X_2}{\|}}{C}-R_2$$

with the proviso that the residual affinity as expressed by the $-\underset{\underset{X}{\|}}{C}-$ group is disturbed by the influence of the groups R_1 and R_2. We have attempted to express the process of isorropesis chemically by stating that the new free period is connected with the equilibrium expressed by

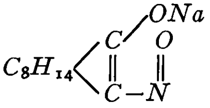


Quite recently[1] we have obtained some experimental evidence in favor of the static existence of the ring form *b*. It is well known that the substances known as the *iso*-nitroso compounds are yellow in alkaline solution. This color, as we have shown, in conjunction with Miss Marsden, is due to the isorropesis occurring with the form

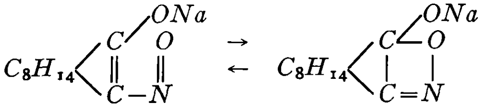


$$R_1-C(=O)-C(=NONa)-R_2$$

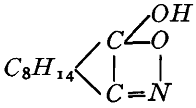
the necessary disturbing influence being provided by the hydrogen atoms upon the radicle R_1 as regards the $-CO-$ group and by the fact that the sodium atom is labile, in the case of the $\overset{|}{\underset{|}{C}}{=}N-$ grouping. Now, in the case of *iso*-nitroso-camphor, the stable form of this compound is yellow in alkaline solution owing to the isorropesis occurring with the form



This may be expressed chemically by the equilibrium



There is direct chemical and spectroscopic evidence that stable *iso*-nitrosocamphor in neutral solution has the form



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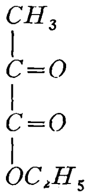
[1] Baly, Marsden, and Stewart, *Chem. Soc. Trans.*, **89**, 1906.

so that our original method of chemically expressing isorropesis has found experimental verification in the case of *iso*-nitroso-camphor.

At the present time we have no physical explanation to offer of the new free period; there is, however, another way of looking at the phenomenon which perhaps may throw more light upon the process. Taking the simplest case of diacetyl

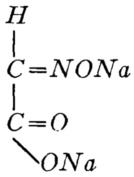
$$CH_3-CO-CO-CH_3$$

there are two CH_3-CO- groups in juxtaposition, and each one of these, by virtue of the potential enol-keto tautomerism they possess, causes or tends to cause the appearance of an absorption band in the ultra-violet. Inasmuch as these two groups mutually influence one another, it is possible that the two free periods in the ultra-violet may so far interfere or combine together to give a new free period in the visible region. On these grounds, therefore, we should look upon the acetyl group or any other group showing enol-keto tautomerism and the benzine nucleus showing benzenoid tautomerism as being potential color systems. The juxtaposition of two of these systems in certain definite ways gives rise to isorropesis or the combination of the two systems to give a new free period. In the compounds described above the new free period is situated in the visible region, so that the substances have visible color. It must be remembered that the conditions may occur in which the isorropic free period is not in the visible region; in this case the substance would not be colored. Such a condition occurs in both pyruvic ester and in *iso*-nitrosoacetic acid in alkaline solution.



$$\begin{array}{l} CH_3 \\ | \\ C=O \\ | \\ C=O \\ | \\ OC_2H_5 \end{array}$$

Pyruvic ester

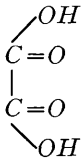


$$\begin{array}{l} H \\ | \\ C=NONa \\ | \\ C=O \\ \diagdown ONa \end{array}$$

Iso-nitrosoacetic acid
(dissolved in sodium hydroxide)

OC_2H_5

In the case of Pyruvic ester compounds the frequency of the isorropic free period is about 3100, which is not in the visible region, and the substances are colorless. It appears that the presence of the hydroxyl oxygen next to the carbonyl group produces this effect, and experiments are at present in progress with a view of explaining this influence. It is interesting to note that the frequency of 3100 obtained with the above two compounds is exactly half-way between the frequency of the isorropesis of diacetyl (2400) and of the enol-keto tautomerism absorption (3800), and further that no isorropesis occurs in oxalic acid where both the carbonyl groups form part of a carboxyl group:



Oxalic acid

It is very noteworthy that the wave-length of the free period of vibration established by isorropesis is about the same as that emitted by the simpler fluorescent organic substances ($\lambda = 4800 - \lambda = 4000$). It may be that there is an intimate connection between fluorescence and isorropesis, and that the former is only a manifestation of the latter. There is nothing inherently improbable in this idea. In both cases, visible color and fluorescence, the free period is established by the isorropesis; in the former case the free period is established by the isorropesis and excited by the incident light and we have absorption, while in the latter case the free period is established and excited by the isorropesis, and we have emission. An important fact bearing on the connection between isorropesis and fluorescence has been recorded by Nichols and Merritt;[1] these authors have observed that, when the fluorescence of fluorescein and certain other substances is excited by a beam of ultra-violet light, a distinct absorption occurs of light of the same wave-length as that emitted by the substance when fluorescent.

CONCLUSIONS

1. When two true ketonic groups $\left(\begin{array}{c}-C-\\ \| \\ O\end{array}\right)$ are in juxtaposition in the molecule, an oscillation (isorropesis) occurs between the residual affinities of the oxygen atoms, which results in the establishment

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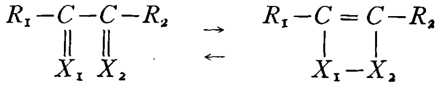
[1] *Phys. Rev.*, **18**, 447, 1904.

of a free period of vibration in the visible region of the spectrum. These substances are therefore colored.

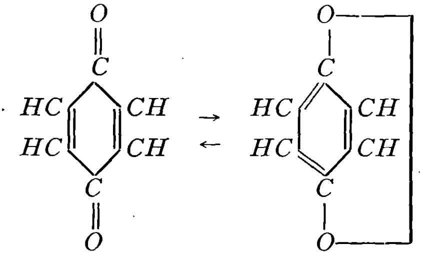
2. This isorropesis occurs also between the residual affinities of the oxygen atoms in the benzenoid quinones, of the nitrogen atoms of the quinonoid form of the nitroanilines, and of the nitrogen and oxygen atoms of the quinonoid form of the nitrophenols. It also occurs between the residual affinities of the oxygen and nitrogen atoms of the *iso*-nitroso compounds.

3. The process of isorropesis may be expressed chemically by the equilibrium expressed by



$$\begin{array}{c}R_1-C-C-R_2\\ \;\;\|\quad\|\;\;\\ \;\;X_1\;X_2\;\;\end{array} \rightleftarrows \begin{array}{c}R_1-C=C-R_2\\ \;\;|\qquad|\;\;\\ \;\;X_1-X_2\;\;\end{array}$$

or



4. It is necessary to assume the transitory existence of a meta-quinonoid linking to account for the phenomena observed with meta-nitroaniline and meta-nitrophenol.

5. Many of the physical and chemical properties of benzene are explained by considering that the benzene ring is elastic and undergoes the same vibrations as are suffered by any elastic ring.

6. The meta-quinonoid linking is possible during one phase of the displacement of the benzene ring.

7. In order to start the isorropesis, it is necessary that some influence be present to disturb the residual affinities upon the atoms concerned.

8. This influence is provided in compounds of the type of diacetyl by the neighboring hydrogen atoms which are attracted by the oxygen atoms; in the benzoquinones it is provided both by the hydrogen atoms and also by the benzenoid tautomerism.

9. Subject to the proviso referred to in 7, there is no doubt that this principle may be extended, and that all the phenomena of visible color are due to the oscillation between residual affinities on atoms or groups of atoms in juxtaposition.

10. Any assumption that two compounds must be fundamentally different in constitution if one is colored and the other white is quite untrustworthy.

11. It is possible that color and fluorescence are evidences of the same phenomenon—isorropesis. In the former case the isorropesis provides the mechanism, and the incident light actuates it; in the latter case the isorropesis both provides and actuates the mechanism.

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London.

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THE CHEMICAL REACTIVITY OF THE CARBONYL GROUP AS MEASURED BY ITS ABSORPTION SPECTRUM

A. W. STEWART AND E. C. C. BALY

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THE CHEMICAL REACTIVITY OF THE CARBONYL GROUP AS MEASURED BY ITS ABSORPTION SPECTRUM

By A. W. STEWART[1] AND E. C. C. BALY

The question as to how far the space relations of atoms within a molecule could affect the properties and reactions of certain compounds was first raised twenty years ago by Wislicenus, and since that time the problem has attracted the attention of many chemists and physicists. Yet, in spite of the great interest which it has aroused, it cannot be said that very great progress has been made in some branches of the subject. An example may be chosen from the work of Menschutkin upon the esterification of aliphatic acids.

By a series of measurements he was able to show that, while a simple acid esterified with ease, the derivatives of the same acid, which were formed by the substitution of methyl groups for hydrogen atoms in the original compound, were much more difficult to esterify. The velocity of esterification was proved to be quite independent of the affinity constant of the acid used, as the following table shows:

Name of Acid	Formula	Velocity of Esterification	Affinity Constant
Acetic	$CH_3.COOH$	3.661	0.00180
Propionic	$CH_3.CH_2.COOH$	3.044	0.00134
Isobutyric	$(CH_3)_2CH.COOH$	1.0196	0.00144
Trimethyl-acetic	$(CH_3)_3C.COOH$	0.0909	0.00098

The most obvious explanation for this phenomenon appeared to necessitate the assumption that the volumes of atoms were not negligibly small when compared with their intramolecular paths of vibration. If this assumption be made, the phenomenon of hindrance can be understood and the cause explained in the following manner. The esterification process requires that the alcohol molecule involved in the reaction should approach very closely to the carboxyl radicle of the acid used. Such an approach will be

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[1] Carnegie Research Fellow.

easy, so long as the groups attached to the carboxyl radicle are not bulky. This is the case in acetic acid. But if for the hydrogen atoms in the acid nucleus we substitute methyl radicles, which are much greater in volume, the alcohol molecule will find much greater difficulty in forcing its way into the neighborhood of the carboxyl group, just as a person would find greater difficulty in walking into a crowded room than into a sparsely filled one.

There can be no doubt that, if atoms have any size at all, this theory of "steric hindrance," as it is called, will hold good; but it cannot be proved that the effects attributed to this cause play any very considerable part in the reactions in question. It seems more probable that the free paths of the atoms in their intra-molecular vibrations are so large in comparison to the size of the atoms themselves that this heaping up of substituents in the neighborhood of the reactive group would have no very marked effect.

Stewart[1] has shown that, when a hydrogen atom near the carbonyl group of a ketone is replaced by a methyl radicle, the result is a decrease in the additive capacity of the carbonyl group. This might have been anticipated from the hypothesis of steric hindrance, since the volume of the methyl radicle must be greater than that of a hydrogen atom. A contradiction between theory and experiment is found in the case where, instead of a methyl radicle, a $-COOEt$ group is introduced into the molecule. In the case of the latter group it is found that, instead of decreasing the velocity of addition of sodium hydrogen sulphite, as its bulk might lead us to predict, it has the contrary effect; for some of these ketones which contain a carboxyl group are much more reactive than the corresponding simple ketone, and, *a fortiori*, than the methyl substituted ketone. The figures found for acetoacetic ester, acetone, and methyl ethyl ketone show this clearly:

		10	20	30	40 Min.
Acetoacetic ester	CH_3COCH_2COOEt	37.4	47.0	56.0	60.0
Acetone	CH_3COCH_3	28.5	39.7	47.0	53.6
Methyl-ethyl ketone	$CH_3COCH_2CH_3$	14.5	22.5	25.1	29.1

The figures give the percentage of bisulphite compound formed

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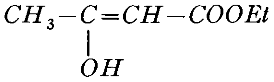
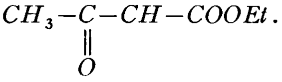
[1] *Chem. Soc. Trans.*, **87**, 185, 1905; *Proc.*, **21**, 78.

by each ketone during the time indicated. It is thus made evident that some new influence has come into play, which tends to mask or modify the steric hindrance due to the more voluminous group.

The carboxyl group in itself, however, is not sufficient to produce this increased reactivity of the carbonyl radicle, as the rate of addition of sodium hydrogen sulphite to ethyl laevulate $CH_3.CO.CH_2CH_2.COOEt$ was found to be slightly lower than that found in the case of methyl propyl ketone $CH_3.CO.CH_2CH_2.CH_3$, which contains a carbon chain of the same length; and a like result was observed in the case of the diketone acetonyl acetone $CH_3.CO.CH_2.CH_2.CO.CH_3$. On the other hand, acetone dicarboxylic ester $COOEt.CH_2.CO.CH_2.COOEt$ has an additive capacity even greater than that of ethyl aceto-acetate. Acetone shows very little sign of tautomeric change; while, on the contrary, acetoacetic ester and acetone dicarboxylic ester are tautomeric compounds. Thus here again theory and experiment appear to be opposed to one another, the true carbonyl compound having much less reactive power than the semi-enolised body. It occurred to us that in this fact was to be found the key of the problem, and that the exceptionally great reactivity of the carbonyl group in tautomeric compounds was due to the actual process of tautomeric change. Acetoacetic ester, under conditions, exists as an equilibrium mixture of the two bodies (I) and (II); and the conversion of the first into the second, and vice versa, is going on continuously.

(I) 

$$CH_3-\underset{\displaystyle OH}{\underset{|}{C}}=CH-COOEt$$

(II) 

$$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH-COOEt.$$

Now, when a molecule of (I) is converted into a molecule of (II), the result is the formation of a carbonyl group from a hydroxyl group. From analogy with the behavior of atoms in the nascent condition, we must suppose that this "nascent carbonyl group" is endowed with a much greater reactivity than that possessed by the ordinary non-nascent carbonyl radicle. This activity need not, however, be occasioned purely by the actual wandering of the hydrogen atom from the oxygen to the carbon; it may be due to some finer play of forces within the molecule which manifests itself in the production of the characteristic absorption of the acetoacetic ester spectrum. The condition into which the hydrogen atom is thrown as a result of this play of forces may be termed a condition of "potential tautomerism," and in it the hydrogen atom will possess a reactive power more or less analogous to that required by an atom as a consequence of the ionisation process.[1]

If we now apply this idea to several cases which have hitherto been classed under the head of steric hindrance, it will be found that they can be satisfactorily explained. Taking the case of the ketones which have already been dealt with by one of us,[2] a marked decrease in the reactivity of the carbonyl group is shown when the hydrogen atoms of acetone are successively replaced by methyl radicles.

In the course of their investigations of the spectra of derivatives of acetoacetic ester, Baly and Desch[3] proved that the equilibrium between the enolic and the ketonic forms produces an absorption band in the ultra-violet region of the spectrum; and they also showed that this band is not due to the shifting of a hydrogen or metallic atom, but is rather to be considered as the result of some intra-atomic change. In the hope of finding some analogous process in the simple ketones, we examined the absorption spectra of several; and we found that a similar absorption band exists there as well. We further noticed that ***the persistence of this band decreases proportionately to the diminution in the reactivity of the ketone's carbonyl group.***[4]

For instance, the following figures show the percentages of oxime formed by various ketones in twenty minutes;[5] and on comparing these amounts with the curves of the absorption spectra shown in Fig. 1, the relation between the two will be evident.

	% Oxime Formed
Acetone, CH_3COCH_3	49·7
Methyl ethyl ketone, $CH_3COCH_2CH_3$	39·2
Methyl propyl ketone, $CH_3COCH_2CH_2CH_3$	37·3
Methyl iso-propyl ketone, $CH_3COCH(CH_3)_2$	31·5
Pinacoline, $CH_3.CO.C\vdots(CH_3)_3$	17·0

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[1] Baly and Desch, *Astrophysical Journal*, **23**, 110, 1906.

[2] Stewart, *loc. cit.*

[3] *Loc. cit.*

[4] The method of observing and plotting the curves of absorption spectra was described in the previous paper (*Astrophysical Journal*, **23**, 110, 1906).

[5] Stewart, *Chem. Soc. Trans.*, **87**, 410, 1905.

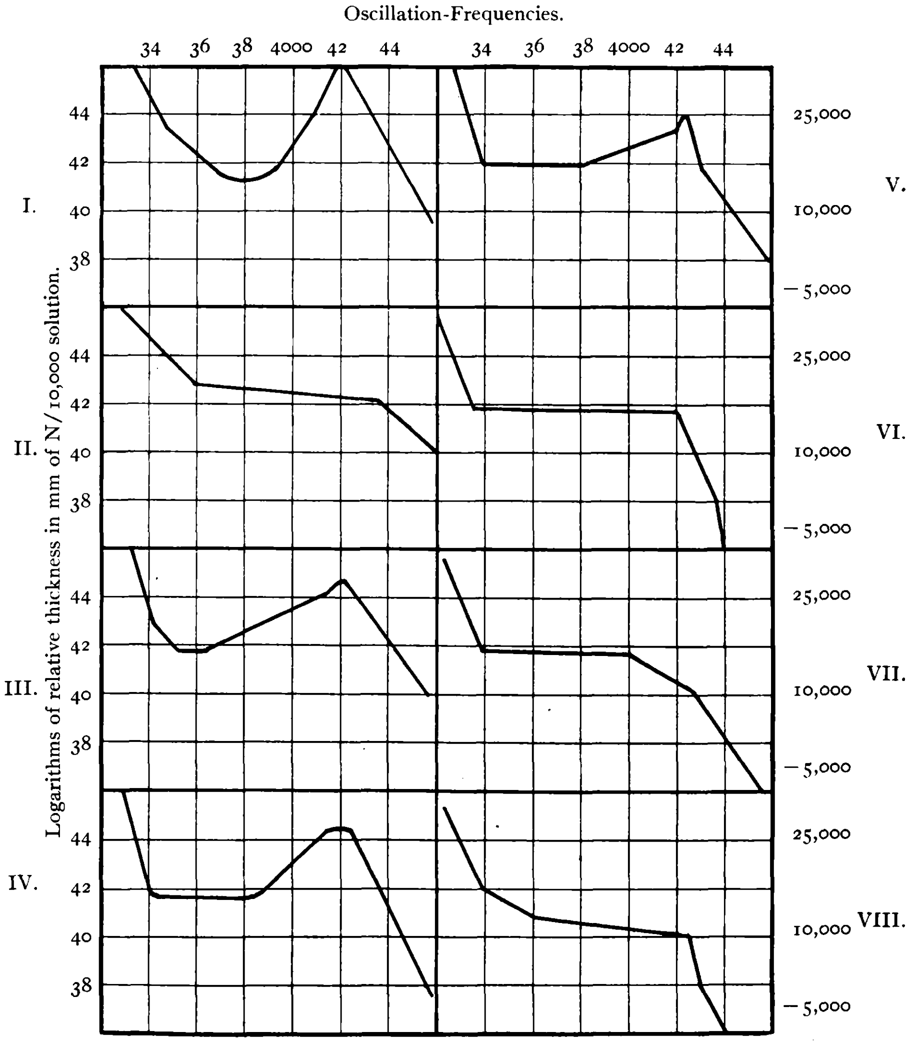

FIG. 1

I.	Acetone.	V.	Methyl iso propyl Ketone.
II.	Acetone (in water).	VI.	Pinacoline.
III.	Methylethyl Ketone.	VII.	Methyl hexyl Ketone.
IV.	Methyl propyl Ketone	VIII.	Methyl nonyl Ketone.

Lapworth[1] showed that the action of halogens upon acetone was preceded by the production of the enolic form of the ketone; and he found, further, that the presence of acids hastened the reaction. Now, he had already shown[2] that the presence of acids brings about a rapid attainment of equilibrium between the tautomeric forms of carbonyl compounds; or, in other words, the addition of acid has a tendency to produce a "nascent carbonyl group." Hence, in the case of acetone itself, not only is there direct spectroscopic evidence in favor of tautomeric change, but the chemical evidence at our disposal is also favorable. Instead of attributing Lapworth's results to the actual formation of the enolic form and an immediate addition of halogen, we prefer to look at them from another point of view. It is obvious, if we consider the change of the group $-CH{=}CH(O\overset{*}{H})-$ into $-CH\overset{*}{H}-CO-$, that the hydrogen atom marked with an asterisk must become "pseudo-nascent" in the process of change. It would therefore be peculiarly liable to chemical action, and would easily be replaced by halogens. The very great ease with which the methylene hydrogen atoms in acetylacetone are replaceable by halogens lends further support to our hypothesis.

In their paper Baly and Desch (*loc. cit.*) stated that acetonylacetone and ethyl laevulate were pure ketonic substances; but on examining the spectra of these substances at greater concentrations than were previously employed, we have been able to detect at one point a rapid extension of the spectrum which corresponds to a very shallow absorption band (Fig. 2). The shallowness of the band indicates that the tautomerism in these two compounds is very weak, which agrees with what has been found with regard to the reactivities of their carbonyl groups. The close agreement between theory and experiment in these cases is very noteworthy.

Now Petrenko-Kritschenko has shown[3] that the speed of phenylhydrazone formation is greatly influenced by the nature of the solvent in which the reaction is carried out. It appeared probable to us that this might be due to the influence of the solvent upon the

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[1] *Chem. Soc. Trans.*, **85**, 32, 1904.

[2] *Ibid.*, **81**, 1503, 1902 and **83**, 1121, 1903.

[3] *Journ. Russ. phys.-chem. Soc.*, **35**, 404, 1903.

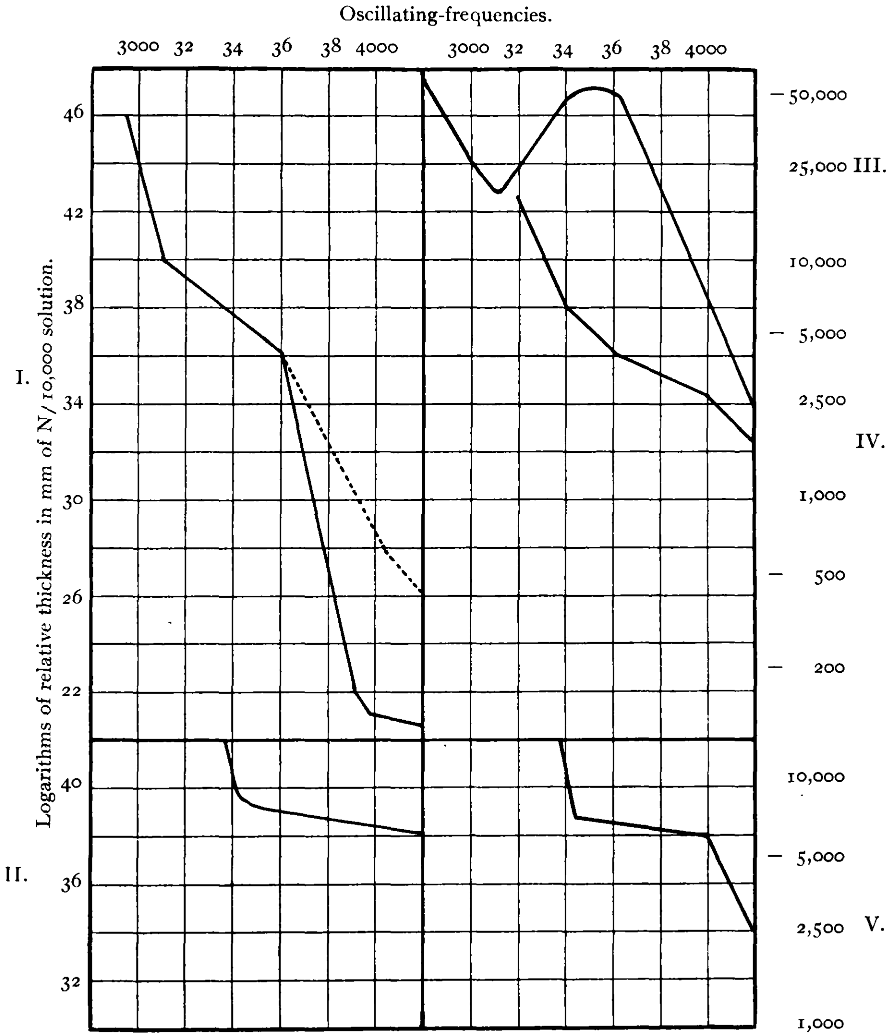


FIG. 2

I. Acetoacetic ester in alcohol (full curve).
The same in water (dotted curve).
II. Ethyl laevulate.
III. Ethyl pyruvate.
IV. Ethyl diethyl aceto acetate.
V. Acetonyl acetone.

tautomerism process; and to test the matter we examined the spectra of acetone and acetoacetic ester in aqueous solution, using as a control in the latter case the spectrum of diethylacetoacetic ester, which is much less tautomeric than the parent substance. From the curves for acetone in alcoholic and aqueous solution it will be seen that the influence of water is very marked, the band in the latter case being much shallower than in the former. The three curves shown in Fig. 2 give the absorption spectra of the acetoacetic ester series; and it is obvious from them that the water has reduced the tautomerism very considerably. It is probable that the greater the unsaturation of the solvent, the less reactivity will be shown by the carbonyl group of the dissolved ketone.

The evidence from simple ketones being so far favorable, we must now examine the case of ketones containing an ethyl carboxylate group. If tautomeric change alone were the cause of the reactivity of the carbonyl radicle, compounds containing the group $-CO-CH_2-CO-$ should be more reactive than those which do not contain it, and the reactivity of the carbonyl group in pyruvic ester (CH_3-$COCOOEt$) should not be at all abnormal, since the group in question does not occur in it; if, however, the reactivity were found to be great in this case, we hoped that some light might be thrown upon the problem by the study of the compound's spectrum.

We therefore decided to compare the rates of addition of potassium hydrogen sulphite to acetone, acetoacetic ester, acetonedicarboxylic ester, and pyruvic ester. The results obtained by the method employed are given in the table below:

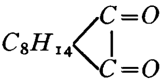
		5	10	15 Min.
Acetone	CH_3COCH_3	5	7	9%
Acetoacetic ester	CH_3COCH_2COOEt	12	18	24
Acetonedicarboxylic ester	$CO:(CH_2COOEt)_2$	30	36	42
Pyruvic ester	$CH_3COCOOEt$	52	64	76

In spite of the precautions taken, these numbers are probably not quite accurate, owing to various causes which cannot be controlled; but the differences between the numbers themselves are very much larger than any possible experimental error under the conditions employed.

An examination of the figures shows that the introduction of a

$-COOEt$ group into acetone increases the additive capacity of the carbonyl group; the introduction of two $-COOEt$ groups still further enhances the reactivity of the carbonyl group; but the most striking effect is produced when, as in the case of pyruvic ester, the carbonyl and carboxyl groups are brought into juxtaposition in the chain. Now, in the case of pyruvic ester, though the compound does sometimes react in the enolic form, it is most improbable that the change of the enolic into the ketonic form is going on at a rate at all comparable to that in which it is occurring in acetoacetic ester or acetonedicarboxylic ester, so that it is not likely that the exceptional reactivity of the carbonyl group in pyruvic ester is due to this kind of tautomerism.

We thought it advisable to examine the spectrum of pyruvic ester, in the hope that some light might thus be thrown on the problem of the activity of the carbonyl group. We found that pyruvic ester gives an absorption band which lies much nearer to the red end of the spectrum than the band given by acetoacetic ester. The origin of the band in the pyruvic ester spectrum might be looked for in two phenomena; either in the enol-keto change of the group CH_3-CO-, or in the interaction of the carbonyl and carboxyl groups of the radicle $-CO-COOEt$. The first explanation is impossible, since, if the band were produced by a similar state of intra-atomic vibration in both instances, it would occur in nearly the same place in the spectrum, while actually the new band has its head with a frequency of 3100, while that of the acetoacetic ester band lies at 3700. Further, since the molecule of pyruvic ester is lighter than that of acetoacetic ester, we should expect to find the band in the latter case nearer to the red end of the spectrum than in the former; while actually the reverse of this is observed.

In order to make certain that the band in question was actually produced by the proximity of two true carbonyl groups in the chain—i. e., that it was not due to the $-COOEt$ group of the carboxylate radicle—we examined the spectra of several α-diketones and found a similar band in all of them, though in them it was situated nearer the red end of the spectrum. For example, in the case of camphorquinone  $C_8H_{14}\left\langle\begin{array}{l}C=O\\ |\\ C=O\end{array}\right.$ (Fig. 3) it will be seen that an absorption band is shown which has a very long persistence. Its head lies at a frequency of 2070.

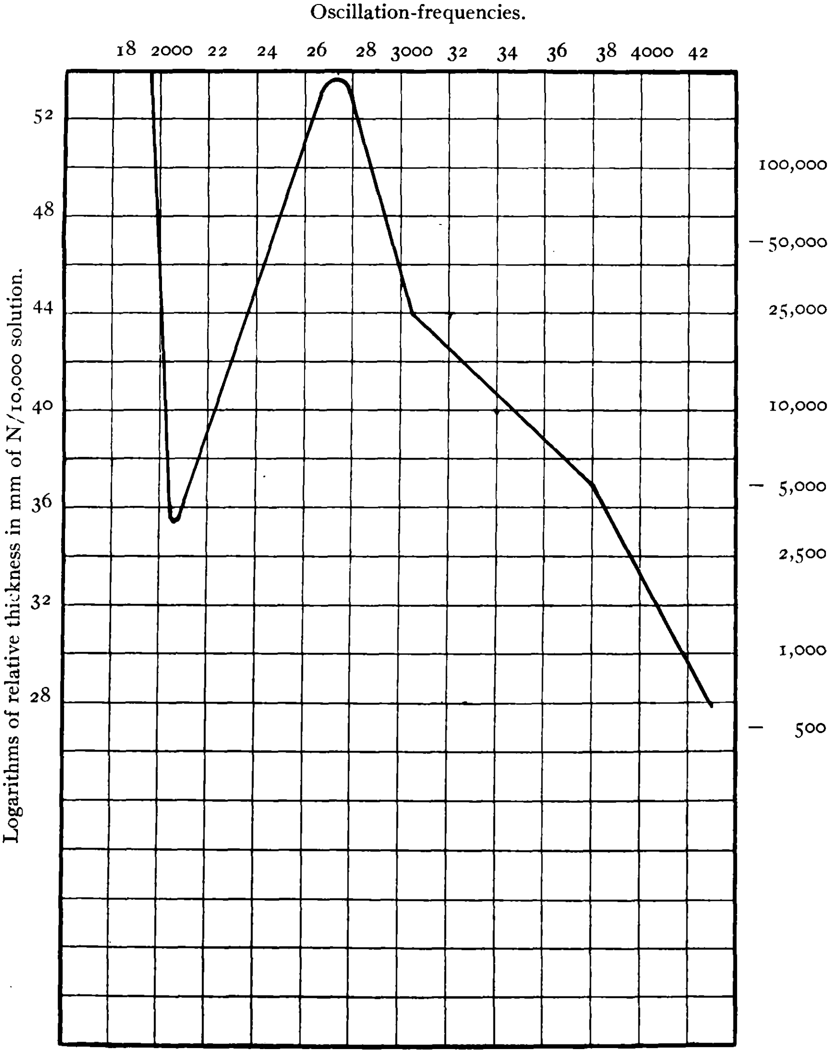
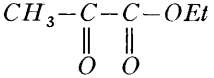


FIG. 3.— Camphor quinone.

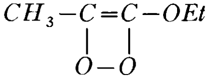
It was thus proved that the type of band in question was due to the two carbonyl groups in the α-position to one another. It has already been pointed out that Baly and Desch concluded that, though the keto-enol absorption band was produced by intra-atomic vibration, it was caused by the change of linkage brought about by the oscillation of the hydrogen atom during the change from the ketonic to the enolic form. From analogy we should expect to find a somewhat similar state of things in the present case. Now, the only possible way in which such a change of linkage can be supposed to occur in pyruvic ester is by imagining that, like acetoacetic ester, it occurs in two forms:

(I)



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OEt$$

(II)



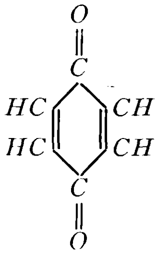
$$\begin{array}{l}CH_3-C=C-OEt\\ \qquad\;\;|\;\;\;\;\;|\\ \qquad\;\;O-O\end{array}$$

It is very hard to indicate exactly what is meant by the aid of the usual structural formulæ, as they only indicate a static condition of the molecule, while what we wish to suggest is essentially a dynamic state. We wish to make it perfectly clear that we do not suppose these two forms necessarily to exist statically; but, owing to the defect of ordinary structural formulæ, it is impossible to write them otherwise if the usual symbols be employed. Our conception can best be comprehended if it be clearly borne in mind that the two formulæ are not intended to represent actual compounds, but merely two phases of the same compound. If this conception of phases be understood, it will be apparent that the change of linkage is continually going on, and that this change will affect the intra-atomic relations of the molecule very much in the same way as they are affected by the phenomena of tautomerism.

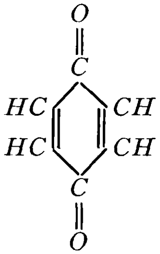
At the same time, it should be noticed that the change of linkage from (II) to (I) would produce what we have already defined as a "nascent carbonyl group" which would have great reactivity. Thus we are led to conclude that substances which show these peculiar absorption bands will in general be more active chemically than other compounds which do not exhibit such selective absorption.

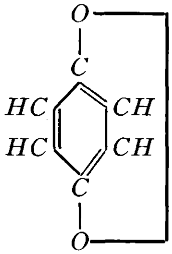
The idea which we have put forward cannot be considered as part of the theory of tautomerism, as, owing to its associations, the name "tautomerism" will always suggest the wandering of a hydrogen atom. It is unfortunate that the name "Desmotropism" has already been employed to denote tautomerism, as it seems well fitted to describe the phenomenon with which we have dealt. We therefore wish to propose the word "Isorropesis" (*ἰσορροπεια*, "equipoise") to describe the process.

The arguments in favor of this theory appeared to us to warrant its application to other classes of compounds, and we proceeded to make a further series of investigations, some of which will be dealt with in a later paper. For the present, quinone



is the only compound which need be described. The known close relation to one another in which the two para-positions in benzene stand, seemed to lend probability to the idea that a band somewhat similar to those observed in compounds containing the group $-CO-$ $-CO-$ might be found in the spectra of the para-quinones. Our anticipations were again justified, as the quinone spectrum has a band almost identical with that of camphor quinone, its head lying at 2150 (see Fig. 4). Now, it is known that quinone can exist in two forms, for both of which chemical evidence has been adduced:





It appears not unwarrantable to assume that in this case also the absorption band is caused by the "make and break of contact" between the two oxygen atoms, as already suggested for pyruvic ester. Thus it may be concluded that the actual wandering of a hydrogen atom is not necessary for the production of these absorption bands. Again, since the result of this "make and break" would be the production of two nascent carbonyl groups, an explanation is thus given of the great chemical activity of the carbonyl radicles in quinone.

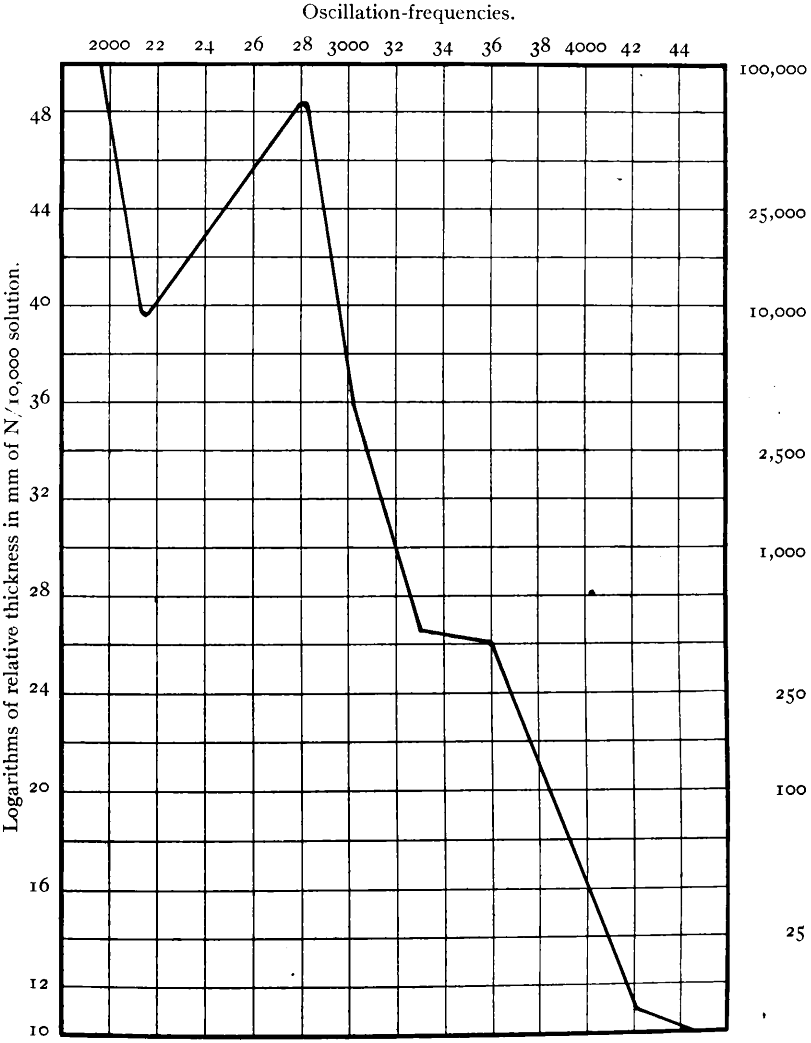
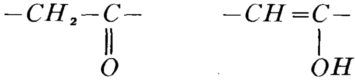


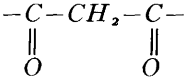
Fig. 4.—Quinone.

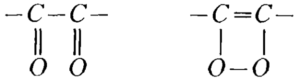
It is thus proved that the two carbonyl groups in the *a* position to one another give rise to a new type of absorption band. From analogy with Baly and Desch's observations that the ultra-violet absorption bands are produced by the change of linkage brought about by the oscillation of the hydrogen atom in the process of enol-keto tautomerism, we should expect to find a somewhat similar change of linkage in the α-diketones. We propose to reserve a full discussion of this process to a further paper in connection with its relation to color, but it may be stated that we are undoubtedly concerned with the residual affinity upon the two oxygen atoms. The free period giving rise to the absorption band is due to a mutual disturbance or an oscillation between these residual affinities.

It would seem that the results described above are of considerable importance, for they show that the chemical reactivity of a ketonic compound can be measured directly by means of the spectroscope. We find that the persistence of the absorption bands given by these compounds is directly proportional to their chemical reactivity. It is a logical conclusion that the chemical reactivity of these compounds is due to a change of linkage within the carbonyl group of the ketone. This change of linkage may either be produced by a wandering hydrogen atom such as occurs in the reversible equilibrium



$$-CH_2-\underset{\underset{O}{\|}}{C}- \qquad -CH=\underset{\underset{OH}{|}}{C}-$$

which occurs or tends to occur in the monoketones and the β diketones containing the  $-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-$ group, or it may be produced by isorropesis or the oscillation between the residual affinities of two carbonyl oxygen atoms in juxtaposition, thus



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}- \qquad \begin{array}{ccc} -C & = & C- \\ | & & | \\ O & - & O \end{array}$$

Furthermore, it is evident that all measurements of the chemical reactivity of a ketonic compound are simply measurements of the amount to which tautomerism is present in the compound. A very great deal of importance has been attached to these measurements in connection with the theory of steric hindrance, but our results, we are sure, will go far to discountenance this theory. There is no doubt that the decrease in chemical reactivity caused by the substitution of hydrogen atoms by groups of atoms is caused, not by the bulk of these atoms, but simply by the fact that fewer hydrogen atoms are available for the tautomeric processes. It is unnecessary to cite in this place the many reactions of ketones which have been measured in support of the theory of steric hindrance, but there is no doubt that they can all be explained more easily and more rationally by the conception of the nascent carbonyl group set forth above.

The method employed for the photography of the absorption spectra of the substances, as mentioned above, has already been described;[1] the compounds were in each case prepared most carefully and satisfactorily answered every test of their purity. Except where especially mentioned to the contrary, the absorption spectra of the substances were observed in alcoholic solution.

CONCLUSIONS

1. The reactivity of any carbonyl group is not inherent in the group itself, but is produced by the action of neighboring atoms upon the carbonyl group rendering it "nascent."

2. Such action may take the form of tautomerism, or of a modification of tautomerism which does not require the actual transfer of a hydrogen atom from one atom to another, but merely some intra-atomic disturbance in the system $-CH_2-CO-$.

3. The action may also take the form of the process which we have termed "isorropesis," in which no actual wandering of the atoms occurs, but in which some oscillation between the residual affinities of the oxygen atoms of the two carbonyl groups is involved.

4. Many cases which at present are accounted for on the hypothesis of steric hindrance can be better accounted for either by tautomerism or isorropesis; and some cases which are in direct contradiction to the steric theory can also be explained. It is therefore claimed that the hypothesis of the "nascent carbonyl group" accounts more satisfactorily for the facts and is superior to explanations based upon the idea of steric hindrance.

5. When the possibility of the formation of a nascent carbonyl

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[1] Baly and Desch, *loc. cit.*

group is excluded, neither the usual ketonic reactions nor an absorption band is observed. The carbonyl radicle may then be considered an "inactive" carbonyl group in contradistinction to a "nascent" one.

6. Inasmuch as both the processes of tautomerism and isorropesis result in the appearance of an absorption band whose persistence is a measure of the amount to which these processes are taking place, it is possible to determine the chemical reactivity of a ketonic compound by observing the persistence of the absorption band.

In conclusion we wish to express our thanks to the Chemical Society of London for a grant toward the expenses of this research; to Professor Collie and Dr. Smiles, for the great interest they have taken in the work; and to Mr. W. B. Tuck, B. Sc., for assistance during the course of the investigation.

THE ORGANIC AND SPECTROSCOPIC LABORATORIES,
University College, London.

FIGURES.

Figure I.

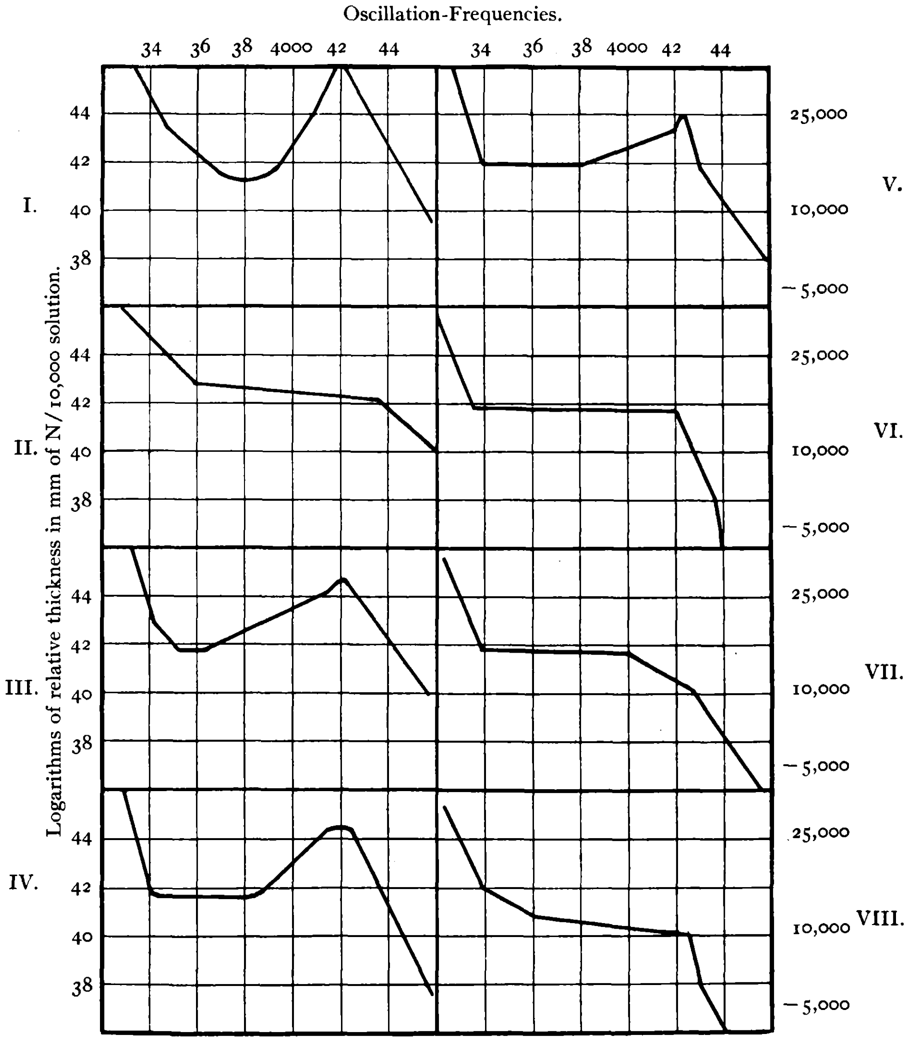


FIG. 1

I. Acetone.
II. Acetone (in water).
III. Methylethyl Ketone.
IV. Methyl propyl Ketone
V. Methyl iso propyl Ketone.
VI. Pinacoline.
VII. Methyl hexyl Ketone.
VIII. Methyl nonyl Ketone.

Figure 2.

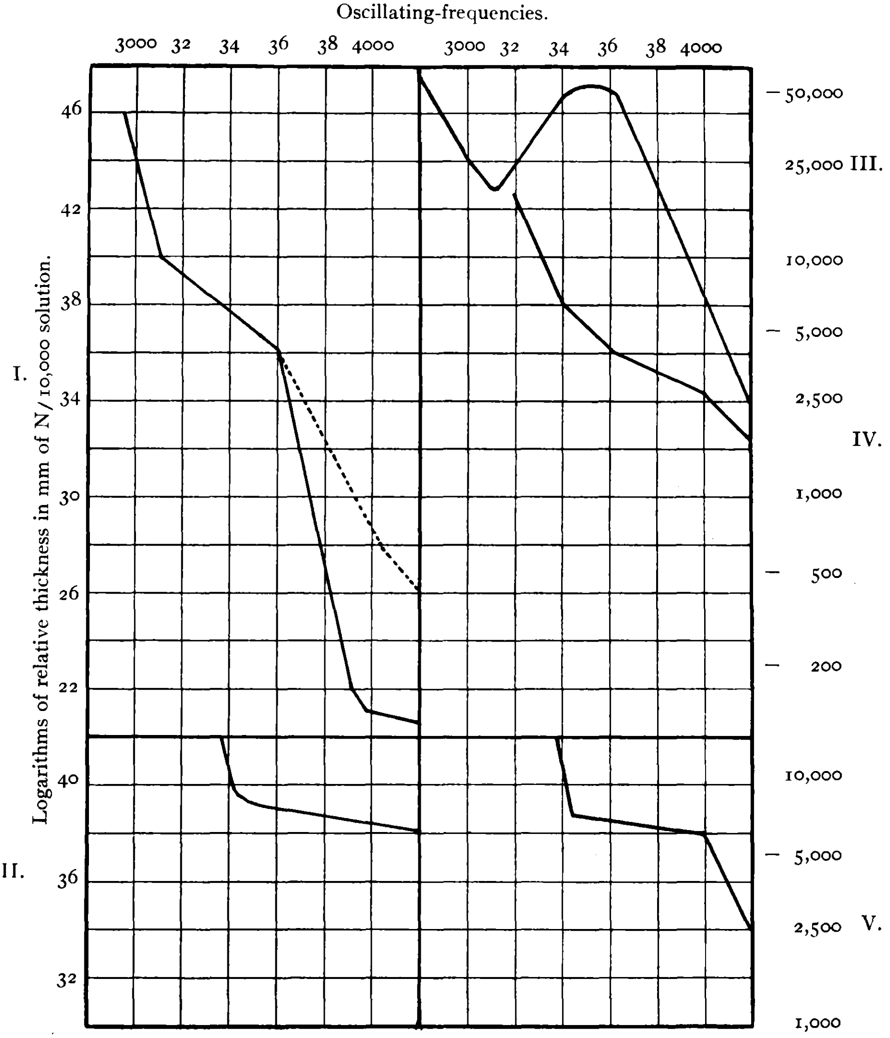


FIG. 2

I. Acetoacetic ester in alcohol (full curve).
The same in water (dotted curve).
II. Ethyl laevulate.
III. Ethyl pyruvate.
IV. Ethyl diethyl aceto acetate.
V. Acetonyl acetone.

Figure 3

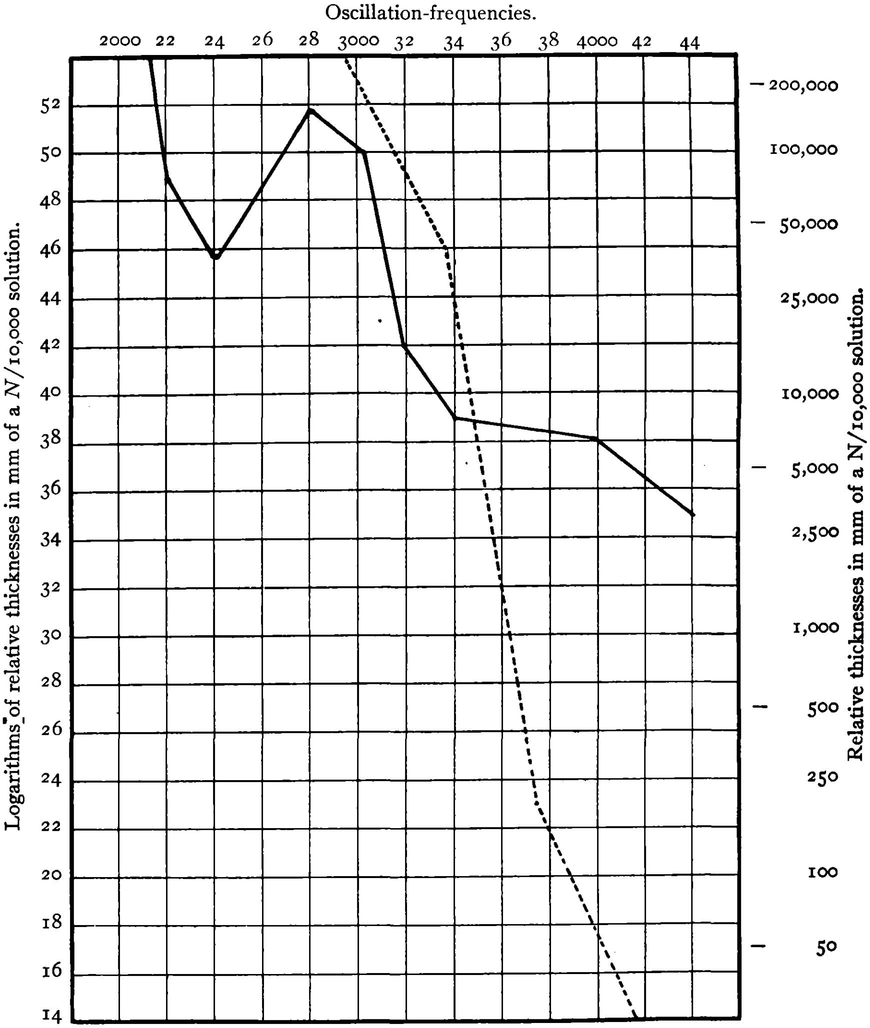


FIG. 3—Diacetyl (full curve): Diacetyl dioxime (dotted curve).

Figure 4.

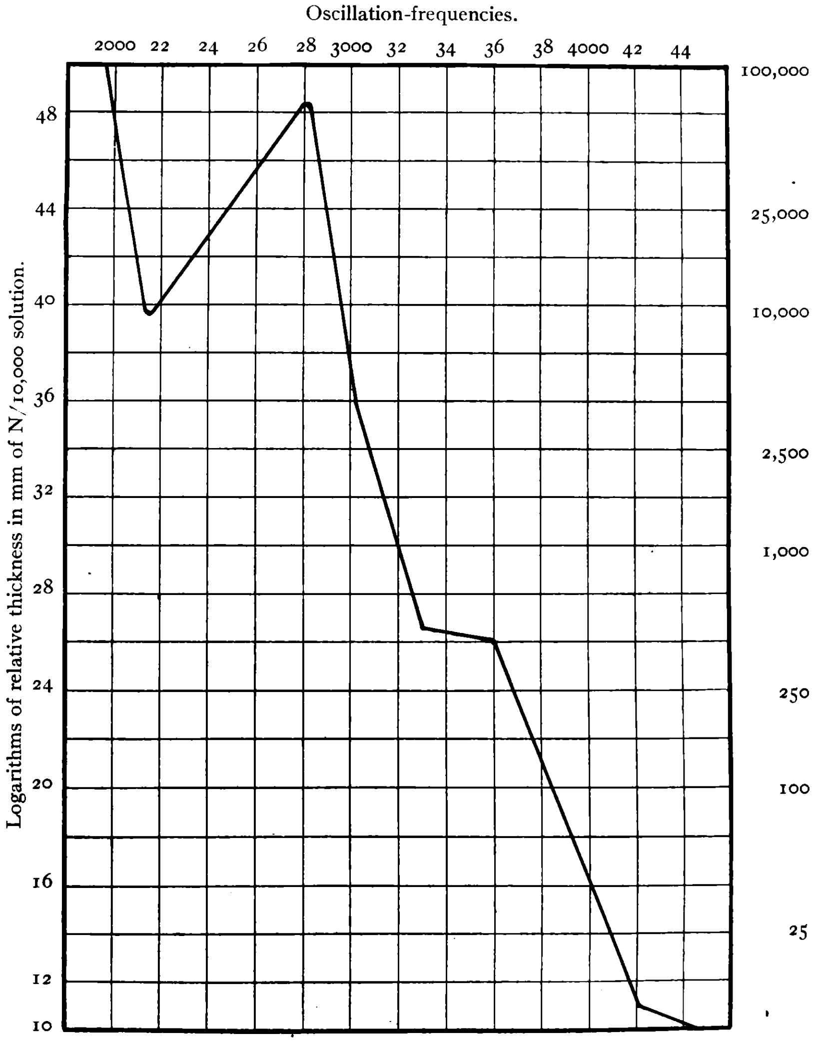


FIG. 4.— Quinone.

Figure 5.

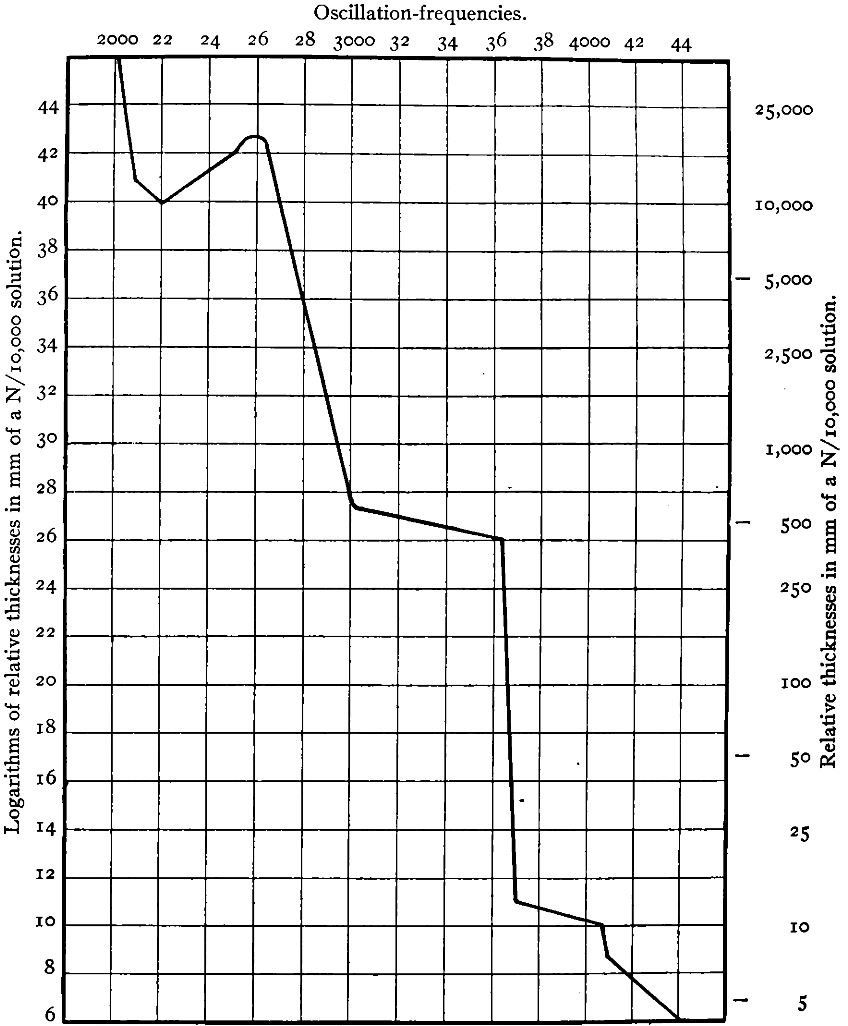
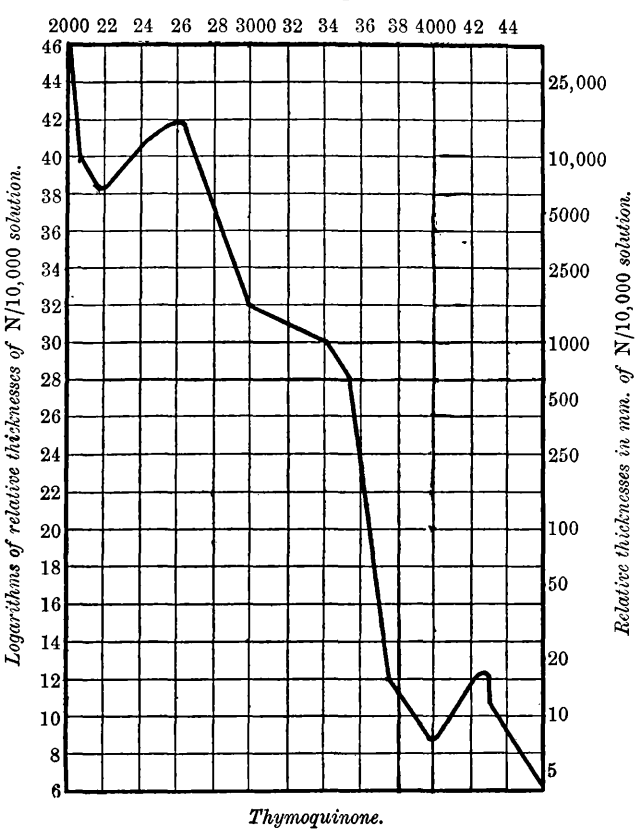


FIG. [illegible]—Toluquinone.

Figure 6.

FIG. 6.



Thymoquinone.

Figure

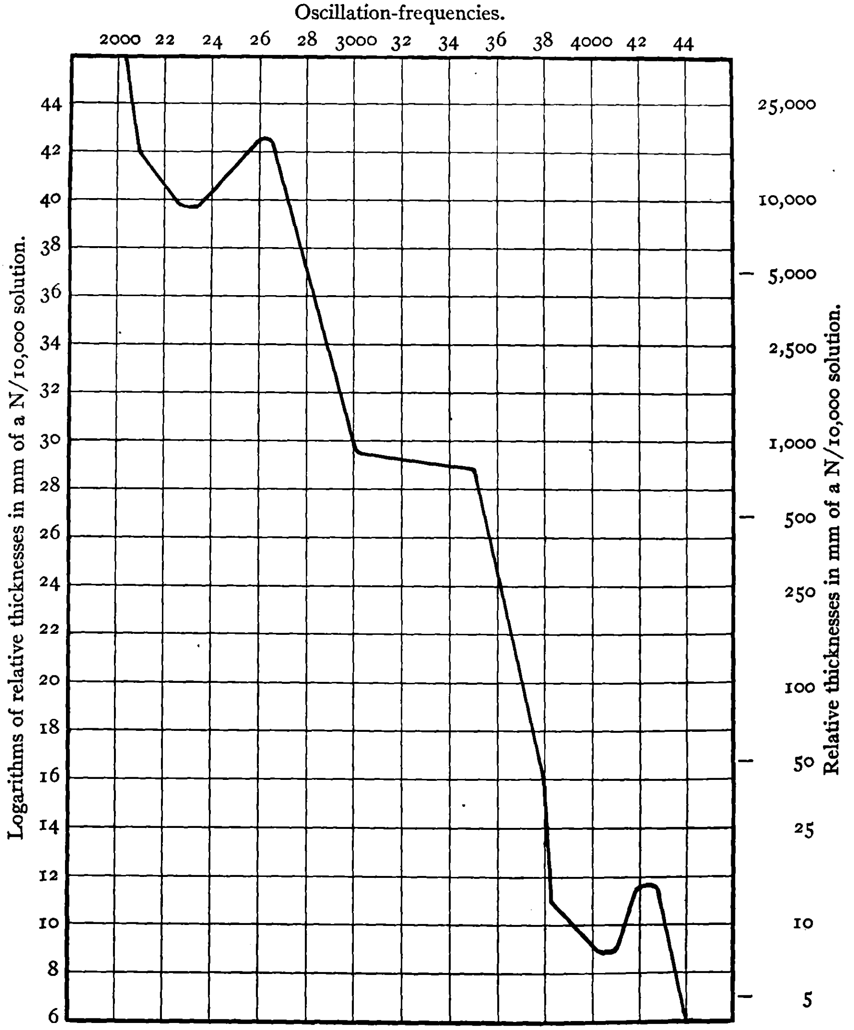
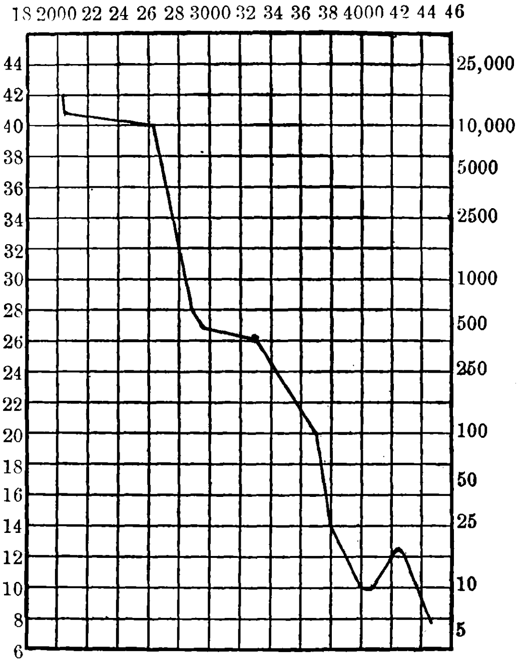


FIG. 7—Para-xyloquinone.

Figure 8.

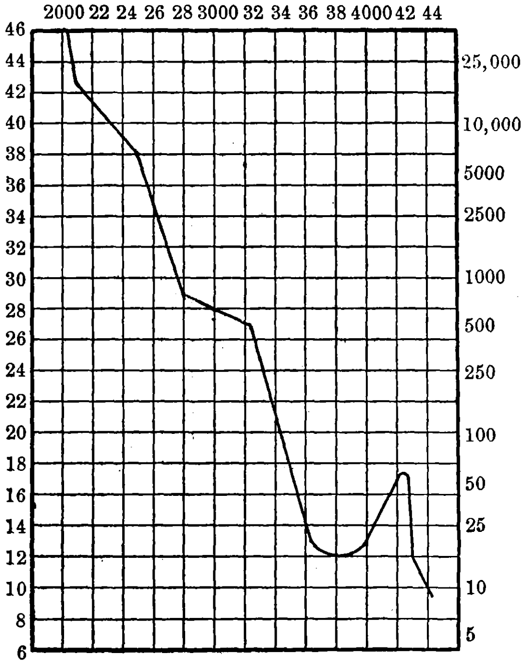
[redacted].



Chlorobenzoquinone.

Figure 9.

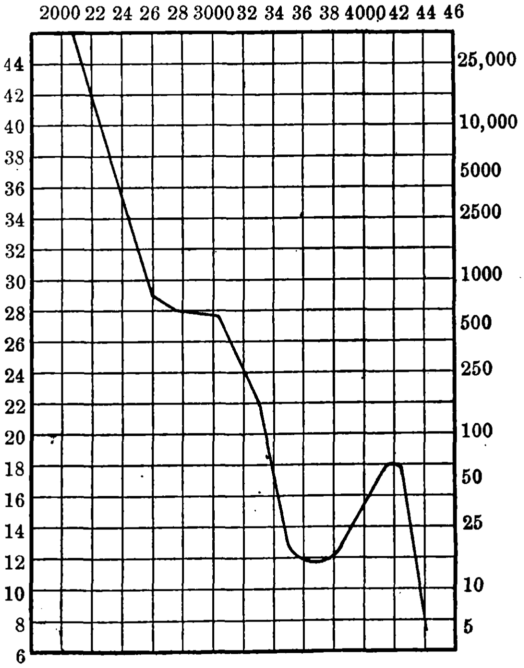
Fig. 9



Dichlorobenzoquinone.

Figure 10.

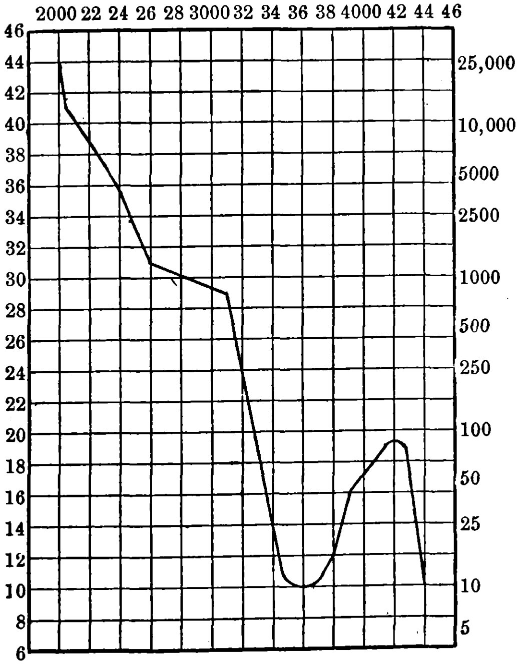
FIG. 10.



Trichlorobenzoquinone.

Figure 11.

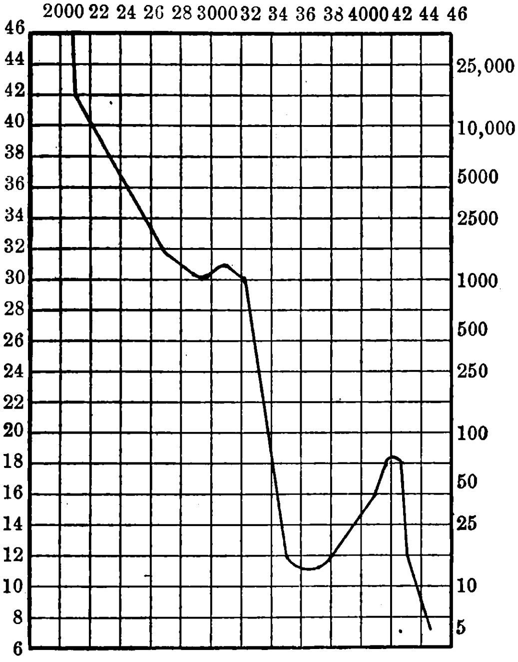
FIG. 11.



Trichlorotoluquinone.

Figure 12.

FIG. 12.



Dichlorothymoquinone.

Figure 13.

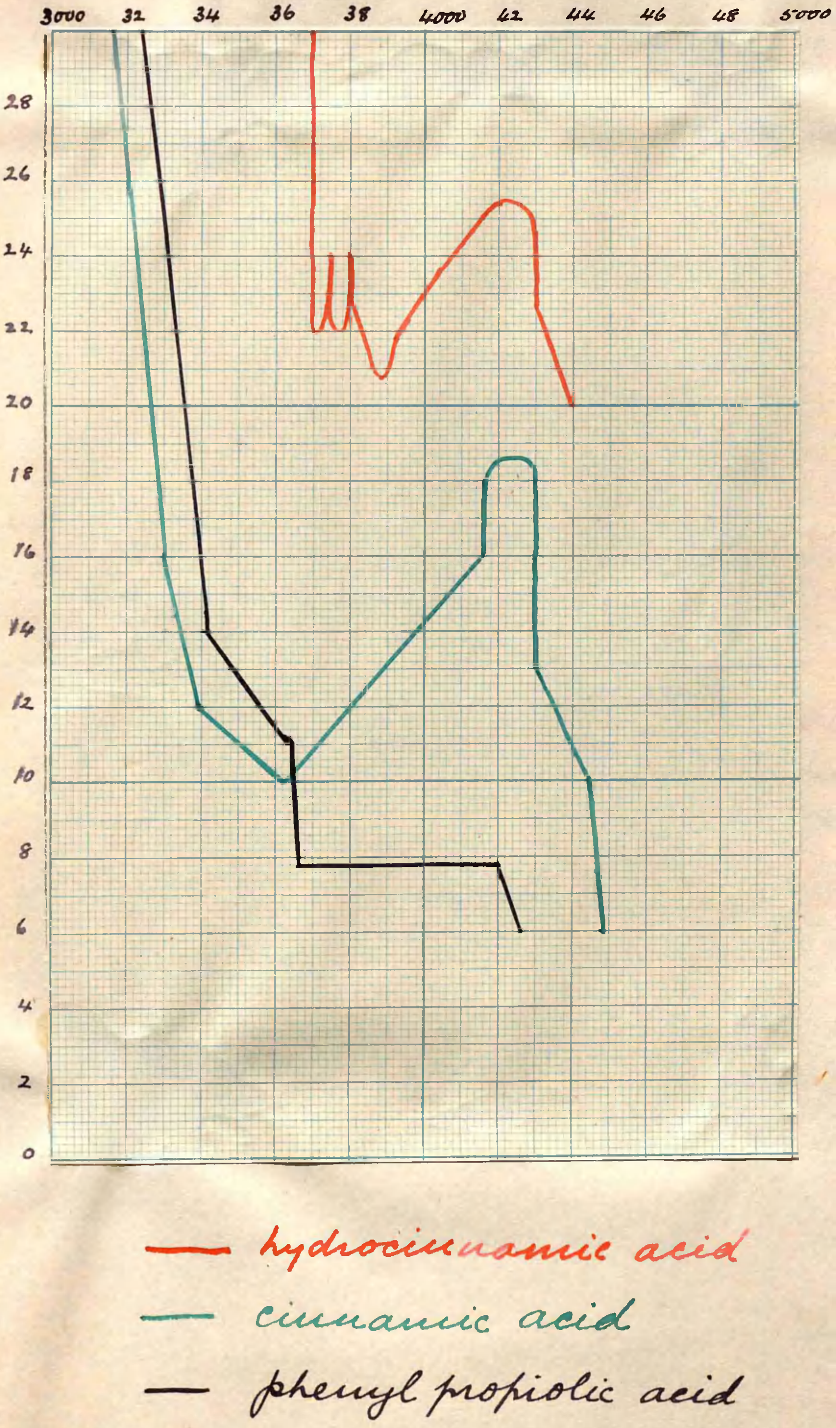
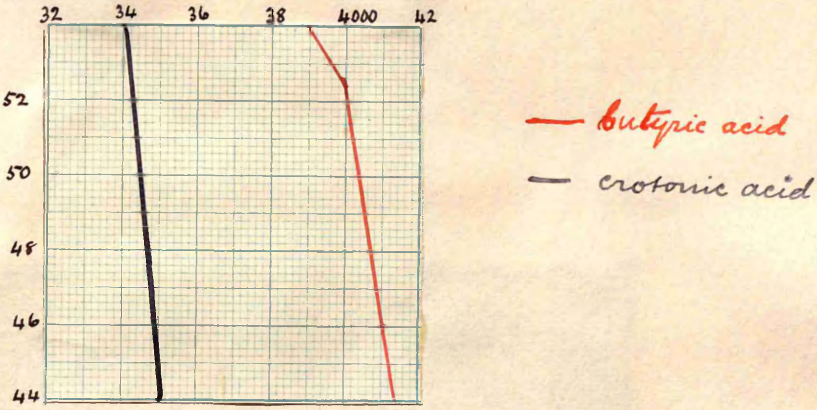

3000
32
34
36
38
4000
42
44
46
48
5000
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
hydrocinnamic acid
cinnamic acid
phenyl propiolic acid

Fig. 14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42
52
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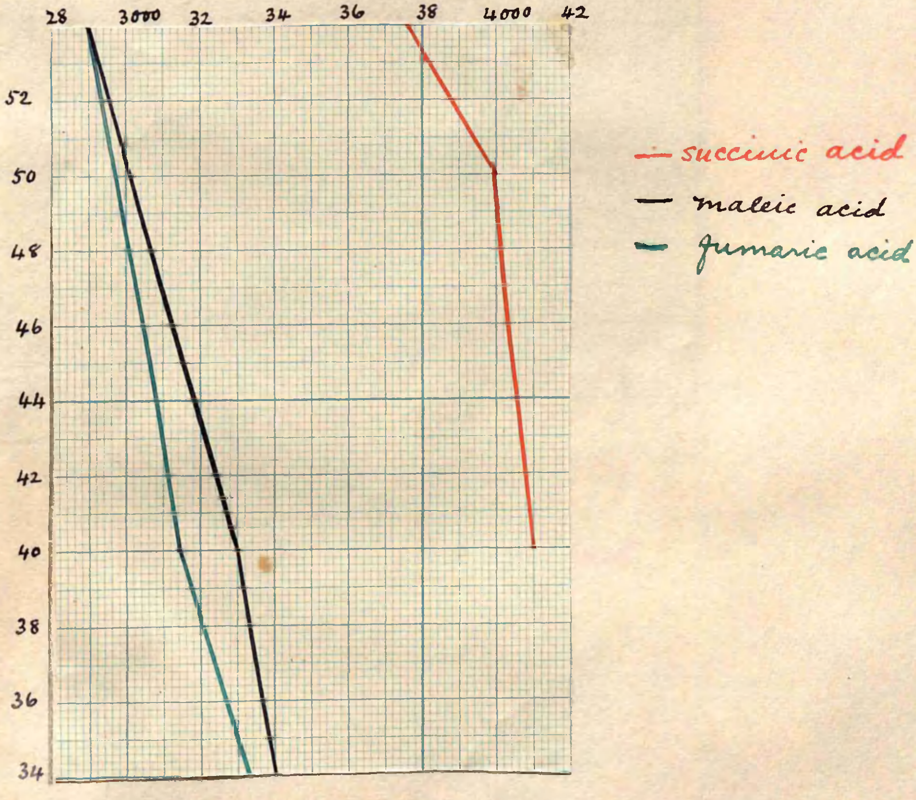
44
butyric acid
crotonic acid

Fig. 15.


28
3000
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4000
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36
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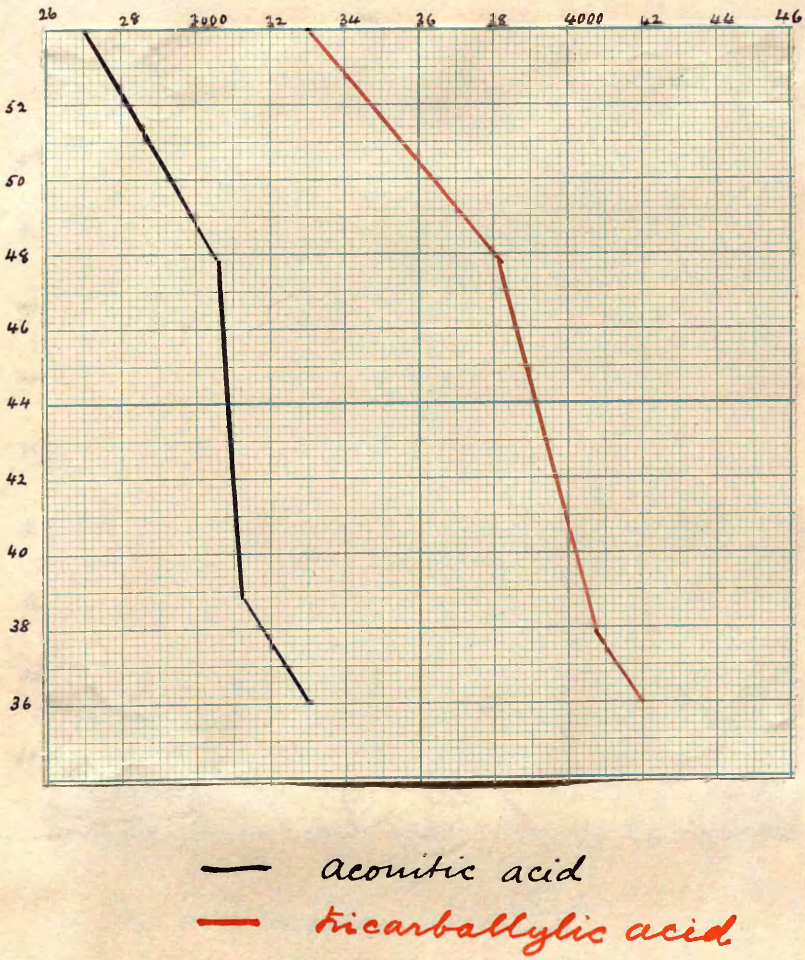
succinic acid
maleic acid
fumaric acid

Fig. 16.



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aconitic acid
tricarballylic acid

Figure 17.


3000
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34
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4000
42
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40
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36
34
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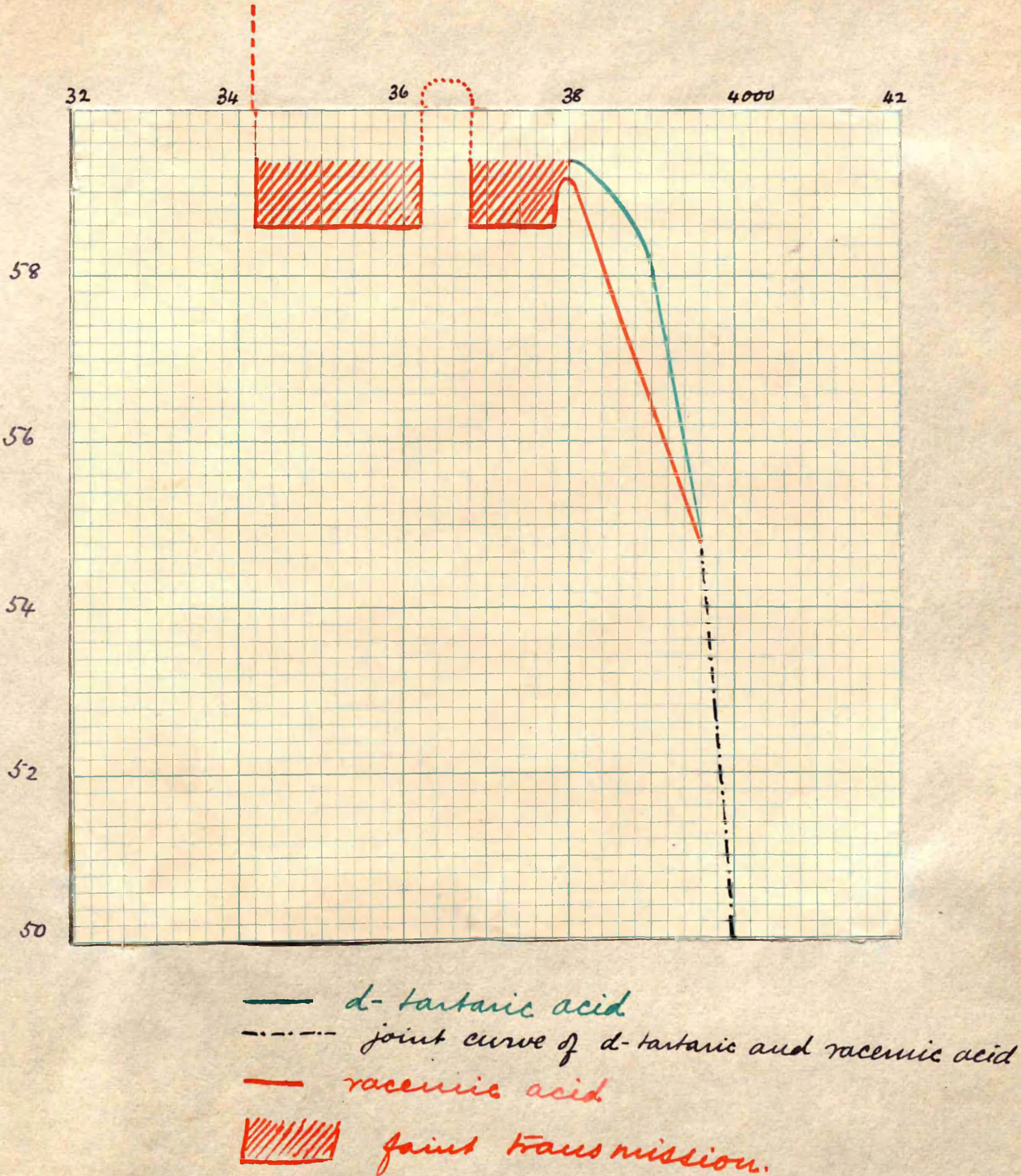
30
— mesaconic acid
— citraconic acid
— itaconic acid

Figure 18.


32
34
36
38
4000
42
58
56
54
52
50
d-tartaric acid
joint curve of d-tartaric and racemic acid
racemic acid
faint transmission.