



TITLE:

Spectroscopic and Photochemical Research on the Diazo-Compounds etc.

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CITATION:

Fukushima, Ikuzo ...[et al]. Spectroscopic and Photochemical Research on the Diazo-Compounds etc.. Memoirs of the College of Engineering, Kyoto Imperial University 1931, 6(3): 179-238

ISSUE DATE:

1931-03-30

URL:

<http://hdl.handle.net/2433/280108>

RIGHT:

Spectroscopic and Photochemical Research on the Diazo-Compounds etc.

By

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(Received Jan. 20, 1931.)

CONTENTS.

Preliminary Remarks.

Part I. Spectroscopic Study of the Diazobenzene Salts etc.

Introduction.

Chap. I. Starting Compounds.

Chap. II. Derivatives with Nitro-Substituent.

Chap. III. Derivatives with Carboxy-Substituent.

Chap. IV. Derivatives with Sulphonic Substituent.

Chap. V. Derivatives with Methyl Substituent.

Chap. VI. Derivatives with Chloro-Substituent.

Chap. VII. Phenyl diazotate and Phenylhydrazine.

Chap. VIII. Derivatives with Hydroxy-, Methoxy- and Ethoxy- Substituent.

Summary.

Part II. The Photolysis of the Diazo-Compounds.

I. Introduction and Absorption Spectrum.

II. Photochemical Absorption Spectrum.

III. Apparatus and Method of Estimation.

IV. Fundamental.

Experimental.

Discussion.

V. Influence of Inner Filter.

Experimental.

Discussion.

VI. Influence of Temperature.

Experimental.

Discussion.

VII. Quantum Efficiency.

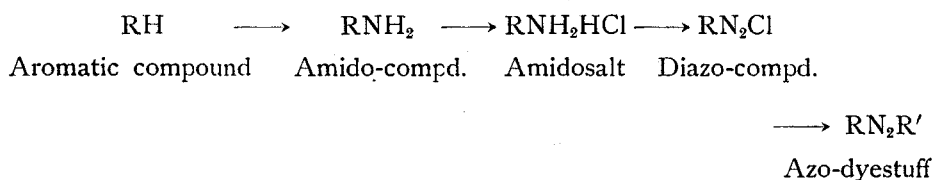
VIII. Summary.

Acknowledgment.

PRELIMINARY REMARKS.

The present article is concerned with the spectro- and photochemistry of the intermediate products of mono-azo dyes.

The mono-azo dyes are generally synthesized through the following stages :



Of these intermediate products, the diazo-compound is the most significant, being the original compound of all the azo-dyes, and presenting so many interesting chemical properties that researches have long been prosecuted on the behaviour of the compounds from the points of view both of theoretical chemistry and of practical application.

The authours have attempted in Part I of the present article to clarify the picture of the structure of these intermediate products by measuring the absorption spectra of a number of compounds of the diazobenzene-family together with their mother substances and the kindred compounds, excepting only a few that cannot be treated in this way. In Part II they are treated according to their photolysis, which is of great importance in connection with the practical problem of dyestuffs. The azo-dyestuff and its intermediate products are mostly stable against light; while most of the diazo-compounds are unstable against light and heat, this being an important factor to be considered during the process of manufacturing azo-dyestuffs. The authours believe that some of these points clarified in this latter part will by analogy be of service in the study of the nature of other dyes.

PART I.
SPECTROSCOPIC STUDY OF THE DIAZOBENZENE
SALTS ETC.

INTRODUCTION.

It is not too much to say that throughout the numerous researches on the diazobenzene salts the chief interest has centered on the structure of those compounds, and we are indebted to a number of chemists for studies through which the idea of the structure has been gradually evolving till now we have Blomstrand's "Diazonium salt" idea. This theory is generally thought to be by far more acceptable than any of those enunciated before or after it¹⁾. Turning to the spectroscopic research in this line, the only article on this subject of which the authours are aware is that by Hantzsch and Lifschitz²⁾, in which allusion is made to the possibility of the diazo-group possessing another structural state than that of the azo-group in view of the notable differences in the ultra-violet absorptions observed in a few cases.

With a view to establishing a more definite idea of the structure of the diazo-group by the aid of spectroscopic phenomena, the authours turned their attention to the changes in the absorption of diazobenzene salts when a different radical is introduced into the various positions in the benzene nuclei. A series of observations was carried out with solutions of those diazobenzene salts, the substances from which they are derived, and some of their derivatives through the substitution with saturated and unsaturated radicals, and those acting both positively and negatively towards the nucleus.

1) Selective literature in chronological order.

P. Griess, A. 1866 **137** 39. Kékulé, Zeitschr. f. chem. 1866 3081.

Blomstrand, Chem. d. Jetztzeit 1869 **4** 272.

Strecker, B. 1871 **4** 786. Erlenmeyer, B. 1874 **7** 1110.

E. Fischer, B. 1877 **10** 1331.

Hantzsch, B. 1895 **28** 1737, 1898 **31** 1612.


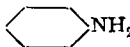
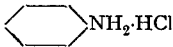

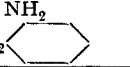
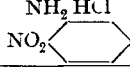

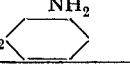
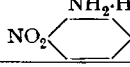

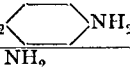
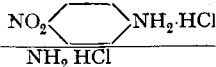

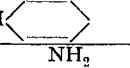
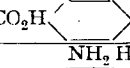


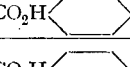

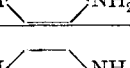
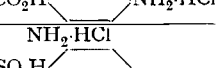
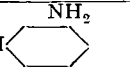
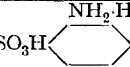
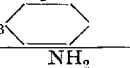
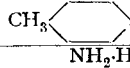


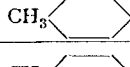

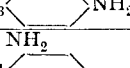
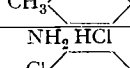

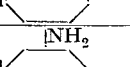
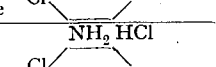

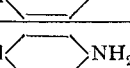
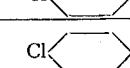

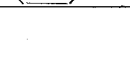
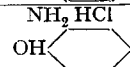

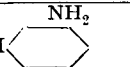
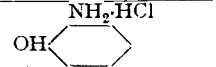

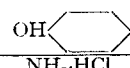

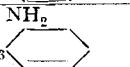
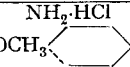

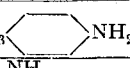
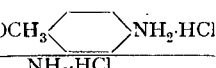
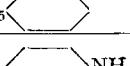
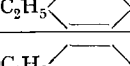




Bambemger, B. 1895 **28** 444.

Cain, Trans. 1907 **91** 1049 &c.


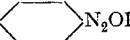
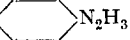
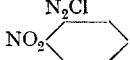
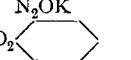
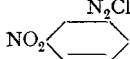

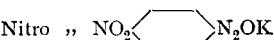
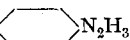
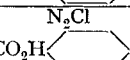
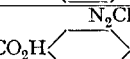
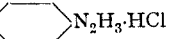

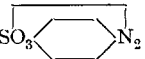
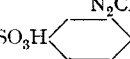
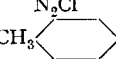
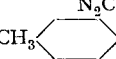

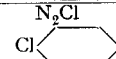
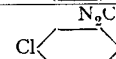
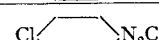
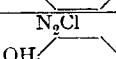
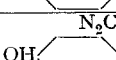
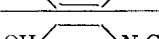
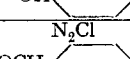
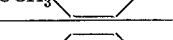
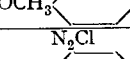
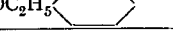
2) B. 1912 **45** 3011.

Cain published, however, the opposition view a short time later. (B. 1913 **46** 101.)

Table

	I	II (Amido)	III (Amido-salt)
1	Benzene 	Aniline 	Aniline hydrochloride 
2	Nitrobenzene 	o-Nitraniline 	o-Nitraniline hydrochloride 
3	" 	m- " 	m- " " 
4	" 	p- " 	p- " " 
5	Benzoic acid 	o-Carboxyaniline 	o-Carboxyaniline hydrochloride 
6	" 	m- " 	m- " " 
7	" 	p- " 	p- " " 
8		Sulphanilic acid 	p-Sulpho-aniline hydrochloride 
9		Metanilic acid 	m- " " 
10	Toluene 	o-Toluidine 	o-Toluidine hydrochloride 
11	" 	m- " 	m- " " 
12	" 	p- " 	p- " " 
13	Chlorobenzene 	o-Chloraniline 	o-Chloraniline hydrochloride 
14	" 	m- " 	m- " " 
15	" 	p- " 	p- " " 
16	Phenol 		o-Amidophenol hydrochloride 
17	" 	m-Amidophenol 	m- " " 
18	" 	p- " 	p- " " 
19		o-Anisidine 	o-Anisidine hydrochloride 
20		p- " 	p- " " 
21		o-Phenetidine 	o-Phenetidine hydrochloride 
22		p- "	p- " "

I.

IV (Diazo)	V (Diazotate)	VI (Hydrazine)
Diazobenzene chloride 	Phenyldiazotate 	Phenylhydrazine 
o-Nitrodiazobenzene chloride 	o-Nitro " 	
m- " " 		
p- " " 	p-Nitro " 	p-Nitro " 
o-Carboxydiazobenzene chloride 	VII (Hydrazine-salt)	
m- " " 	Phenylhydrazine hydrochloride 	
p- " " 		
p-Diazobenzene sulphonic acid 		
m-Sulphodiazobenzene chloride 		
o-Methyldiazobenzene chloride 		
m- " " 		
p- " " 		
o-Chlorodiazobenzene chloride 		
m- " " 		
p- " " 		
o-Hydroxydiazobenzene chloride 		
m- " " 		
p- " " 		
o-Methoxydiazobenzene chloride 		
p- " " 		
o-Ethoxydiazobenzene chloride 		
p- " " 		

The compounds that are dealt with in the present work may be conveniently grouped in Table 1.

The absorptions are shown by Hartley-Baly diagrams in which the ordinates stand for the logarithm of the depth of the $m\mu/5,000$ -solution in mm., and the abscissas for the number of waves per one mm. For the light source the authors employed a condensed spark passed in the air between copper electrodes with a potential difference of 15,000 V. The spectrograph used was an Adam Hilger one, with quartz lens and prism, the plates being "Ilford Process Plates".

CHAPTER I. STARTING COMPOUNDS.

(ref. 1st row in Table I.)

The absorption diagrams of the four compounds,

C_6H_6	$C_6H_5NH_2$	$C_6H_5NH_2HCl$	$C_6H_5N_2Cl$
Benzene	Aniline	Aniline hydrochloride	Diazobenzene chloride
I.	II.	III.	IV.

are given in Fig. 1.

It may be noted that although there takes place an essential change in the absorption spectrum with the transition from benzene (I) to aniline (II), aniline hydrochloride (III) resumes the characteristic absorption of benzene proper. This was observed already by Baly and others¹⁾. By far the most significant point here, however, is the fact that the absorption diagram of diazobenzene chloride (IV) preserves the essential feature of the benzene bands, which are situated at 3700 to 4200 ($r. \text{ \AA}$). Observing these relationship among the four compounds, we find that when benzene is converted into its amido-substitution product, some essential change in absorption follows, while with the transition into its salt-form (III), the absorption resumes again the characteristic of benzene proper, which still survives in the absorption of diazobenzene chloride (IV)²⁾. This shows that

1) Baly and Colly, J. chem. Soc. **87**, 1332.

2) It is observed in various cases that the benzene derivatives with the substituent, which has an ammonium nitrogen atom binding directly to the nucleus, preserve characteristic of benzene in their absorption. (ref. Ley and Urlich, B. 1909, **42**, 3441. The absorption of phenyl-trimethyl-ammonium chloride is shown in Fig. 1.)

only the amido-compound (II) is something utterly different from the structural point of view.

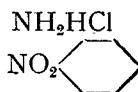
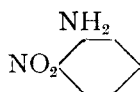
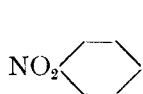
CHAPTER II. DERIVATIVES WITH THE NITRO-SUBSTITUENT.

In the present chapter are set forth the cases in which substitutions were made in the fundamental compounds mentioned above, the unsaturated nitro-group behaving positively towards the nucleus being introduced into the benzene nucleus.

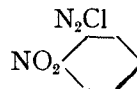
1. The ortho-compounds. (ref. 2nd row in Table I.)

The absorptions of these four compounds, namely

Nitrobenzene (I), o-Nitraniline (II), o-Nitraniline hydrochloride (III),



o-Nitrodiazobenzene chloride (IV).

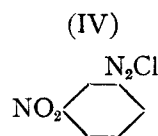
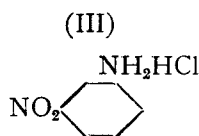
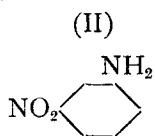
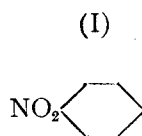


are shown in Fig. 2.

Starting from nitrobenzene, a great change in the absorption is observed to attend the transformation into nitraniline; while with the further change into compound (III) the absorption returns again to that of nitrobenzene (I). The diazo-compound (IV) also gives an absorption curve which is very similar to that of nitrobenzene in its most important parts. The amido-compound alone presents a different sort of absorption.

2. The meta-compounds. (ref. 3rd row in Table I.)

Fig. 3 represents the absorption diagrams for the four meta-compounds:

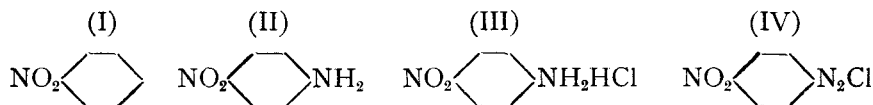


In the figure, the absorptions of both nitraniline hydrochloride (III)

and its diazo-compound (IV) keep the essential feature of nitrobenzene (I), that of the amido-compound (II) only diverging abnormally from the other three.

3. The para-compounds.

Fig. 4 shows the diagrams of the four compounds of the para substitution products.



The pervading analogous relationship is evident, the amidosalt (III) and the diazo-compound (IV) displaying the characteristic bands of the original compound. The amido-compound (II) alone betrays its peculiarity.

CHAPTER III. DERIVATIVES WITH CARBOXYL-SUBSTITUENT.

(ref. rows 5th, 6th & 7th in Table I.)

The above mentioned relationship prevails among the carboxyl-substitution products. Figs. 5, 6 & 7 show the ortho-, meta- and para-compounds respectively. As is obvious from the figures, the diazo-compounds (IV) equally possess the main selective benzene bands, in the same chromatic position as those of benzoic acid and the amidosalts (III). The amido-compounds show the peculiar absorptions.

CHAPTER IV. DERIVATIVES WITH THE SULPHONIC SUBSTITUENT.

The derivatives obtained by substitution with the unsaturated, positive sulphonic radical were then investigated. (The ortho-compound was not measured.) Without exception, the reiterated analogous relationship still holds with these sets of compounds.

1. The meta compounds. (ref. 9th row in Table I.)

Fig. 8 shows the diagram for the meta-compounds. Only meta-anilinesulphonic acid (metanilic acid) (II) has its center of absorption in a different chromatic position from those of (III) & (IV), which lie at the

same wave-number.

2. The para-compounds. (ref. 8th row in Table I.)

As is clearly shown in Fig. 9 the same thing can be said of the para- as of the meta-compounds.

CHAPTER V. DERIVATIVES WITH THE METHYL SUBSTITUENT.

1. The ortho-compounds. (ref. 10th row in Table I.)

Comparing Fig. 10 with Fig. 1, an exact similarity is recognized so far as the most important part is concerned. Here too only the amido-compound, i. e. toluidine, shows a different sort of absorption.

The same is true of the meta-compounds and the para-compounds; only in the latter case, however, the center of absorption of the diazo-compound is slightly shifted towards the red by 11 m μ .

2. The meta-compounds. (ref. 11th row in Table I.)

The modes of absorption are shown in Fig. 11.

3. The para-compounds. (ref. 12th row in Table I.)

Fig. 12 shows the para-compounds.

CHAPTER VI. DERIVATIVES WITH THE CHLORO- SUBSTITUENT.

(ref. rows 13th, 14th & 15th in Table I.)

The chloro-substitution products present such a similarity to the methyl compounds that one can safely assert that they are identical. Only chloroaniline (II), the amido-compound, affords an anomalous absorption, while the diazo-compound (IV) retains the characteristic absorption of chlorobenzene. That the para-diazo-compound alone has the center of absorption somewhat displaced (12 m μ toward the red) is quite similar to the case of the methyl compounds. These diagrams are shown in Figs. 13, 14 and 15.

Summarizing the foregoing cases we may make the following observations:

First, the benzene substitution products with whatever radical, be it

positive or negative, saturated or unsaturated, at any position of the nucleus of benzene, are always attended with either a pronounced or an essential change in the mode of their absorption, as the original compounds are converted into the amido-form. In the second place, when those compounds are further converted into their salt-forms, the absorption tends to show again the characteristic bands of the original substances. Furthermore, these characteristic benzene bands of the original compounds are still maintained in the cases of the diazo-compounds. And all the diazo-compounds show congeneric absorptions. In other words, the amidosalt-radical, as well as the diazo-salt-radical, when introduced into any position in the nucleus of benzene, does not materially disturb the original condition of the starting substances, thus standing in strong contrast with the behaviour of the amido-radical. Or, more concretely, the diazo-radical, has an effect similar to that of the amidosalt-radical ($-\text{NH}_2\text{HCl}$), but showing quite a different behaviour from the unsaturated group of atoms of the amido-radical ($-\text{NH}_2$).

On the amido-compounds in the preceding cases, we may make the following remarks. The amido-radical, when it is made to coexist in the same benzene nucleus with one of these unsaturated radicals, such as $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, greatly affects the absorption spectrum, causing in most cases the disappearance of the characteristic aniline-band, producing besides very divergent and irregular absorption curves even among their isomers. (ref. Figs. 16, 17 & 18.)

The case is quite otherwise when the amido-radical coexists with the negative group, but without unsaturated linking, in the same benzene nucleus. Figs. 19, 20, 21 & 22 are cases in which the amido-radical is found with some such negative group as $-\text{CH}_3$, $-\text{Cl}$, $-\text{OH}$, $-\text{OCH}_3$, or $-\text{OC}_2\text{H}_5$. In all cases the characteristic bands of aniline are equally apparent.

CHAPTER VII. PHENYLDIAZOTATES & PHENYLHYDRAZINE.

Researches on diazotates have been carried out as extensively as on

the diazo-salts¹⁾. As to spectroscopic researches, however, there is a scarcity of literature²⁾. As in the previous experiments, the effect of substitution on the change in the absorption of both diazotates and hydrazines was observed, and efforts were made to find out their position relatively to the compounds already treated.

As is shown in Fig. 23, potassium anti-phenyldiazotate has its absorption band at a position indicating a considerably longer wave length than diazobenzene. However, when the nitro-group is introduced the mode of absorption undergoes a great change. In the case of the para-compound, the center of absorption is found to shift as much as $60\text{ m}\mu$ towards a position of longer wave length. And the ortho-compound also presents a peculiar sort of longer wave absorption. That the absorption of diazobenzene mentioned above is not the like, is clearly shown by Fig. 23. The same is true of phenylhydrazine; i. e. its nitro-substitution product presents a marked change in absorption, as is shown in Fig. 24.

As in the above cases, the effect of the nitro-group upon phenyldiazotate and phenylhydrazine as well, being quite identical with the case of aniline, utterly differs from that of the amidosalt- and the diazo-radical.

The authors accordingly investigated the change that attended the conversion of phenylhydrazine into its salt-form at the second nitrogen linking. This is mentioned here because of its particular interest though it has no direct bearing on the present problem. From the various instances of the amidosalts mentioned previously one might well expect that $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \text{H} \\ \text{NH}_2 \end{smallmatrix} \cdot \text{HCl}$ would show an absorption similar to that of $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$, and this was verified, as is clearly indicated in Fig. 25. It is equally

-
- 1) V. Meyer (B. **21** 15). Japp. u. Klingemann (B. **24** 2264).
Von Pechmann (B. **24** 3255). Bambemger (B. **24** 3264, B. **26** 495).
Pechmann Foobenius (B. **27** 672). Bambemger (B. **27** 679, 1948).
Hantzsch (B. **27** 1702, 1857). Bambemger (B. **27** 2596).
Hantzsch (B. **27** 1865) (A. **325** 226; B. **28** 1734, 1900) (B. **29** 1003, B. **33** 2517).
Bambemger (B. **27** 3212; **28** 225, 829; **29** 457; A. **313** 97).
Hantzsch (B. **32** 1703; **35** 2964; **36** 3097, 4361; **37** 3030).
Recently; L. Cambi, L. Szegő (B. **61** (1928) 2081).
A. Hantzsch: (B. **62** (1929) 1235 etc.).
 - 2) Hantzsch and Lifschitz: (B. **45** 3011). Dobbie and Tinkler (Trans. 1905 **87**, 273).

worthy of remark, however, that the absorption is fairly hyposochromic as compared with aniline, while, on the other hand, it is well recognized in the cases of *o*-nitraniline hydrochloride and some others that the amido-salt-radical, combined directly with the nucleus of benzene, exerts a bathochromic effect.

An analogous phenomenon has already been observed with much interest by H. Ley¹⁾ with styrolene: viz. when the methyl radical, which is known to display a weak auxthochromic effect, was substituted in the position of the α carbon of styrol $C_6H_5-CH=CH_2$ the absorption shifted towards a position indicating shorter wave length; while when substitution was carried out at the β carbon, the absorption band was shifted in the opposite direction.

CHAPTER VIII. INVESTIGATION OF DIAZO-PHENOLS, -ANISIDINES, AND -PHENETIDINES.

(ref. rows 16, 17 and 18 in Table I.)

It is known that when hydroxydiazobenzene chlorides²⁾ are prepared, HCl is very apt to be separated from the products in the presence of water. Hantzsch and others³⁾ observed dissociation degrees of these diazo-amidophenols to be remarkably higher, and assumed that these compounds show different structural states than ordinary diazo-salts. We have measured the absorption spectra of the dilute water solutions of diazo-phenols, -anisidines, and -phenetidines and ascertained the above assumption, observing the exact analogy which exists among the compounds.

Fig. 26 shows the absorption diagrams of *ortho*-amidophenol hydrochloride, diazotized *ortho*-amidophenol, and phenol. Quite unlike the diazo-salts of the kind already treated, the diazo-compound of the present set shows a strongly deformed absorption curve compared with those of both amidophenol hydrochloride and phenol. The absorption curve has

1) B. 1918, 51, 1808.

2) Cameron, Amer. Chem. Journ. 20, 229; Schmidt, B. 1, 67.

3) B. 29, 1522.

undergone a remarkable shift to a position of longer wave length, presenting a strong selective absorption of the so-called chinone-type. The diagrams of the meta- and the para-compounds are given in Figs. 27 & 28. The para-compounds too give a considerably deformed curve, while the meta-diazo-compound alone shows a weak chinone absorption. The characteristic band of phenol is also seen in this case. The ortho- and para-compounds of anisidine and phenetidine present identical absorption curves (ref. Figs. 29 & 30). The diazotized derivatives of amidophenol, anisidine and phenetidine equally present the singular absorption at the chromatic position of longer wave length, proving that they are in a more or less different state from that of the diazo-salts treated in the preceding chapters. This chapter will suffice to show that the diazotized amido-phenol, -anisidine, and -phenetidine as compared with the diazo-compounds already treated are all in a radically different state from the structural point of view.

SUMMARY.

1. The amido-, the amidosalt-, and the diazo-radical, were each introduced into the nucleus of benzene, and the absorption spectra obtained show that only the amido-compound is anomalous, in that the original essential of benzene proper is missing, while the other two retain it.

2. The relation among the four different types of compounds in 1. exists without exception in all cases where $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{CH}_3$ or $-\text{Cl}$, are further introduced into the nucleus of benzene in the ortho, meta, or para positions.

3. On still closer observation it has been found that the amido-radical, negative towards the benzene nucleus, coexisting with the unsaturated group i. e. $-\text{NO}_2$, $-\text{COOH}$ or $-\text{SO}_3\text{H}$, acting positively towards nucleus, brings about the disjointed deformation of the characteristic aniline absorption curve, and exhibits chaotic irregularity even among the isomers; while the amido-radical, coexistent with the negatively acting group such as $-\text{CH}_3$, $-\text{Cl}$, $-\text{OH}$, $-\text{OCH}_3$ or $-\text{OC}_2\text{H}_5$, retains equally the characteristic band of aniline. At any rate, the amido-radical thus introduced into the benzene

nucleus causes the disappearance of the band of the original substance.

4. Unlike the above, the amidosalt- and also the diazo-salt-radical do not cause the disappearance of the characteristic band of the original compound, independent of the coexisting positive, unsaturated group such as $-\text{NO}_2$, $-\text{SO}_3\text{H}$ and $-\text{COOH}$, or the negative radical such as $-\text{CH}_3$ and Cl , in the benzene nucleus, and regardless of the position with respect to the nucleus.

5. Phenyl diazotate and phenylhydrazine have been subjected to substitution at the nucleus with $-\text{NO}_2$, and absorption bands have been found in positions indicating longer wave lengths, quite similar to the case of aniline.

6. Notwithstanding the general tendency of the amidosalt-radical to exhibit a bathochromic effect when it is substituted for the H-atom of the benzene nucleus, this radical, nevertheless, exhibits a hypsochromic effect in the case of phenylhydrazine, where the substitution is effected by replacing the H-atom indirectly combined with the benzene nucleus.

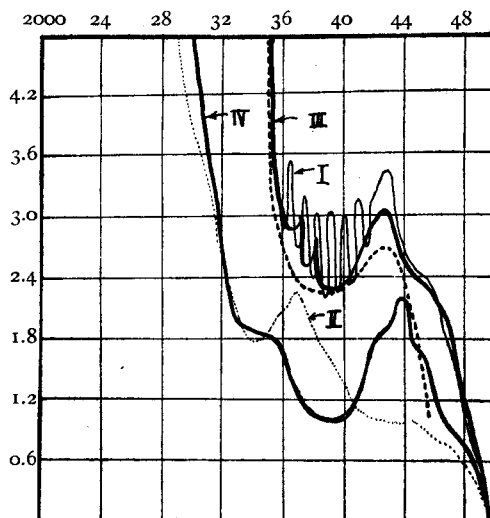
7. The absorption spectra of the diazotized amidophenols, anisidines and phenetidines have been measured, and found to give the singular absorption at chromatic positions of longer wave lengths, thus revealing very different structural conditions. Such singular absorption proved very weak in the case of the meta-compound.

8. To sum it all up in a word we may say that the diazobenzene family and the amidosalt-family are congeneric, and, as for the structure, especially the valency of the first N-atom, $>\overset{\vee}{\text{N}}\equiv$ is to be accepted as correct. However, in cases where $-\text{OH}$, $-\text{OCH}_3$, or $-\text{OC}_2\text{H}_5$ exist in the benzene nucleus, the diazo-compounds present an utterly different absorption, thus showing a different state in the structure from that when these are not present. The optical behaviour of the amido-, diazotate- and hydrazine-compounds is quite the opposite of that of the diazo-salt-, and amidosalt-compounds.

The physical constants (m. p. and b. p.) of the fundamental compounds that are dealt with in the present work were measured by the authors as given below :

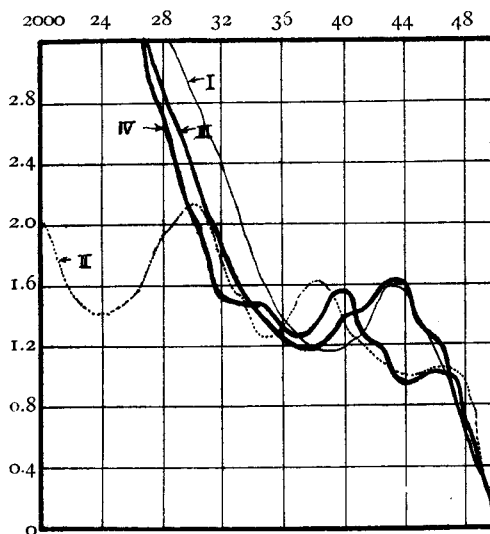
O-Nitraniline (m.p. 70°C); m-Nitraniline (m.p. 112°); p-Nitraniline (m.p. 147°); o-Amidobenzolic acid (m.p. 144°); m-Amidobenzoic acid (m.p. 171°); p-Amidobenzoic acid (m.p. 188°); m-Amidophenol (m.p. 123°); p-Amidophenol (m.p. 185°, *Kahlbaum's* "scientific pure" chemicals were purified through sublimation); Benzoic acid (m.p. 122°); o-Anisidine (b.p. 217°); p-Anisidine (m.p. 58); o-Phenetidine (b.p. 226°); p-Phenetidine (b.p. 245°); o-Toluidine (b.p. 198°); m-Toluidine (b.p. 200); p-Toluidine (m.p. 45°); o-Chloraniline (b.p. 206°); m-Chloraniline (b.p. 228°); p-Chloraniline (m.p. 70°); Aniline (b.p. 182°); Nitrobenzol (b.p. 206°).

Fig. 1.
(ref. 1st row in Table I.)



- I — Benzene c1ccccc1
 II Aniline Nc1ccccc1
 III — Aniline hydrochloride Nc1ccccc1.[Cl-]
 IV — Diazobenzene chloride [Cl-].[N+]#Nc1ccccc1
 V - - - - Phenyl-tri-methylammonium chloride [Cl-].N(C)(C)C1=CC=CC=C1

Fig. 2.
(ref. 2nd row in Table I.)



- I — Nitrobenzene O=[N+]([O-])c1ccccc1
 II o-Nitraniline Nc1ccc([N+](=O)[O-])cc1
 III — o-Nitraniline hydrochloride Nc1ccc([N+](=O)[O-])cc1.[Cl-]
 IV — o-Nitrodiazobenzene chloride [Cl-].[N+]#Nc1ccc([N+](=O)[O-])cc1

Fig. 3.
(ref. 3rd row in Table I.)

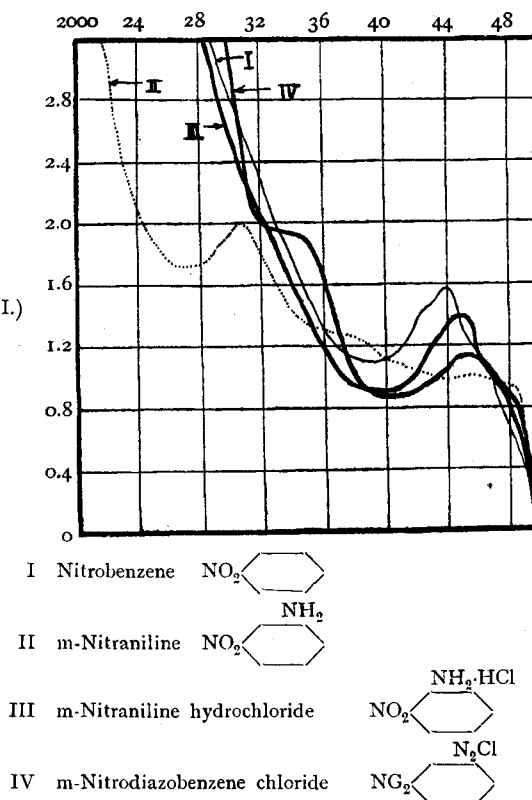


Fig. 4.
(ref. 4th row in Table I.)

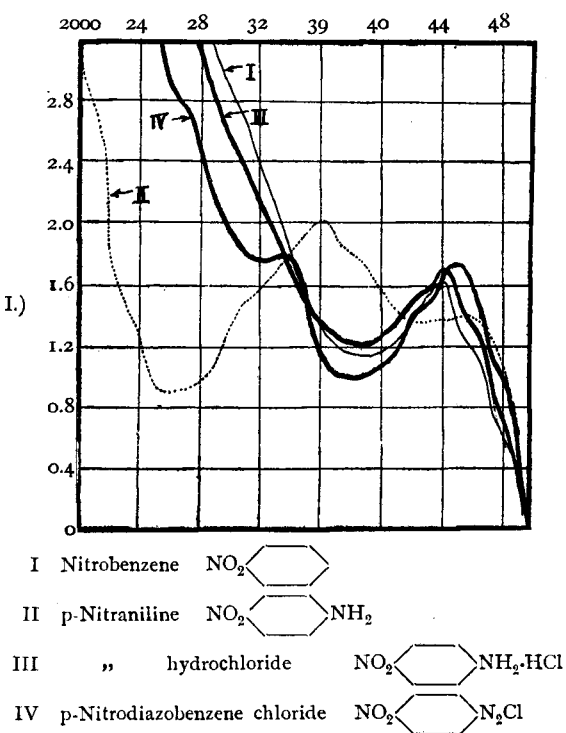


Fig. 5.
(ref. 5th row in Table I.)

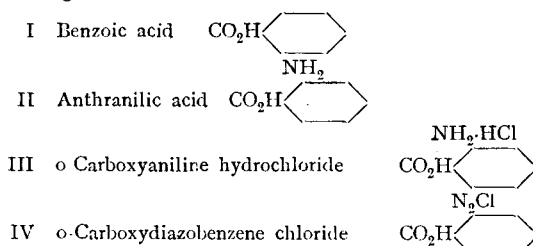
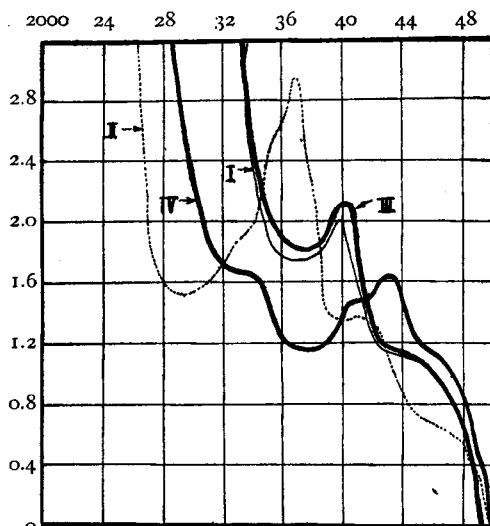


Fig. 6.
(ref. 6th row in Table I.)

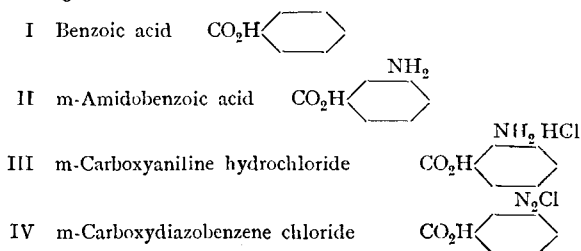
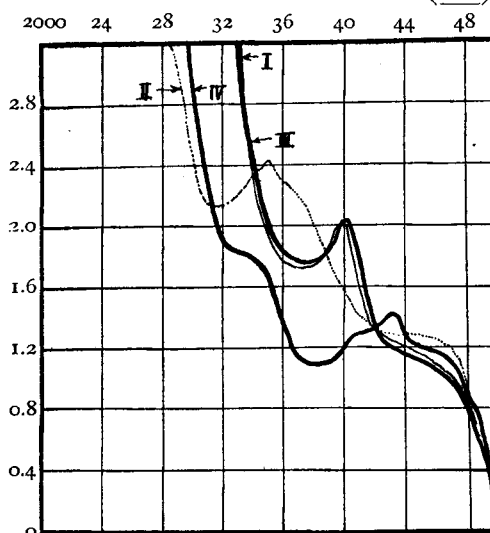


Fig. 7.
(ref. 7th row in Table I.)

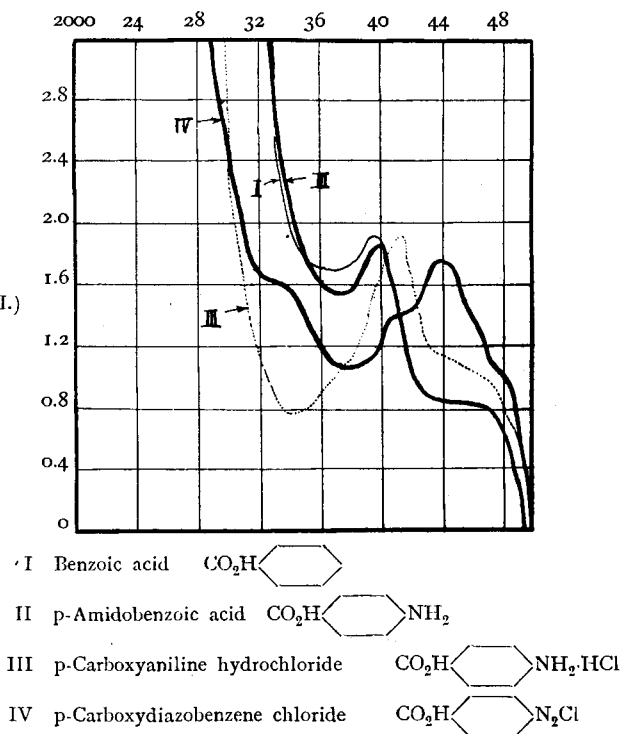
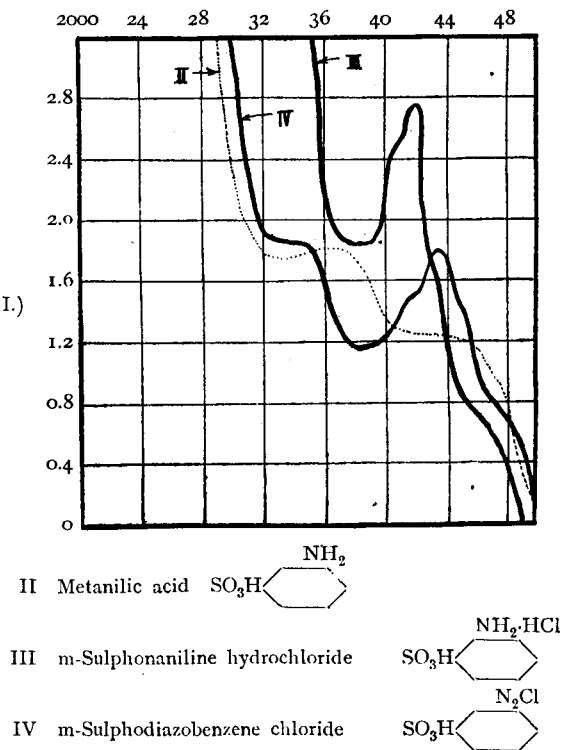


Fig. 8.
(ref. 6th row in Table I.)



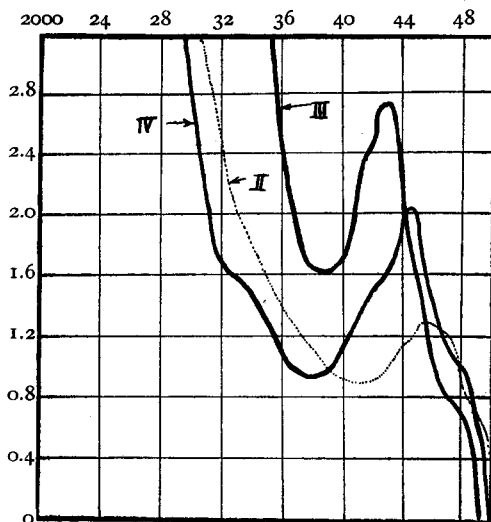


Fig. 9.
(ref. 8th row in Table I.)

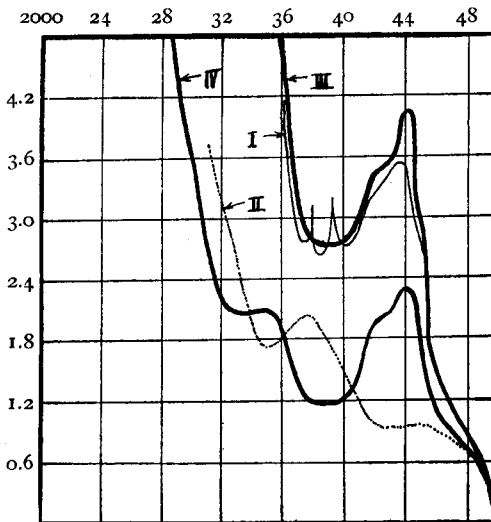
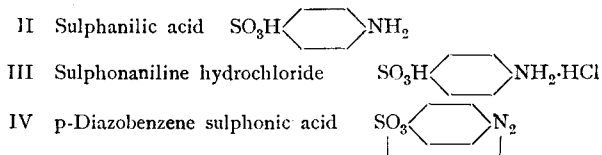
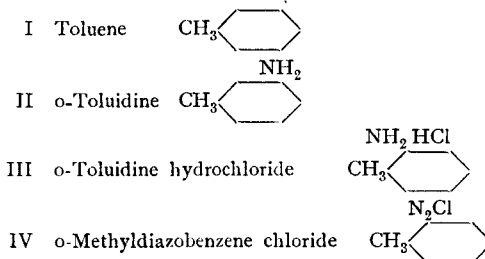


Fig. 10.
(ref. 10th row in Table I.)



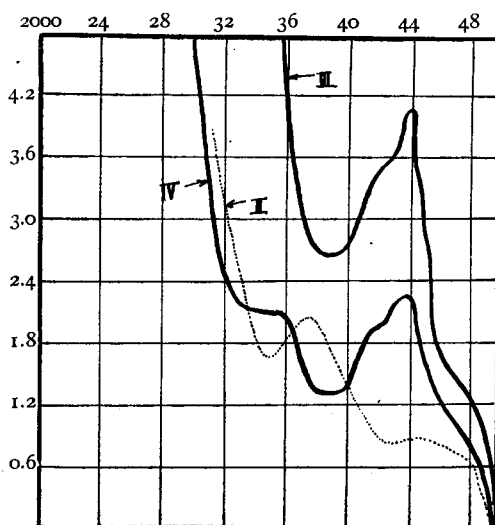


Fig. 11.
(ref. 11th row in Table I.)

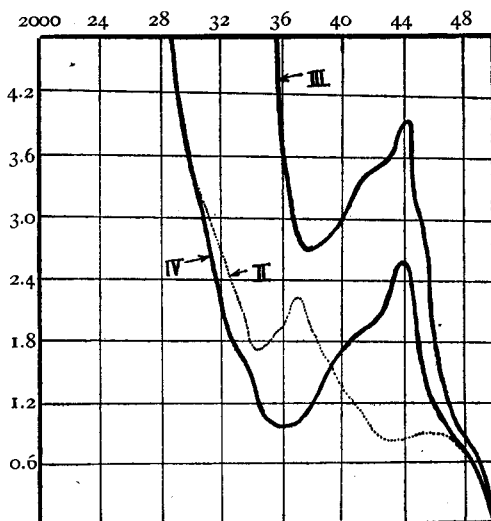
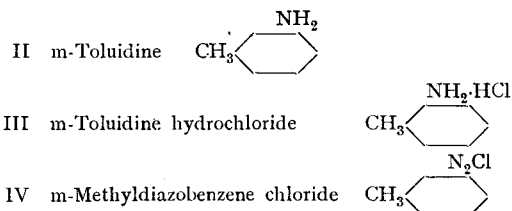


Fig. 12.
(ref. 12th row in Table I.)

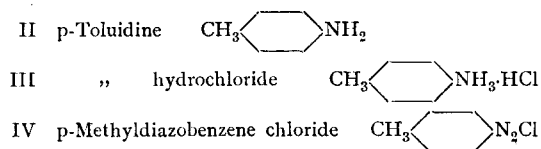


Fig. 13.
(ref. 13th row in Table I.)

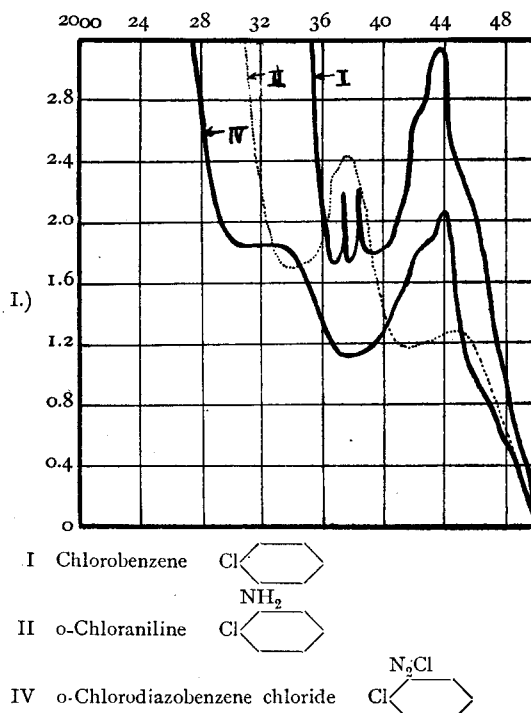


Fig. 14.
(ref. 14th row in Table I.)

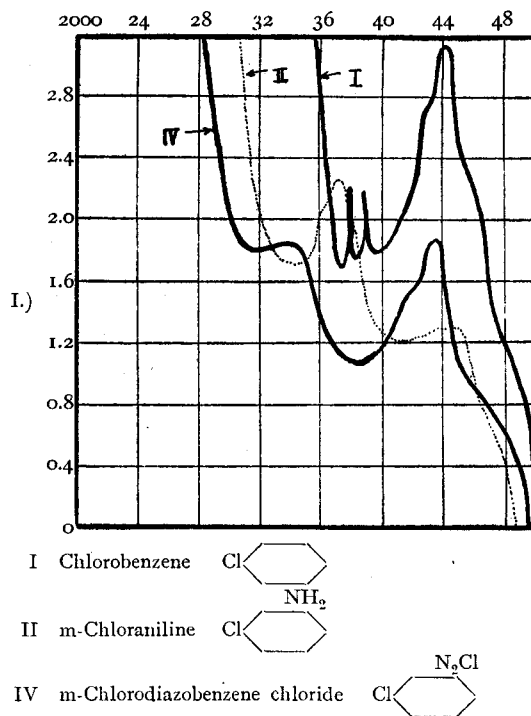


Fig. 15.
(ref. 15th row in Table I.)

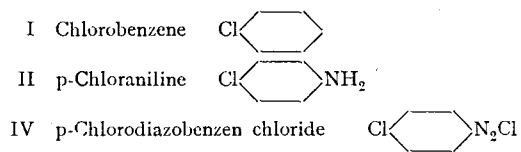
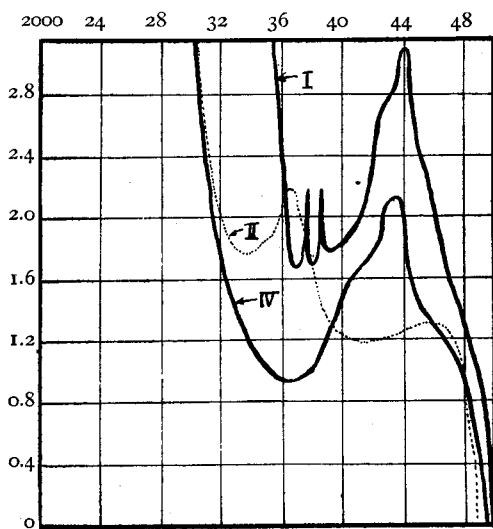
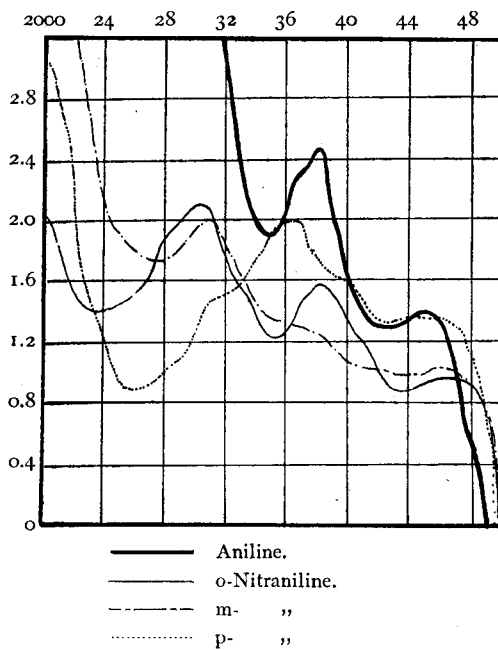


Fig. 16.



— Aniline.
 - - - o-Nitraniline.
 - - - m- "
 p- "

Fig. 17.

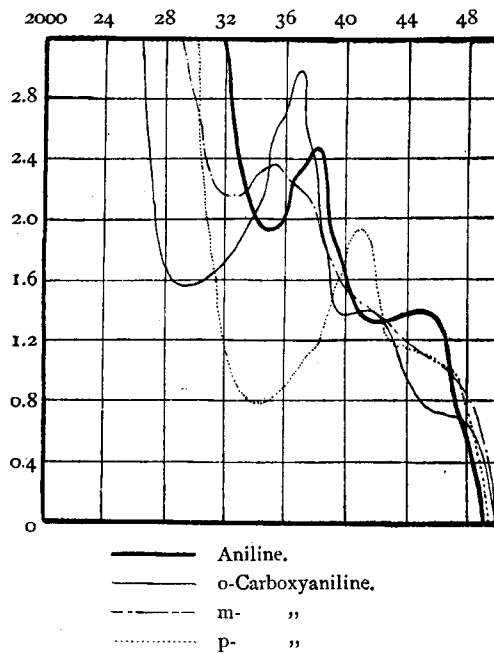


Fig. 18.

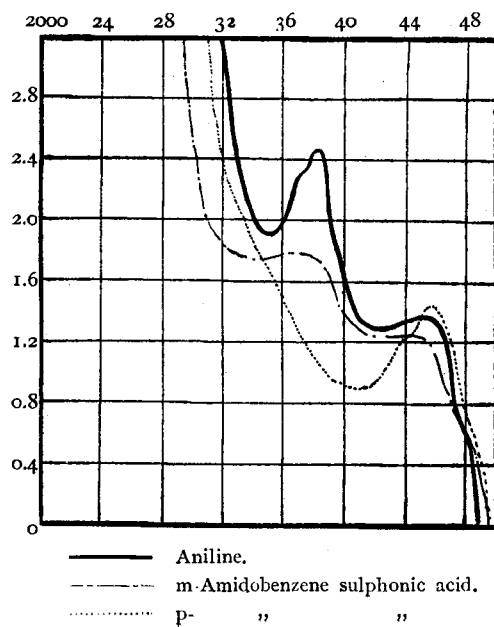


Fig. 19.

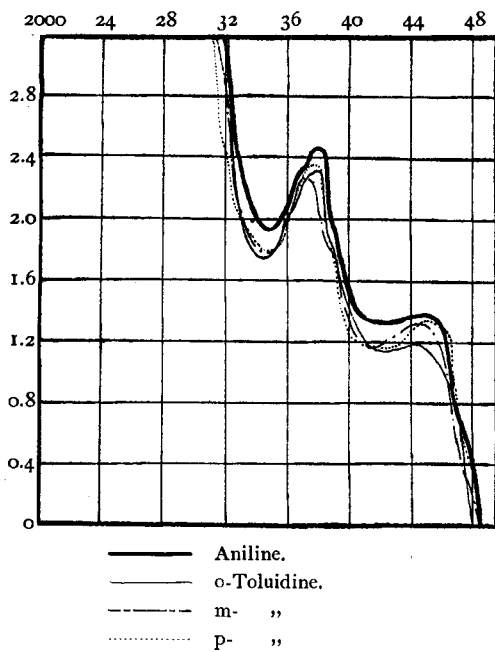


Fig. 20.

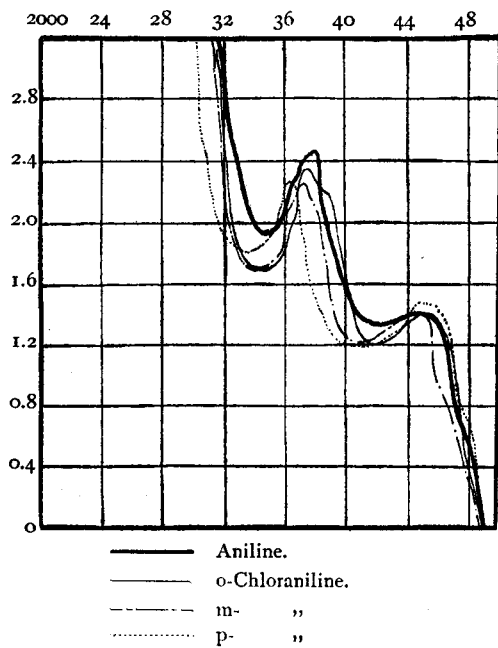


Fig. 21.

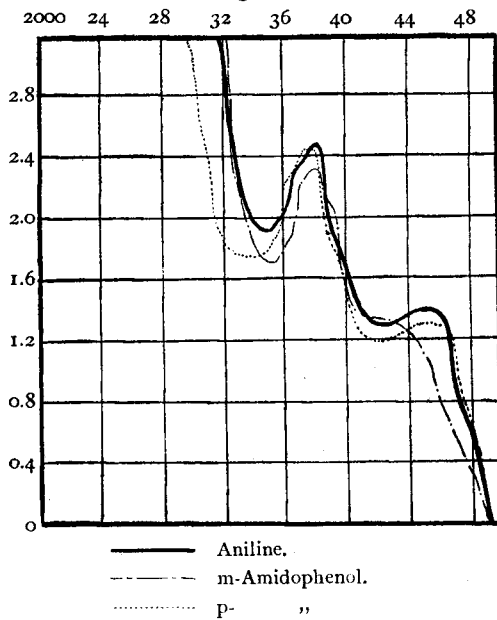


Fig. 22.

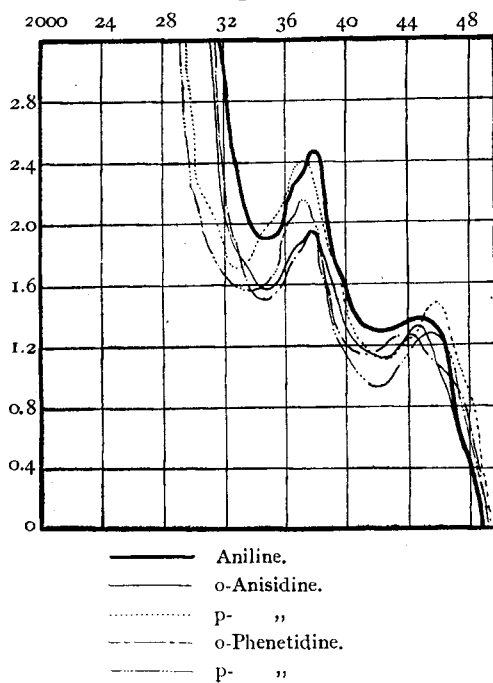


Fig. 23.

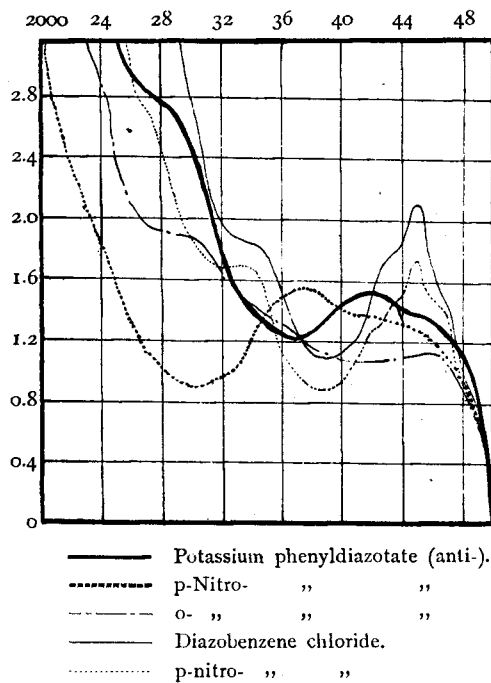


Fig. 24.

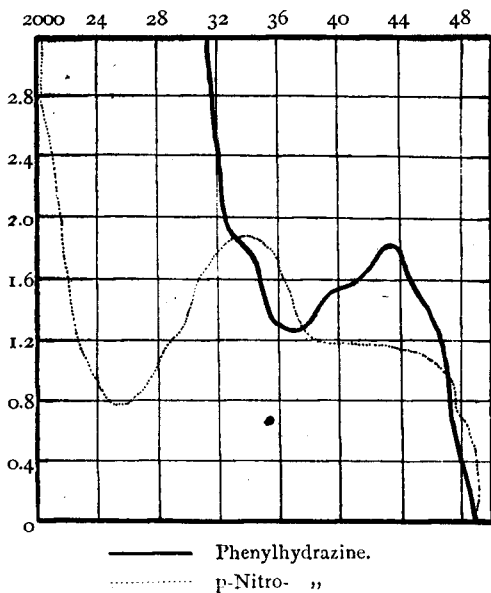


Fig. 25.

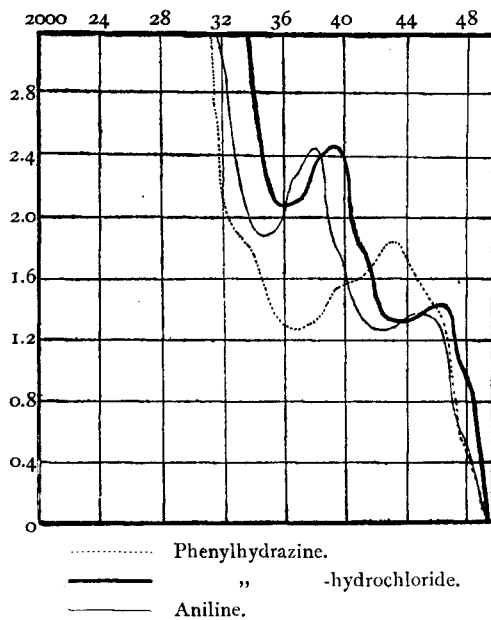


Fig. 26.

(ref. 16th row in Table I.)

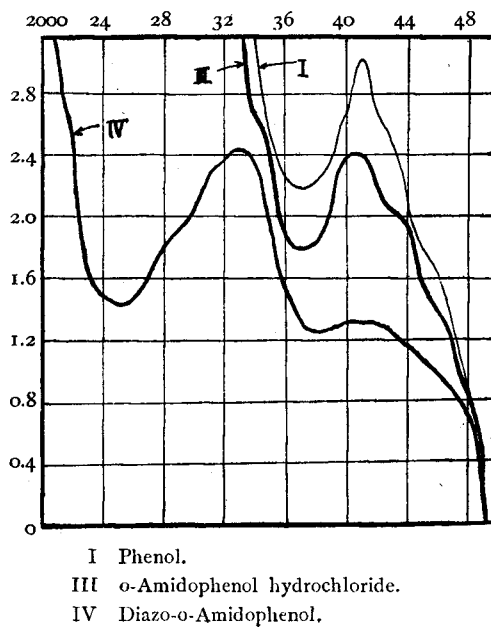
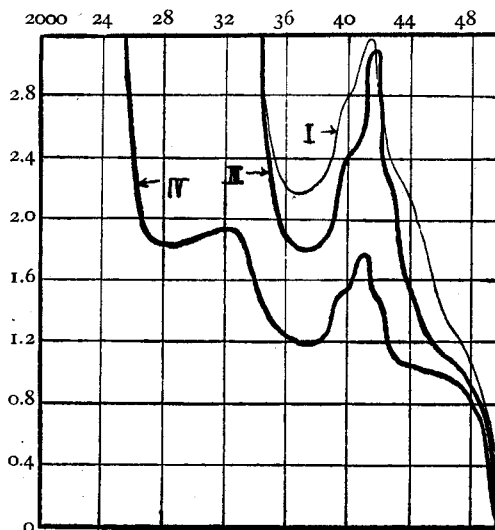
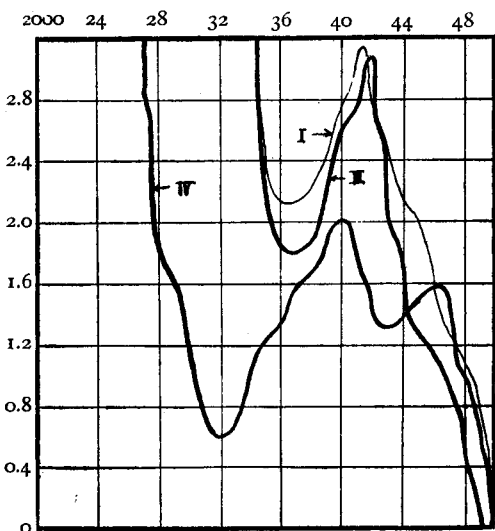


Fig. 27.
(ref. 17th row in Table I.)



- I Phenol.
- III m-Amidophenol hydrochloride.
- IV Diazotized m-amidophenol.

Fig. 28.
(ref. 18th row in Table I.)



- I Phenol.
- III p-Amidophenol hydrochloride.
- IV Diazo p-amidophenol.

Fig. 29.

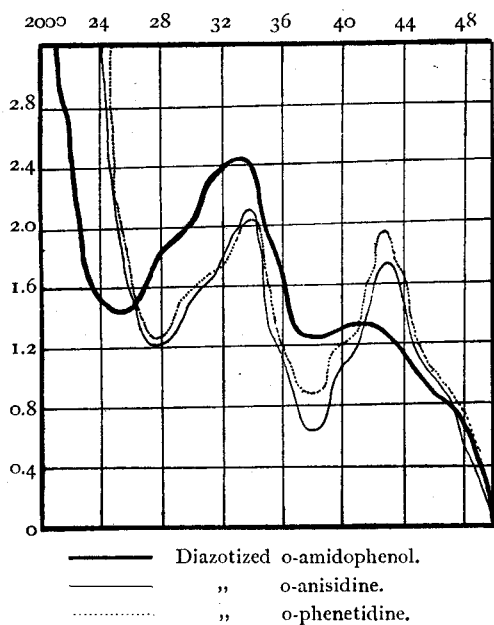
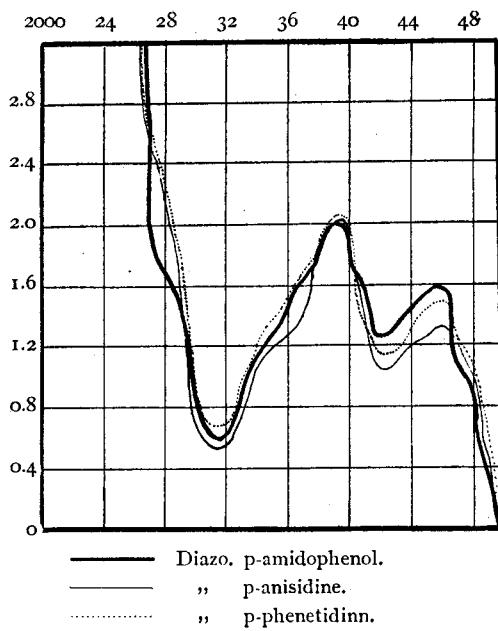


Fig. 30.



PART II. THE PHOTOLYSIS OF THE DIAZO-COMPOUNDS.

I. INTRODUCTION.

In spite of the fact that numerous researches upon the diazo-compounds have been reported, the literature on the photochemical reactions, especially quantitative studies, is rather scanty. However, attention has so long been drawn to the sensitiveness of the diazo-compounds to light, that a number of patents have been applied for in respect of devices connected with the typing process to which the diazo-compounds are applied. Reference may here be made to the early devices and researches of A. Feer¹⁾, Green, Cross and Bevan²⁾, O. N. Witt³⁾, Andresen⁴⁾, Anilin Fabrikation, Berlin⁵⁾, and M. Schön⁶⁾, etc.; these, having a direct bearing on the so-called "Diazo-typing Process," are still being followed up by people along various lines⁷⁾.

Andresen⁸⁾ was the first to remark on the photolysis of the diazo-compounds. He held the view that photochemical decomposition is effected by the same sort of reaction as in the case of thermal decomposition. Later Otto Ruff and Stein⁹⁾ studied the relation between light sensitivity and the kinds of nuclei of the diazo-compounds, and the influence of substitutions upon the sensitiveness, together with the sensitivity of the diazotized 3-amidocarbazol. Orton and Coates¹⁰⁾ investigated the modes of decomposition of the diazonium salts under solar light. Seywitz and Mounier¹¹⁾ reported their experiments on the influence of temperature and

-
- 1) D.R.P. 53455 (1889).
 - 2) D.R.P. 56606 (1890).
 - 3) Photo. Korresp. 1890, **27**, 568.
 - 4) Photo. Korresp. 1895, **32**, 284.
 - 5) D.P.R. 82239 (1894).
 - 6) D.R.P. 111416 (1899).
 - 7) Recent patents.
Institute of physical and Chemical Research, Japan.—Jap. Pat. 76865, 78556 (1928).
Filma Kalle & Co.—D.R.P. 422972 (1924) etc.
 - 8) Photo. Korresp. 1895, **32**, 284.
 - 9) B. 1901, **34**, 1668.
 - 10) Trans. 1907, **91**, 35.
 - 11) Compt. rend. 1928, **186**, 953.

the pH value upon the photolysis of the diazo-compounds. In connection with the typing process, Kögel¹⁾ studied the photolysis of quinone diazides.

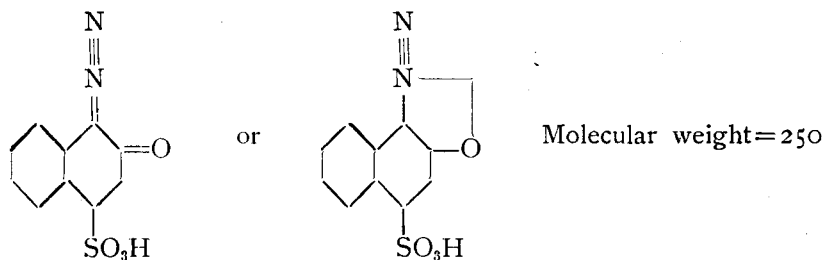
As for the quantitative studies, however, the authors can refer only to the latest work published this year by Schröter²⁾, who measured the quantum efficiencies of the photolysis of diazotized amidonaphtol sulphonate (2·1·4·) and p-amidophenylamine sulphate under various conditions.

Now the light sensitivity of the diazo-compounds, though it has been skilfully applied in the "Diazo-typing process", is at the same time a most important factor to be considered during the process of manufacturing azo-dyestuffs.

The present authors investigated the photolysis of the diazo-compounds quantitatively with the light-thermostat. The compounds which are dealt with in the present paper are 1·2·4· Diazo-Naphtol-Sulphonic acid (called D. N. S. hereafter) and Diazo-Benzene-Sulphonic acid (D. B. S. hereafter). The former is being used in the "Diazo-typing process" and the latter for the most part in the manufacture of azo-dyestuffs.

The following supplementary notes on the compounds may be given:—

(I) D. N. S.



The sample was prepared by diazotizing 1·2·4· amidonaphtol sulphonic acid in the presence of a small quantity of copper sulphate³⁾, which was synthesized from pure β -naphtol according to Böniger's method⁴⁾, the resulting bright yellow crystalline substance being quite soluble in a small quantity of water with a slight acidic character.

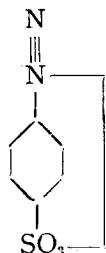
1) Z. wiss. Photo. 1926, **24**, 20.

2) Z. wiss. Photo. 1930, **28**, 1. (Z. Elektrochem. 1928, **34**, 602.)

3) D.R.P. 171027.

4) B. **27**, 23.

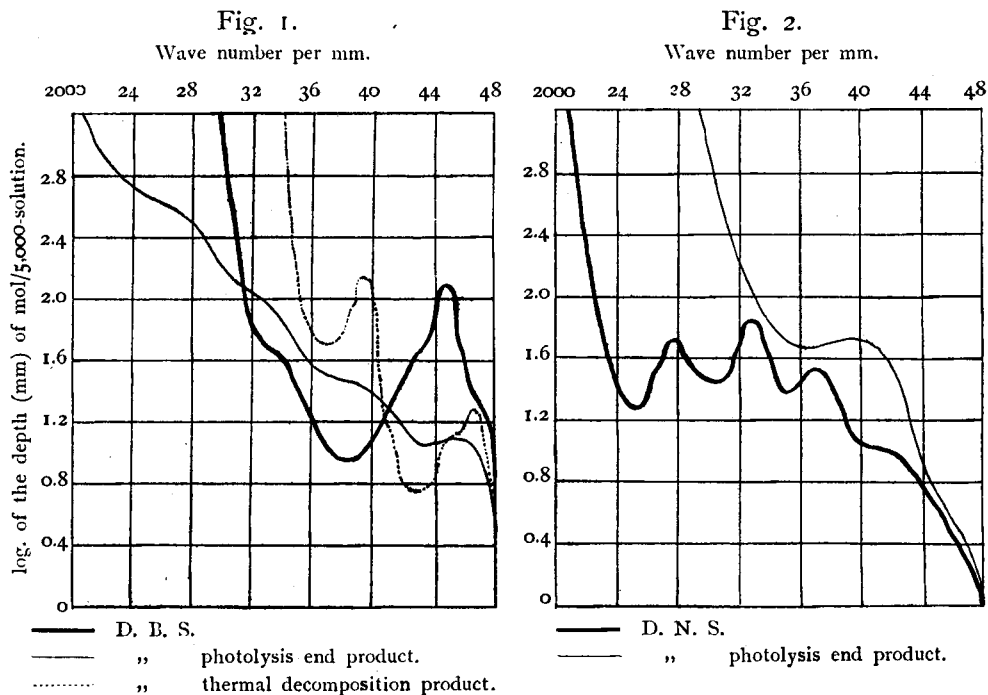
(II) D. B. S.



Molecular weight=184

This was obtained through diazotizing pure sulphanilic acid, and drying after recrystallizing three times from warm water of 60°C, a pure white crystalline substance of an explosive nature being produced.

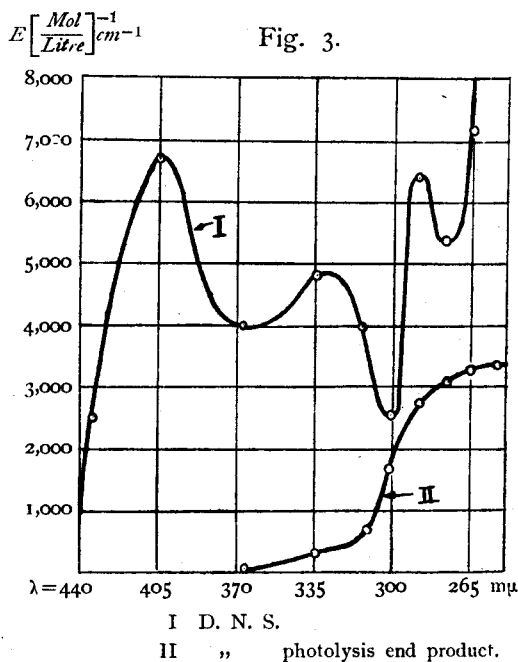
The absorption spectra of the two compounds are shown in Figs. 1 and 2.



In the present paper a brief reference will also be made to the absorption spectra of the end products of photo- and thermal decomposition. In fig. 1 are shown these absorption spectra in the case of D. B. S. together with that of the original. Decomposition was carried out

in aqueous solutions¹⁾, complete decomposition being ascertained on examination with alkaline solution of H-acid. A glance at the diagrams shows at once an evident disagreement between the two decompositions.

In the case of D. N. S., only the absorption spectrum of the end product of the photolysis was measured, because it did not decompose even in its boiling state. The extinction coefficients of the two compounds were also measured for several wave lengths by means of the photographic method of V. Henri²⁾. The result is shown in fig. 3.



1) As for the thermal decomposition, this was carried out through heating the solution to boiling for some time till the compound was completely decomposed. Photochemical decomposition was carried out through exposing the solution to the beams of light of a mercury lamp. The solution was cooled by ice blocks during the exposure.

2) B. 1912, 45, 2819; Étude de photochimie, Paris 1919.

$$E = \frac{I}{cd} \log \frac{J_0}{J} = \frac{I}{cd} \log \frac{t}{t_0}$$

t_0 = Time of exposure for solvent

t = Time of exposure for solution

We can find the value of E by measuring t_0 and t .

II. PHOTOCHEMICAL ABSORPTION SPECTRUM.

We may now turn our attention to the light absorbed in the case of different wave lengths, reacting chemically upon the compounds, i. e. the photochemical absorption spectrum. For the purpose of measuring the absorption, we employed the quartz spectrograph in which a sheet of paper, thinly coated with the compound, and serving as a photographic dry plate, was exposed to a light from the iron arc lamp. Then the patterns of the photochemical absorption were easily distinguished by developing the paper with the azo-components.

It was elucidated, under the above conditions, that D.N.S. could be decomposed only by light with a wave length shorter than about 450 $m\mu$, and that in the case of D.B.S. the longest wave length which reacted chemically upon the compound was situated at the position of about 380 $m\mu$ ¹⁾.

III. APPARATUS AND METHOD OF ESTIMATION.

Apparatus: The apparatus employed for the experiments is schematically shown in fig. 4.

The light source used was a quartz mercury lamp. To keep the temperature around the lamp constant, the lamp was fixed in a draught, the opening for which could be easily regulated. The voltage supplied was 110.V. The potential difference between the two terminals of the lamp and the streaming current were kept constant by slightly regulating the variable rheostat and the opening of the draught. In order to make certain that the radiated light energy was constant, a sensitive

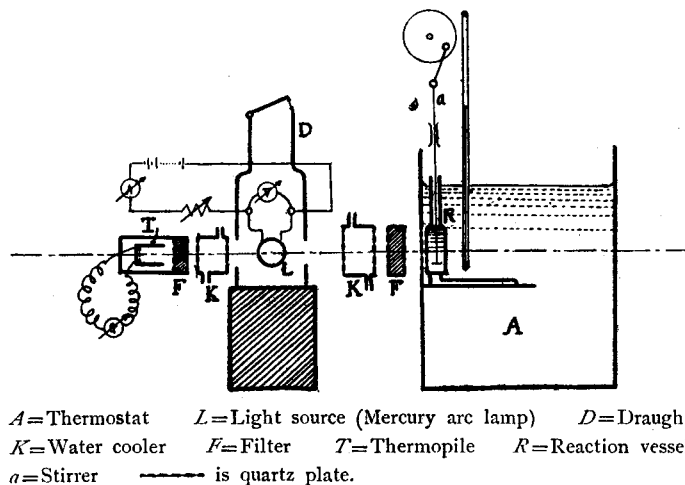
1) According to Einstein's theory of photochemical equivalent (Ann. d. Phys. 1912, **37**, 832), the following relationship holds between ν , the smallest frequency which acts chemically, and A , the free energy of the primary photo-reaction for photochemical gram equivalent, i.e.

$$A = N h \nu = \frac{N h c}{\lambda}$$

N (Avogadro-Loschmidt number) h (Planck const.) c (Velocity of light) and λ gives the longest wave length which acts chemically; as we have seen in the above case.

However, it has been shown experimentally that in most cases the result of observation disagrees with that from the theory.

Fig. 4.



thermopile connected to a mirror galvanometer was installed. It was ascertained that the energy from the lamp was constant, with a maximum deviation of only 10%, some 40 minutes after the lamp was started.

For the experiments, the monochromatic ray of $\lambda=366\text{ m}\mu$ and general rays were employed. As for the filter for $366\text{ m}\mu$, special ultra-violet dark glass of 5 mm thickness was used, monochromatic separation being ascertained on examination with a quartz spectrograph.

For the reaction vessel, a drum-like glass receptacle, with a quartz plate on the exposed side, and with a capacity of 10 c.c. was employed. The front area of the vessel was about 10 cm^2 . It was arranged so that the whole area of the quartz surface should be uniformly exposed to the beams of light falling at right angles to the surface.

The Method of Estimation:

(1) D. N. S. Reference has already been made to the extinction coefficients of this compound with rays of various wave lengths before and after the photolysis (ref. Fig. 3). The bright yellow solution of D. N. S. (the compound has a strong selective absorption in the visible region of the spectrum; the extinction coefficient, measured photographically, amounting to 7,500 at $\lambda=405\text{ m}\mu$) bleaches up to the point of being almost colourless during the photolysis. Utilizing its absorptive character the authors esti-

mated the concentration of D. N. S. by means of colorimetry. The instrument used, was a Dubosq-Colorimeter with two quartz cylinders. On making a preliminary examination, to test the applicability of the law of Beer-Lambert, it was clearly ascertained that the law held good for the solutions of D. N. S. with a concentration between $\frac{mol}{200}$ and $\frac{mol}{2,000}$, and with a deviation of not more than 10%. Prior to the measurement, the solutions were diluted with four times their volume of water.

(II) D. B. S. For the estimation of D. B. S. which had been thoroughly recrystallized, the method of titration was employed. $\frac{Mol}{200}$ solution of pure sodium β -naphtholate, containing an excess of sodium acetate, was used as the normal solution¹⁾. The end point of the titration was determined when the diazo-solution no longer developed colour with the solution of H-acid on a filter paper. Thus, the titrated solution, when filtered from the dyes produced, (here a spoonful of common salt is added to help the separation of the dyes) still gives only a slight colour with an alkaline solution of H-acid. It was ascertained that titration gives a satisfactory result for the estimation of D. B. S. which has been purified by being recrystallized several times from warm water. The experimental error was within ± 0.05 c.c.

IV. FUNDAMENTAL.

Experimental (No. 1).

To facilitate discussion later on, the two fundamental cases are first dealt with.

(I) $\frac{Mol}{200}$ D. N. S.-solution was decomposed by the monochromatic light of $\lambda=366 m\mu$. The result obtained is shown in table I and fig. 5, where a =initial concentration, x =change of concentration on exposure. The temperature was 20°C.

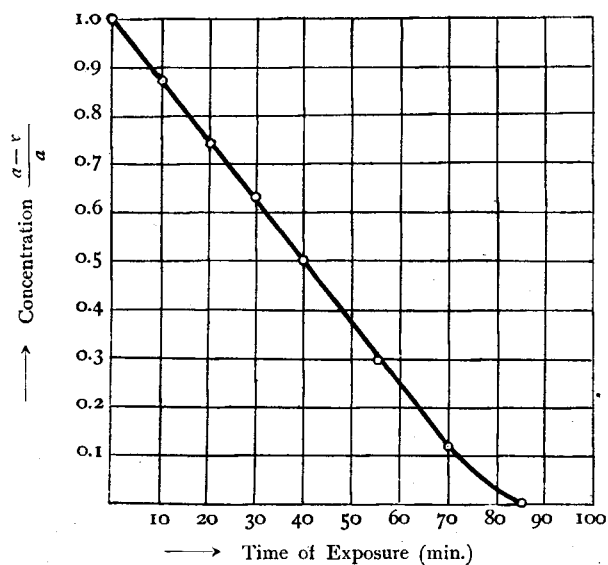
1) O. Schwalbe, B. 1905, 38, 2198, etc.

Recently E. Yamamoto (J. Soc. Chem. Ind., Japan 1929, 32 B. 279) employed the method of titration of the diazo-solution.

Table 1. ($\lambda = 366 \text{ m}\mu$)

Time of Exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	Decomposition velocity $\frac{x}{a}/t$
10	0.87	0.0130
20	0.74	0.0130
30	0.63	0.0123
40	0.50	0.0125
55	0.29	0.0129
70	0.13	0.0124
85	0.01	(0.0116)
		mean 0.0127

Fig. 5.



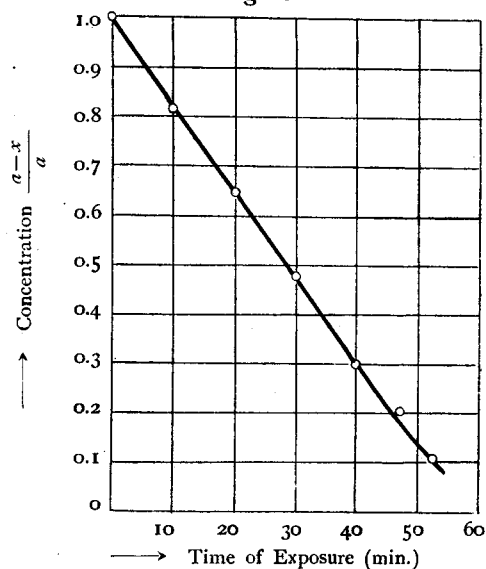
The decomposition per minute is almost constant during the progress of the photolysis, and the Concentration-Time diagram shows a straight line. However, it may be noted here that the velocity gets a little slower towards the completion of the photolysis.

(II) $\frac{\text{Mol}}{200}$ D. B. S. solution 10 c.c. was decomposed at 2°C . The total wave length of the lamp was employed. The result is shown in table 2 and fig. 6. (a and x denote the volume of $\frac{\text{mol}}{200}$ β -naphthol-solution.)

Table 2.

Time of exposure (t) (min.)	Concentration ($a-x$)	Decomposition velocity $\frac{x}{t}$
0	9.75	—
10	8.50	0.175
20	6.35	0.170
30	4.66	0.170
40	2.93	0.171
47	2.01	0.164
52	1.05	0.167
		mean 0.170

Fig. 6.



It is to be observed here also that the velocity of decomposition is almost independent of the concentration of the diazo-solution.

As is evident in the two cases, the decomposition is both the reaction of zero-order.

Discussion.

In the case of photolysis of D. N. S.-solution by $\lambda=366 \text{ m}\mu$, it must be noted that the end product of the decomposition is also able to absorb the same light. We will now consider the influence of the effect of

extinction of the end product upon the photolysis of the D. N. S. original, and explain the foregoing result.

In the simplest case of photolysis, it is generally considered that the mass of the compound lost in unit time is proportional to the quantity of light absorbed. (Grotthus, Draper, and Van't Hoff etc.¹⁾)

This relationship can be expressed in a kinetic equation as follows, that is, so far as Beer-Lambert law of absorption holds good,

$$-\frac{d(a-x)}{dt} = K \frac{J_0}{l} [1 - e^{-i(a-x)l}] \dots \dots \dots (1)$$

J_0 =Light intensity l =depth of solution i =absorption constant K =velocity constant
 a =initial concentration x =change of concentration

Now the total absorption of the system, which consists of the components whose absorption constants and concentrations are respectively $i_1, c_1; i_2, c_2; \dots \dots \dots$, is

$$\phi = S J_0 [1 - e^{-i_1 c_1 l - i_2 c_2 l \dots}] \dots \dots \dots (2)$$

S =exposed surface area

Next, according to Langendyk²⁾ and Weigert³⁾ the absorption of each component alone is generally as follows.

$$I_m = \frac{i_m c_m}{\sum i c} \cdot \phi \dots \dots \dots (3)$$

Applying the above relationship to the case of D. N. S.-photolysis, we obtain the following equations (we assume here tentatively that the excited molecule of D. N. S. reacts with the water molecule directly to its end product, and that the latter is chemically inactive⁴⁾):

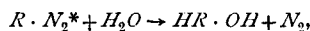
$$-\frac{d(a-x)}{dt} = K \frac{J_0}{l} \cdot \frac{i_1(a-x)}{i_1(a-x) + i_2 x} \cdot [1 - e^{-i_1(a-x)l - i_2 x l}] \dots (4)$$

1) The applicability of this law to the "total reaction" (photoreaction+the following secondary reactions thereof) is not universal. In cases where the secondary reactions are effected either through the unchanged photolyte or other foreign substances, the velocity of the secondary reactions must be taken into consideration. If the secondary reaction is the slowest the concentration of the substances which take part in the same reaction affects the velocity of the total reaction, standing in contrast with the cases when the primary reaction is the slowest.

2) Z. phys. Chem. 1925, **120**, 301.

3) Weigert: Optische Methode der Chemie, Leipzig, (1927) S. 355.

4) The reaction may be written down



in which $R \cdot N_2^*$ being excited molecule of D. N. S. (ref. Z. wiss. Photo. 1930, **28**, 1.)

$$\text{or } \frac{i_1 - i_2}{i_1} \int \frac{dx}{1 - e^{-i_1(a-x)t - i_2xt}} + \frac{i_2 a}{i_1} \int \frac{1}{a-x} \cdot \frac{dx}{1 - e^{-i_1(a-x)t - i_2xt}}$$

$$= K \frac{J_0}{l} \int dt \dots \dots (4')$$

Where i_1 and i_2 are respectively the absorption constant of D. N. S. and its photolysis product for the line of $\lambda=366 \text{ m}\mu$. When i_1 is very large, i.e. in the case of complete absorption, the foregoing equations are simplified and can be integrated as follows.

$$\frac{i_1 - i_2}{i_1} x - \frac{i_2 a}{i_1} \ln(a-x) = K \frac{J_0}{l} t + C \dots \dots (5)$$

In order to satisfy the condition ($t=0, x=0$)

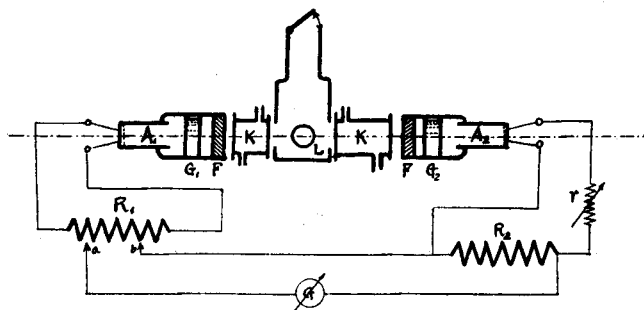
$$\frac{i_1 - i_2}{i_1} x + \frac{i_2 a}{i_1} \ln \frac{a}{a-x} = K \frac{J_0}{l} t \dots \dots (6)$$

$$\text{or } M \cdot \frac{x}{a} + N \cdot \log \frac{a}{a-x} = K \frac{J_0}{al} t \dots \dots (6')$$

$$\left(M = \frac{i_1 - i_2}{i_1} \quad N = 2.3 \frac{i_2}{i_1} \right)$$

Now in order to examine equation (6) or (6)', we must know the exact value of i_1 and i_2 . For this purpose the thermoelectric method was employed. The apparatus employed is shown in fig. 7.

Fig. 7.



where

L =Light source, Quartz mercury lamp, G_1, G_2 =receptacles. K =Water cooler. F =Filter for the monochromatic light of $\lambda=366 \text{ m}\mu$. A_1, A_2 =Thermopiles. R_1, R_2 =Rheostat of 50Ω . R_1 is furnished with subdivisions at distances of 0.5Ω . R_1 serves as a potentiometer. r =regulatable rheostat. G =Mirror galvanometer. This serve as a zero-instrument. R' =Resistance between a & b

$$\text{then } E = \frac{I}{cd} \log \frac{J_0}{J} = \frac{I}{cd} \log \frac{50}{R'}$$

The results of the measurement are given in the following tables.

Table 3.
E-Values of D. N. S. for the line of 366 m μ .

<i>C</i> (Mol/Litre)	$\frac{I}{5,000}$	$\frac{I}{7,500}$	$\frac{I}{10,000}$	$\frac{I}{12,500}$	$\frac{I}{20,000}$
$E \cdot 10^{-1}$	350	347	356	345	356

mean mol $E \cdot 10^{-1} = 351$ (% $E = 140$)

Table 4.
E-Values of Photolysis end product of D. N. S. for the line of 366 m μ .

<i>C</i> (Mol/Litre)	$\frac{I}{250}$	$\frac{I}{500}$	$\frac{I}{1,000}$	$\frac{I}{1,000}$
$E \cdot 10^{-1}$	3.71	3.04	3.58	3.34

mol $E \cdot 10^{-1} = 3.42$

Applying the above measured values, we have

$$M = 0.99 \quad N = 0.02$$

Applying these values to equation (6)', we find that the second factor of (6)' is practically negligible compared with that of the first through the greater part of the photolysis, i. e.

$$Mx \doteq K \frac{I_0}{l} \cdot t = K' \cdot t \dots \dots \dots (7)$$

Hence, it is to be observed in the case of the photolysis of D. N. S., brought about by the wave length of 366 m μ , that the extinction of its end product exercises too small an influence to affect the velocity of decomposition; and it decomposes with a constant velocity during the greater part of the photolysis, as equation (7) shows.

V. INFLUENCE OF INNER FILTER.

Experimental (No. II).

The present chapter deals with the case when D. N. S. is homogeneously mixed in solution with another soluble compound serving as an inner filter. As such, the authors employed acidic solution of quinine

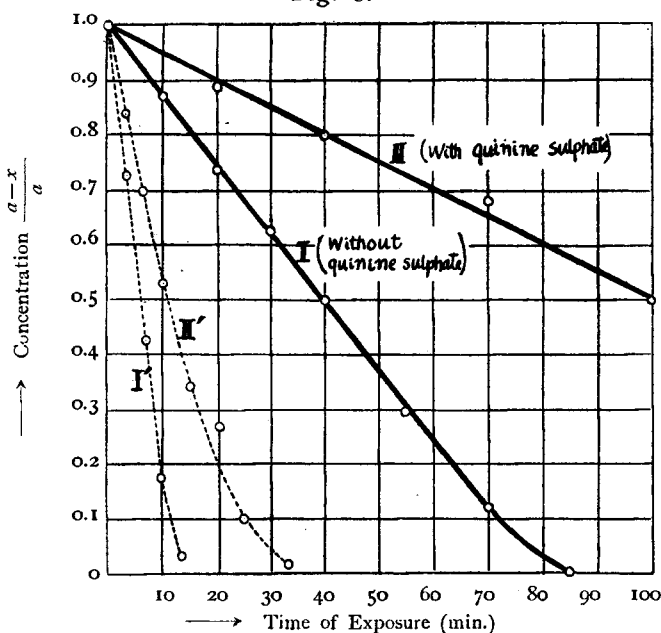
sulphate, beingf airy stable to light. The light employed was monochromatic ray of $\lambda=366\text{ m}\mu$.

(1) The concentration of D. N. S. was $\frac{\text{mol}}{200}$ (0,125%); quinine sulphate, 0.6% ; H_2SO_4 , 0.5 *N*. The energy from the light source and the other conditions in general were quite the same as in the case of Experiment No. I. The result is shown in Table 5 and Fig. 8.

Table 5.
($\lambda=366\text{ m}\mu$)

Without quinine sulphate			Quinine sulphate 0.6%-sol.		
Time of exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	Decomposition velocity $\frac{x}{a}/t$	Time of exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	Decomposition velocity $\frac{x}{a}/t$
10	0.87	0.0130	20	0.88	0.0060
20	0.74	0.0130	40	0.80	0.0050
30	0.63	0.0123	70	0.68	0.0045
40	0.50	0.0125	100	0.50	0.0050
55	0.29	0.0129			mean 0.0050
70	0.13	0.0124			
		mean 0.0127			

Fig. 8.



A comparison of the two cases may be made in the figure; II being the result in cases where quinine sulphate was added, and I, the result where it was not added. The mean velocity constant in the former case was 0.005, while in the latter it amounted to 0.013.

The decomposition velocity is thus shown to be reduced by adding quinine sulphate.

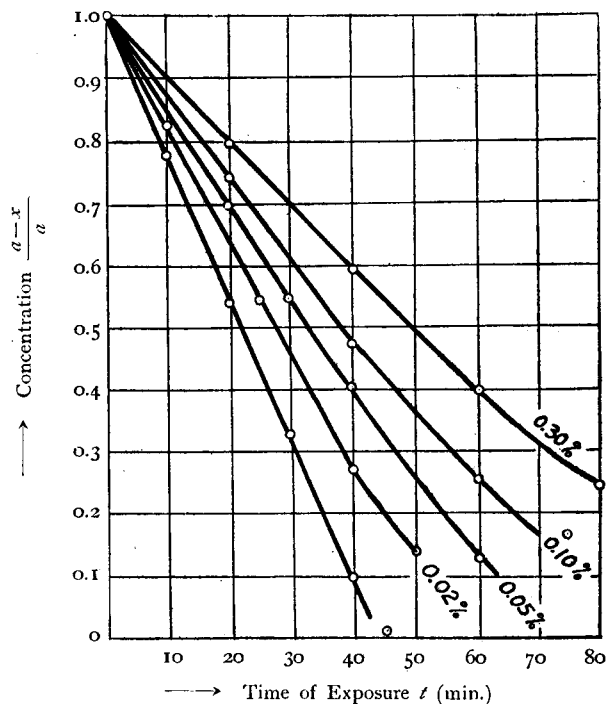
(II) Experiments were carried out for several solutions, containing various concentrations of quinine sulphate. The results are shown in the following table and figure (Table 6 and Fig. 9). It can clearly be seen that as the concentration of quinine sulphate increases, the decomposition velocity of D. N. S. is the more reduced.

Table 6.

$\lambda = 366 \text{ m}\mu$ Conc. of D. N. S., $\text{mol}/500$ (0.05%); H_2SO_4 IN

Concentration of quinine sulphate (%)	Time of exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	Decomposition velocity $\frac{x}{a} / t$
0	10	0.78	0.0220
	20	0.54	0.0230
	30	0.33	0.0223
	40	0.10	0.0225
			mean 0.022
0.02	10	0.83	0.0170
	25	0.54	0.0184
	40	0.27	0.0182
	50	0.14	0.0172
			mean 0.018
0.05	20	0.70	0.0150
	30	0.55	0.0150
	40	0.41	0.0148
	60	0.13	0.0145
			mean 0.015
0.10	20	0.75	0.0125
	40	0.47	0.0132
	60	0.26	0.0123
	75	0.17	0.0111
			mean 0.012
0.30	20	0.79	0.0105
	40	0.59	0.0102
	60	0.40	0.0100
	80	0.25	0.0094
			mean 0.010

Fig. 9.



(III) A similar relationship holds also in cases where the solutions were decomposed by the total wave length of the lamp. Table 7. Fig. 8 I' and II'.

Table 7.

Without quinine sulphate			Quinine sulphate 0.6% sol.		
Time of exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	$\frac{x}{a} / t$	Time of exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	$\frac{x}{a} / t$
3	0.73	0.090	3	0.84	0.053
6	0.47	0.088	6	0.70	0.050
10	0.17	0.083	10	0.53	0.047
13	0.04	0.074	15	0.35	0.043
			20	0.27	0.037
			25	0.10	0.036
			33	0.02	0.029

The decomposition velocity is thus shown to be reduced by the

addition of quinine sulphate in the photolysis effected by both the monochromatic and general rays.

Discussion.

When the compound serving as inner filter (Extinction $i' c'$) is chemically inactive, the decomposition velocity of D. N. S.-solution for the ray of $\lambda=366 \text{ m}\mu$ is given as follows, now that the factor of i_2 no longer comes into consideration :

$$-\frac{d(a-x)}{dt} = K \frac{J_0}{l} \cdot \frac{i_1(a-x)}{i_1(a-x) + i' c'} \cdot [1 - e^{-i_1(a-x)l - i' c' l}] \quad (1)$$

Now if we can limit the condition so that the extinction of the inner filter is very large, then the whole system will always absorb the light completely throughout the whole course of the photolysis. Hence, by means of integration the following equations are obtained:—

$$x + \frac{i' c'}{i_1} \ln \frac{a}{a-x} = K \frac{J_0}{l} \cdot t \dots \dots \dots (2)$$

or
$$\frac{x}{a} + 2.3 \frac{i' c'}{i_1 a} \log \frac{a}{a-x} = \frac{K J_0}{a l} \cdot t \dots \dots \dots (2)'$$

We will now compare the results of the foregoing experiments with that calculated from equation (2)'. As for the extinction coefficient of D. N. S. at $\lambda=366 \text{ m}\mu$, we obtained by the thermoelectric method $\text{mol } E=3510$, i. e. $\% E=140$, on recalculation.

Next as regards the extinction coefficient of quinine sulphate solution, we adopted the value $\% E=95.3$, measured by Weber¹⁾ by means of the fluorescence-method. (The values of the extinction coefficient of potassium chromate, measured in the same way by him, are in fairly complete agreement with ours²⁾). Hence we obtain the following tables:—

1) Z. Elektrochem. 1930, 36, 29.

2)

Table 9.
E-Values of K_2CrO_4 -solutions. ($\lambda=366 \text{ m}\mu$)

C (Mol/Litre)	$\frac{1}{5,000}$	$\frac{1}{10,000}$
Measured by the authours	4225	4110
Measured by Weber	4268	4074

Table 8 a. (ref. Table 5.)

Concentration of quinine sulphate (%)	Time of exposure (t) (min.)	Rate of decomposition of D. N. S. $\left(\frac{x}{a}\right)$	
		Measured	Calculated
0.60	20	0.12	0.06
	40	0.20	0.11
	70	0.32	0.19
	100	0.50	0.27

Table 8 b. (ref. Table 6.)

Concentration of quinine sulphate (%)	Time of exposure (t) (min.)	Rate of decomposition of D. N. S. $\left(\frac{x}{a}\right)$	
		Measured	Calculated
0.02	10	0.17	0.17
	25	0.46	0.42
	40	0.73	0.63
	50	0.86	0.75
0.05	20	0.30	0.25
	30	0.45	0.37
	40	0.59	0.47
	60	0.87	0.65
0.10	20	0.25	0.18
	40	0.53	0.34
	60	0.74	0.48
	75	0.83	0.56
0.30	20	0.21	0.09
	40	0.41	0.17
	60	0.60	0.24
	80	0.75	0.31

It may be noted here that the measured values are all rather larger than the calculated.

In this disagreement, however, the influence of the fluorescent light from quinine sulphate, which was disregarded in the equations, must above all be taken into consideration. As a matter of fact, quinine sulphate re-emits part of the absorbed light as a fluorescence, whose spectrum is

situated in the blue region. And D. N. S., as we have observed, can absorb this light and is thereby decomposed (ref. Chap. II, p. 213). Accordingly the experimental values in this case are to be considered as a resultant of the decomposition by the primary and the secondary light sources, with the result that larger values are obtained¹⁾.

VI. INFLUENCE OF TEMPERATURE.

Although the chemical reaction in general is decidedly affected by temperature, in the ideal case of pure photochemical reaction, the temperature has no effect upon the reaction velocity at all. As a matter of fact it has been well ascertained in the various examples that the temperature coefficient in the pure photochemical reaction is almost equal to unity. Next, even when pure chemical reaction, i. e. the thermal reaction, occurs is parallel, the foregoing may be true, so far as the said reaction is chemically independent of the photo-reaction. Here Plotnikow insists upon his "Addition Theory". But that theory is true only when the mutual independence of the two different reactions holds. If there is mutual interaction of reactions, various complex phenomena must follow. Hence it is most important to investigate, first, the influence of temperature upon the reaction in order to be fully aware of the nature of the decomposition reaction.

1) Plotnikow holds somewhat different view as regards the mode of distribution of the total absorbed energy. (*Z. wiss. Photo.* 1926, **24**, 305 etc.). He insists that the light energy absorbed by a system, which consists of several components, is distributed among each component in proportion to each single and separate absorption, i. e.,

$$I_m = \frac{1 - e^{-i_m \rho_m l}}{\sum (1 - e^{-i_e l})} \cdot \phi$$

In the case of our experiments, in which the absorption constants of D. N. S. and quinine sulphate being very large, it follows

$$I_m = \frac{1}{2} \cdot \phi$$

But the results of experiments are clearly in helpless disagreement with the above, because the decomposition velocity becomes slower as the amount of quinine sulphate increases. Lately Weber (*Z. Electrochem.* 1930, **36**, 26) also obtained the result, which, being contrary to the result from Plotnikow's formula, but is in complete agreement with that from Langendyk's formula with a correction.

Experimental (No. III).

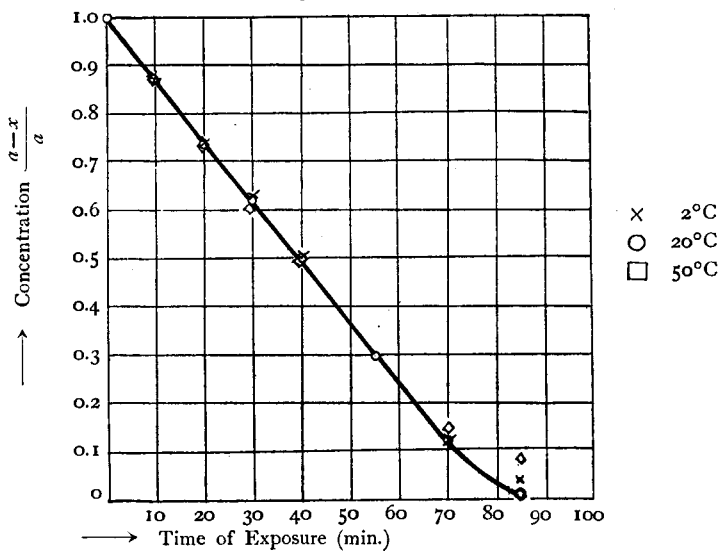
(I) D. N. S. The $\frac{\text{mol}}{200}$ -solution was decomposed at temperatures of 2°C, 20°C, and 50°C, by the monochromatic light of $\lambda=366 \text{ m}\mu$. The results are shown in Table 10 and Fig. 10.

Table 10.

 $\lambda=366 \text{ m}\mu$.

Temperature (°C)	Time of exposure (t) (min.)	Concentration $\left(\frac{a-x}{a}\right)$	Decomposition velocity $\frac{x}{a}/t$
2	10	0.88	0.0120
	20	0.74	0.0130
	30	0.64	0.0120
	40	0.51	0.0122
	70	0.12	0.0125
	85	0.04	(0.0113)
20	10	0.87	0.0130
	20	0.74	0.0130
	30	0.63	0.0123
	40	0.50	0.0125
	55	0.29	0.0129
	70	0.13	0.0124
	85	0.01	(0.0116)
50	10	0.87	0.0130
	20	0.74	0.0130
	30	0.62	0.0127
	40	0.50	0.0125
	70	0.16	0.0120
	85	0.08	(0.0107)

Fig. 10.



Evidently, judging from the above data, the temperature is utterly independent of the rate of decomposition.

(II) D. B. S.

The solution of this compound is decomposed also by heat, as well as the other compounds of the diazonium benzen family. Hence, the photolysis of this compound becomes fairly complicated, as the thermal decomposition must be taken into consideration at higher temperatures. At the same time we investigated the single thermal decomposition. Reference has already been made to the decomposition of D. B. S.-solution at 2°C, where the thermal decomposition is practically negligible. And in this case, it was observed that the values of $\frac{x}{t}$ were always constant, regardless of the concentration. (ref. Chap. IV.)

Now the result of the photolysis at various temperatures, namely at 2°C, 22°C, 45°C, and 60°C are shown in the following tables and figure. (Table 11 a and 11 b, Fig. 11.)

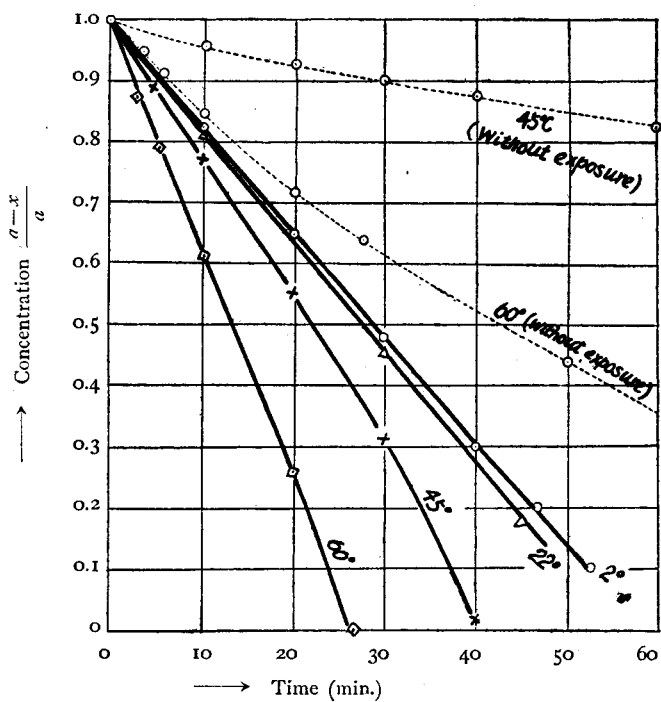
Table 11 a.

Temperature (°C)	Time of exposure (t) (min.)	Concentration (a-x)	Decomposition velocity $\frac{x}{t}$
2	0	9.75	—
	10	8.00	0.175
	20	6.35	0.170
	30	4.66	0.170
	40	2.93	0.171
	47	2.01	0.164
	52	1.05	0.167
	mean		0.170
22	0	9.78	—
	10	7.95	0.183
	30	4.48	0.177
	45	1.67	0.180
	mean		0.180

Table 11 b.

Temperature (C°)	Time (min.)	Concentration ($a-x$)	
		Exposed	Not exposed
45	0	9.49	9.49
	5	8.44	—
	10	7.45	9.14
	20	5.32	8.82
	30	3.06	8.57
	40	0.20	8.30
	60	—	7.80
60	0	8.30	8.30
	3	7.25	7.89
	5	6.62	7.63
	10	5.14	7.00
	20	2.16	5.95
	27	0.11	5.30

Fig. 11.



Surveying the foregoing results, it is first to be noted that the rates of decomposition at 2°C and 22°C give values quite close to each other and that, on the other hand, in the case of 45°C and 60°C their velocity is notably larger. But, now we may turn our attention to the dark reaction. Although the decomposition effected by the dark reaction at 2°C and 22°C is practically negligible within short time limits, the dark reaction must be considered when the temperature is 45°C and 60°C. Therefore, the foregoing results obtained at 2°C and 22°C must clearly be regarded as decomposition effected merely through the action of light. On the other hand, the results in the case of 45°C and 60°C are the resultants of the action of *Light* and *Heat*. The amounts of decomposition by the thermal effect alone are also given in the foregoing table 11 b, and they are shown in dotted lines in fig. 11. But it must be emphasized here that we cannot assume rashly that the amount of single photochemical decomposition can be calculated arithmetically from the foregoing data.

Now returning once more to the results obtained at 2°C and 22°C, the values of $\frac{x}{t}$ are always constant in each case, and yet the values of each are quite close together. In other words, it may be said that the temperature influence is very small in the region of 2°C and 22°C, showing that the photolysis of D. B. S. solution at these temperatures is practically a pure photochemical reaction, like that of D. N. S. as was mentioned above. In order to draw the more definite conclusion from the results obtained at 45°C and 60°C, it is necessary to study further in consideration of the thermal reaction coming into play.

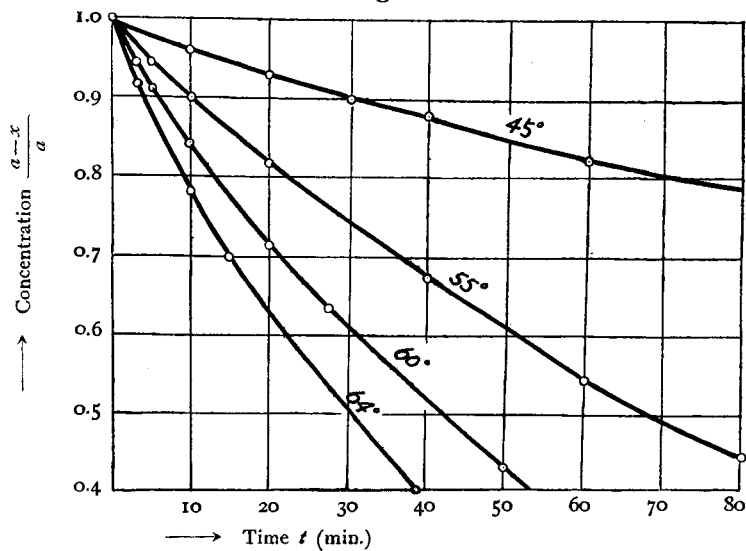
As for the thermal decomposition, this was carried out at 45°C, 55°C, 60°C, and 64°C¹⁾. The results obtained are shown in Table 12 and Fig. 12. The decomposition proceeds with the velocity of the monomolecular reaction.

1) Muller and Hausser (Compt. rend. 1892, 114, 549) studied the thermal decomposition of D. B. S.-solution. The velocity constant measured by them is well in agreement with ours.

Table 12.

Temperature (C°)	Time (t) (min.)	Concentration (a-x)	$k = \frac{1}{t} \ln \frac{a}{a-x}$
45	0	9.49	—
	10	9.14	0.00375
	20	8.82	0.00366
	30	8.57	0.00340
	40	8.30	0.00336
	60	7.80	0.00327
55	0	8.47	—
	5	8.04	0.0104
	10	7.64	0.0103
	20	6.92	0.0101
	40	5.70	0.0099
	60	4.61	0.0101
	80	3.75	0.0102
60	0	8.30	—
	3	7.89	0.0169
	5	7.63	0.0168
	10	7.00	0.0170
	20	5.95	0.0166
	27	5.30	0.0166
	50	3.55	0.0170
64	0	8.30	—
	3	7.71	0.0246
	10	6.53	0.0240
	15	5.80	0.0239
	40	3.31	0.0230

Fig. 12.



As can be seen above, the decomposition velocity of D. B. S.-solution increases roughly three times with every increases of 10°C. And in this case, a linear relationship is observed to exist between the values of $\frac{1}{T}$ and $\ln k$ as shown in Table 13 and Fig. 13, which is in agreement with the equation of Arrhenius, namely,

$$\frac{d \ln k}{dT} = -\frac{Q}{RT^2} \quad \text{or} \quad \ln k = C - \frac{Q}{RT}, \quad \text{where } C = 29.04$$

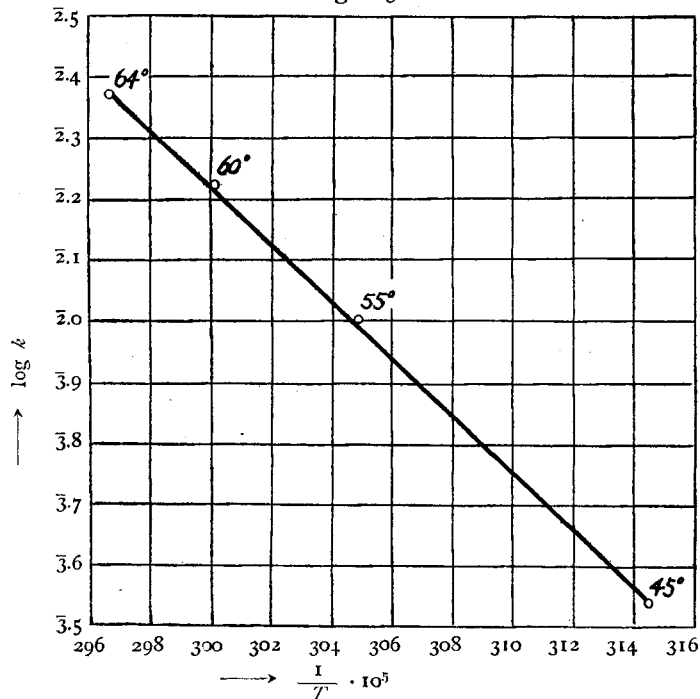
$$\frac{Q}{R} = 11033$$

are calculated.

Table 13.

t (°C)	$\frac{1}{T} \cdot 10^5$	k	$\log k$
45	314.5	0.00349	3.5428
55	304.9	0.0102	2.0086
60	300.3	0.0168	2.2253
64	296.7	0.0239	2.3784

Fig. 13.



At higher temperatures, the photo-reaction is accompanied by a thermal decomposition as just mentioned, attended by a resultant complexity. Here we want to treat the above results kinetically in order to elucidate the nature of this photolysis.

Discussion.

With regard to the thermal decomposition of D. B. S.-solution, it was observed that the following kinetic equation holds good.

$$-\frac{d(a-x_1)}{dt} = k(a-x_1) \dots \dots \dots (1)$$

Next, as regards its photochemical decomposition, it proceeds with a constant velocity independent of the concentration, namely,

$$-\frac{d(a-x_2)}{dt} = K \dots \dots \dots (2)$$

Now, supposing that these two sorts of reactions chemically independent of each other, the following equation is obtained.

$$-\frac{d(a-x)}{dt} = k(a-x) + K \dots \dots \dots (3)$$

By integration

$$-\frac{1}{k} \ln [K + k(a-x)] = t + c \dots \dots \dots (4)$$

In order to satisfy the condition ($t=0, x=0$)

$$\ln \frac{K + k \cdot a}{K + k(a-x)} = k \cdot t \dots \dots \dots (5)$$

Thus, assuming the mutual independence of the two sorts of reactions the above relationship must hold between k , the velocity constant of the thermal decomposition, and K , that of the light reaction.

As the values of k were determined by measurement, those of K can be calculated from equation (5). And applying to the equation the experimental results obtained at 45°C, we have the following table:—

Table 14.

 $t=45^{\circ}\text{C}$ $k=0.00349$

Time of exposure min.	Concentration ($a-x$) c.c.	K (calculated)
0	9.49	—
5	8.44	0.178
10	7.45	0.175
20	5.32	0.183
30	3.06	0.193
40	0.20	0.216

If, then, the foregoing assumption is true, the values of K calculated above ought to be constant, and not merely constant, but also their magnitude must be practically equal to the values measured at 2°C and 22°C .

Surveying the above table we find that the values of K keep constant in the earlier stages of the decomposition, and, furthermore, they are in agreement with the values which were obtained, at 2°C , and 22°C (ref. Table 11 a p. 228). Therefore, in this case, the foregoing assumption proved to be justifiable. In other words, it may be safely said that, in the earlier stages of decomposition, the simple additive relationship practically holds between the two sorts of reactions, and the decomposition by light should be regarded as a pure photochemical reaction.

However, so far as the later stages of the decomposition are concerned, the assumption must be abandoned, as the values of K increase towards the completion of the reaction.

Now it follows that, in the photolysis of D. B. S.-solution at 45°C , in the earlier stages, the decomposition is practically additive, both light and heat being concerned; but as the reactions proceed, the decomposition becomes violent by degrees, till the additive relationship holds no longer. *Here the two sorts of reactions cease to be accepted as chemically independent.*

This is recognized more clearly in the case of 60°C , where the thermal decomposition is more noticeable. The values of K are calculated as follows:—

Table 15.

60° $k=0.0168$

Time of exposure min.	Concentration ($a-x$) c.c.	K (Calculated)
0	8.30	—
3	7.25	0.218
5	6.62	0.211
10	5.14	0.204
20	2.16	0.222
27	0.11	0.238

Now the values of K are larger by far than those which have just been dealt with, and, furthermore, they increase towards the end of the decomposition. Here the two sorts of reactions, observed separately, stand by no means in a simple additive relationship.

Hence, as may be seen above, it can be said, so far as the thermal decomposition is inappreciable, that the photolysis of D. B. S. may be regarded as a pure photochemical reaction; but as the thermal decomposition grows more appreciable, this characteristic begins to disappear, the compound decomposing more rapidly than is conditioned by the theoretical equation. As a matter of fact, as shown in Table 11 b, near the end of the decomposition, the solution is decomposed strangely enough with a velocity two times, or more, that of the earlier stages. Here, secondary, tertiary, and more complex reactions are being brought about, as the result of the mutual interaction of the photo- and thermo-chemical reactions. This phenomenon, where the diazo-compound is decomposed through light more easily with than without accompanying thermal reaction, is a matter of importance in the practical process of manufacturing azo dyestuffs.

VII. QUANTUM EFFICIENCY.

According to Einstein's theory, it follows that 1 molecule is decomposed each by just a single quantum absorbed, hence

$$\varphi = \text{Quantum efficiency} = \frac{\text{Number of decomposed molecules}}{\text{Number of absorbed quanta}} = 1$$

However, in many cases the quantum efficiency φ is smaller than unity. Therefore, it seems to be of interest to study the relationship between the absorbed light energy and the amount of decomposed substance.

The quantum efficiency of the photolysis of D. N. S.-solution by $\lambda=366\text{ m}\mu$ was measured. The energy from the lamp was measured by means of a Ruben's thermopile connected to a mirror galvanometer. The absolute value of the light was estimated by Gerlach's method¹⁾ with a Hefner-lamp as a standard.

Experiment (No. 4).

(I) $\frac{\text{Mol}}{1000}$ -solution of D. N. S. was decomposed. The experimental data and calculation are shown below.

Table 16.

	Intensity of the light (HK)*	Area of exposed surface (cm ²)	Time of exposure (sec)	Initial concentration (Mol/Litre)	Change of concentration (Mol/Litre)	Volume of solution (cm ³)
I	4.2	9.3	$4.20 \cdot 10^3$	$1.00 \cdot 10^{-3}$	$0.71 \cdot 10^{-3}$	10
II	4.2	9.3	$2.82 \cdot 10^3$	$1.00 \cdot 10^{-3}$	$0.53 \cdot 10^{-3}$	10

$$(I) \text{ Absorbed quanta} = 1.76 \cdot 10^{14} \cdot 4.2 \cdot 9.3 \cdot 4.20 \cdot 10^3 = 29 \cdot 10^{18} (h\nu)$$

$$\text{Decomposed molecules} = 0.71 \cdot 10^{-3} \cdot 6.06 \cdot 10^{23} = 4.3 \cdot 10^{18}$$

$$\varphi = \frac{4.3 \cdot 10^{18}}{29 \cdot 10^{18}} = 0.15$$

$$(II) \text{ Absorbed quanta} = 1.76 \cdot 10^{14} \cdot 4.2 \cdot 9.3 \cdot 2.82 \cdot 10^3 = 19 \cdot 10^{18} (h\nu)$$

$$\text{Decomposed molecules} = 0.53 \cdot 10^{-3} \cdot 6.06 \cdot 10^{23} = 3.2 \cdot 10^{18}$$

$$\varphi = \frac{3.2 \cdot 10^{18}}{19 \cdot 10^{18}} = 0.17$$

Mean quantum efficiency $\varphi=0.16$.

1) Physik. Zeitschr. 14, 577.

*) Energy of 1 HK = $945 \text{ erg cm}^{-2} \text{ sec}^{-1}$
 $h\nu$ for $366 \text{ m}\mu$ line = $5.37 \cdot 10^{-12} \text{ erg}$.

VIII. SUMMARY.

(1) The photochemical absorption spectra of the diazo-compounds were measured, and the rays which act chemically were elucidated.

(2) The photolysis of D. N. S. and D. B. S.-solutions was observed quantitatively by employing the light-thermostat. (Concentration of the solution was $\frac{mol}{200}$).

It was observed that the decomposition proceeds with the constant velocity independent of the concentration.

It was shown theoretically that the influence of the decomposition product of D. N. S. upon the photolysis is negligible.

(3) The influence of quinine sulphate upon the decomposition velocity of D. N. S. was observed. By adding quinine sulphate the decomposition velocity of D. N. S. was reduced. And the more quinine sulphate was added, the slower became the velocity. The result was compared with those from the kinetic equation which was derived by applying Langendyk-Weigert's distribution theory. The experimental values of $\frac{x}{a}$ were rather larger than those obtained from the equation; and the result was discussed.

(4) The influence of temperature upon the photolysis of D. N. S. and D. B. S. was studied, and the nature of the decomposition was made clear.

(I) Temperature influence upon D. N. S. is negligible. The photolysis is practically a pure photochemical reaction.

(II) Temperature influence upon D. B. S.-photolysis is also negligible in the region of 2°C and 22°C. The results obtained at 45°C and 60°C showed some complexity.

In order to make clear the nature of this photolysis, the thermal decomposition of the solution was thoroughly studied.

From the theoretical point of view, it was shown numerically how the pure photo-reaction of D. B. S. is disturbed by the thermal reaction, and how the decomposition is accelerated, together with its practical meaning.

(5) It was found by measurement that the quantum efficiency of the photolysis of D. N. S.-solution at $\lambda=366\text{ m}\mu$ was 0.16.

ACKNOWLEDGMENT.

The authors wish to express their deepest thanks to Prof. M. Kimura, College of Science of the Kyoto Imperial University, and to Prof. M. Miyata, College of Engineering of the Kyoto Imperial University, for their valuable advices and kind revision.
