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An Experimental Investigation of Certain Phases of the Reaction of Meta Dinitrobenzene and Carbonyl Compounds

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AN EXPERIMENTAL INVESTIGATION OF
CERTAIN PHASES OF THE REACTION OF
META DINITROBENZENE AND CARBONYL
COMPOUNDS

By
William Elson

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of Master
of Science in Loyola University

February

1942

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to his advisor, Dr. George Schmeing, Chairman of the Department of Chemistry of Loyola University for his unwavering interest and valuable guidance, and to Mr. Raymond Melchione, also of the Department of Chemistry of Loyola for his numerous practical and helpful suggestions.

The increasing use, within recent years, of certain aromatic compounds for solvent purposes, has presented numerous problems in the field of industrial hygiene, problems that have necessitated intensive investigation of the physiological and chemical properties of these substances.

These investigations, early in their course, revealed the high toxicity of these compounds and their detrimental physiological effect upon workers exposed to their vapors for prolonged periods of time. With this discovery the importance of a method of accurately determining their concentration in contaminated air became paramount, and several investigators turned their attention to the solution of this problem. The researches of these workers, have within recent years, resulted in the publication of several workable procedures which now play an important role in controlling the industrial hazards inherent in the wide spread use of these compounds.

The methods of analysis devised, though necessarily differing in method, facility of determination, and resulting accuracy, have almost without exception

one fundamental basis- the reaction of the dinitro derivative of the aromatic substance with a carbonyl compound to generate a color that can be quantitatively compared to a known standard.

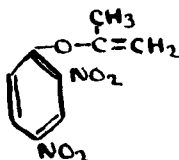
The importance of this reaction in all of these procedures might lead one to assume that it has been subject to considerable investigation. Strangely enough, however, a search of the literature reveals that it has been the object of but little study, despite the fact that it has been known for over forty years. Consequently, because of its importance in the procedures mentioned above, and because of its fundamental theoretical interest, certain of its phases have been studied experimentally and are the concern of this thesis.

The fact that meta dinitro benzene, and related aromatic substances, give color reactions with aldehydes and ketones, in the presence of a base, seems to have been first observed by Janovsky¹ in 1891, who proposed the reaction as test for dinitro compounds. The following year, 1892, the reaction was extended by von Bitto² to serve as a test for aldehydes and ketones in a paper in which he

1. Janovsky, Ber. 24 971, 1891
2. von Bitto, Ann 269 37, 1892

tabulated a number of these compounds which would give the reaction.

In the year 1910, Reitzen and Stamm³ found that when a solution of 1,2,4 chloro-dinitrobenzene in acetone, is slowly added to sodium acetone in a current of dry hydrogen, a deep violet coloration is produced, and decided that the color formation was an instance of the Janovsky test. A brown powder was the final product of the reaction mixture of the formula $C_9H_3O_5N_2$ for which the authors proposed the structure:



and decided that the reaction was strictly analagous to the color produced by adding potassium hydroxide to an acetone solution of 1,2,4 chloro-dinitrobenzene. They also listed color reactions given by numerous nitro compounds with acetone and potassium hydroxide, as well as meta dinitrobenzene, potassium hydroxide and aliphatic cyclic substances containing the group CH_2CO- .

3. Reitzen & Stamm, J. Prakt. Chem. 81 168, 1910

In 1923 Taylor and Rinkenbach⁴ made a more extensive study of the reaction, considering various nitro compounds, and substituted compounds. These investigators found that simple mono nitro derivatives gave no color, dinitro compounds a purple, and trinitro derivatives a blood red coloration. They further considered the effect of substituent groups upon the color formation and found that the amino, hydroxyl and substituted amino groups tended to inhibit the color, and that richly substituted rings do not give the color.

In 1933 Peronnet and Truhart⁵ adapted the reaction to a quantitative determination of benzene in air, nitrating the benzene to the dinitro compound by drawing the contaminated air through a mixture of concentrated sulfuric acid and fuming nitric acid, extracting with sodium carbonate solution and ethyl alcohol, and then warming with a dilute levulose solution. The resulting color was then compared with a known standard.

Two years later, in 1935, Szecsenyi-Nagy⁶ extended Janovskys reaction to detecting benzene in organs, convert-

4. Taylor & Rinkenbach, U.S. Bureau of Mines Bull. 219, 122, (1923)

5. Peronnet & Truhart, Bull. soc. chim 53, 1464 (1933)

6. Szecsenyi-Nagy, Biochem. 28, 175, 178 (1935)

ing the benzene to the dinitro compound by the method of Joachimogli⁷ and then dissolving the dinitro compound in acetone, adding sodium hydroxide and matching the color with a standard.

In 1935 Schrenk, Pearce, Yant⁸ modified the reaction of Peronnet and Truhart by using methyl-ethyl ketone and potassium hydroxide to generate the color.

The following year 1936, the same authors⁹ extended their method, by introducing slight modifications, to the determination of toluene.

-
7. Joachimogli, Biochem. Z. 70, 93 (1915)
 8. Schrenk, Pearce, Yant, Reports of Investigations, Bur. of Mines, R.I. 3323 (1935)
 9. Ibid. R.I. 3387 (1936)

EXPERIMENTAL PROCEDURE

The experimental investigation was directed at three phases of the reaction of dinitro compounds and carbonyl compounds:

1. Attempts to isolate the colored substance.
2. The mechanism of the color formation and the role of the reactants.
3. The relation of color intensity to concentration of the dinitrobenzene in dilute solutions.

Attempts at Isolation

The dinitrobenzene used in these experiments was obtained from the Eastman Kodak Company and recrystallized from ethyl alcohol. The ethyl-methyl ketone, also an Eastman product, was carefully fractioned and the portion boiling between 79-80 degrees collected.

The color is generated readily by simply adding potassium hydroxide solution (40%) to a solution of dinitrobenzene in ethyl-methyl ketone and shaking the mixture. The color produced varies from a light red-violet to a deep purple violet, depending upon the concentration of the dinitro solution.

In all attempts at isolation of the color, a large excess of the ketone was used in order to insure as much

as possible, complete reaction of the dinitro compound. One gram of dinitrobenzene (.006 moles) was dissolved in five hundred grams of the ketone (6 moles). This solution was then shaken with two grams of a forty per-cent solution of potassium hydroxide. Upon the full development of the color the KOH layer was with-drawn. The colored solution was then concentrated by evaporation of the ketone under reduced pressure.

Early in the investigation purple colored crystals were obtained upon evaporation of the solution, that at preliminary examination seemed to be the colored substance. Examination, however, showed these to be crystals of the original dinitrobenzene with an adsorbed layer of the purple color. Upon complete drying, this color quickly disappeared. In no case could crystals, other than these, be obtained, even on prolonged cooling of the concentrated solutions in freezing mixtures. In every case in which the solvent was evaporated the color on the crystals soon disappeared- the color evidently being dependent upon adsorbed ketone. Often the color could be regenerated on the surface of these crystals by simply exposing them to vapors of the ketone.

If these solutions, from which the KOH had been

withdrawn, were warmed the color changed to a light brown. The same behavior was noted upon exposure of the solution to light. If, however, the KOH solution was allowed to remain in contact with the ketone solution the color was quite stable and could be refluxed for several hours without appreciable change; likewise such solutions could be exposed to light for ten to twelve hours without decomposition.

If the solutions of the dinitrobenzene were made more concentrated and heated with potassium hydroxide a vigorous reaction took place, during which the purple color disappeared and a brown resinous solid material remained similar to that observed by Reitzen and Stamm with acetone and chlorodinitrobenzene.

From the results of these experiments it must be concluded that the color is stable only in solution; that this stability is greatly increased by the presence of potassium hydroxide solution, and that the colored substance cannot be isolated, at least by the common methods of separation.

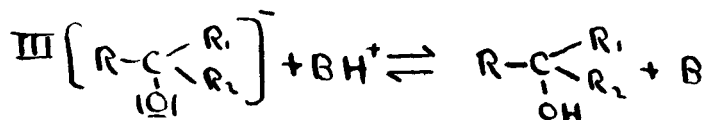
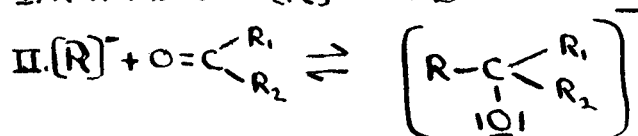
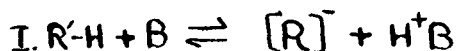
Possible Mechanism and Role of the Reactants

When the reaction is examined from the standpoint of nature of the overall reaction mechanism, and the part played by each of the reactants, the most logical hypothesis seems to be that the color formed is an intermediate product in an carbonyl addition type reaction.

According to the most recent theories, as postulated by Hammett¹⁰, this type reaction involves three essential components;

1. A carbonyl compound.
2. An acid component, or proton donor.
3. A base catalyst, or condensing agent.

The general reaction can be accounted for in a mechanism of the following type:



If the hypothesis, that the color formation is related to this type of reaction, is correct then the

10. Physical Organic Chemistry, Hammett, Mc Graw-Hill Co. 1940, Chap. XI

three necessary components listed above should be present, and should function in the role characteristic of the theoretical demands of this type of reaction.

That the first component, a carbonyl compound, is present is evident. That it is necessary for this type of reaction seems indicated by the fact that a search of the literature reveals nonsimilar reaction of dinitro compounds with substances other than those containing a carbonyl group.

The existence of a proton donor in the reaction mixture, however is not as apparent. That the nitro group has often an activating effect in certain molecules is well known; thus the activating effect in certain aliphatic compounds, and the sensitizing effect which renders the ortho hydrogens in dinitrobenzene easily susceptible to oxidation have both been noted. In general, however, the desensitizing of the nitro group on the benzene ring raises a doubt as to the possibility of dinitrobenzene serving as a proton donor in a reaction such as that in question. Recent investigation, however, shows that this actually takes place in the presence of base.

Kharasch, Brown and Mc Nab¹¹ have found by measuring the

11. Kharasch, Brown & Mc Nab, J. Org. Chem 2 (1939)

proton exchange in deuterio alcohol, that the nitro group markedly reduces the electronegativity of the phenyl radical, and consistent with the low electron density around the carbon atom, facilitates the removal of a proton by hydroxyl groups.

On the basis of these considerations, therefore it would seem that the existence of the dinitrobenzene as the acid component, or proton donor, has strong theoretical basis. In order to augment this evidence by actual experimental data, an attempt was made to determine the active positions in the benzene ring, by carrying out the reaction procedure with related compounds in which successive ring positions in the dinitrobenzene molecule were systematically blocked. The nitro derivatives used in these experiments were prepared from the corresponding hydrocarbon, or substituted hydrocarbon, by the procedure of Shriner and Fuson¹².

The results of these experiments are arranged diagrammatically in Table I.

From the table the following conclusions may be drawn:

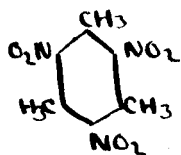
12. Identification of Organic Compounds, Shriner and Fuson, John Wiley and Co., New York, N. Y.

TABLE I.

Figure

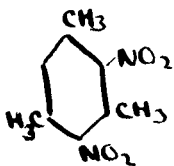
Color Reaction

1.



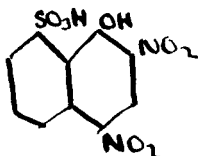
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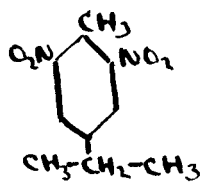
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3.



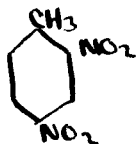
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4.



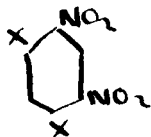
+

5.



+

6.



x indicates active positions

Figure 1. 2-4-6 trinitromesitylene. The negative reaction of this compound indicates that at least one of the ring positions must be open and unsubstituted.

Figure 2. 2-4 dinitro-mesitylene. The fact that this compound does not give the reaction is evidence that the position meta to both nitro groups, the 6 position in this substance, is not the active position. This is apparent since the six position is the only one unsubstituted and capable of taking part in the reaction.

Figure 3. 2-4 dinitro-3sulphono-1 naphthol. The negative reaction of this substance indicates that the position ortho to the two nitro groups, the three position, is not the active position since it is the only ring position that is not blocked.

Figure 4. 2-6 dinitro-para-cyamene. From the positive reaction of this substance two inferences may be drawn:

1. The confirmation of the conclusions of Figs. 2 and 3. The meta and common ortho positions are both blocked, and therefore cannot be essential since the reaction still takes place.

2. One, or both, of the two positions ortho to the nitro groups must be active, and essential to the

reaction. This conclusion necessarily follows since the two positions in question, are the only positions unsubstituted and available for the reaction.

figure 5. 2-4 dinitro-toluene. The positive reaction of this compound in which one of the ortho positions is effectively blocked, demonstrates that only one of the positions is essential for the reaction.

Conclusion: The experimental evidence obtained by successively blocking possible active ring positions in the dinitrobenzene molecule, indicates that only the positions ortho to each nitro group are able to participate in the reaction, and that only one of these positions is necessary for the reaction.

Secondly, the location of the active position- ortho and not meta to the two nitro groups, coupled with the evidence of Khrarasch, and that to be presented later regarding the role of the base, is strongly indicative of a proton transfer from one of these positions as the initial step of the reaction.

Role of the Potassium Hydroxide

Since the carbonyl addition theory demands the presence of a proton acceptor, or base catalyst, two experiments were devised to confirm or disprove, the action of the KOH in this role.

1. The relation of color intensity to KOH concentration.

In this experiment 10cc of a one-tenth molar solution of meta dinitrobenzene in ethyl-methyl ketone was added to each of five tubes. To these tubes was then added, 0.1cc, 0.3cc, 0.5cc, 0.7cc, 0.9cc respectively, of a 40% solution of KOH in water. The tubes were then allowed to stand. The color developed rapidly in the tubes containing the high concentrations of KOH; slowly in those of lower concentration. On standing all became equal in intensity.

2. Conductance changes in the reaction mixture.

In this experiment the change in conductance of an acetone-water solution of KOH, upon the addition of an acetone solution of meta dinitrobenzene was measured. The acetone was substituted for the ethyl-methyl ketone in this experiment since its miscibility with water was more conducive to this type of measurement.

To a mixture of seventy-five cc of water and seventy-five cc of acetone contained in a four hundred cc beak-

I NaOH + H₂O + acetone

II Blank. NaOH + H₂O + acetone
+ acetone solution of ϕ -NO₂
NO₂

III NaOH + H₂O + acetone + acetone
solution (1M) of ϕ -NO₂
NO₂

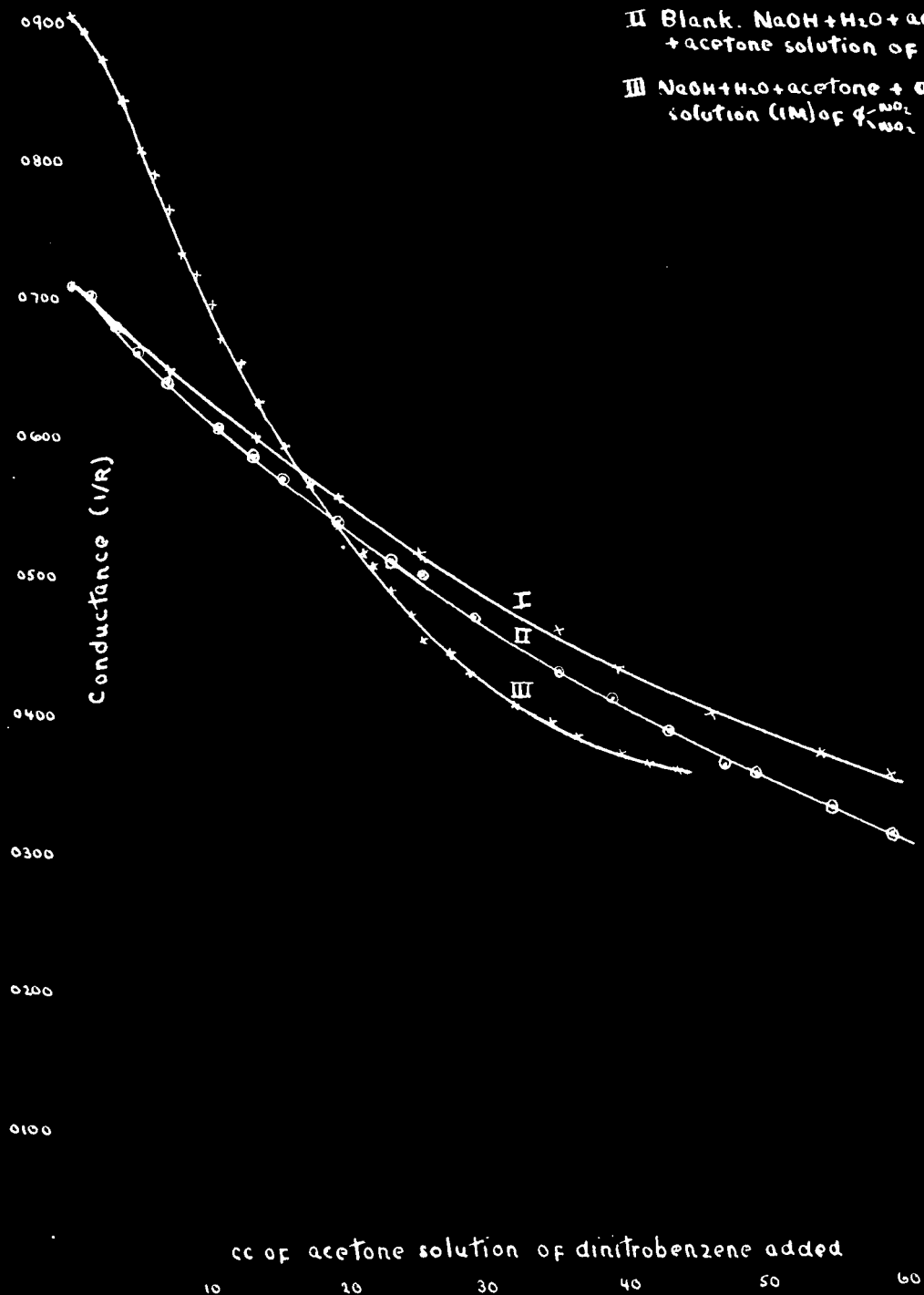


TABLE II.

cc of dinitro- benzene solution added	R	C
0.0	14.1	0.0710
1.6	14.2	704
1.9	14.4	695
3.1	14.7	680
4.8	15.1	663
7.1	15.6	642
11.0	16.5	606
13.1	17.0	588
15.1	17.5	572
19.2	18.6	537
23.2	19.5	513
25.1	20.0	500
29.1	21.3	470
33.1	23.2	431
39.1	24.3	412
43.1	25.7	389
47.1	27.2	368
49.2	28.0	357
53.3	30.1	332
59.3	31.9	314

TABLE III.

c.c. of dinitro- benzene solution added	R	C
0.0	11.1	0901
1.0	11.2	895
2.0	11.5	872
3.5	11.9	842
4.0	12.1	830
4.5	12.3	815
5.0	12.4	808
6.0	12.8	783
7.0	13.1	765
7.5	13.2	760
8.0	13.7	732
8.5	13.9	721
9.0	14.0	715
9.5	14.2	706
10.0	14.4	696
10.6	14.6	686
11.1	14.9	672
11.5	15.3	655
12.0	15.6	650
12.5	15.8	634
13.0	16.1	622
13.0	16.3	615

13.6	16.3	0815
14.0	16.5	607
14.9	16.9	593
15.6	17.2	583
16.0	17.5	572
16.9	17.8	562
17.5	18.1	553
18.0	18.2	549
18.6	18.5	541
19.1	18.7	534
19.6	18.9	529
20.2	19.1	524
21.1	19.4	516
21.9	19.8	505
22.5	20.0	500
23.0	20.2	495
24.0	20.9	478
24.5	21.2	471
25.1	21.5	464
25.6	21.8	458
26.0	22.0	454
27.1	22.6	442
27.6	23.0	435
28.6	23.4	427

29.1	24.0	0413
30.0	24.2	413
31.0	24.5	408
32.0	24.9	402
33.0	25.2	397
34.1	25.4	394
34.5	25.6	390
35.5	25.9	386
36.6	26.2	382
37.5	26.5	377
39.6	27.0	370
41.6	27.5	364
43.7	28.1	358
45.6	28.5	351
48.6	29.1	344

TABLE IV.

c.c. of acetone added	R	C
0.0	14.1	0710
7.1	15.4	649
13.1	16.7	600
19.2	18.0	556
25.0	19.3	518
35.0	21.7	462
39.1	22.9	436
47.1	25.1	398
54.1	26.9	372
55.2	27.1	369
59.2	28.0	357

er was added 13.5cc of ten per-cent KOH solution. Two platinum electrodes, connected through a dynamometer conductance meter, dipped into the solution. The conductance of this solution, as measured in reciprocal ohms, was taken as the initial reading of R. An acetone solution of dinitrobenzene, 3 grams in 100cc (.018 molar) was then added slowly from a burette. Readings were taken after addition, the color developing with the first few drops of the dinitro solution.

This procedure was then repeated with a 0.5 molar solution of the dinitrobenzene.

In a third experiment the same procedure was followed with the exception that pure acetone was substituted for the dinitro solution. The data from these experiments are contained in Tables II, III, and IV. The corresponding plots are represented by curves 1, 2, and 3, in Fig. I.

Discussion

The results of the first experiment, in which the rate of the color formation, but not the final intensity, are shown to be related to the KOH concentration, indicates that the KOH did not enter into direct combination with either of the other reactants. If such combination had taken place a gradation in the final intensity of the solutions should have been noted.

When the data obtained in the first two part are plotted as conductance volume of dinitro solution added-curve, it will be seen that a smooth, unbroken curve results in both cases. This is contrary to what might be expected if the KOH were being used up in actual chemical combination. If this were true, the conductance should fall off as the KOH was removed from the reaction mixture to a nearly constant value. The curve, therefore, would show a break in the region of molar or equivalent values of concentration. The general smoothness of both of the curves indicates that the fall conductance is due largely to a dilution effect. This is confirmed in the plot of the third part of the experiment, in which only acetone was added to the KOH-acetone-water solution. This curve shows the same smooth drop off in conductance and the same general shape as the other curves though the dinitrobenzene was absent from the mixture.

From the results of these two experiments it may be concluded that the potassium hydroxide does not enter into permanent combination with either of the other components of the reaction mixture, and is present as a base catalyst.

Conclusion

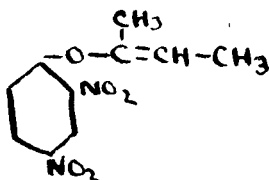
On the basis of the above theoretical and exper-

imental evidence, it would seem indicated that the only logical hypothesis in regard to the mechanism of the color formation, would be that the reaction is of the carbonyl addition type, and that the color is due to an intermediate in this reaction which probably consists of the following steps:

1. A proton exchange between the base and the dinitro compound; such exchange taking place at one of the positions ortho to one of the nitro groups in the dinitrobenzene molecule.

2. The unstable addition of the carbonyl compound at this point in some manner conducive to color formation.

3. The decomposition of this intermediate into a stable final product, which on the basis of the work of Reitzen and Stamm before cited, probably has the following structure:



COLOR INVESTIGATION

The purpose of these experiments was two-fold:

1. The determination of the percent transmission-wave length curve of the color as generated in a dilute di-nitro solution.

2. The determination of the color intensity-concentration relation in dilute solutions.

Absorption Curve

In this experiment and those subsequent all color intensity measurements were made with the Coleman Company Spectrophotometer.

The percent transmission-wave length curve was determined by developing the color, by the usual method, in a solution containing 0.01 mg. per c.c. The percent transmission of this solution was then measured at intervals of fifteen millimicrons throughout the range of 300-800 millimicrons. The data for this curve (IV) are contained in Table V.

Color-Concentration Relation

In determining the color-concentration relation the respective solutions were made up from a primary standard containing 0.01 mg. of meta dinitrobenzene per c.c. of methyl ethyl ketone; the reagents used meeting the specifications set forth in the beginning of the experimental

portion of this report.

The color reaction was carried out with 20 c.c. aliquots of these solutions by adding 3 c.c. of 40% potassium hydroxide to each solutions and allowing the mixtures to stand, with frequent shaking, over a period of one hour. During this time the solutions were well protected from light. Measurements of the percent transmission were made at a wave length of 550 millimicrons.

These data (VI) when graphed as a log of the percent transmission-concentration curve (not included) yielded a straight line between the concentration values 0.0002 mg. to 0.001 mg. per c.c.

100

Curve II

90

80

70

60

50

40

30

20

10

% Transmission

wave length

300

400

500

600

700

800

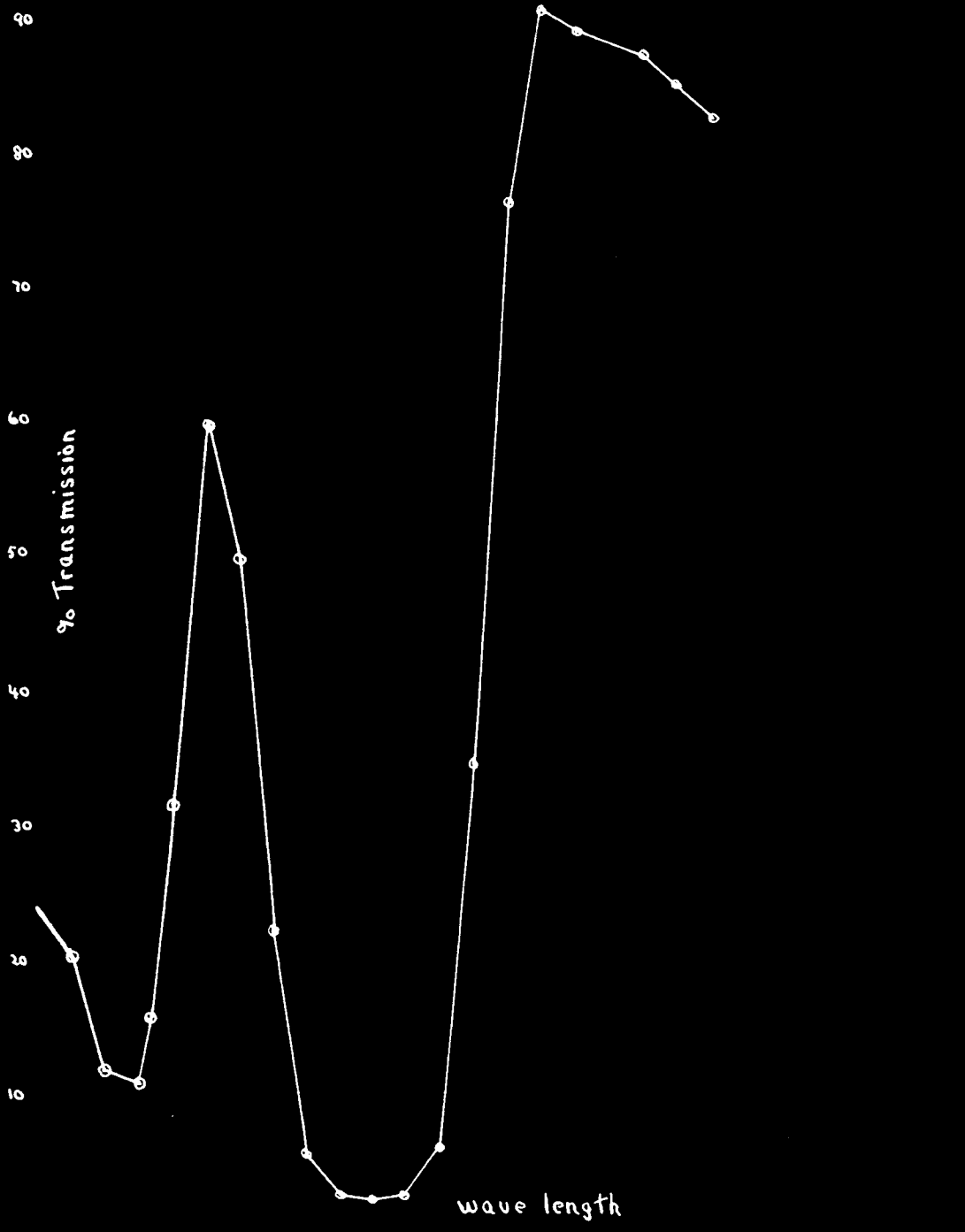


TABLE V.

Absorption Curve

Wave length	% transmission
400	8.2
415	24.0
425	40.8
440	64.9
455	73.1
470	68.1
485	57.5
500	44.0
515	31.0
530	20.3
545	14.0
560	11.2
575	12.5
590	20.0
605	36.8
620	60.5
635	80.1
650	91.0
665	94.0
680	94.1

TABLE VI.

Concentration mg./c.c.	% transmission
0.0001	88.0
2	87.2
3	84.8
4	82.7
6	78.4
8	76.1
10	70.5
12	65.0
14	55.4
16	42.8
20	42.2
30	31.9

The thesis, "An Experimental Investigation of Certain Phases of the Reaction of Meta Dinitrobenzene and Carbonyl Compounds", written by William Elson, has been accepted by the Graduate School with reference to form, and by the readers whose names appear below, with reference to content. It is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

George M. Schmeing, Ph.D.

November 28, 1941

Joseph D. Parent, Ph.D.

November 13, 1941

