

A QUANTITATIVE EXAMINATION OF THE  
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NO<sub>2</sub>-RADICAL IN THE PRESENCE OF  
HIGHLY-COLORED REACTION PRODUCTS

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BENZENE RING...

BY

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.....

A QUANTITATIVE INVESTIGATION OF THE  
REPLACEMENT OF NITRO-GROUPS  
IN THE BENZENE RING  
AS PREDICTED BY THE ELECTRONIC CONCEPTION OF POLARITY.

- by -

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*Approved*  
E.H.A.



## TABLE OF CONTENTS

### INTRODUCTION.

- A. A statement of the Electronic Conception of Valence as applied to the polarity of various groups substituted in the benzene ring.
- B. The purpose of the work undertaken, and an explanation of how Part II led to Part I.

### REVIEW.

- A. A review of some studies in replacement of nitro-groups in various benzene derivatives by other workers, and a comparison of their results with those predicted by the Electronic Theory.

### PART I.

- 1. The various methods of estimating the amount of replacement that had occurred, with facts leading to the abandonment of each;
- 2. Reasons for the final decision regarding the use of alcohol as a solvent;
- 3. The final method of analysis evolved as being most suitable under the conditions.

### PART II.

- 1. The various procedures used in effecting the substitution of the nitro-group
- 2. Tables and discussion of the results.

THE REPLACEMENT OF NITRO-GROUPS  
IN THE BENZENE RING.

INTRODUCTION

A.

The latest conception of the atom as consisting of a positively-charged nucleus surrounded by a rotating system of negative electrons, now almost universally accepted, leads to the following conclusion:

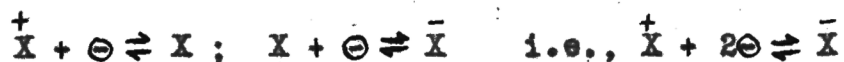
The neutral atom, by the gain of one electron may become negatively charged; conversely, by the loss of one electron the atom may become positively charged.

This important statement is the basis of the theory of the Electronic Conception of Valence, as presented by H.S. Fry.<sup>1</sup>

From it, the following important suppositions are made:

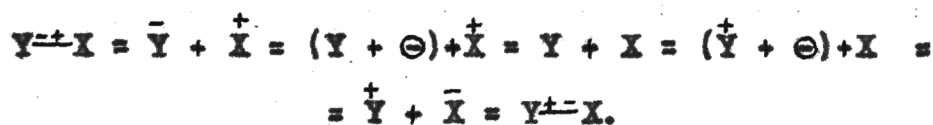
- (i) The diatomic molecule,  $X_2$ , may be considered to undergo a process of "electronic dissociation" represented thus:  $X_2 = \overset{+}{X} + \bar{X}$ .
- (ii) Any other diatomic molecule, undergoing the same process, would likewise give:  $Y_2 = \bar{Y} + \overset{+}{Y}$ . On combination with a molecule of:  $(X_2 =) \overset{+}{X} + \bar{X}$ , the two possible forms  $Y^{\pm}X$  and  $Y^{\pm}X$  may be imagined to result in a condition of "electronic tautomerism".
- (iii) In the representation:  $X_2 = \overset{+}{X} + \bar{X}$ , according to the nature of the element X one or the other of the two

forms  $\overset{+}{X}$  and  $\bar{X}$  will tend to be the more stable; if the electron be designated by the symbol  $\ominus$ , the conversion of one form to the other may be represented thus:



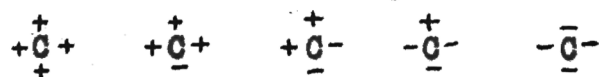
This of course assumes some substance to be present which is capable of supplying the electrons.

(iv) The above scheme may now be represented as a possible explanation of the tautomerism mentioned under (ii):

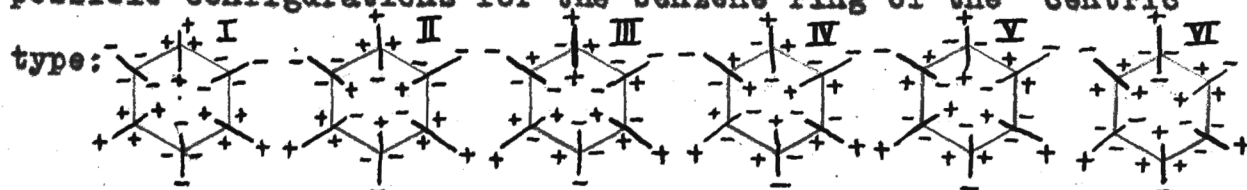


Now, the actual existence of  $\overset{+}{X}$  and  $\bar{X}$  may be supposed in the following cases:  $\overset{+}{Na}\bar{H}$  and  $\overset{+}{H}\bar{F}$ , where  $X=H$ , since Na and F are respectively considered to be one of our most characteristic positive and negative elements. Again, a similar argument holds for  $\overset{+}{H}\bar{Cl}$  and  $\overset{+}{H}-\bar{O}-\bar{Cl}$  in the case of Cl, and further, in the case of iodine, we have the fact that ICl hydrolyzes thus:  $ICl + \overset{+}{H}-\bar{O}H = \overset{+}{H}\bar{Cl} + \overset{+}{I}-\bar{O}H$ , showing I to be  $\overset{+}{I}$  in  $\overset{+}{I}\bar{Cl}$ , whereas we are led to suppose it is  $\bar{I}$  in  $\bar{H}\bar{I}$ .

There is no reason to suppose that this effect is limited to univalent atoms, and therefore we have the following five possibilities for the quadrivalent carbon atom:

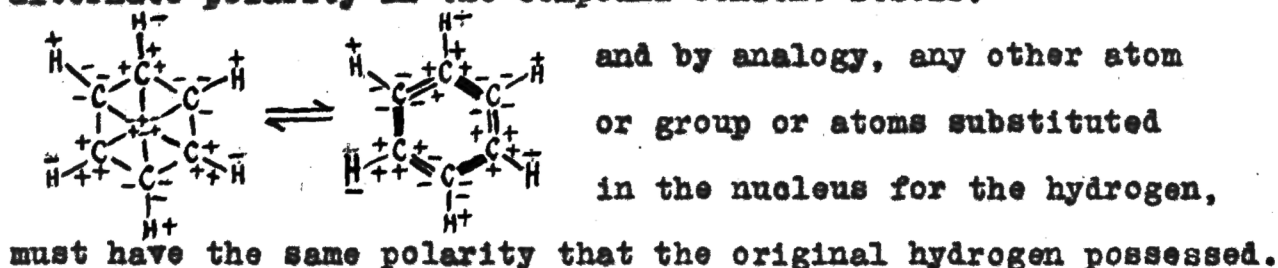


which, when combined in every conceivable manner in the form of a closed ring of six carbon atoms, give six and only six possible configurations for the benzene ring of the "centric" type:

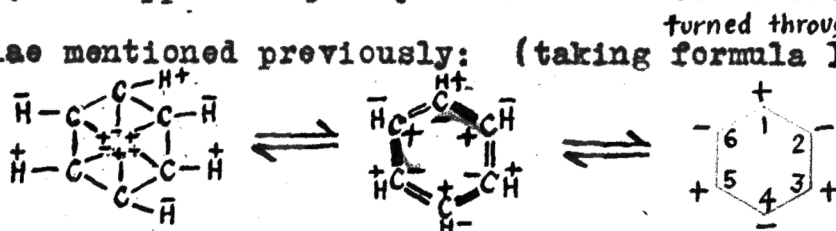


It will be noted that the preceeding six formulae may be converted to conform with the Kekulé type by joining the centric bonds in pairs, thereby obtaining either contraplex or duplex double bonds as the case may be; but it is quite immaterial which type is considered -- in either case the outer bonds have alternate positive and negative values in each of the six possibilities.

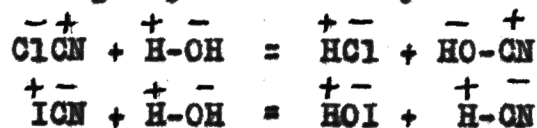
The underscored statement above is the key to the electronic explanation of substitution in the benzene nucleus, since this fact demands the existence of hydrogen atoms of alternate polarity in the compound benzene itself:



Since the full formula of the benzene nucleus is very awkward to work with, the following abbreviation will be henceforth used, and applies equally well to either of the six possible formulae mentioned previously: (taking formula I<sub>A</sub> as an example.)



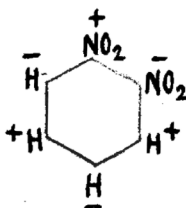
Finally, the electronic tautomerism may be extended not only to introduce the existence of positive and negative atoms, but of total polarity of groups of atoms, as in the case of the CN group recorded by Nef:<sup>2</sup>



The tendency of any particular atom or group is to act with more or less preference for a certain polarity, though in some cases this preference is very slight,<sup>3</sup> and leads to the following classification of some of the commoner substituents in the benzene ring:

OH, Cl, Br, I, NH<sub>2</sub>, CH<sub>3</sub>, etc., where the tendency  $\bar{X}$  exceeds  $\overset{+}{X}$ ,  
 CO<sub>2</sub>H, COH, SO<sub>3</sub>H, NO<sub>2</sub>, etc., where the tendency  $\overset{+}{X}$  exceeds  $\bar{X}$ .

That any group may function positively or negatively is at once evident in the consideration of the di-substituted ortho benzene compound in the light of the present theory:



### B.

The preceding brief outline of the logical sequence of facts that lead to the theory of alternate polarity of the carbon atoms in the benzene ring suffices to introduce the actual subject of this investigation; namely, to gather evidence either for or against the above theory by experimental replacement of variously-oriented nitro groups in benzene compounds. The replacement was to be effected by alkali-metal hydroxides, since the only conceivable reaction: (taking a simple case)

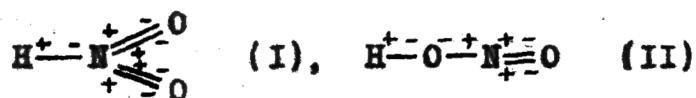
$$\text{C}_6\text{H}_4(\overset{\pm}{\text{NO}_2})_2 + \text{NaOH} = \text{C}_6\text{H}_4(\overset{+}{\text{NO}_2})(\overset{-}{\text{OH}}) + \text{Na}\overset{+}{\text{NO}_2}\overset{-}{\text{O}}$$

would result in a differentiation between positive and negative nitro groups since only  $\bar{\text{NO}}_2$  can be imagined to partake in the

formation of characteristic  $\text{Na}^+\text{NO}_2^-$  where the mutually satisfied polarities are acceptedly distributed as indicated.

At this point it may be well to consider the electronic structure of the  $\text{NO}_2$ -group itself.

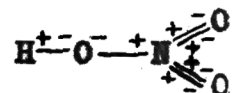
Nitrous acid,  $\text{HNO}_2$ , presents two possibilities of form but only one possibility of polarity with respect to the  $-\text{NO}_2$  group:-



It is evident that

the nitrite formed is derived from form (II), while form (I) is possibly that from which the nitroparaffins are derived.

Since, however, the  $\text{NO}_2$ -group is only introduced into the benzene ring directly through the agency of  $\text{HNO}_3$ , not  $\text{HNO}_2$ , it will be found that the only possible electronic formula of nitric acid contains a  $\text{NO}_2$ -group that is positive instead of negative as



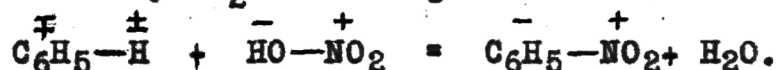
in the case of nitrous acid. This fact

leads to the important conclusion that only those  $\text{NO}_2$ -groups which have <sup>not</sup> been directly substituted in the ring should be replaceable by alkali hydroxides, since the positive, directly-substituted group would not tend towards the formation of  $\text{Na}^+ - \text{NO}_2^-$ . Any such replacement as might occur in the latter case may however be explained by the process of tautomerism mentioned under (iv) on page II.

Let us now examine the possibilities of distribution of these positive and negative  $\text{NO}_2$ -groups in the ring.

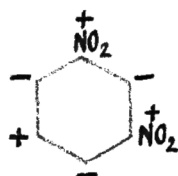
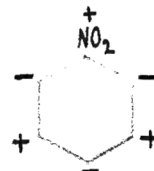
Commencing with benzene itself, suppose it to be

mono-substituted by  $\text{NO}_2$  according to the reaction:



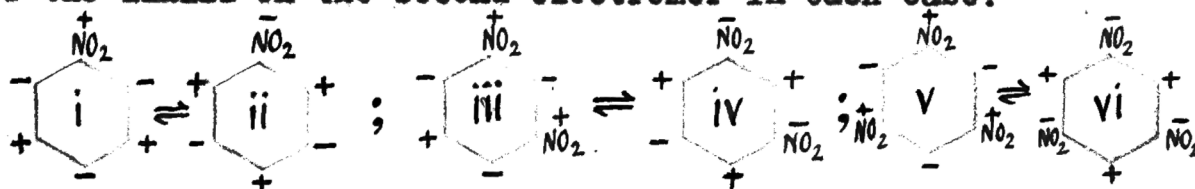
Since the  $\text{NO}_2$  has been shown to have the tendency to react as a positive group, it is logical to assume the replacement of a positive hydrogen as previously explained; this eliminates three alternate positions in the ring as not being favorable for substitution, leaving only one possibility:

for the electronic formula of nitrobenzene since each of the remaining three positions are equivalent. A similar argument leads to the following



as the only possible di-nitrobenzene since positions 3 and 5 are equivalent not only in polarity but from the standpoint of isomerism.

Finally, the product of the final direct nitration of benzene leads to the symmetrical 1-3-5 trinitrobenzene, and no other direct nitration products have ever been observed<sup>4</sup> except in minute traces. The action of alkali-hydroxides on the above three compounds should theoretically be nil, though any replacement actually occurring might be explained by the action of the alkali on the second electromer in each case:

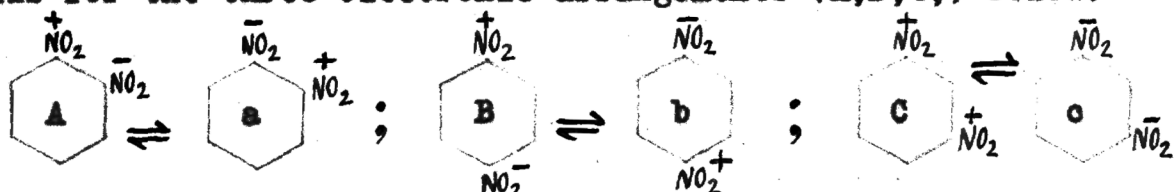


The curious fact now presents itself that the symmetrical 1-3-5 trinitrobenzene when acted upon by  $\text{NaOCH}_3$ , instead of giving traces of the compound (i) below as might be expected from the electromer (vi) above, actually gives<sup>5</sup> (ii):



If the indirect nitration of the benzene ring be now allowed, we find that many combinations of polarity of the  $\text{NO}_2$ -group are now possible. No second nitrobenzene should be formed, since the nitro group, having a positive tendency, would always give the one electromer where the group is positive.

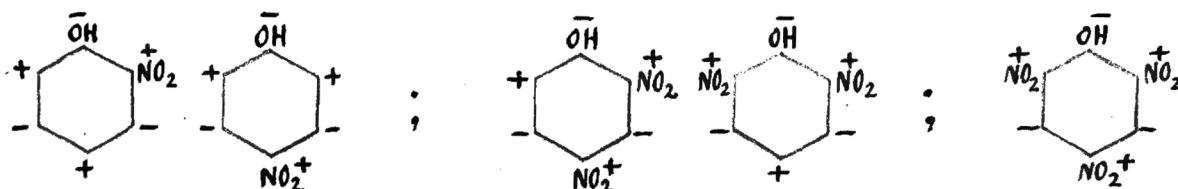
The isomeric demand for three di-nitro benzenes calls for the three electronic arrangements (A,B,C,) below:



together with their respective electromers, (a,b,c.).

It is noticed that the electromers (a,b,) should present no difference in behavior towards  $\text{NaOH}$  to their originating forms (A,B,); all four having one negative nitro group in common, which should be replaceable. If C, (which should not be acted upon) gives appreciable quantities of c, then both  $\text{NO}_2$ -groups should be replaced equally but not necessarily quantitatively. This is a very important conclusion.

If a negative group such as OH is already in the ring; following the laws of isomerism and the electronic theory, a directly-substituted  $\text{NO}_2$ -group has a choice of two positions in which to enter, instead of only one as in the case where the group already in position ( $\text{NO}_2$ ) is positive. These two possibilities together with the possibilities of further direct nitration are indicated below:





Experimentally, it is found that the products formed by direct nitration of phenol agree with these five formulae, and that any other isomers must be formed indirectly.

The introduction of more than three nitro groups in the benzene ring is exceedingly difficult, the fourth group having to be substituted by very indirect methods, and in all cases, the compounds so formed are most unstable. Such would be expected from the considerations presented above.

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The object of this investigation therefore resolves itself into the converse problem of ascertaining if the replacement of the variously-substituted nitro groups occurs in such a manner as to support the theory which has been advanced to interpret their original introduction.

This replacement, performed by the agency of NaOH, KOH, (possibly  $\text{NaOC}_2\text{H}_5$  and  $\text{KOC}_2\text{H}_5$ ), should lead to the formation of sodium or potassium nitrite in either case. It was expected that by quantitative estimation of this nitrite combined with investigation of the product of substitution, no difficulty should be experienced in following the progress of the substitution. Many methods of analyzing nitrites have been made standard, and should prove adaptable to this case, it was thought.

When the actual analysis came to be made however, difficulties<sup>a</sup> rose which hindered the progress of the investigation for over a year. The discussion of these and their final solution will form the topic of PART I.

THE REPLACEMENT OF NITRO-GROUPS  
IN THE BENZENE RING.

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A review of some studies in replacement of nitro-groups in various benzene derivatives by other workers, and a comparison of their results with those predicted by the Electronic Theory.

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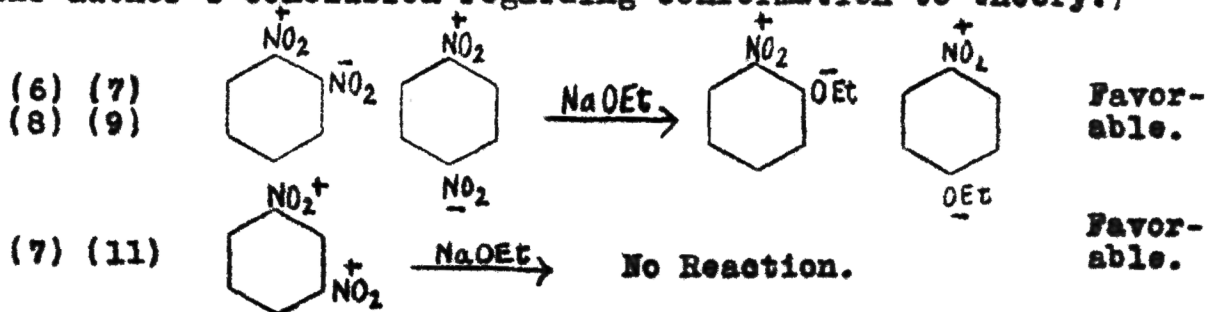
A.

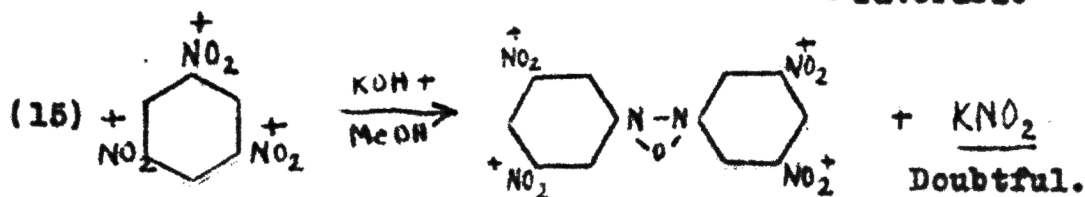
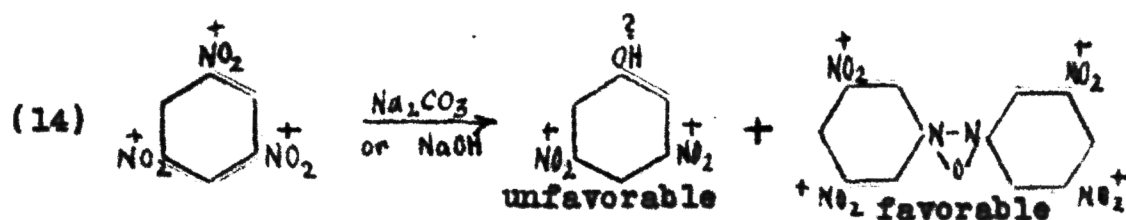
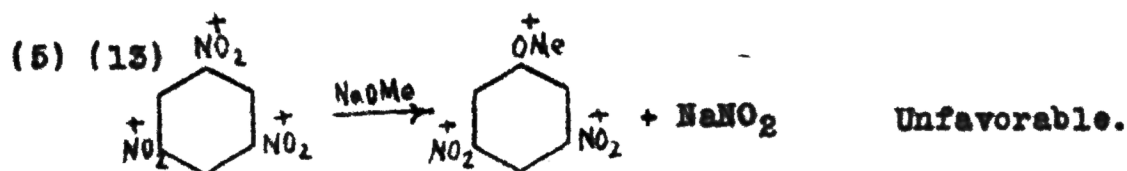
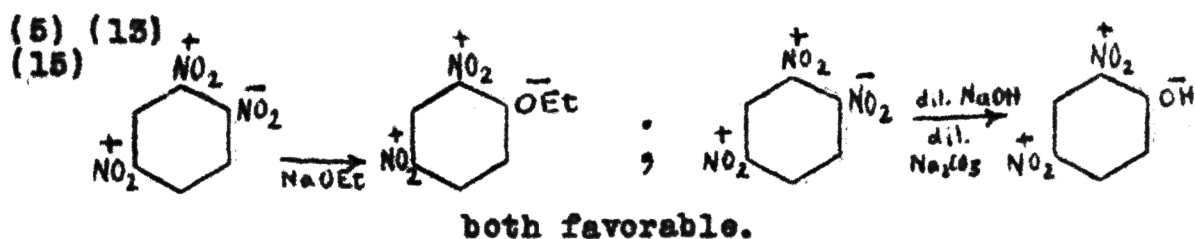
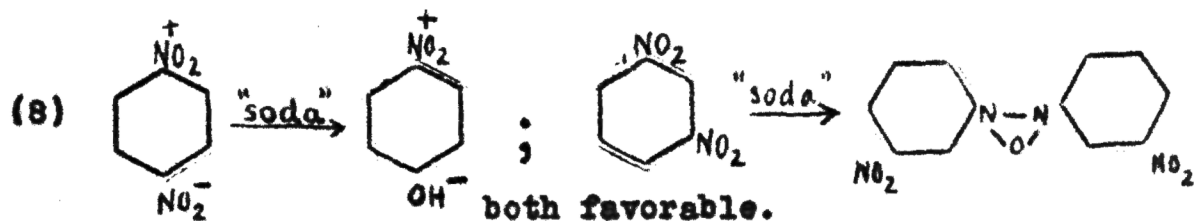
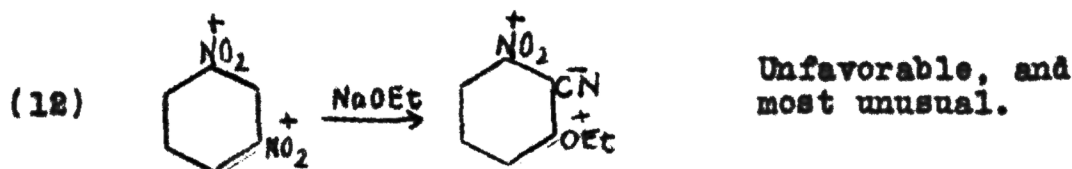
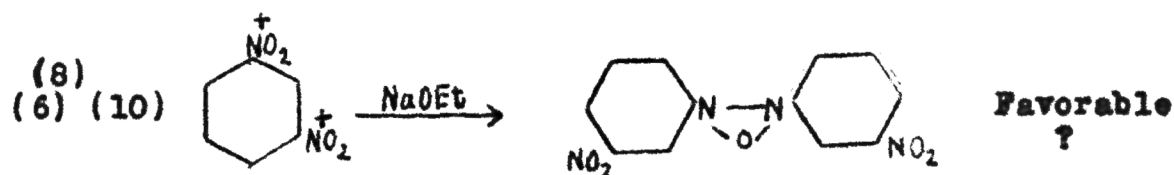
Consideration will first be given to purely nitro-derivatives of benzene, then to more complex compounds.

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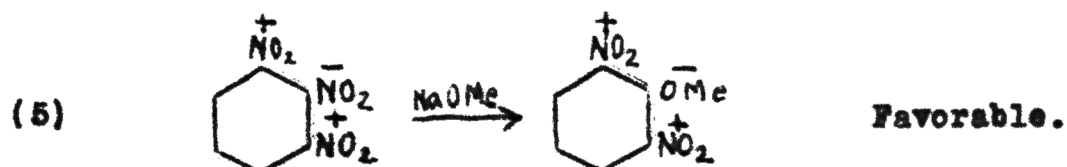
No evidence in the literature reviewed could be found bearing on the direct replacement of the  $\text{NO}_2$  in nitrobenzene by alkali-hydroxides.

In abstracts published by the Journal of the Chemical Society, London, of the work done by C.A. Lobry de Bruyn (de B.) much valuable information was gathered concerning the behavior of poly-nitro benzene compounds. Taking these in order of complexity the following facts are noted: (The numerals in parentheses refer to the list of references at the close of this work; the words "favorable" and "unfavorable" refer to the author's conclusion regarding conformation to theory.)



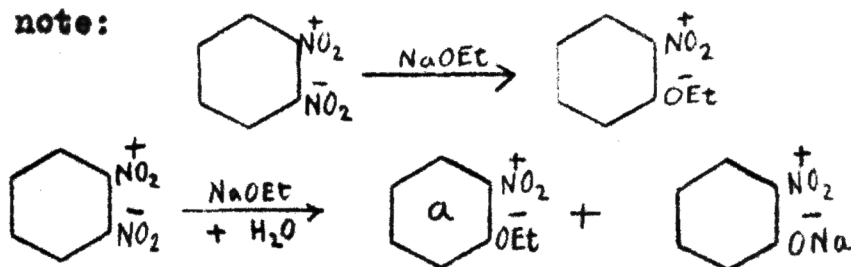


The last three results make the validity of the original assumption of three positive nitro-groups questionable.



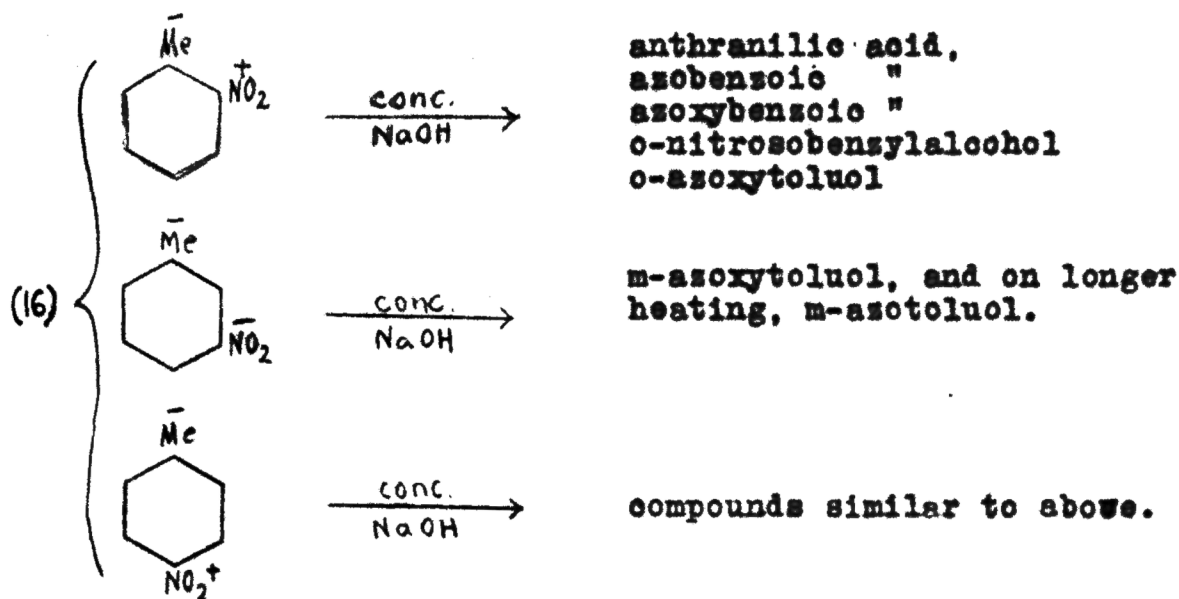
Lobry de Bruyn finally states<sup>(6)</sup> that the action of alcoholic KOH or even of aqueous alkalies<sup>8</sup> on nitro-compounds usually yields complicated azo-derivatives although  $\text{KNO}_2$  is nearly always formed at the same time. See also (18).

With respect to the influence of water on the course of the reactions of sodium ethylate, Lobry de Bruyn<sup>10</sup> has the interesting note:

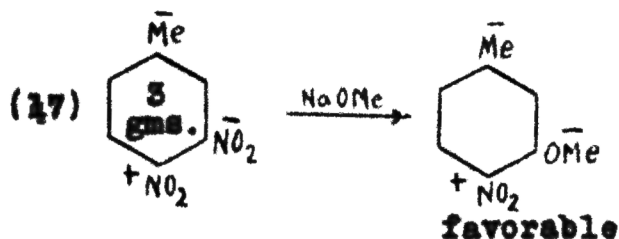
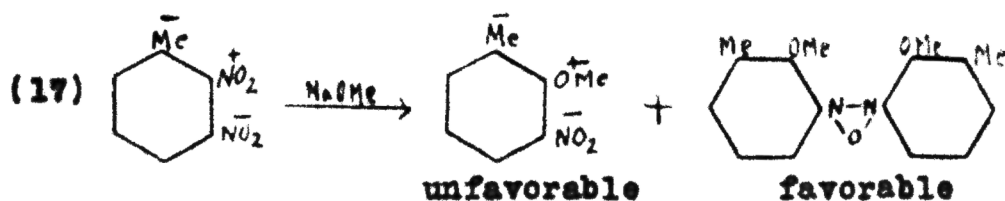


where the % of the (a) compound increases rapidly with the % of alcohol present.

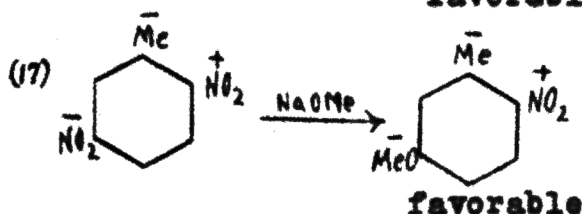
Passing on to the more complex nitro-compounds, various workers have contributed the following:



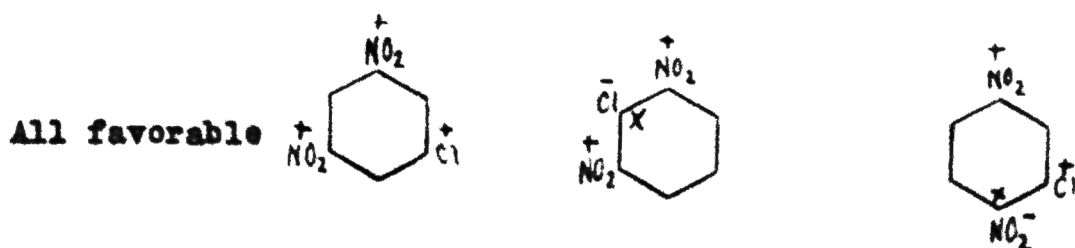
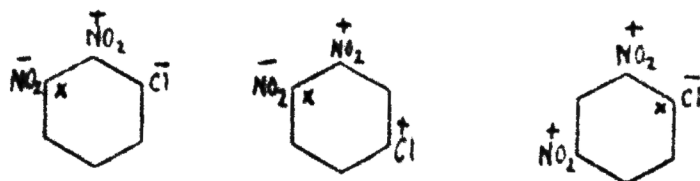
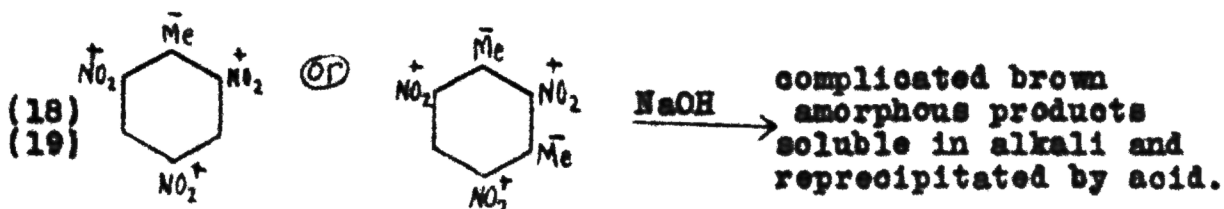
This general complexity of action is further borne out by the following reactions, and by the reference (18):



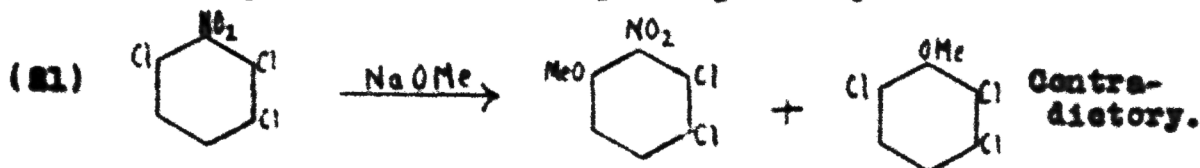
also .8gm black insol. product  
(probably stilbene der.)  
and .5gm of a dark red resin-  
ous product soluble in  
alkalies.



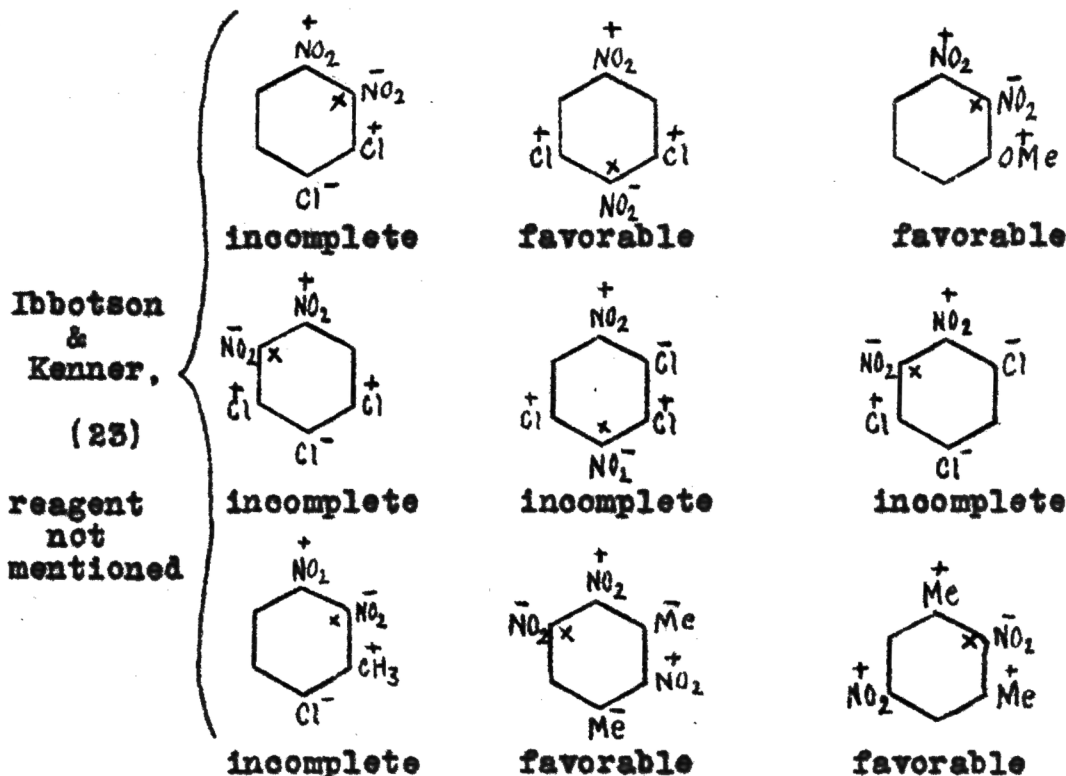
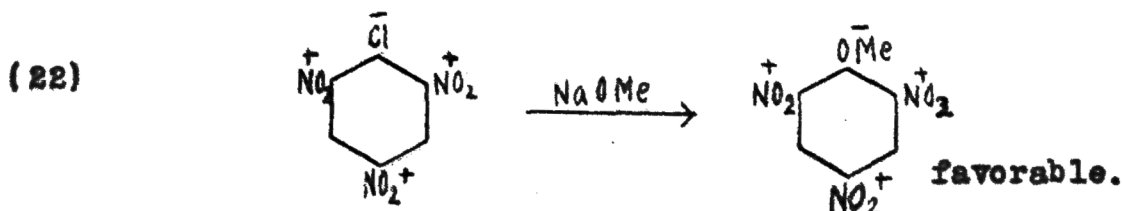
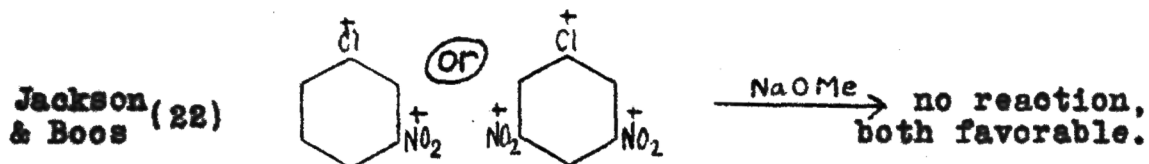
(only a very small yield)



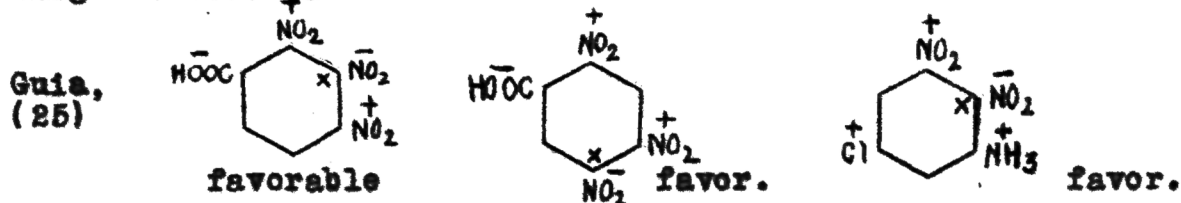
The above six compounds were investigated by Holleman<sup>20</sup>  
by letting them react with NaOMe. The group replaced is marked  
by an "x". Replacement is incomplete probably in the first case.



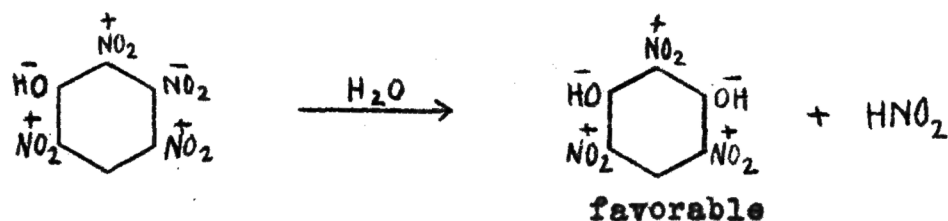
There now follow some cases that do not fall in any particular grouping, ~~and in most cases~~ <sup>most of which</sup> were recorded with an entirely different object in view on the part of the worker.



In commenting upon the above six compounds, the word "unfavorable" is not used when a negative chlorine atom fails to be displaced as expected; "incomplete" reaction probably being the true cause.



Finally, the following interesting case showing the ease with which a fourth nitro-group is displaced, is drawn from Cohen:<sup>24</sup>



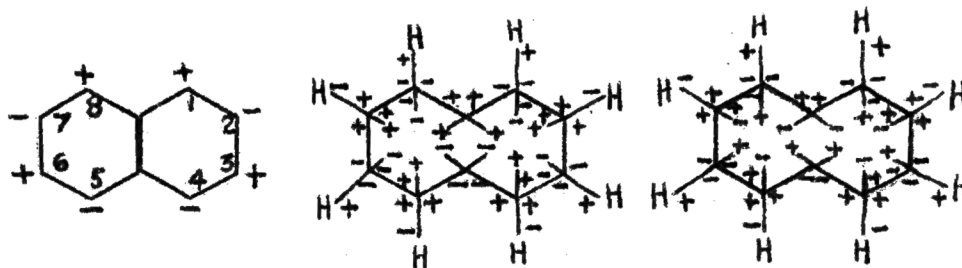
Many other cases of displacement of nitro-groups may be found in the literature, but in many cases the object in view was so entirely different, that the author does not feel justified in including any other than those where the reagents used would indicate the formation of nitrites.

It will be seen that the author has based his assumptions of polarities of the original compound upon the fact that any  $\text{NO}_2$ -group replaced must have borne a negative sign, hence giving a starting-point from which to evaluate the remaining groups. This has in a few cases led to somewhat anomalous results, but nevertheless remains the most probable indication of the said polarities.

The often-mentioned production of azoxy-compounds as reaction products indicates a reducing action of the reagent; if this is so, the simultaneous formation of a nitrite does not seem very plausible, as it would be oxidized to nitrate by the liberated oxygen; the reducing power of the reagent not being sufficiently strong to keep the nitrite as such. The reaction may however be much more complex, as indicated by the concomitant formation of still more complicated compounds.

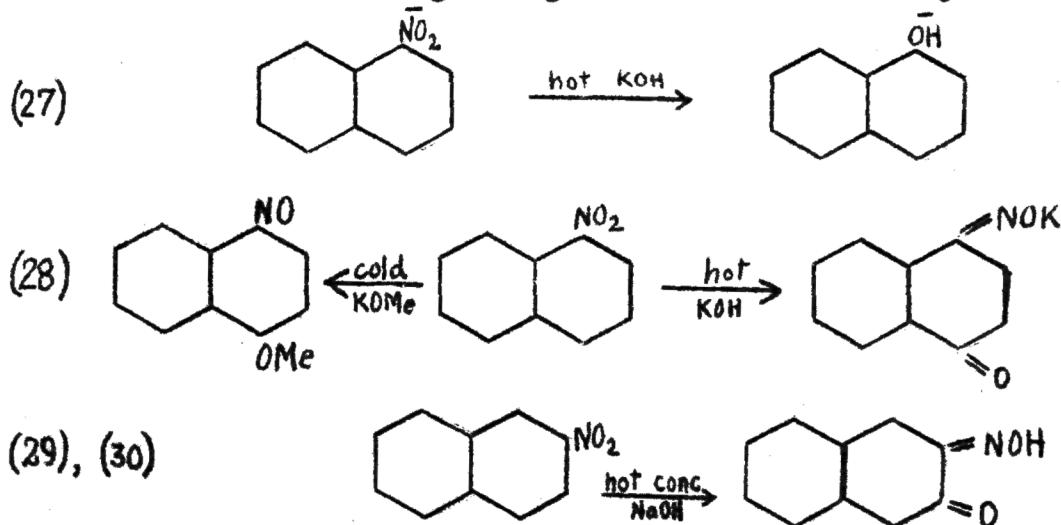
In concluding this review, it may be well to mention the comparative paucity of information regarding the nitro-compounds of naphthalene with respect to the action in question.

Fry,<sup>26</sup> following the same argument as for benzene, derives the same abbreviated formula from the only two possible electronic forms that can be constructed from the different



combinations of the six types of carbon atoms previously mentioned. It will be seen that the polarities are distributed symmetrically about a vertical centre line, causing the polarity of the hydrogen atoms to be non-alternating. This leads to the probable difference in behavior that may be expected between 1-5 and 1-8 di-substituted naphthalene derivatives (the most common derivatives) due to the fact that in the 1-5 compounds the substituents should have different polarities while in the 1-8 compounds, the polarities should be the same.

The following examples show a diversity of reaction:





THE REPLACEMENT OF NITRO-GROUPS  
IN THE BENZENE RING.

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EXPERIMENTAL -- PART 1.

1. The various methods of estimating the amount of replacement that had occurred, with facts leading to the abandonment of each.

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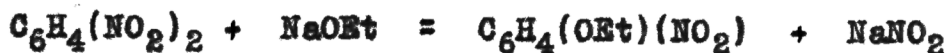
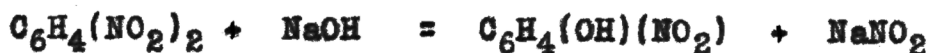
- (A) Titration of excess alkali;
  - (a) by added indicator,
  - (b) by first formation of precipitate,
  - (c) by electric conductivity measurement
- (B) By the use of "nitron" to quantitatively precipitate nitrite as nitron nitrate;
- (C) Reduction of nitrite to  $\text{NH}_3$  by means of aluminium in the alkaline solution;
- (D) Measurement of volume of nitric oxide liberated by action of mercury and conc.  $\text{H}_2\text{SO}_4$  ;
- (E) Titration of iodine liberated by the action of potassium iodide on the nitrous acid.

.....

A.

(a)

The first method of analysis that suggested itself was due to consideration of the equations:



It is seen that alkali is used up without being replaced by an equivalent amount of other alkali. Thus, if the titration of the alkali used against a standard acid were known, the

amount of alkali used up in the reaction could be found by titration of the remaining alkali in the reaction-mixture against the same standard acid. This difference of alkali could then be converted directly to terms of  $\text{NO}_2$  replaced by a simple calculation.  $\text{HCl}$  was chosen as the acid most suitable and a formula derived to give the % of replacement directly from the titrations had the following form:

$$\frac{(\text{diff. HCl Tit'n})(\text{norm. HCl})}{1000} \times (\text{mol. wt. of } \text{NO}_2) = \text{gms. } \text{NO}_2 \text{ replaced,}$$

$$\frac{(\text{gms. } \text{NO}_2 \text{ replaced})(\text{mol. wt. of substance})}{(\text{wt. substance})(\text{no. } \text{NO}_2 \text{ groups})(\text{mol. wt. } \text{NO}_2)} \times 100 = \% \text{ of replacement.}$$

To ensure equal conditions regarding  $\text{CO}_2$ -absorption during heating, loss of alkali by action on the glass, etc., a "blank" was run with each set of experiments, consisting of an identical concentration and amount of the reagent alone, whose titration after heating was taken as initial amount of reagent used.

Phenolphthalein, unaffected by  $\text{HNO}_2$ , was first used as an indicator and worked very well for the "blanks". When the reaction-mixture came to be titrated however, the first real difficulty arose. They were invariably of a deep red or brown color which so effectually masked the color-change of the indicator that the end point could not be determined within .5 cc. This error becomes greatly magnified in the calculation as will be seen. Lessening the concentration of the acid gave a larger titration but a greater error in determining the end-point.

It was observed that when acidity was established, the muddy solution cleared with formation of a curdy blackish-

brown precipitate, leaving an amber solution. Back-titration of excess acid caused the muddiness to reappear, but with no greater success in determining the end point.

Methyl red was next tried, but with no greater gain in accuracy. A few other biological indicators were tried also, with no better result.

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b.

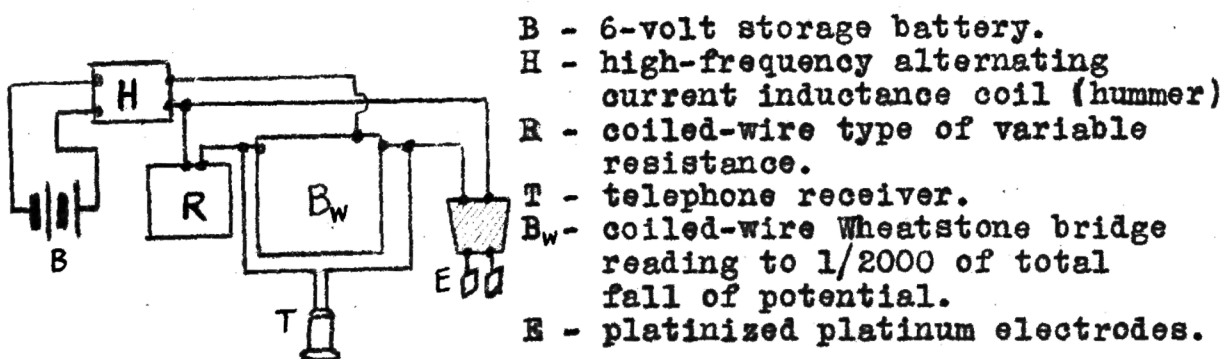
By observation of the first signs of the above mentioned precipitate (a sign of acidity) a consistent titration could be obtained for several compounds, while others gave an obscure, gradually-forming precipitate, and some no precipitate at all. Hence this method was not sufficiently general.

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c.

The need of a new method of titration not depending on a color-change was now felt, and led to the adoption of an electrical conductivity method whereby the abrupt change in conductivity of a strong base (NaOH) during titration with a strong acid (HCl), due to change from excess  $\text{OH}^-$  ions to excess  $\text{H}^+$  ions, marks the neutralization point.

The reaction mixture was poured into a 400 cc beaker and rinsed with distilled water to a volume of 250 cc. The heat of solution was allowed to dissipate before titration. The apparatus was quite standard, being as follows:

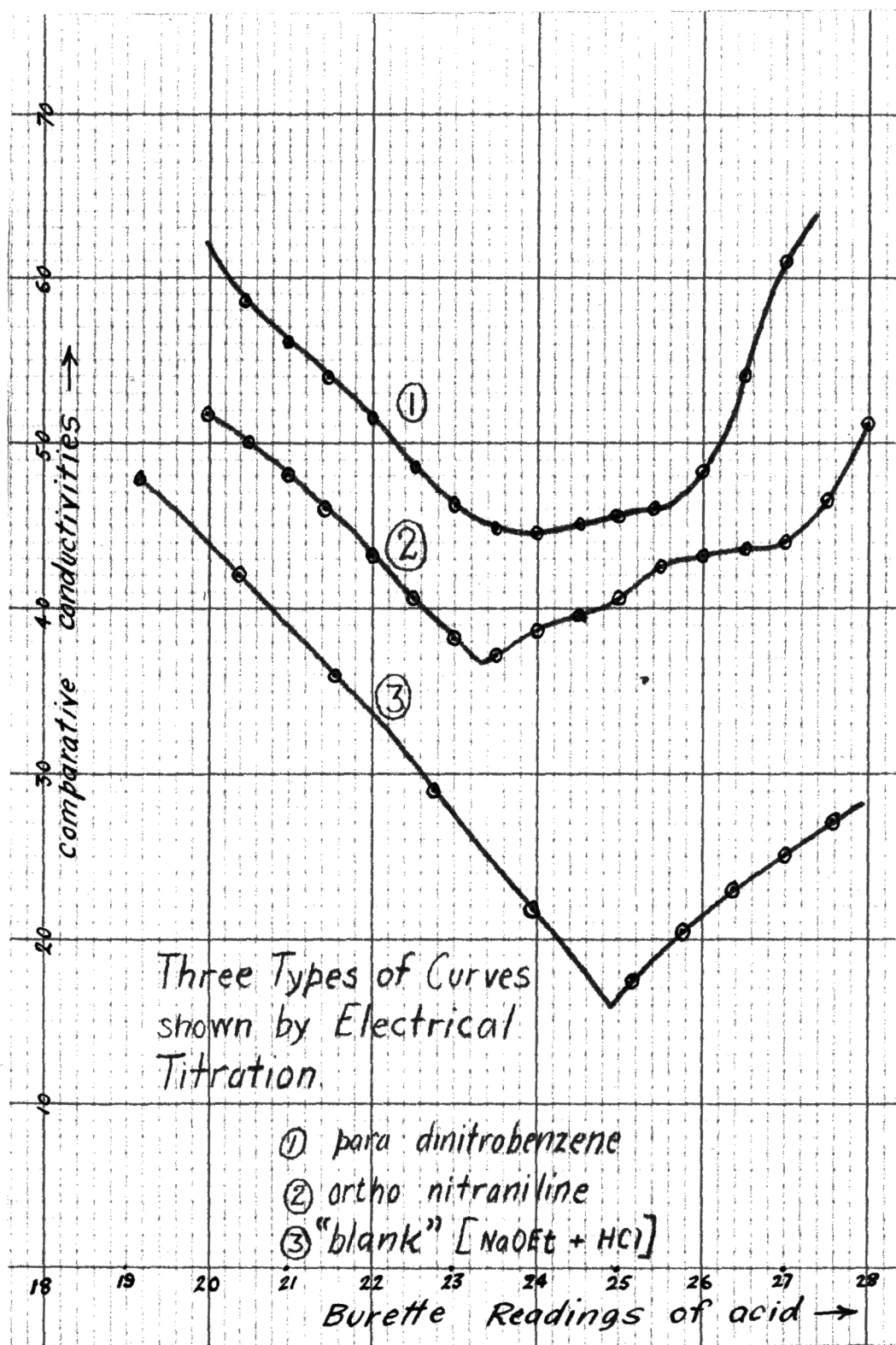


The electrodes "E" were made from two pieces of Pt foil one cm. square, rigidly held one cm. apart by glass supports. The leads were of Pt wire sealed in glass tubes to within  $\frac{1}{8}$  cm. of the foil. These had to be freshly platinized at the end of about six titrations to maintain a sharp minimum of sound.

The readings were taken by immersing the two electrodes into the solution in the beaker, and after running in about  $\frac{2}{3}$  the calculated amount of acid, "R" was adjusted to give a weak hum in "T". The contact roller of "B" was now oscillated back and forth about the minimum sound position until the ear became used to the minimum, which was then fixed with as much accuracy as possible. This requires a quiet room and considerable patience, and the end point is often disconcerting in its eccentricity. The burette reading of the acid and the dial reading on "B" are noted, and the process is repeated after the addition of every 2 cc. for about 8 or 10 cc., then every cc. until the dial readings cease to increase and begin to decrease, ending with a few more readings 2 cc. apart.

The burette readings plotted against the dial readings give a curve with a minimum at the burette reading corresponding to the end-point. (See Plate 1.)

PLATE I.



It was subsequently found that: (i) The depth to which the Pt foil was immersed (notwithstanding the glass lead tubes) considerably influenced the sound minimum; (ii) the same effect resulted from the accidental proximity of anything such as the side of the beaker, glass stirring rod, etc.; (iii) the minimum would be different if redetermined after the solution had stood even too short a time for the absorption of CO<sub>2</sub> to have taken place appreciably; (iv) the minimum for a "blank" titration was always sharp and concave downward whereas the minimum for an actual run was always more or less rounded and convex downward. (Minimum here refers to the shape of the graph.) This fact showed that the complexity of the solution (containing NaOH, NaOEt, EtOH, NaCl, and the organic substance) was influencing the shape of the curve to a degree that allowed as much error to creep into the determination of the end point as was experienced with an indicator. The formation of a precipitate at the end point as mentioned under (b) also doubtlessly influenced the curve.

Therefore the method was discarded in favor of a method which would not depend on the determination of the small amount of alkali used up in the presence of such a large excess.

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#### B.

"Nitron" (a handy commercial abbreviation for 1:4 diphenyl 3:5 endoanilo 4:5 dihydro 1:2:4 triazole) is a yellowish crystalline powder <sup>sparingly</sup> ~~scarcely~~ soluble in water and

alcohol, soluble in dilute acetic acid. When the acetic acid solution is added to any solution acidified with dilute  $\text{H}_2\text{SO}_4$  and warmed, any  $\text{HNO}_3$  originally present (or set free by the  $\text{H}_2\text{SO}_4$ ) in the second solution is deposited on cooling in ice water in the form of a  $\text{HNO}_3$  addition-product of nitron.<sup>31</sup>

This addition-product of nitron nitrate is extraordinarily insoluble in water, of the same order as  $\text{AgCl}$  and  $\text{BaSO}_4$ .<sup>32</sup>  $\text{HNO}_2$  gives a similar precipitate less insoluble,<sup>33</sup> and other acids such as  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HAc}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{C}_6\text{H}_5\text{COOH}$ , etc., give no precipitate.<sup>34</sup> The nature of the metal originally associated with the acid radical is immaterial.<sup>35</sup> Its use for  $\text{NO}_2$ -determination in organic compounds is confirmed,<sup>36</sup> and  $\text{H}_2\text{O}_2$  may be used to oxidize liberated  $\text{HNO}_2$  to  $\text{HNO}_3$ .<sup>37</sup> Several methods for its use are given, the simplest being as follows:<sup>35</sup>

Add 10-12 drops of dilute  $\text{H}_2\text{SO}_4$  for each .1 gm. of suspected  $\text{NO}_3$  per 100 cc. of solution. Heat almost to boiling and add 10 cc. of a 10% solution of nitron in 5% acetic acid for each suspected .1 gm. of  $\text{NO}_3$ . Cool at  $0^\circ\text{C}$ . for 5-8 hours, filter through a Gooch crucible containing Swedish filter paper, washing first with a saturated solution of nitron nitrate, then with 3-5 cc. water at  $0^\circ\text{C}$ . Dry at  $110^\circ\text{C}$ . Each gram of dry precipitate represents .1228 gm. of  $\text{NO}_2$ .

This is the procedure followed, with the modifications mentioned below, to suit the circumstances.

The reaction-mixture was poured into a beaker and titrated with dilute acetic acid until the solution was just decidedly alkaline as determined by spot-plate trials. In this

state it was evaporated almost to dryness to expel any alcohol. (When NaOEt was used as a reagent, the alcohol present would tend to dissolve the nitron nitrate). The distillate was condensed and extracted with solvents to aid in identification of compounds formed.

To oxidize the  $\text{NaNO}_2$  to  $\text{NaNO}_3$ , 10 cc of a 3% solution of  $\text{H}_2\text{O}_2$  were now added, and the excess destroyed by boiling again almost to dryness. Water was now added to 100 cc and the solution acidified with .1 N acetic acid (which does not liberate  $\text{HNO}_3$  from its salts) to cause the usual precipitate formed on acidification. This curdy mass (if any) was filtered off and the washings added to the filtrate; any precipitate was later treated for identification. The more or less light-colored filtrate was now treated with nitron as described above.

In this way, several compounds were analyzed, but as usual, a flaw soon developed. It apparently depends upon the nature of the organic compound whether the nitron nitrate comes down as a true precipitate, a mass of fine white needles in spangles, or a crystalline creamy mass so fine that it passes through the pores of the Gooch crucible. In some cases where replacement was known to have taken place, no precipitate at all could be induced either by long standing (weeks) or by inoculation. All manner of variations of procedure were tried, with no better result; and it was finally decided that unless the method would work for all compounds desired, it would have to be discarded, and a still different angle of the problem approached.



### C.

The next mode of attack was suggested by the Kjeldahl method of nitrogen determination, namely, reduction of the nitrite to ammonia.

Aluminium in solid form was added directly to the reaction-mixture in its container, and a small piece of paraffin introduced to prevent frothing. On gentle heating, a vigorous exothermic reaction set in between the alkali and the aluminium with evolution of hydrogen and ammonia.

Trials were made on known amounts of pure  $\text{AgNO}_2$  treated with  $\text{NaOH}$  to provide a known amount of nitrite. The gases evolved were led through a condenser and introduced into a definite volume of standard  $\text{H}_2\text{SO}_4$  by means of an adapter dipping under the surface of the acid. After the action was over, the solution was boiled for a few minutes to drive out all ammonia, and the excess  $\text{H}_2\text{SO}_4$  titrated with  $\text{NaOH}$  (.1 N.) to determine the amount of ammonia produced.

In no case could over 75% of the calculated value be exceeded, and after a few trials with actual runs of an organic compound which proved no better, the method was dropped.

### D.

In the presence of mercury, concentrated  $\text{H}_2\text{SO}_4$  has the property of decomposing  $\text{HNO}_3$  and  $\text{HNO}_2$  (or  $\text{KNO}_3$  and  $\text{KNO}_2$ ) into nitric oxide at a moderate heat, quantitatively. If this method could be made practicable, it would be very

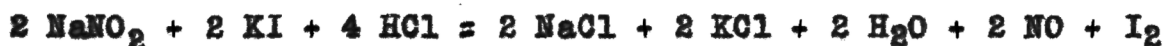
very desirable because of the fact that precautions would not be necessary to prevent the nitrite from oxidizing to nitrate, since both liberate the same equivalent of nitric oxide.

Trials were made with known amounts of nitrite (from  $\text{Ag NO}_2$ ) in an apparatus especially adapted for collecting the gas from contact with mercury. This will not be described at this stage, since exactly the same apparatus was used for the final successful method of analysis, and this present method proved to be useless; never more than 5-10% of the expected volume of nitric oxide could be obtained from the known nitrite.

#### E.

An appeal to H.S. Fry for information regarding the method of analysis used by other workers in reporting results on this replacement elicited the statement that no general method was available. The following suggestion however was submitted.

When  $\text{HNO}_2$  is liberated from a nitrite in the presence of hydriodic acid by means of the simultaneous action of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  on potassium iodide and the nitrite, nitric oxide and iodine are quantitatively liberated (or produced,) from the  $\text{HNO}_2$  according to the reactions:<sup>38</sup>



The iodine may now be titrated in the usual manner:



In the hope that the end point of the titration of the iodine using starch as an indicator would be more definite than that of previous titrations attempted, trials were again made with a known nitrite before actual attempts to analyze an organic compound were performed. The procedure was as follows:

The solution of the nitrite being already neutral, needed no preliminary partial acidification, so twice the calculated amount of KI was at once dissolved in the solution. An excess of 1 N. HCl was run in from a pipette, causing the mixture to turn deep amber from the liberation of the iodine. Standard  $\text{Na}_2\text{S}_2\text{O}_3$  (.1005 N.) was run in from a burette until the color had been almost removed, when a few drops of starch solution were added. Addition of further  $\text{Na}_2\text{S}_2\text{O}_3$  now produced an apparent end point; however, as effervescence of NO was still in progress, it was noticed that the blue color of the starch compound kept reappearing at the surface of the mixture, and required more  $\text{Na}_2\text{S}_2\text{O}_3$  to remove it. On vigorous stirring, the clear solution could be transformed to a deep blue-black as often as desired apparently. By the time an end point had been obtained which lasted for five minutes, it was found that over four times the required  $\text{Na}_2\text{S}_2\text{O}_3$  had been added!

Variations in procedure were now made such as:

- (i) adding the HCl and  $\text{Na}_2\text{S}_2\text{O}_3$  very slowly and carefully to avoid effervescence of NO as much as possible;
- (ii) adding almost the calculated amount of  $\text{Na}_2\text{S}_2\text{O}_3$  before the HCl was added, with the purpose of combining with almost

all the iodine as liberated, so that the solution could be boiled to expel the NO without appreciable loss of iodine from volatilization due to its low concentration. On titrating the cooled solution for the remaining iodine and adding the total volume, the amount of  $\text{Na}_2\text{S}_2\text{O}_3$  used was still far too great, as was also the case in (i).

(iii) Benzene was added to the solution before acidification to act as a protecting agent to prevent the liberated NO from combining with the atmospheric oxygen at the immediate surface of the liquid. It was thought that possibly the formation of  $\text{NO}_2$  at the surface might be the cause of the continued return of the blue color there. The iodine liberated dissolved in the benzene however, and even the titration of that iodine still in the aqueous solution required more  $\text{Na}_2\text{S}_2\text{O}_3$  than the calculated amount.

(iv) Instead of using  $\text{Na}_2\text{S}_2\text{O}_3$ , the iodine was titrated with  $\text{KMnO}_4$ , which loses its color and acts as its own indicator. On running in .1 N.  $\text{KMnO}_4$  from a burette into the strongly acid solution ( $\text{H}_2\text{SO}_4$ ), it was found that the color was removed just as promptly after 10 times the calculated amount had been run in, as when the supposed end point was reached!

Hence this method had to be discarded, for if it would not yield the true value of a known nitrate, it was much less likely to do so in a more complicated reaction-mixture.

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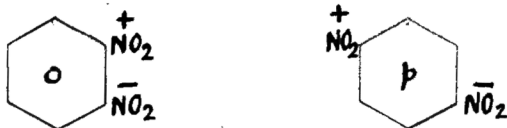
## EXPERIMENTAL -- PART I.

### E.

Reasons for the final decision  
against the use of alcohol as  
a solvent

.....

In all the cases mentioned under(1) where different methods of analyses were being tested, whenever an actual organic compound was used to provide the experimental conditions of a typical run, either ortho or para dinitrobenzene:



were chosen because they are the simplest poly-nitro compounds of benzene which should contain nitro-groups of different polarity.

Now the repeated use of NaOEt, NaOMe, KOEt and KOMe throughout the literature reviewed previously, as a reagent to effect substitution of the nitro-group, is undoubtedly due to the fact that so few of the organic nitro compounds are soluble in aqueous alkalies, phenols excepted.

Furthermore, it has been shown that in a great many cases the action of the alcoholate or alcoholic alkali is more complex than one would be led to suppose, whereas in those instances where the aqueous alkali was used, the reaction usually proceeded more normally.

It was noticed in this investigation that the result

of the action of alcoholic alkali on these compounds invariably was of a dark chocolate or muddy brown color with a slight sediment. Now the expected replacement products, ortho or para nitrophenetole (or possibly sodium nitrophenolate) are all nearly colorless or of a clear red color. Hence here is proof that secondary reactions are going on simultaneously.

Three efforts were made to avoid this possibility by testing other possible solvents in place of alcohol. This is rather difficult, since the requirements call for a solvent in which both the alkali and organic compound shall be mutually soluble. Acetone will dissolve in a weak aqueous alkaline solution, and most organic compounds dissolve readily in acetone, but its use is at once prohibited by its proneness to enter into reactions.

- (i) BENZENE -- Since organic compounds dissolve fairly readily in benzene, it might be expected that the reaction at the interface with the aqueous solution of the alkali might lead to complete substitution if the two liquids were kept agitated for a sufficient time by refluxing.

OBJECTION- The benzene boils off and froths in the condenser.

- (ii) BENZENE plus  $\text{CCl}_4$  -- by "weighting" the benzene with the heavier carbon tetrachloride, the solution of the organic compound would be forced to boil up through the alkali.

OBJECTION- The temperature necessarily must be low, and even so, the benzene tends to boil away.

- (iii) WATER ---- By increasing the concentration of the alkali, the boiling point may be so raised as to cause many of the organic compounds to melt, forming an emulsion on refluxing, which presents a reacting surface of large extent.

OBJECTION-None except slowness of action .

The results obtained by the use of the aqueous alkali alone as the reagent were so satisfactory that a further innovation was introduced in the form of an inert atmosphere. Its purpose was meant to be twofold; it would prevent the oxidation of any nitrite produced by excluding atmospheric oxygen, and might possibly lessen any tendency still remaining to form complex products. The result was most encouraging, producing, in the case of para dinitrobenzene, a clear red solution with no trace of sediment. The color almost exactly matched that of a synthetic solution of sodium para nitrophenolate of the same concentration, thus giving strong indication that the replacement was as expected. The details of the procedure are given later in PART II. This method was finally adopted entirely.

#### EXPERIMENTAL ----- PART I.

##### 3.

The final method of analysis evolved.

.....

With the apparent replacement taking place satisfactorily as described just above, all that remained to perfect the investigation was a certain method of analysis.

The author finally evolved such a method by combining the principles of methods "D" and "E" under (1).

It will be remembered that by the action of HI on  $\text{HNO}_2$ , nitric oxide was liberated simultaneously with the iodine. Previous experience with the volumetric measurement of NO in method "D" had not led to much encouragement; however, as a last hope it was decided to ascertain if the quantitative yield of NO was more closely approached under these conditions.

A trial with a small amount of  $\text{KNO}_2$  gave a much larger volume than had been obtained before, and more exact measurements were then undertaken using exact amounts of  $\text{NaNO}_2$  obtained from pure  $\text{AgNO}_2$  by double decomposition with NaOH.



Each molecule of  $\text{HNO}_2$  produces a molecule of NO. The actual replacement obtained was 97.2 % of the theoretical. All that now remained to ensure success was a trial to be made with an organic compound. As usual, para dinitrobenzene was chosen, and the resulting volume of NO given upon analysis after 44 hours of refluxing was 94.2 % of the expected volume for total replacement of one nitro-group.

The successful method of analysis had at last been obtained.

.....

NOTE: Since for every  $\text{NO}_2$ -group displaced from an organic compound, a molecule of  $\text{NaNO}_2$  appears, which in turn gives rise to one molecule of NO, the simple relation <sup>holds</sup> ~~appears~~ that for every  $\text{NO}_2$  displaced from a gram-mol of the organic compound, 22,400 cc of NO at N.T.P. are formed.



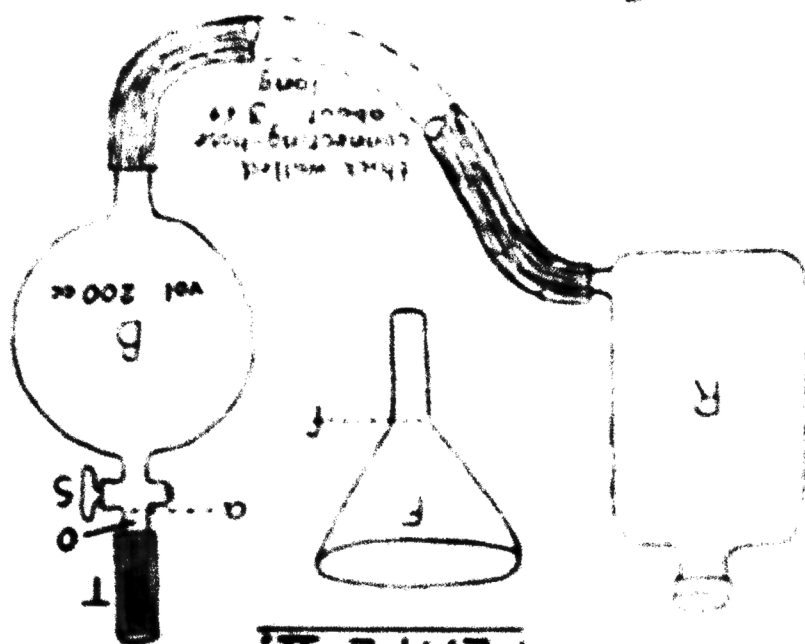
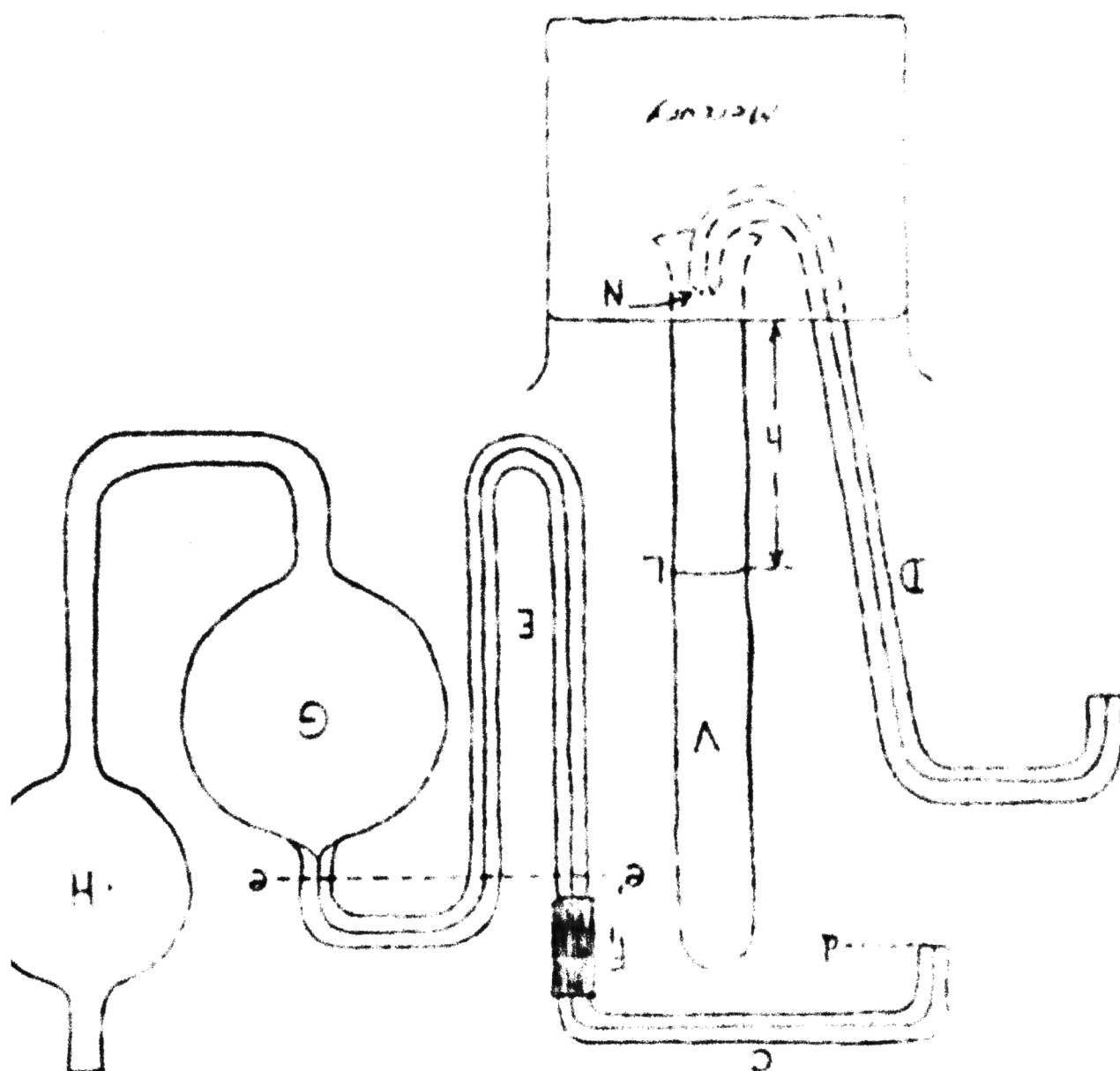


PLATE II.

The exact procedure of analysis will now be described with the help of the diagrams opposite.

A  $1\frac{1}{2}$ " funnel "F" with a short stem fitted into the short piece of rubber tubing "T" which fits tightly over the outlet "O" from the stopcock "S" serves as a means of introducing the reaction-mixture from the refluxing flask into the reaction-bulb "B". This is accomplished by raising the reservoir "R", full of mercury, until it fills "B" "S" "O" "T" and "F" up to the level "f". "S" is closed, "R" is lowered a few inches below "B", and about two grams of KI crystals are placed dry in "F". "F" is now filled from the refluxing flask directly, "S" is opened slightly, allowing the reaction-mixture to be sucked into "B", being careful to always keep "F" at least  $\frac{1}{2}$  full.

When all the reaction-mixture and the necessary rinsings of boiled water have been sucked through, "B" will be probably  $\frac{1}{2}$  full of the reaction-mixture plus dissolved KI, and  $\frac{1}{2}$  full of mercury. A small bubble of air may be located just below "S". "R" is now lowered three feet below "B" to create a vacuum space in "B" which effectually collects any dissolved air or gas into a larger bubble below "S" when the vacuum is released by raising "R". This bubble is expelled by again bringing the level of the liquid to "f", half filling "F" with boiled water and allowing it to run into "B" until "S" "O" "T" and "F" as far as "f" are full of water only, and "B" contains no trace of air consequently.

The remainder of "F" is now filled with moderately strong HCl which is allowed to run into "B" by lowering "R" and opening "S". When the level of the acid has reached "a", "S" is tightly shut and the flask "B" well shaken. If any replacement has occurred, "B" rapidly becomes half-filled with the liberated NO, forcing mercury into R. "O" and "T" are now filled with boiled water by means of a capillary pipette (not shown).

"H" and "G" are the two bulbs of an ordinary gas absorption apparatus which is filled with concentrated NaOH. A short piece of tubing connects "H", the capillary, with another piece of capillary tubing "C" about three inches long. By using compressed air in "H", the alkali in "G" is forced through "C" until a drop hangs from "d". This drop is placed in contact with the top of the liquid in "T" and the free end of "C" quickly forced into "T".

By now raising "R" above "C" and opening "S", the NO is allowed to pass into "G" until the liquid in "B" reaches "S". "S" is then closed tightly, "R" lowered away below "B"; when raised again, as much as 10 cc more gas will be found in "B" that had previously not been given off. This is passed into "G", and the process repeated as often as gas is found to collect in "B" (usually about six times; vigorous shaking of "B" while under reduced pressure assists greatly.)

NOTE: The action of conc. NaOH on NO is very slow. <sup>39</sup>

When the final bubble of gas has been passed over, instead of causing the liquid in "B" to stop at "S", it is allowed to flow to "e" thus forcing every last trace of NO from "B" into "G", where the CO<sub>2</sub> liberated by the acid from the carbonate always found in the NaOH used for the reagent is absorbed.

While the CO<sub>2</sub> is being absorbed in "G", "C" is disconnected from the short piece of rubber tubing "F". (A seal of liquid between "e'" and "e" keeps the gas in "G")

A long piece of capillary glass tubing bent as shown at "D" is fitted into "F", and when the CO<sub>2</sub> has been removed, compressed air is forced into "H" to drive the liquid seal through the capillary. When the liquid which was at "e" has almost reached the tip "N" of "D", a pinchcock on the compressed air tube is closed, keeping a small liquid seal in place at "N" while "N" is being introduced under the mouth of "V". "V" is a gas-measuring tube graduated to 50 cc filled with mercury and inverted in a beaker full of mercury as shown. When "N" is safely under the mouth of "V", the pinchcock is released and the NO completely transferred into "V".

"D" is now removed and "V" (still inverted in the mercury) set aside to assume room temperature if necessary.

"B" is emptied and completely rinsed by successive washings of hot water to be ready for the next run. The liquid emptied from "B" may now be examined for recognition of the product formed.

It is now seen that this technique provides a method of accurately measuring the volume of NO liberated without allowing access of atmospheric oxygen at any stage. When "V" has assumed room temperature, this is read on a thermometer close by, the reading of the level "L" of the mercury is taken, and the difference "h" between the two mercury levels is measured by a small celluloid scale. The gas in "V" is assumed to be saturated with water vapor at the temperature "t" if the tube "V" was wetted before filling with mercury.

If "w" = vapor pressure of water at "t", "L" = vol. of gas,

"p" = atmospheric pressure, then:

$$\frac{p - w - h \text{ (in mm.)}}{760} \times \frac{273}{273+t} \times L = \text{volume of NO at N.T.P.}$$

THE REPLACEMENT OF NITRO-GROUPS  
IN THE BENZENE RING.

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EXPERIMENTAL - PART II.

1.

The various procedures used in effecting the actual replacement of the nitro-group.

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During the earlier part of this work, as has been above explained, practically all runs made were used up in trials of different methods of analyses. Not only did these trials prove fruitless, but in many cases the technique of the actual replacement-action was at fault.

In PART I, (2), reasons were given why the use of alcohol as a solvent should be abandoned, and in (3) the use of an inert atmosphere was proven desirable.

Consequently, little will be mentioned regarding the early procedures, and more attention devoted to the final technique adopted.

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Duplicate samples of the compound in question were introduced in amounts of .5 gm. each into thick-walled 5/8"-

bore soft-glass tubes some 30 cm. in length, having a round seal at the bottom. If the substance was solid it was pulverized before weighing; if liquid, it was weighed in a very thin-walled glass weighing bulb which would break when dropped into the tube. The neck of the tube was then constricted, leaving a small funnel-shaped end, through which half the desired volume of double-strength reagent was first introduced, followed by an equal volume of absolute alcohol (when NaOEt was being used) or of water (when NaOH was being used). This gave the desired volume of proper concentration, and provided a means of incidentally rinsing out the constriction so that adhering alkali would not prevent a perfect seal.

After sealing, the tubes were placed in a horizontal bomb furnace heated by gas to 110-120°C. ~~by gas~~. Considerable difficulty was experienced in keeping the temperature constant.

When removed after cooling, the contents were in all cases a deep chocolate muddy brown color, with a resinous sediment along that side of the tube that was bottom-most.

Taking the usual precautions regarding opening the tubes, no pressure was ever experienced on opening any tube containing nitro compounds.

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Exactly similar tubes were later heated in a circular rack suspended in a boiling water bath. The temperature could thus be kept constant, but admitted of only one regulation. By first heating the tubes to about 90°C., cooling to 70° and vigorously shaking before final raising of the

temperature to  $100^{\circ}$ , the solution of the compound in the reagent was assured. Since the heating could not be continued overnight, a similar opportunity was taken for shaking each morning, as in some cases the tubes were heated for a total of 48 hours.

Despite the fact that the tubes were shaken, evidence was sometimes found of undissolved product, and as the method of analysis being tried at the time did not allow the use of a larger volume of reagent, a second procedure was tried.

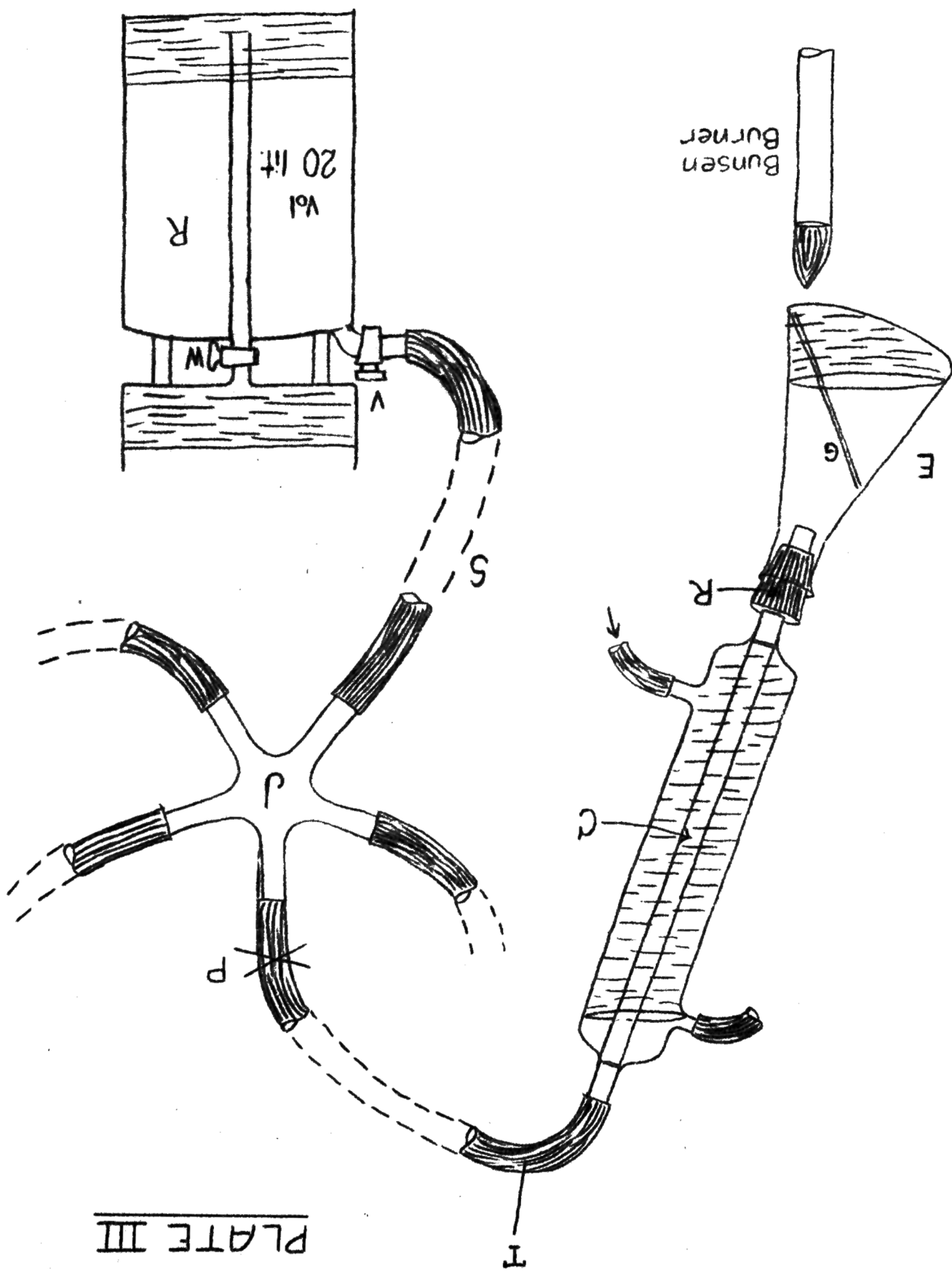
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To allow greater agitation during heating, the principle of refluxing was tried. The weighed samples were introduced into 150-cc Florence flasks and the reagent added in two portions as before to facilitate rinsing. Small upright water condensers were attached, fitted with  $\text{CaCl}_2$ -tubes at the upper extremity to exclude  $\text{CO}_2$  which would change the concentration of the alkali during the long period of refluxing. The flasks were heated to the boiling point of the reagent ( $80\text{--}85^{\circ}\text{C}$ . depending on the concentration of the  $\text{NaOEt}$ ) on an electric hotplate. No trouble was experienced with bumping.

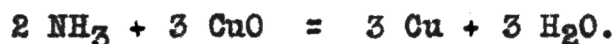
This method led to the final one adopted of refluxing with water solutions of  $\text{NaOH}$ , and very little change in the mode of heating was made until the inert atmosphere idea was introduced, which will next be described.

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As an inert atmosphere, hydrogen was first used but soon discarded as being too dangerous. Nitrogen then was



adopted, being<sup>at</sup> first manufactured by passing ammonia from a tank of liquid ammonia over heated copper oxide in a long pyrex glass tube:



Later, a tank of compressed nitrogen free from oxygen became available. The actual mode of operation may be followed from references to Plate III opposite.

The substance and reagent are introduced in the 150-cc Erlenmeyer flask "E" which is connected to a small water condenser "C" by means of a tight rubber cork. A flexible rubber tube "T" about two feet long and of  $\frac{1}{4}$ "-bore is connected to the upper end of the condenser tube.

The free end of "T" is now connected to the tank of nitrogen, the cork "R" loosened, and "T", "C" and "E" are thoroughly swept out with nitrogen. With the nitrogen at about 10 lbs. pressure, the cork "R" is tightly fitted into "E" and the pinchcock "P" closed before removing "T" from the nitrogen supply.

"T" is now slipped over one of the arms of a five-armed glass joining-tube "J". The rubber connections of three similar condensers are connected to the remaining three free arms of "J" while the fifth arm is connected to a tube "S".

"R" is a reservoir of nitrogen from which the gas can be forced by opening the valve "W" allowing water to flow in and the gas to escape through the valve "V".

When all four condensers with their appended Erlenmeyers are in readiness, the four pinchcocks (P) are opened one after the other, allowing the nitrogen under 10 lbs. pressure in the four systems to escape and sweep out all the air in "S" which is immediately connected to the valve "V" which is then left open.

A small non-luminous flame about  $\frac{1}{2}$ " in height is now lit under the lowest portion of the Erlenmeyer flasks, an ordinary Bunsen burner being quite suitable. The capillary glass tube "G" open at both ends, serves admirably to prevent "bumping".

The four condensers are clamped at a slight angle in stands, and the water may be run from one to the other in series. It is important that "T" does not collapse at the point "T", otherwise a sudden bump of the liquid will blow the flask off the condenser instead of being dissipated in the reservoir "R" which is only needed for such an emergency.



## EXPERIMENTAL -- PART II.

### 2.

#### Tables and discussion of results.

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The fact has already been often mentioned that the early part of this work was taken up in a search for a suitable method, and until this was discovered, the results obtained were of little use. However, in a few cases, one mode of analysis was used long enough to make a few comparisons of the influence of varying such factors as time, temperature, normality of reagent, etc. A few of these will be included.

In all, over 75 separate runs were made and used in the search for the proper analysis; another 25 were made in perfecting the final method and in making larger quantities of the compounds for identification, and finally, 47 runs have been made to date using the final method, with plans laid out for several more to be subsequently done.

The chemicals used were purchased from the Eastman Kodak Chemical Works of Rochester, N.Y., U.S.A. The M.P. of those compounds common enough commercially to have consistently uniform M.P. data recorded, was in each case found to be sufficiently close to the recorded value to warrant the assumption of probable sufficient purity for those compounds which have inconsistently recorded melting points.

TABLE 1.

Samples of dinitrobenzene, refluxed with alcoholic NaOH, and analyzed (?) by titration with indicator.

	iso- mer	weight in gms.	reagent		temp. (°C.)	time (hrs)	replacement		
			co.	norm.			calc.	obs.	
1	o	.6000	50	.500	84	6	50%	38.0%	favorable to theory
2	o	"	"	"	"	11	"	41.8	
3	o	"	"	"	"	24	"	42.4	
4	o	"	"	.910	88	6	"	76.4	
5	m	"	"	.128	79	24	0	36.0	unfavorable
6	m	"	"	.300	81	15	0	43.0	
7	p	"	"	.500	84	5	50	44.9	favorable
8	p	"	"	"	"	8	"	33.3	
9	p	"	"	"	"	18	"	41.8	
10	p	"	"	"	"	24	"	43.0	
11	p	1.0000	"	.183	80	25	"	23.8	
12	p	.5000	"	.871	120	6	"	47.8	
13	p	1.0000	"	.910	88	6	"	68.5	

Runs 1,2,3, show an increasing replacement with increase of time, other circumstances being equal.

Runs 8,9,10, show a like relation, indicating that the progress of the reaction slows up at the end of about 15 hrs.

1,4, show increased replacement with increase of concentration, but 4 exceeds the theory.

Like relations could be drawn from the following two tables, but the accuracy of the results do not warrant it.

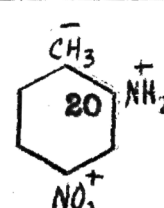
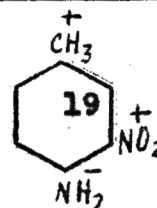
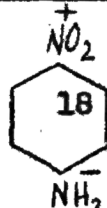
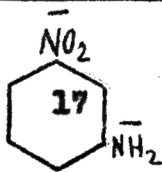
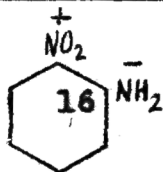
In commenting on the favorability, only the general trend of the figures is taken into account, no attention being paid to such exceptions as 4 and 13.

In the following cases, the signs attributed to the groups are distributed in such a way as to satisfy the polarity of the greatest number of groups according to the scheme given on page IV of the INTRODUCTION.

TABLE 2.

Samples of various compounds, refluxed with  
alcoholic NaOH, and analyzed (?) by the  
electrical conductivity titration method.

	iso-mer	weight in gms.	reagent		temp. (°C.)	time (hrs)	replacement		
			cc.	norm.			calc.	obs.	
NITROBENZENE									
14	-	.8800	50	.111	79	24	0%	1.8%	Favorable
15	-	1.0000	60	.183	80	25	0	0.5	
NITRANILINE									
16	o	.9990	50	.500	81	44	0	7.5	Favorable
17	m	1.0000	50	.500	81	44	100	46.0	"
18	p	1.0020	50	.500	81	44	0	0.9	"
NITRO AMINO TOLUENE									
19	3:4	.9990	50	.500	81	44	0	0.0	Favorable
20	4:2	1.0000	50	.500	81	44	0	14.5	Unfavorable



In 14,16,18, there should be no question about the indicated polarities; in 17 it is evident one group must have a polarity contrary to its tendency, and in view of the observed replacement, the NO<sub>2</sub> group naturally is chosen.

In 19 and 20, no arrangement will give all groups their normal polarity; in each case two have been satisfied with the result that the replacement in 20 should not be expected.

In all cases, there is a sufficiently large excess of reagent always added to combine with all the NO<sub>2</sub> in the compound plus a generous excess to displace any possible equilibrium.

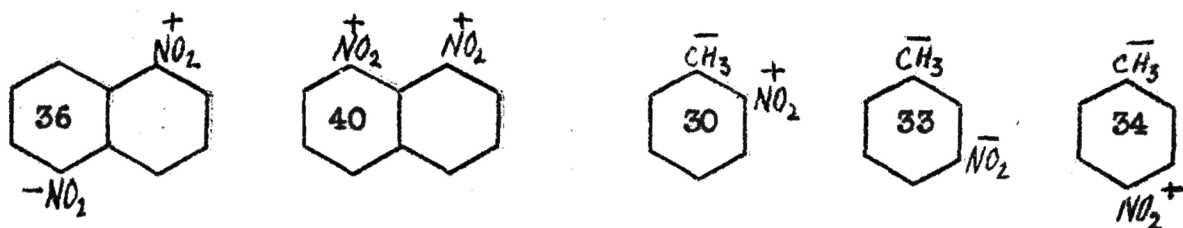
TABLE 3.

Samples of various compounds, sealed in tubes with alcoholic NaOH and heated in a water bath. Analyzed (?) partly by electric titration (designated by #) and the remainder by titration with an indicator.

	iso-mer	weight in gms.	reagent		temp. (°C.)	time (hrs)	replacement			
			cc.	norm.			calc.	obs.		
NITRANILINE										
21	o	1.0000	20	.562	100	31	0%	11.4%	#	Doubtful
22	o	1.0000	22	.476	100	52	0	15.4		
23	o	1.0010	22	.476	100	70	0	19.9		
24	m	1.0000	24	.531	100	4	100	23.4	#	Favorable
25	m	1.0000	20	.562	100	30	100	38.2	#	
25	m	.9940	22	.476	100	54	100	31.0		
26	p	1.0000	24	.531	100	4	0	12.3	#	Favorable
27	p	1.0000	20	.562	100	31	0	9.0	#	
28	p	1.0010	22	.476	100	52	0	7.4		
29	p	.9990	22	.476	100	70	0	26.5		
NITROTOLUENE										
30	o	1.0000	24	.531	100	4	0	12.3	#	Doubtful
31	o	1.0000	22	.476	100	52	0	15.4		
32	o	1.0010	22	.476	100	70	0	19.9		
33	m	.9940	22	.476	100	54	100	31.0		Favorable
34	p	1.0010	22	.476	100	52	0	7.4		Doubtful
35	p	.9990	22	.476	100	70	0	26.5		
DINITRONAPHTHALENE										
36	1:5	.7010	25	.486	100	2	50	32.7	#	Favorable
37	1:5	.6980	25	.486	100	2	50	41.5	#	
38	1:5	1.0000	24	.562	100	30	50	26.8	#	
39	1:5	1.0000	18	.374	100	32	50	26.4	#	
40	1:8	1.0000	24	.562	100	31	0	25.9	#	
41	1:8	1.0000	24	.562	100	30	0	20.2	#	Unfavorable
42	1:8	1.0000	18	.374	100	33	0	25.0	#	
43	1:8	1.0000	18	.374	100	31	0	25.9	#	

Runs 21 to 35 show the influence of time upon the result very well, since temperature is constant and concentrations nearly so.

The results are discussed on the next page with the formulae.



Referring to the formulae for nitraniline given on page 31, the unexpected replacement in runs 21,22,23 may be due to action on the electromer, since it is seen that the rate of substitution is very slowly increased with time. This would indicate the slow conversion of the stable electromer to the unstable one.

The same explanation may hold for cases 30,31,32, for here the groups have their proper sign and no replacement should be expected. For 33, as in the case of 17, the polarities must be chosen. Since replacement has occurred, the  $\text{NO}_2$  has been given the negative.

The results for 36 are exactly as predicted; for 40 they are not. In 1:8 dinitronaphthalene, as was shown on page 7, there are two positive positions in the 1-8 carbon atoms, or if the formula be turned up side down, there are two negative positions. Since  $\text{NO}_2$  tends to act positively, it is logical to assume the two nitro groups would occupy the two positive positions, and would have very little tendency to revery to the electromer. The facts in runs 41 to 43 do not bear this out.

The melting points of the various compounds separated from the reaction-mixtures as indicated previously, are here appended, and do not favor the theory of straightforward substitution.

	o	m	p
M.P. of dinitro benzenes (a)	117	90	171
M.P. of nitro phenetoles	58		58
M.P. of nitro phenols	45.2	96	114
M.P. of compounds found from (a)	46		58
M.P. of nitranilines (b)	71	114	146
M.P. of amino phenetoles		(all liquids)	
M.P. of amino phenols	170	123	184d.
M.P. of nitro phenetoles	58		
M.P. of nitro phenols	45.2	96	114
M.P. of compounds found from (b)	63	137	139
M.P. of nitrotoluenes (c)	-10.5	16	52
M.P. of methyl phenetoles			
M.P. of methyl phenols		(all liquids)	
M.P. of compounds found from (c)	38, 51	47, 52	128, 138

Here all the possibilities of substitution are taken into account, and only in the case of the dinitrobenzenes are the products of the reaction positively identified.

Since any method depending on titration would not necessarily show from the analysis whether it was the nitro group being replaced or not, melting point data is essential for ascertaining the course of the reaction. In the final analysis adopted, the replacement of the nitro group is positively identified, since NO can only be formed from the nitrite liberated.

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TABLE 4.

Various compounds refluxed in an atmosphere of nitrogen with aqueous NaOH, and analyzed by the author's own method.

Before giving the table, it may be mentioned that the products of reaction from ortho and para dinitrobenzene were positively recognized as ortho and para nitrophenol. In the case of the meta compound, it was recovered practically quantitatively unchanged, agreeing very well with the analysis result.

TABLE 4.

		weight.	Vol. of NO at N.T.P.			% Replacement	
(1)	AgNO <sub>2</sub>	.2997	43.6 calc.	40.2 obs.	100 calc.	92.3 obs.	
(2)	AgNO <sub>2</sub>	.2998	43.6 "	41.5 "	100 "	95.1 "	
(3)	AgNO <sub>2</sub>	.2997	43.6 "	42.3 "	100 "	97.1 "	

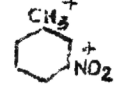
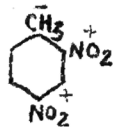
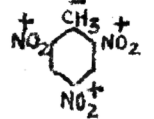
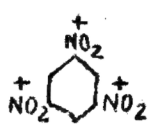
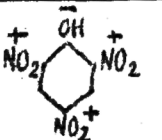
	iso-mer	weight in gms	reagent vol	norm	time (hrs)	% replacement calcul. obs.		
DINITROBENZENE								
44	o	.7007	50	1.0	15	50	32.6	favorable
45	m	.7010	50	1.0	4	0	3.3	
46	m	.3516	50	1.0	15	0	3.5	favorable
47	m	.5012	50	0.5	44	0	6.4	
48	p	.3482	50	1.0	0.5	50	45.8	
49	p	.3502	50	1.0	1.5	50	44.7	favorable
50	p	.3494	50	1.0	44	50	47.1	
NITRANILINE								
51	o	.2995	50	1.0	3	0	0.0	favorable
52	o	.3025	25	2.0	17	0	0.0	
53	m	.2995	50	1.0	3	100 or 0	0.0	
54	m	.3015	25	2.0	15	100 or 0	0.0	doubtful
55	m	.3060	25	5.0	17	100 or 0	2.5	
56	p	.2995	50	1.0	3	0	0.0	
57	p	.3004	25	2.0	17	0	0.0	favorable
NITROPHENOL								
58	m	.3052	25	2.0	17	100	0.0	unfavorable
NITROTOLUENE								
59	m		25	2.0	17	100 or 0	0.0	 ?
DINITROTOLUENE								
60	2:4	.4230	25	1.0	2.3	0	21.1	 ?
61	2:4	.4250	25	2.0	6	0	29.8	
62	2:4	.3985	25	4.0	20	0	20.	
TRINITROTOLUENE								
63	sym	.5002	25	1.0	3	0	32.	 unf
64	sym	.5036	25	0.5	24 (KOH)	0	31.2	
TRINITROBENZENE								
64	sym	.4980	25	0.5	4 (KOH)	0	27.5	 unf.
65	sym	.4980	25	4.0	2	0	1.3	
66	sym	.4038	25	2.0	40	0	30.6	
67	sym	.3990	25	2.0	50	0	28.9	
TRINITROPHENOL								
68	sym	.5002	30	0.5	4 (KOH)	0	12.3	 unf.
69	sym	.5027	30	0.5	8 (KOH)	0	24.1	

TABLE 4. (cont.)

	iso- mer	weight in grm	reagent		time (hrs)	% Replacement		
			vol	norm		calcul.	obs.	
DINITRONAPHTHALENE								
70	1:5	.4987	50	1.0	8	50	0.0	
71	1:5	.4989	50	2.0	43	50	0.0	
72	1:5	.5000	25	4.0	20	50	0.0	
73	1:5	.4996	25	6.0	18	50	7.6	
74	1:5	.5000	25	10.0	15	50	9.7	
75	1:8	.4957	50	1.0	8	0	8.6	
76	1:8	.4984	50	2.0	43	0	11.8	
77	1:8	.5010	25	4.0	20	0	4.3	
ALPHA-NITRONAPHTHALENE								
78		.3953	25	2.0	15	0	0.0	
79		.3990	25	10.0	15	0	0.0	
TRI NITRONAPHTHALENE								
80	138	.5012	25	2.0	0.2	0	11.7	
81	138	.5063	25	2.0	18	0	32.4	
82	138	.5078	25	5.0	8	0	17.0	
83	138	.5022	25	5.0	12	0	20.0	
84	138	.5085	25	5.0	24	0	16.2	

Discussing this table in full would be a lengthy process; the figures speak for themselves.

Runs 44 to 50 need no comment; nitraniline was discussed on page 31, but runs 53,54,55 would tend to show that the tendency for the nitro group to be positive is greater than the tendency for the amino group to be negative in the meta form, where one must show its superiority. This contradicts the conclusions in table 2. Run 58 is decidedly contradictory. Runs 59,60,61,62 are doubtful because of the possibility of tautomeric change to the electromer being very great.

Runs 63 to 69 are, however, unfavorable; the groups all have their proper sign, and especially in the case of 68 and 69, there should be no tendency whatever towards electromerism.

Runs 78,79, are entirely as expected, whereas



runs 70 to 77 are almost contradictory. By referring to the formulae, the 1:5 isomer has certainly one replaceable group, while the 1:8 could only show replacement by most unlikely electromerism. The replacement noted must, however, be due to this change. This brings us to the final case where in 1:3:8 trinitronaphthalene, the three positive  $\text{NO}_2$  groups should show the least tendency of all towards electromerism. The results deny this.

In practically all of Table 4 the time factor is used in arranging the results -- this may not be the best arrangement, for the speed of reaction is dependant on two factors: (i) the rate of action of the reagent on replaceable groups, (ii) the rate of tautomeric change in an effort to produce replaceable groups. Unless many experiments are carried out with a determination of these rates in view, no satisfactory results or conclusions can be made.

Attempts to identify products in most cases tend to show that possibly more complex reactions have been taking place than has been suspected, exactly the result that many other workers have found.

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In conclusion, the author wishes to make clear the fact that he believes either (i) the Electronic theory of alternate polarity does not hold, or (ii) that the tautomeric changes predicted by the theory so predominate as to render any speculation on the course of an untried replacement futile.

The author takes this opportunity to express  
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