

[CONTRIBUTION FROM THE SANDERS CHEMICAL LABORATORY OF VASSAR COLLEGE]

THE DINITRO DERIVATIVES OF PARA-DICHLOROBENZENE

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Several years ago an investigation into the reactions of the dinitro derivatives of *p*-dichlorobenzene was undertaken in this laboratory at the suggestion of Professor E. P. Kohler. At that time only 2 of the possible 3 isomeric dinitro-dichlorobenzenes had been isolated. One, crystallizing in flat plates, of which the melting point has been variously recorded as 104–106°, was proved to be 2,6-dinitro-1,4-dichlorobenzene.¹ The other, crystallizing in needles melting at 101°, was generally assumed to be 2,3-dinitro-1,4-dichlorobenzene, an assumption which we have confirmed by reducing to the corresponding diamine and condensing this with benzil to *p*-dichloro-diphenyl-quinoxaline. The existence of the third isomer was indicated by the work of Morgan and Norman² and Hartley and Cohen³ who reduced the crude nitration product and separated the *p*-dichloro-*p*-phenylenediamine (m. p. 162–163°) from the reaction mixture, but the dinitro derivative itself had never been separated.⁴

The work done in this laboratory on the separation of the products of nitration showed that it was possible by careful crystallization from alcohol to isolate a product of distinct crystalline habit, melting sharply at 81°. Nason⁵ reduced this compound to 2,5-dichloro-1,4-phenylenediamine, the identity of this being fixed by the melting point and by oxidation to *p*-dichloroquinone. Although the yield of the reduction product was small (33%) this could easily be accounted for as due to faulty separation, and the constitution of the compound melting at 81° was supposed to be established as 1,4-dichloro-2,5-dinitrobenzene.

A study of the reaction of alcoholic ammonia on the 3 isomeric *p*-dichloro-dinitrobenzenes disclosed the surprising fact that the main product of the reaction with the 81° compound was identical with that obtained from the 2,6-dinitro-1,4-dichlorobenzene melting at 106°, but the work was interrupted for a time before the reaction could be thoroughly investigated. Meantime Holleman and his students⁶ took up the study of the dinitro-*p*-dichlorobenzenes and showed that a fourth product melting at 119° could be obtained. For the isolation of this substance they took

¹ Korner, *Jahresber.*, **1875**, 324. Ullmann and Sane, *Ber.*, **44**, 3731 (1911).

² Morgan and Norman, *J. Chem. Soc.*, **81**, 1378 (1902).

³ Hartley and Cohen, *ibid.*, **85**, 865 (1904).

⁴ The statement of Hartley and Cohen, Ref. 3, that the compound melting at 105° was the *p*-dinitro derivative had no experimental basis and was obviously erroneous.

⁵ Nason, *THIS JOURNAL*, **40**, 1602 (1918).

⁶ Hollander and van Haeften, *Proc. Acad. Sci. Amsterdam*, **22**, 661 (1920). Holleman and Hollander, *Rec. trav. chim.*, **39**, 435 (1920). Holleman, Hollander and van Haeften, *ibid.*, **40**, 323 (1920).

advantage of the fact that the different isomeric dinitro-*p*-dichlorobenzenes react with alcoholic ammonia at different rates. Starting with the crude product of nitration, treatment with saturated alcoholic ammonia at room temperature converts the 2,6-dinitro-1,4-dichlorobenzene fairly rapidly to 4-chloro-2,6-dinitro-aniline, melting at 145°, while the other isomers react more slowly. On evaporating the alcohol, dissolving the organic residue in benzene, and extracting the benzene solution with conc. sulfuric acid the amine is dissolved in the acid and the unchanged isomers can be recovered from the benzene. The residue from the evaporation of the benzene is then dissolved in saturated alcoholic ammonia and heated on a water-bath under a reflux condenser, ammonia being passed in from time to time to replace that lost by evaporation. Under these conditions the 2,3-dinitro-1,4-dichlorobenzene is converted into 3,6-dichloro-2-nitro-aniline, and after 24 hours the procedure described above is repeated. After the amino compound has been extracted by acid as before, evaporation of the benzene leaves the product melting at 119°. Holleman believed this compound to be 2,5-dinitro-1,4-dichlorobenzene, and confirmed his hypothesis by synthesizing it from *p*-dichloro-acetanilide and from *p*-chloro-aniline, the intermediate products being identified in each case.

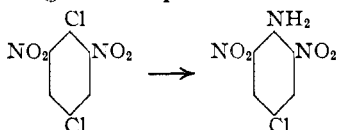
Although Holleman refers to Nason's paper in passing, he makes no attempt to explain the nature of the product melting at 81°. He evidently obtained the same product, but failed to purify it, as he states⁷ that after separating the 105° and 101° isomers from the crude nitration product he obtained a white mass of cauliflower-like crystals with indefinite melting point, which could not be separated into its components by crystallization. We have had no difficulty whatever in separating a product which melts within 0.5°, the melting point remaining unchanged after 5 or 6 recrystallizations from alcohol or as many crystallizations from half a dozen different solvents in succession. Moreover, this substance can be sublimed and distilled unchanged. On distillation in a vacuum it boils at a constant temperature, the melting point of the distillate being identical with that of the undistilled material. Analysis gives values corresponding closely to the formula $C_6H_2(NO_2)_2$ ⁵ and molecular-weight determinations indicate a monomolecular form. In its reactions with alcoholic ammonia, with aniline, with sodium alcoholates, and on reduction 2 classes of derivatives are invariably formed, one corresponding to the *meta*-dinitro and the other to the *para*-dinitro derivative. An element of confusion was introduced by Nason's failure to obtain any trace of *meta*-diamine on reduction, but it appears that this was due to the method used for extraction, since modification of the procedure in this respect has resulted in a greatly improved yield, comprising the 2

⁷ Holleman, Hollander, and van Haefen, Ref. 6.

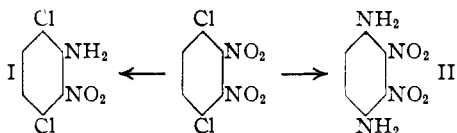
diamines, the *meta* isomer being present in largest amount as was to be expected from our other experiments.

Granting that the 119° compound isolated by Holleman represents the true 2,5-dinitro-1,4-dichlorobenzene, there remain two possible hypotheses as to the nature of the 81° substance. It may be a eutectic, or it may be a molecular compound, the two constituents present being in either case the *meta* and *para* isomers. A study of the freezing-point curves has shown conclusively that the latter hypothesis is correct, and that the substance in question is a molecular compound of the 2 isomers, the proportions being probably 2 molecules of 2,5-dinitro-1,4-dichlorobenzene to 3 of 2,6-dinitro-1,4-dichlorobenzene. The molecular-weight determinations show that it exists in solution only in its dissociated state, which explains the results obtained with alcoholic ammonia and the other reagents used. In this, as well as in the shape of the freezing-point curve, it shows an interesting analogy to the behavior of racemic compounds.⁸

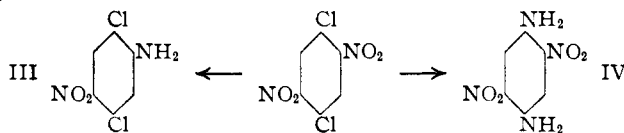
A study of the behavior of the 3 isomers toward alcoholic ammonia has shown that with 2,6-dinitro-1,4-dichlorobenzene the sole product of the reaction is, as might be expected, 2,6-dinitro-4-chloro-aniline.



2,3-Dinitro-1,4-dichlorobenzene gives two products, over 91% of the original substance being transformed to the corresponding dichloro-aniline (I), while between 8 and 9% forms 2,3-dinitro-1,4-diamidobenzene (II).



Similar products are obtained from 2,5-dinitro-1,4-dichlorobenzene, 73% going to form the nitro-aniline (III), while 27% is transformed into diamine (IV).



Experimental Part

Separation of the Isomeric Dinitro Derivatives.—The crude product obtained from

⁸ Raoult, *Z. physik. Chem.*, **1**, 186 (1887). Purdie and Walker, *J. Chem. Soc.*, **67**, 638 (1895). Frankland and Pickard, *ibid.*, **69**, 123 (1896). Adriani, *Z. physik. Chem.*, **33**, 459, 467 (1900).

the nitration of *p*-dichlorobenzene as described by Nason⁵ was dissolved in 95% alcohol, in the proportion of 100 g. of material to 3 liters of alcohol, cooled in ice and filtered; 2,6-dinitro-1,4-dichlorobenzene separated in a comparatively pure state. Two or at the most three recrystallizations from alcohol gave a pure product. The alcoholic filtrate from which this isomer had been separated was then distilled. It has been found that if the quantity of alcohol distilled is limited to between 600 and 650 cc. of distillate per liter of filtrate in winter, or between 700 and 750 cc. in summer, and the residue allowed to cool very gradually in the water-bath overnight, a fraction consisting of the substance melting at 81° crystallizes in reasonably pure state. One recrystallization from alcohol results in a product melting at 81–81.5°. After this has been filtered and the filtrate cooled in a freezing mixture, a fraction consisting of fairly pure 2,3-dinitro-1,4-dichlorobenzene separates. When the quantity of alcohol distilled varies much from the limits given, a mixture of both of these substances is obtained on cooling. It is almost invariably true that after the substance melting at 81° has separated slowly at room temperature, the isomer melting at 101° can be obtained by cooling the filtrate in a freezing mixture.

For the separation of the 2,5-dinitro derivative the procedure followed was a slight modification of that suggested by Holleman,⁶ 25 g. of the product melting at 81° was treated with 175 cc. of 4 *N* alcoholic ammonia and allowed to stand at room temperature for 24 hours or more. Under these conditions the *meta* derivative is entirely transformed into the dinitrochloro-aniline, while the *para* derivative which reacts more slowly with ammonia remains for the most part unacted upon. The alcohol was then evaporated by suction and the residue covered with conc. sulfuric acid. After standing for several hours with frequent stirring the mass was filtered through a Gooch filter. The undissolved residue was well washed with sulfuric acid and then with water until all the acid was removed. One recrystallization from chloroform gave lemon-yellow crystals which melted sharply at 117.5°, but corresponded in all other particulars with the description given by Holleman. When the reaction time was shortened to much less than 24 hours, and especially if the temperature of the laboratory was low during that time, the product instead of being pure 2,5-dinitro-1,4-dichlorobenzene was contaminated with unaltered 81° substance, and the resulting mixture was practically impossible to purify by recrystallization. There seems to be no room for doubt that it is to such a mixture as this that Holleman refers⁹ when he speaks of obtaining in some cases a substance which crystallized well but melted between 80° and 105° instead of at the expected 119°.

Molecular-weight Determinations.—The Molecular weight of the substance melting at 81° was determined by the lowering of the freezing point of benzene.

Analyses. Subs., 3.028, 4.647, 7.172; 100 g. of benzene: 0.67°, 1.02°, 1.57° depression. Calc. for C₆H₂O₄N₂Cl: 237. Found: 226, 227, 228.

Similar determinations of the molecular weight of 2,5-dinitro-1,4-dichlorobenzene (119°) and 2,6-dinitro-1,4-dichlorobenzene (105°) gave values of 227 and 226, respectively.

Sublimation and Distillation.—The substance melting at 81° sublimes without change on a boiling water-bath. Five g. of the substance was distilled in a vacuum and boiled at a constant temperature of 198° at 61 mm. The melting point of the distillate was found to be identical with that of the undistilled material. For purposes of comparison the boiling points of the 3 substances melting at 117°, 105° and 81°, respectively, were determined under atmospheric pressure. The substance melting at 117° boiled at 304° for some time. Towards the end of the distillation the boiling point rose to 305°, this change being probably due to the slight decomposition taking place. The compound melting at 105° boiled at 302°, rising gradually to 303°, with somewhat more

⁹ Holleman, Hollander and van Haeften, Ref. 6.

marked decomposition. The boiling point of 312° given by Jungfleisch appears to be erroneous. The 81° substance boiled at 302.5° , the temperature rising to 303° at the end of the distillation.

Freezing-point Curves.—2,6-Dinitro-1,4-dichlorobenzene was obtained by the method referred to above and was recrystallized from alcohol until successive crystallizations caused no change in the melting point. The true melting point was determined from the cooling curve. The substance was melted in a test-tube fitted with a cork through which extended a platinum stirrer and a thermometer graduated to 0.1° , the amount of material used being sufficient to cover the bulb and reservoir of the thermometer up to the immersion line. This test-tube was placed within a larger tube, serving as air jacket, in a sulfuric acid bath kept at a temperature 5° below the approximate melting point. After the usual supercooling, as crystals appeared the temperature rose to the melting point where it remained constant for some time (5 to 10 minutes). This method gave a value of 104.9° , a slightly lower value than that obtained in a capillary tube.

2,5-Dinitro-1,4-dichlorobenzene was obtained by the reaction with alcoholic ammonia as described above, and recrystallized repeatedly from alcohol. The melting point of the pure substance as shown by the cooling curve was 117.1° instead of 119° as given by Holleman.

The 81° substance was obtained from the crude nitration product and purified by recrystallization from alcohol. The cooling curve obtained with this substance was interesting. From a minimum of 78.7° where crystallization began the temperature rose very slowly to 81.2° , this rise extending over a period of 25 minutes (bath at 75°). It remained steady at 81.2° for 7 minutes and then dropped off gradually as the contents of the tube became too solid to stir. In the case of both the 2,5- and the 2,6-dinitro derivatives the rise from minimum to maximum was very rapid, occupying only 1.5 and 1 minute, respectively.

For the investigation of the freezing-point curve of mixtures of the two dinitro derivatives the procedure was practically the same as that just described. The bath was kept at a temperature of from 4° to 6° below the approximate melting point. Duplicate determinations showed that variations of 2° or even more in the temperature of the bath caused no variation in the behavior of the melt which could be detected by the thermometer employed. The mixture was stirred continually during the cooling, and temperature readings were taken every half minute. With mixtures ranging from 35 to 50% of the *para* isomer the readings were continued until solidification made stirring impossible. Duplicate determinations were made for each mixture, practically perfect checks being obtained in every case.

The selection of the true freezing point of a mixture has been discussed by Bell¹⁰. As this author points out, the minimum point in the cooling curve (A, Fig. 1) is not the true freezing point because of the variable degree of supercooling involved and also because of the difficulty of observing accurately the appearance of the first small crystal. On the other hand, Bell objects to the

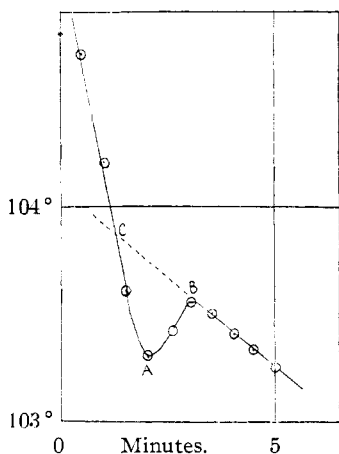


Fig. 1.—Cooling curve of mixture 75% of 2,5-dinitro- and 25% of 2,6-dinitro-1,4-dichlorobenzene.

¹⁰ Bell, *J. Ind. Eng. Chem.*, **11**, 1125 (1919).

common usage of adopting the maximum point on the curve (B, Fig. 1) on the ground that this represents the temperature of equilibrium between the crystals and a liquid

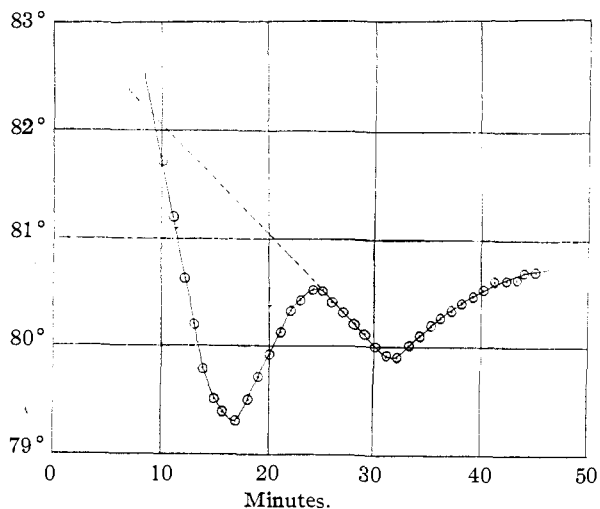


Fig. 2.—Cooling curve of mixture 41.4% of 2,5-dinitro- and 58.6% of 2,6-dinitro-1,4-dichlorobenzene.

which has a different composition from that present when crystallization began. He, therefore, chooses as the true freezing point that obtained by extrapolating the cooling curve, liquid-crystals, back to the point where it cuts the cooling curve of the liquid (C, Fig. 1), this being, in the case illustrated, the theoretical point where crystals of 2,5-dinitro-1,4-dichlorobenzene would be in equilibrium with a liquid mixture of 75% of 2,5-dinitro- and 25% of 2,6-dinitro-1,4-dichlorobenzene. The curve shown in this figure is typical of mixtures containing a high percentage of either component. It should be noted that the minimum (A) on the figure is not the point at which crystals first appeared. As a rule, crystals were visible during the half minute or minute preceding the minimum, the location of A varying with the extent of supercooling.

Until mixtures ranging from 39 to 46% of the *para* isomer were reached, the extrapolated points were obtained without difficulty. Within this range, however, extrapolation proved impracticable: Fig. 2 shows the behavior of a mixture containing

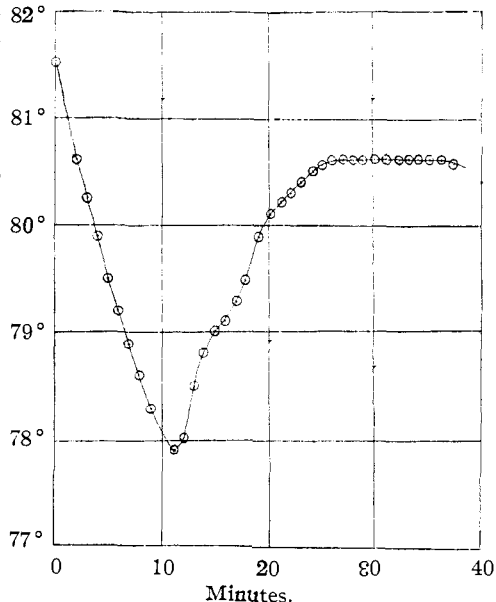


Fig. 3.—Cooling curve of mixture of 44.0% of 2,5-dinitro- and 56.0% of 2,6-dinitro-1,4-dichlorobenzene.

41.4% of the *para* isomer. After prolonged supercooling the temperature rose to 80.5°, fell to 79.9°, and then gradually rose again to 80.7°. During this last rise the mixture was

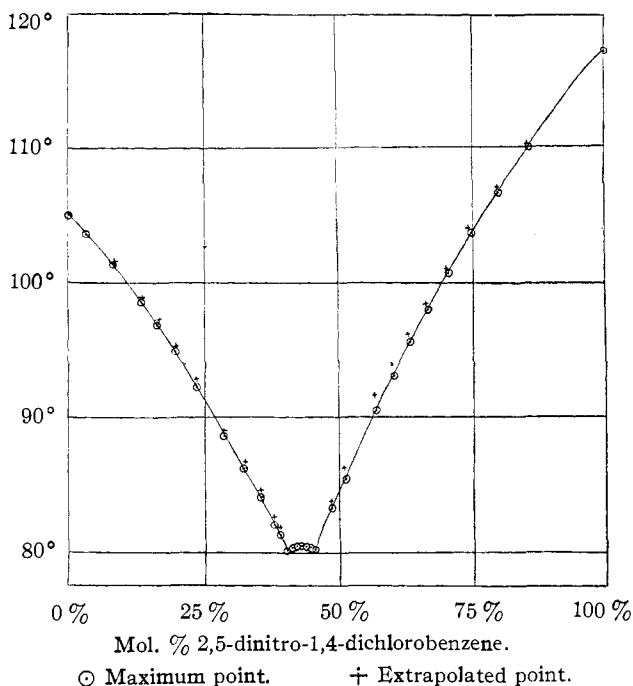


Fig. 4.—Binary system 2,6-dinitro- and 2,5-dinitro-1,4-dichlorobenzene.

thick with crystals. Fig. 3 shows the cooling curve of a mixture with 44.0% of this isomer. Crystals began to form at a temperature of 78°. The slow rise of the temperature to 80.6°, the highest point reached, took 15 minutes. These curves are typical of all obtained within the range mentioned.¹¹ In every case the temperature reached was between 80.5° and 80.9°. With 42–45% of the *para* isomer present the mixture became too thick to stir before there was any indication of a falling temperature.

In order to obtain a consistent curve, it was plotted from the maximum points throughout. The result is shown in Fig. 4, the circles indicating the freezing points as taken from the maxima. For purposes of comparison the points obtained by extrapolation, where this was possible, are indicated by crosses on the same curve. It will be observed that the difference between the curves obtained by the two methods is very slight.

From the slope of the curve it is obvious that a possible eutectic of the two isomers would separate at approximately 78°, more than 2° below the point at which the break indicating compound formation appears. One point was obtained on the continuation of that portion of the curve along which the *para* isomer separates. When two duplicate

¹¹ A precisely similar type of curve was obtained by Guida [*Gazz. chim. ital.*, **50**, 2, 101 (1920)] in the interval of compound formation between 2,4-dinitrotoluene and 2,4,6-trinitrotoluene, this being, however, the only analogous case which we have found in the literature.

determinations were made, however, no maximum appeared, but the temperature rose continuously to 80.6°. This single point probably lies on the metastable portion of the curve.

The curve indicates clearly the formation of a compound in the range 40–46% of *para* isomer, corresponding nearly to 2 molecules of 2,5-dinitro- to 3 of 2,6-dinitro-1,4-dichlorobenzene. This being the case, the extrapolated freezing points in this range should be the points obtained by continuing the cooling curve, *liquid-crystals of compound*, back to the cooling curve of the liquid (compound plus either component). To determine the points where the solid compound was in equilibrium with liquid containing varying amounts of the components the freezing-point curve for the system, 81° substance plus 2,6-dinitro-1,4-dichlorobenzene, was studied. The points obtained lay on a smooth curve as shown in Fig. 5. These points were plotted by calculating the percentage composition of the mixtures in terms of the components, assuming that the 81° substance consists of the 2 isomers in the proportion of 43% of 2,5-dinitro- to 57% of 2,6-dinitro-1,4-dichlorobenzene, and correspond very satisfactorily to points on the large curve given in Fig. 4.

The following experiment was carried out in order to observe the behavior of the 81° compound when kept for a considerable time at its melting point. A convenient bath which remained constant to within 0.1° was prepared by immersing a coil of Nichrome wire in glycerol in a Dewar flask. A current was passed through the wire and the resistance adjusted till the temperature could be kept constant at the desired point. When the bath had been constant for an hour at this temperature a test-tube fitted with thermometer and stirrer and containing the melted substance in which crystallization had just begun was placed in an air jacket immersed in the glycerol. The mass was stirred constantly and the temperatures of the system, *liquid-crystal*, and the bath were read every 15 minutes. Readings showed a variation of only 0.1° in the temperature of the melt over a period of 3 hours, the thermometer remaining at 81.4–81.5° (corr.). A similar determination was made with material obtained by melting together the 2 isomers in the proportion of 2 parts of the *para* to 3 of the *meta* isomer, cooling, and recrystallizing from alcohol. The product thus obtained was kept for 2.5 hours at the temperature 81.4–81.5°, liquid and crystals remaining in equilibrium over the whole period. There is, therefore, no doubt as to the identity of the product obtained from nitration and that prepared by mixing the isomers in the proportions given, nor as to its compound nature. The true melting point appears to be 81.2° ± 0.3°.

When the bath had been constant for an hour at this temperature a test-tube fitted with thermometer and stirrer and containing the melted substance in which crystallization had just begun was placed in an air jacket immersed in the glycerol. The mass was stirred constantly and the temperatures of the system, *liquid-crystal*, and the bath were read every 15 minutes. Readings showed a variation of only 0.1° in the temperature of the melt over a period of 3 hours, the thermometer remaining at 81.4–81.5° (corr.). A similar determination was made with material obtained by melting together the 2 isomers in the proportion of 2 parts of the *para* to 3 of the *meta* isomer, cooling, and recrystallizing from alcohol. The product thus obtained was kept for 2.5 hours at the temperature 81.4–81.5°, liquid and crystals remaining in equilibrium over the whole period. There is, therefore, no doubt as to the identity of the product obtained from nitration and that prepared by mixing the isomers in the proportions given, nor as to its compound nature. The true melting point appears to be 81.2° ± 0.3°.

Reaction of the Isomeric Dinitro-*para*-dichlorobenzenes with Alcoholic Ammonia

Reaction with 2,6-Dinitro-1,4-dichlorobenzene.—The *meta*-dinitro derivative reacts quite readily with saturated alcoholic ammonia, even at room temperature, but the rate of reaction varies considerably with the proportions used. With 15 g. of the dinitro derivative to 100 cc. of 4 *N* alcoholic ammonia some of the original material remained unchanged at the end of 4 days' standing at room temperature or after heating to 100° in a pressure flask for 8 hours. With 9 g. of dinitro derivative in 100 cc. of alcoholic ammonia the reaction was complete after 2 days at room temperature, and with 10 g. in

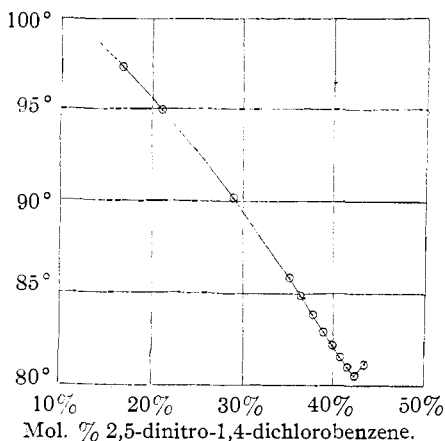


Fig. 5.—Binary system 2,6-dinitro-1,4-dichlorobenzene and 81° compound.

100 cc. reaction appeared to be complete after heating for 5 hours on the water-bath. The only organic product which could be detected was 2,6-dinitro-1,4-chloro-aniline, melting at 145°. This was verified by a determination of the amount of ammonium chloride produced, as follows. Ten g. of 2,6-dinitro-1,4-dichlorobenzene was heated with 100 cc. of 4 *N* alcoholic ammonia in a pressure flask on the water-bath for 5 hours. At the end of this time the alcohol was distilled, and the residue extracted with 150 cc. of dry benzene to remove the greater part of the organic material and then with water to dissolve the ammonium chloride. The water solution was made up to 500 cc. and the chloride titrated with silver nitrate and potassium thiocyanate solution, using a sodium light to eliminate the difficulty caused by the yellow color from the organic material dissolved. A slightly higher degree of accuracy, as indicated by duplicate experiments, can be obtained by repeating the benzene extraction until fresh portions of benzene show no coloration, but for our purpose the difference was too slight to compensate for the additional time required. In three successive experiments the ammonium chloride from 10 g. of 2,6-dinitro-1,4-dichlorobenzene was found to be 2.230, 2.230 and 2.26 g., or an average of 2.24 g., corresponding to 9.92 g. of original material converted into the dinitro-chloro-aniline. We assume, therefore, that in the case of this isomer the reaction goes entirely in this direction, the deviation noted being due to experimental error.

Reaction of 2,3-Dinitro-1,4-dichlorobenzene.—The *ortho*-dinitro derivative reacts with alcoholic ammonia, giving as the chief product 2-nitro-3,6-dichloro-aniline, m. p. 67°, which was identified by melting at the same temperature when mixed with a specimen on hand. Along with this a small quantity of a secondary product was formed, which was much less soluble than the nitro-aniline in all the common solvents and which can therefore be separated from the mixture of the two by fractional crystallization from either benzene or alcohol. This product gave the usual color tests for a *para*-diamine.

Analysis. Calc. for $C_6H_4Cl_2N_2$: N, 15.8. Found: 16.0.

2,3-Dinitro-1,4-diamidobenzene crystallizes in microscopic needles, mustard-yellow in color, which tend to collect into a flocculent mass. It melts with decomposition between 241–250°. It is sparingly soluble in alcohol, ether, benzene and chloroform.

Since no monochloro derivative is formed in this reaction, determination of the ammonium chloride formed should give a measure of the proportion of the dinitro derivative converted into diamine. Three determinations in which 10 g. of the *ortho*-dinitro derivative was heated with 100 cc. of 4 *N* alcoholic ammonia in a pressure flask to 100° for 5 to 8 hours gave 0.371, 0.415, and 0.381 g. of ammonium chloride, or an average of 0.389 g., indicating that between 8 and 9% of the dinitro derivative is converted into the *o*-dinitro-*p*-phenylenediamine by the replacement of both chlorine atoms by amine radicals, while the remainder forms the dichloronitro-aniline by replacement of one nitro group by an amino group.

Reaction of 2,5-Dinitro-1,4-dichlorobenzene: 2,5-Dinitro-1,4-diamidobenzene.—The *para* derivative reacts slowly with alcoholic ammonia, giving 2 organic products. That formed in greater amount is the 4-nitro-3,6-dichloro-aniline, melting at 153°, as mentioned by Holleman. There is formed at the same time a secondary product which usually separates from the reaction mixture in the form of small, greenish black, metallic-looking balls about 1 mm. in diameter. They are hard and brittle, and when broken open frequently show a yellow nucleus of occluded material from the reaction mixture. When the alcoholic solution is cooled rapidly this product is deposited as a dark brown amorphous-looking powder which adheres very tenaciously to filter paper. It is insoluble in benzene and can be separated from the dichloronitro-aniline by evaporating the alcohol to dryness, grinding the residue in a mortar and extracting repeatedly with benzene until the yellow color is entirely removed. On washing the ammonium chloride from the residue a chlorine-free product is obtained which dissolves in hot alcohol to give a dark

red solution and separates on cooling in small reddish brown needles. It is soluble in acetone and in conc. sulfuric acid, but very sparingly so in chloroform, carbon tetrachloride and ether. It melts with decomposition at 295–300°. While we have not as yet obtained a sufficient amount of this material in a pure state to complete its identification we have found that it gives the usual tests for a *para*-diamine, and this, together with the high melting point, the absence of chlorine, and the analogy with the reaction of the *ortho*-dinitro isomer, may be regarded as sufficient evidence of its identity as 2,5-dinitro-*p*-phenylenediamine.

Chloride determinations gave 1.23 and 1.24 g. of ammonium chloride in two experiments in which 10 g. of the *para*-dinitro derivative was heated on the water-bath with alcoholic ammonia for 20 and 23 hours, respectively. From this it follows that about 27% of this derivative is converted into the diamine by the replacement of the two chlorine atoms, while the other 73% goes to form the dichloronitro-aniline by replacement of one nitro group.

Reaction of the Substance Melting at 81°.—Fifteen g. of the substance was heated with 100 cc. of 4 *N* alcoholic ammonia in a pressure flask to 100° for about 6 hours. On cooling, orange-colored needles separated, through which were scattered a quantity of small black balls identical with those produced in the reaction between alcoholic ammonia and the 2,5-dinitro derivative. The supernatant liquid was decanted from the crystals, which were practically pure except for the presence of a little ammonium chloride, later removed by dissolving in benzene, filtering, evaporating to dryness and recrystallizing from 95% alcohol. The product melted sharply at 145°. The liquid, which had been decanted was evaporated to dryness, the residue dissolved in benzene, and filtered to remove the ammonium salts. The filtrate was evaporated to dryness once more and the residue dissolved in absolute alcohol. When the amount of alcohol used is carefully regulated, 2,6-dinitro-4-chloro-aniline separates first and can be filtered off. Further evaporation of the alcohol results in the separation of a deep-yellow flocculent mass which can be purified by repeated crystallization from chloroform. It is necessary, however, to remove the 2,6-dinitro-4-chloro-aniline fairly completely by the first procedure, as in the presence of this substance chloroform fails to effect a separation. When pure, the yellow substance melts at 153°, the melting point of 2,5-dichloro-4-nitro-aniline.

There are, therefore, 3 organic products obtained by heating the dinitro derivative of *p*-dichlorobenzene melting at 81° with alcoholic ammonia under pressure at 100°; 2,6-dinitro-4-chloro-aniline, formed from the *meta* isomer; 2,5-dichloro-4-nitro-aniline, formed from the *para* isomer; and 2,5-dinitro-1,4-diamidobenzene, formed from the same source. At the beginning of the work it was hoped that the study of this reaction would throw some light upon the nature of the substance melting at 81° and the relative proportions in which its constituents are present, but it proved impossible to obtain any but roughly qualitative results. When the reaction is carried on at 100° the original constituents are entirely converted into the amido derivatives, but the separation of these involves a large number of recrystallizations, in the course of which a very considerable amount of material is carried off in the vapor of the boiling solvents. At room temperature the 2,5-dinitro-1,4-dichlorobenzene reacts much more slowly than the other component, and with a smaller proportion of the nitro-aniline present we were able to make the separation with less loss of material. Starting with 15 g. of the 81° substance and treating it with 4 *N* alcoholic ammonia at room temperature for 48 hours, the proportions of the various products obtained were as follows: 8.0 g. of chloro-aniline, corresponding to 8.75 g. of 2,6-dinitro-1,4-dichlorobenzene; 2.9 g. of nitro-aniline, corresponding to 3.32 g. of 2,5-dinitro-1,4-dichlorobenzene; 2.6 g. of unaltered 2,5-dinitro-1,4-dichlorobenzene. According to these figures there should have been present in the original material 8.75 g. of the *meta* and 5.9 g. of the *para* derivative, corresponding to

58.1 and 39.3%, respectively,—figures which show fairly good agreement with the proportions calculated from the freezing-point curves.

Reduction of the Substance Melting at 81°.—The method adopted was a modification of that used by Nason.⁵ Ten g. of the substance, 30 g. of stannous chloride, and an excess of granulated tin were heated with 100 cc. of conc. hydrochloric acid on the water-bath for about 5 hours. After filtering off the residual tin, the excess of hydrochloric acid was evaporated, 250 cc. of benzene added, and the acid liquid was treated with sodium hydroxide in the presence of the benzene. Under these conditions no black precipitate forms and the precipitated tin hydroxide dissolves readily in the excess of sodium hydroxide. After shaking the mixture thoroughly, the benzene was separated, dried, and distilled to half volume on the water-bath. As it cooled 1.5 g. of practically pure *para*-diamine separated, melting at 164°. This was identified by comparing it with a specimen on hand. On concentrating the benzene solution 3.5 g. of impure material separated which was recrystallized, first from chloroform and then from 50% alcohol. The product obtained was in the form of fine needles melting at 105.5° and was identified as the *meta*-diamine by melting with specimens obtained by the reduction of 2,6-dinitro-1,4-dichlorobenzene both by stannous chloride and by titanium trichloride. A second extraction with benzene gave only 0.2 g. of the *para*-diamine, although it was evident from the very dark color of the aqueous liquid that this still contained a considerable quantity of organic material. The 2 diamines can be very readily distinguished, both by melting point and crystalline form. The *meta*-diamine is much more readily soluble in benzene. Both have a trace of brownish pink color which is probably due to a slight impurity, but which we have found impossible to remove entirely. When impure they darken very rapidly if exposed to the air in a moist state, this tendency decreasing as they are purified.

Reduction of 1,4-Dichloro-2,3-dinitrobenzene: 1,4-Dichloro-2,3-diamidobenzene.—Ten g. of 1,4-dichloro-2,3-dinitrobenzene was reduced as described above. After the addition of sodium hydroxide solution the mixture was distilled with steam. Very fine white crystals of 1,4-dichloro-2,3-diamidobenzene separated from the distillate, forming a felt. The crystals were pure white when first distilled, but rapidly turned brown on exposure to the air, this tendency lessening, however, as the substance was purified. The diamine is very soluble in alcohol and in ether. Recrystallization from 50% alcohol gave pure white, silky needles melting at 98°.

Analysis. Calc. for $C_6H_6Cl_2N_2$: N, 15.8. Found: 16.0.

Condensation of 1,4-Dichloro-2,3-diamidobenzene with benzil; 1,4-Dichloro-diphenyl-quinoxaline.—To a solution of 2.3 g. of benzil in hot alcohol, 2 g. (a slight excess) of 1,4-dichloro-2,3-diamidobenzene was added, and the mixture was heated on a water-bath. Crystals began to separate almost immediately, but the heating was continued for 1.5 hours. The product was very soluble in benzene, sparingly in alcohol. It was recrystallized from a mixture of benzene and alcohol, from which it separated in minute white needles melting at 214°.

Analysis. Calc. for $C_{20}H_{12}N_2Cl_2$: C, 68.3; H, 3.4. Found: C, 68.3; H, 3.5.

Summary

1. The product melting at 81° obtained from the nitration of *p*-dichlorobenzene has been shown to be a molecular compound of 2,5-dinitro- and 2,6-dinitro-1,4-dichlorobenzene, the proportions approximating 2 molecules of the former to 3 of the latter.

2. A quantitative study of the reaction of alcoholic ammonia with the isomeric dinitro-*p*-dichlorobenzenes shows that in the case of the *meta*-

dinitro derivative the sole product is the dinitrochloro-aniline formed by replacement of the chlorine atom *ortho* to the 2 nitro groups by an amino group. In the case of the *ortho*- and *para*-dinitro derivatives the main reaction is the replacement of 1 nitro group by an amino group to give the dichloro-aniline, while at the same time there is formed a comparatively small amount of dinitro-*p*-phenylenediamine by replacement of both chlorine atoms. The amounts of the diamines formed correspond to 27% of the 2,5-dinitro- and 8.5% of the 2,3-dinitro-1,4-dichlorobenzene.

3. The constitution of 2,3-dinitro-1,4-dichlorobenzene, melting at 101°, has been proved by reducing to the *p*-phenylenediamine and condensing this to quinoxaline.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE OXIDATION OF ISOPROPYL ALCOHOL WITH POTASSIUM PERMANGANATE¹

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The work presented in this paper on the oxidation of *isopropyl* alcohol is a continuation of a series of studies made in this laboratory on the oxidation of certain organic compounds by means of potassium permanganate in the presence of potassium hydroxide.² The purposes of our investigation were as follows: (a) to determine by exact quantitative data the relationship of the initial alkalinity to the character and amounts of the products formed; (b) to determine the relationship of the temperature to the character and amounts of the oxidation products; (c) to ascertain the course followed by the reactions involved in the oxidation of *isopropyl* alcohol by means of alkaline permanganate.²

The literature shows that only a small amount of work has been done on the oxidation of *isopropyl* alcohol. When Berthelot³ oxidized this substance by means of potassium chromate and sulfuric acid, acetone was the only oxidation product. He obtained the oxidation products of acetone when the reaction mixture was more concentrated. Remsen and Emerson⁴ oxidized a series of alkyl side chain aromatic compounds and found that the *isopropyl* group was more easily oxidized by acid reagents than by alkaline ones. Hetper⁵ oxidized *isopropyl* alcohol and acetone with potassium permanganate in both acid (phosphoric) and alkaline solution.

¹ Presented at the Chicago meeting of the American Chemical Society, September 1920.

² THIS JOURNAL, **34**, 1086 (1912); **38**, 375 (1916); **41**, 1267, 1385 (1919).

³ Berthelot, *Ann. chim. phys.*, **23**, 212 (1872).

⁴ Remsen and Emerson, *Am. Chem. J.*, **8**, 262 (1887).

⁵ Hetper, *Z. anal. Chem.*, **50**, 355 (1911); **51**, 417 (1912).