296. *A Mode of Studying Nitration. Part II. Isomeric Ratios in Dinitrobenzene.*

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The work here described is an outcome of that by Hetherington and Masson (J., 1933, 105; regarded as Part I) in which were examined the influences of acid concentration upon the extent of conversion of mono- into di-nitrobenzene. In that work, the question of the variability of the proportions of the three isomerides was not studied; and it forms the theme of the present communication.

Holleman's work upon this question was based upon the analyses of the final yields of six nitrations by him and de Bruyn (*Rec. trav. chim.*, 1900, **19**, 79). In four of these, fuming nitric acid of four different concentrations (95·2, 83·1, 87·1, and 92·1 mols. %) was the sole nitrating agent, the temperature being 0° in the first case and 30° in the others. In the other two nitrations, sulphuric acid was mixed with the nitrobenzene before nitric acid was added; the mixed concentrations, which were the same for each nitration, can be approximately reckoned from the data as $66{\cdot}5H_2SO_4 + 10HNO_3 + 23{\cdot}5H_2O$ (in mols.). One nitration was done at 0°, the other at 40°. Despite the intermingling of variables, Holleman and de Bruyn were able to conclude that a rise in the temperature of nitration lowers the relative yield of *m*-dinitrobenzene; that the introduction of sulphuric acid increases the ratio of *p*- to *o*-; and that water does not modify the isomeric ratios, which remain the same during the course of a nitration. The last conclusion was drawn from the experiments with aqueous nitric acid only. The proportion of *m*-dinitrobenzene varied only from 93·5 to 90·9% of the total yield; that of *o*- from 4·8 to 8·5%; that of *p*- from *ca.* 0·3 to 1·7%.

Wyler (*Helv. Chim. Acta*, 1932, **15**, 23) has lately made a more extended study of temperature-effects, in which, having worked out a chemical method of determining the *m*-content, he showed clearly how this fell from 95% of the yield, at − 17° to − 10°, to 85% at 124—129°. He used one mixture of acids for the four lower temperatures and another for the four upper temperatures; the compositions of the acids can be approximately reckoned in the former case as $77H_2SO_4 + 19HNO_3 + 4H_2O$, and more exactly in the latter as $57H_2SO_4 + 25HNO_3 + 18H_2O$ (in mols.). He noted an apparent fluctuation in the proportion of *m*-dinitrobenzene at temperatures over 100°; our work suggests that this may have been due to trinitrobenzenes, which (if they were formed) we find would have been included as *o*- and *p*-dinitrobenzene by his analytical method.

Wyler's data for the ratio *o*/*p* depend upon a method of thermal analysis with which he supplemented his chemical determination of the *m*-content. Unfortunately, our study of this matter shows that this part of Wyler's work is not securely based, and we are obliged to give no more than qualitative weight to his *o*/*p* ratios. We discuss the basis of the thermal analysis in the succeeding paper; meanwhile, we may accept from Wyler's data a general statement that a rise in the temperature of nitration increases the yield of *o*- at the expense of that of *p*-dinitrobenzene.

Our work concerns mainly the influence of the composition of the acid (H_2SO_4, HNO_3, H_2O) upon the isomeric ratios resulting from the complete nitration of mono- to di-nitrobenzene. Twenty-three nitrations, covering a wide range of acid composition, were done at 35·0°, the temperature used in Part I (*loc. cit.*), and two at 0° and 60°. The procedure in our nitrations was essentially the same as in Part I; we have given special attention to the working up of the yield without subjecting it to alteration before analysis; to the methods of analysis themselves; and to the sources of by-products in the nitrations.

FIG. 1.

Each arrow describes the change in molar composition of the acid during a nitration, and the figure on the arrow is the percentage of meta-*isomeride in the dinitrobenzene formed.*

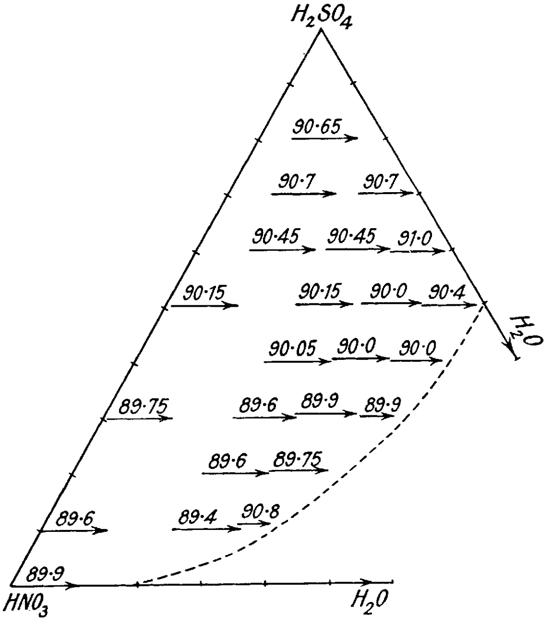
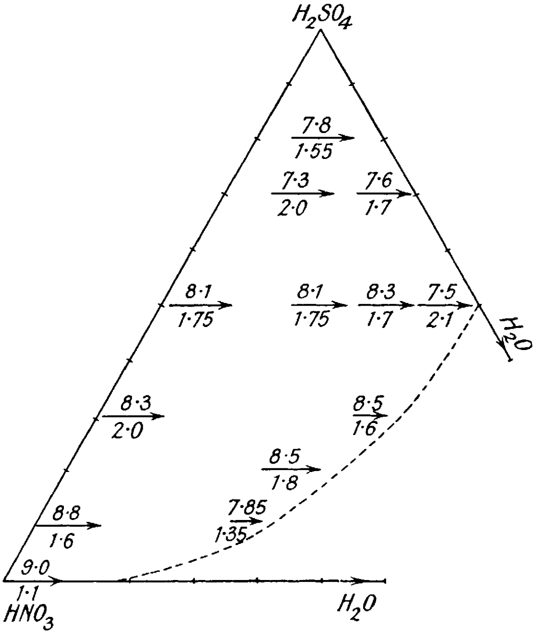


FIG. 2.

Showing percentages of ortho-*isomeride* (*above the arrow*) *and of* para-*isomeride* (*below*) *in the dinitrobenzene formed.*



Survey of Results.—The mode of expressing the compositions of acids during each nitration is that developed in Part I, involving molecular percentages and triangular plotting. In Fig. 1, each arrow describes the whole course of a separate nitration; and the number on an arrow gives the percentage of *m*-compound in the dinitrobenzene formed. The boundary curve, taken from Part I, marks the concentrations at which the acids cease to nitrate. Fig. 2 shows, in the same way, for those 13 of the same nitrations in which the other isomerides were determined, the percentages of ortho (above the arrows) and of para (below them). Both diagrams refer to a nitration temperature of 35°.

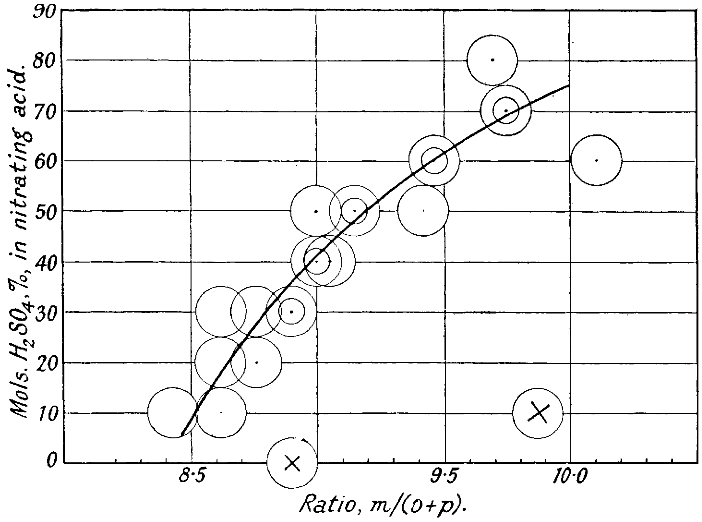
In general, these results show a remarkable constancy of composition. Any mixture of sulphuric and nitric acids which will nitrate nitrobenzene at all, yields at 35° a product whose percentage composition (and ranges) can be stated as: *m*- 90·1 (89·6—91·0); *o*- 8·1

(7·3—9·0); *p*- 1·7 (1·1—2·1)%. On closer examination, however, one definite influence upon the nature of the product becomes plain: that of the sulphuric acid. This is best seen in Fig. 3, where the ratios $m/(o + p)$ are plotted against the sulphuric contents of the nitrating acids. The changes being small, analytical aberrations (corresponding with the diameters of the circles) are naturally magnified in the diagram; nevertheless, it is seen that, on the average, each increase of 10% in the molecular percentage of sulphuric acid causes an increase of 0·2—0·25 in the numerical ratio $m/(o + p)$. (Deviations which are probably genuine are in absolute nitric acid, and in the other acid marked in Fig. 3 as ×, which was barely capable of performing nitration.)

During the course of a full nitration (shown, for instance, by a chain of arrows along a horizontal line in Figs. 1 and 2), no material change occurs in the proportion of any of the three isomerides. This is another instance of the dominant influence of the sulphuric content, which of course remains constant during any given nitration.

FIG. 3.

Nitrations of nitrobenzene at 35·0°. *Showing the influence of the* H_2SO_4 *content of the acid upon the composition of the dinitrobenzene formed.*



The numerical ratio o/p, owing to the smallness of the *p*-content, is too easily affected by slight analytical aberrations to be usefully stated, and the separate percentages of each isomeride are more instructive. The *o*-content ranges from 9·0% of the yield, in nearly absolute nitric acid, to 7·3% in a sulphuric-rich mixture. The trend is well shown in the series of acids along the left-hand edge of Fig. 2. The small *p*-content seems to alter simultaneously in the opposite sense, 1·1 to 2·0%.

On the hypothesis mentioned in Part I, *viz.*, that the proved formation of a salt with the cation $PhNO_2{\cdot}H^+$ is responsible for *m*-nitration, the smallness of the change in the ratio $m/(o + p)$ implies that sulphuric and nitric acids do not greatly differ in their ability to form salts with nitrobenzene. But such change in the ratio as does occur (cf. Fig. 3) shows sulphuric acid as the more effective of the two in this respect; and this is in line with the fact, established in Part I, that water sooner nullifies the activity of nitric acid than of sulphuric acid in the nitration of mononitrobenzene. Hantzsch, in his work on anhydrous nitric and sulphuric acids, assigns to sulphuric rather than to nitric acid the rôle of supplying anions, as in his " nitronium hydrogen sulphate," akin to his crystalline compound " nitronium perchlorate."

We find, further, that when glacial acetic acid replaces sulphuric acid in a mixture with fuming nitric acid ($52HOAc + 39HNO_3 + 9H_2O$, in mols.), no nitration of nitrobenzene takes place at 35°. It is to be presumed that the acetate of the complex cation

$PhNO_2{\cdot}H^+$ is not formed, in accordance with the feeble acidity of acetic acid and with the view that the acetic acid molecule itself enters the cation of a salt with nitric acid. Nor can one assign the failure of acetic acid in promoting the *m*-nitration merely to its lack of dehydrating power; for an experiment in which the acetic acid of the above-named mixture was replaced by an equal number of molecules of acetic anhydride showed that here also no nitration took place at 35°.

Hence, it appears to be proved that in ordinary nitration mixtures the sulphuric acid acts because it is simultaneously a strong acid and a dehydrator; and the hypothesis put forward in Part I, embodying this requirement, is strengthened.

Temperature Effect.—One only of our mixed acids was examined, of composition H_2SO_4 50·0, HNO_3 29·6, H_2O 20·4 mols. %. Used at three different temperatures to nitrate 10 mols. of nitrobenzene per 100 mols. of the mixed acid, it gave dinitrobenzene of the following compositions:

	Percentages.			Ratios.	
Temp.	*m*-.	*o*-.	*p*-.	$m/(o+p)$.	o/p.
0°	93·7	5·8	0·5	14·9	12
35	90·15	8·1	1·75	9·15	4·6
60	87·3	11·5	1·2	6·9	9·6

The results of Holleman and de Bruyn and of Wyler are in broad agreement with these data, as regards the influences of temperature upon the ratio $m/(o + p)$ and upon the production of the *o*-compound.

A reason for the decrease in *m*-content at the higher temperatures may be sought in the same hypothesis as has been mentioned; for the complex between nitrobenzene and acid, whose formation is slightly exothermic, will naturally be present in smaller concentration at high temperatures than at low.

Side Reactions.—The yields of dinitrobenzene collected in the 25 nitrations ranged closely round a mean value of 96·8% on the nitrobenzene taken. Of the loss (3·2%) a part was accounted for by the solubility of the three dinitrobenzenes in the aqueous liquors which resulted from the dilution and neutralisation of the nitration mixtures after the completion of reaction. Quantitative measurements of solubility in appropriately chosen liquors showed that 2% had been lost from this cause. If we may assume that the respective solubilities of the three isomerides in the saline liquors are in practically the same ratios to each other as in pure water (a point not specifically studied), then the 2% thus lost has scarcely affected the composition of the 96·8% which was analysed. The correction might raise the *p*-content by 0·2 unit % and the *o*-content by the same amount; but this is offset by the behaviour of *m*-dinitrobenzene which is noted below.

The remaining loss of 1·2% was shown to be mainly due to the formation of yellow nitrophenolic substances. Colorimetric measurements on the diluted and neutralised nitration liquors gave similar values for all the nitrations; the shade and depth of colour matched those of a dilute solution of *o*-nitrophenol (1 part) and *p*-nitrophenol (4 parts) in 22,000 parts of aqueous sodium sulphate (2280 parts) and nitrate (415 parts). The yellow colour was easily extractable with ether from the acidified liquors; hence it was not due to picric acid, and in any case the sensitive test with cyanide for this substance gave only faint indications. About 15% of the colouring matter was volatile in steam, like *o*-nitrophenol; on the other hand, *o*- and *p*-nitrophenols are not stable in the mixed acids used in the nitrations. The precise identity of these products was of less immediate interest to us than their origin; for if they come from the preferential decomposition of any one or two of the dinitrobenzenes (especially the para), the isomeric ratios found in the yield will not be the true ratios formed in nitration. Direct tests with each dinitrobenzene isomeride in a mixed acid at 35° proved that *o*- and *p*-dinitrobenzene, once they are formed, are quite stable during a nitration, but that *m*-dinitrobenzene slightly decomposes to form yellow compounds. The quantity of these, however, as measured tintometrically, accounted for only a small part of the substances in the actual nitration liquors. Finally, the colour production in the nitrations was traced principally to a direct reaction of mononitrobenzene with the acids; for a mixed acid of concentration just too aqueous to nitrate it gave, when treated with it for 12 hours at 35°, enough colouring matter to account for what had been observed.

The net result of all the experiments on the losses of yield is that preferential losses, as between the isomerides, are negligible with the treatment adopted; and that therefore the stated compositions of the various yields can be accepted as showing the genuine proportions in which the isomerides were initially formed.

EXPERIMENTAL.

Nitrations.—These were carried out essentially as described in Part I, though on a smaller scale. Normally 10 mols. of nitrobenzene were taken per 100 mols. of the mixed acid, and the yield of dinitrobenzene in each case was about 25 g. With those acids which were near the border line of nitrating power, the proportion of nitrobenzene taken was appropriately reduced. In no case was any nitrobenzene left when reaction had ceased. A thermostat was used for maintaining the mixtures at 35·0°, and care was taken that from the start of each nitration the temperature did not vary from this value. All ingredients were weighed.

The zones of heterogeneity described in Part I (pp. 110, 111) were defined more accurately than before: the boundary between heterogeneous and homogeneous nitrations at 35° in sulphuric-rich acids proves to lie somewhat nearer to the H_2SO_4–H_2O side of the triangular diagram than was represented in Part I.

Treatment of Yields.—Each finished nitration mixture was diluted, with cooling, to a measured extent, and exactly neutralised with aqueous sodium hydroxide; after standing, the dinitrobenzene was filtered off, washed with a definite quantity of water, and sucked dry. It was then melted, with vigorous shaking, under 100 c.c. of water, and filtered after being cooled to the measured temperature of the room with shaking, and the process was thrice repeated; the acidity of the washings was proved by titration to vanish in each case. The solid, now almost white, was dried for a day in a covered Petri dish on a plate kept at 60°. It was then weighed, finely ground, replaced for some days on the hot plate, with occasional stirring, and finally kept in a vacuum desiccator over phosphoric oxide, before being used for analysis. Products thus treated were proved free from sulphate and from non-volatile matter.

Analysis of Isomeric Dinitrobenzenes.—Much time was spent in testing reactions reported as discriminating between the isomerides; the reagents studied included hydrazine, piperidine, aqueous sodium sulphite, aqueous and alcoholic alkali, and sodium methoxide in anhydrous methyl alcohol. Certain results of the hydrolytic and alcoholytic experiments are all that need be indicated here.

Systematic experiments were made on the behaviour of the three isomerides, separately and together, towards aqueous potassium hydroxide. The reaction was carried out under reflux at the b.p., for periods from 2 to 8 hours, with different concentrations and proportions of alkali. The hydrolysis was followed by measuring iodometrically the nitrite formed in the hydrolysis to nitrophenoxide, air being excluded from the titrations. The numerical results may be summarised as follows: *m*-dinitrobenzene undergoes negligible hydrolysis in boiling 0·2*N*-potassium hydroxide, but in 0·5*N*-alkali, decompositions other than hydrolysis occur, forming dark solutions. Atmospheric oxygen is not concerned in these decompositions. The other two isomerides are much more reactive, but even after long refluxing in 0·2*N*-potassium hydroxide they are incompletely hydrolysed, the highest values got being 95% for *p*- and 89% for *o*-dinitrobenzene. The *p*-isomeride is definitely the most reactive towards alkali. When the *o*- and *p*-isomerides are part of a mass of molten dinitrobenzene, they react still more slowly with the liquid. No aqueous alkali of concentration sufficient to hydrolyse all the *o*- and *p*-isomeride leaves the *m*-isomeride unattacked; hence this method is unfitted for analysis.

The reactions with sodium methoxide in methyl alcohol were examined. L. de Bruyn (*Rec. trav. chim.*, 1894, **13**, 114) states that *o*- and *p*-dinitrobenzene react with it quantitatively to form the nitro-anisoles, and that the *m*-isomeride is mainly reduced to 3 : 3′-dinitroazoxybenzene. Wyler (*loc. cit.*) found that the rigorous exclusion of water inhibits the last of these three reactions only, and he developed accordingly his analytical method for determining the *m*-content. We tested this carefully, except that we did not use potassium methoxide, which Wyler prefers to sodium methoxide. Essentially, the determination depends upon using a known amount of methoxide and, after refluxing the reagents for a definite time, titrating back the excess of methoxide with a freshly standardised solution of acetic acid in methyl alcohol. An external indicator is necessary, thymol-blue being used by us. Without giving details, we may say that we confirmed de Bruyn's and Wyler's conclusion that *o*- and *p*-dinitrobenzene react quantitatively, one nitro-group being affected in each case. We found also that **1** : **3** : **5**-trinitrobenzene (for a stock of which we thank Messrs. Imperial Chemical Industries, Ltd.) reacts quantitatively, one nitro-group being removed. But even the purest *m*-dinitrobenzene that we could prepare was not quite immune from reaction with dry methyl-alcoholic sodium methoxide; and a specimen which had already been repeatedly submitted to the process, and had m. p. 90·3°, continued to react when re-treated. Under working conditions, we found that a correction of 0·3 unit should on this account be subtracted from the apparent figure for the percentage of $o + p$ in the sample analysed. The correction was not quite regular, and 0·3 is a mean figure.

All the nitration products were thus analysed; and when the resulting data for the *m*-contents are compared with those obtained by the independent method of thermal analysis which we meanwhile developed (see following paper), the concordance is found to be fairly good. There was, nevertheless, a small and irregular discrepancy between the two methods, amounting to a few tenths per cent.; and since the thermal method affords a complete determination of each of the three isomerides and was proved to be reliable, whereas the chemical method determines only one isomeride and had the above-mentioned small element of caprice, however carefully we applied it, we prefer the thermal results. The methoxide data at least ensure that in the thermal method the proper region of the triangular diagram of *o*-*m*-*p* m. p. isotherms is being used.

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