34. *A Mode of Studying Nitration.*

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THE work here summarised was entered upon in order to learn why a dehydrating agent, such as sulphuric acid, is required in many aromatic nitrations; for the withdrawal of a reaction product (as such) cannot of itself facilitate a reaction which is irreversible, and ordinary nitration is irreversible. Evidently, then, the prejudicial influence of water in nitrations must be due to its acting upon one of the initial reagents; and the first obvious hypothesis is that if water were allowed to be present it would hydrate nitric acid, and that only unhydrated nitric acid (rendered so by sulphuric acid) could perform the reaction $RH + HNO_3 \longrightarrow RNO_2 + H_2O$. Such a mechanism was, in fact, put forward in connexion with the " nitration " of cellulose by Kullgren (A., 1908, i, 768) largely on the basis of the work of Saposchnikoff (*Z. Ges. Schiess Sprengstoffw.*, 1904, **24**, 453; *Z. physikal. Chem.*, 1904, **49**, 697) and others. Saposchnikoff made valuable experiments upon the vapour pressures of nitric acid in its mixtures with sulphuric acid, which showed clearly the hydration of sulphuric acid at the expense of that of the nitric acid; and he drew attention to a rough parallelism between the partial pressure of nitric acid vapour and the nitrogen content of the " nitrocellulose " which the acid mixture would yield. A survey of this subject has lately been made by Farmer (*J. Soc. Chem. Ind.*, 1931, **50**, 75T), using Hantzsch's ideas of the existence of acids in a " pseudo-acid " form. It would not, however, be safe to apply to true aromatic nitrations inferences drawn from reversible aliphatic esterifications; and still less from esterifications of a heterogeneous colloidal material, in which not only the formation of sulphuric esters but also rates of selective diffusion play a considerable part (also cf. Berl and Klaye, A., 1908, i, 504).

From the work of Veley and Manley (J., 1903, **83**, 1015), Schaefer (*Z. anorg. Chem.*, 1916, **98**, 70), and Hantzsch (*Ber.*, 1925, **58**, *B*, 941) on the optical and other properties of aqueous nitrates, nitric esters, solutions of nitric acid, and sulphuric–nitric mixtures, it has been inferred by Hantzsch (*loc. cit.*) that in the two last-named cases nitric acid is present not only as ionised $(H_3O)^{\bullet}(NO_3)'$ and non-ionic $HO{\cdot}NO_2$, but also as " nitronium " salts, analogous to the isolated crystalline compounds $2HClO_4,HNO_3$ and $HClO_4,HNO_3$ or $(H{\cdot}HNO_3)^{\bullet}ClO_4'$. Hantzsch's work on electrical conduction and molecular weights in absolute sulphuric acid is also taken into account. Thus, in highly concentrated nitric acid, the polymeric form $H_2N_2O_6$, recognised by earlier workers, is regarded by Hantzsch and Wolf as nitronium nitrate; and in sulphuric solutions of nitric acid the corresponding acid sulphate is believed to be present.

The experiments on aromatic nitration here described were chiefly upon the influence of acid composition on the formation of dinitrobenzene from mononitrobenzene. This case is initially suitable because, on the one hand, it is a mononitration only, trinitrobenzene not being appreciably formed, and on the other hand, isomeric dinitrobenzenes are produced in only small quantity relatively to the meta-compound. (In the present work we have not examined the variability of this proportion.)

When a stoicheiometric excess of nitrobenzene is shaken, for periods ranging from 1 hour to 24 hours, with a mixture of sulphuric acid, nitric acid, and water, the reaction may go to completion, all the nitric acid being used for dinitration; or it can come to a practical standstill, both nitric acid and nitrobenzene remaining together in the mixture. The point at which the reaction ceases (whether with complete or with only partial consumption of the reagents) is determined mainly by the relative proportions of the three inorganic compounds, in the manner described below. The proportion of excess unused nitrobenzene is not without an influence on the end-point reached, as will be shown. The dinitrobenzene produced appears to have no great influence, but our tests of this were not numerous. Temperature, within our limits, appears to play only a minor part in determining how far the reaction goes. It will be shown that the " cessation " of reaction, due to water, is really a decrease of velocity to a negligible though doubtless still finite value; but so marked is this decrease that it amounts to a stoppage, and in the present communication it will be convenient to express it in this way.

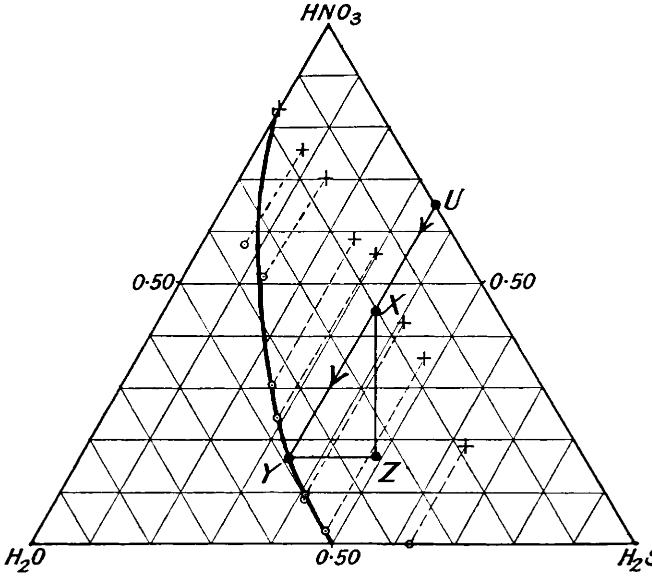
The study of the concentration changes in a nitration can best be made rational by considering *molar fractions* in the ternary mixture H_2SO_4–HNO_3–H_2O, and by plotting these triangularly. Clearly, since during nitration each molecule of nitric acid that disappears is replaced by a molecule of water, the molar fraction of sulphuric acid remains unaltered from start to finish. The path followed, throughout nitration, by the composition of the ternary acid mixture (" the acid ") is therefore shown in the triangular diagram along the fixed parallel which designates that particular molar fraction of sulphuric acid. (This simplicity is, of course, altogether obscured when weight percentages are used.)

Accordingly, we plot in Fig. 1, and tabulate on p. 113, the result of each of a systematic set of nitrations (Expts. 1, 8, 13, 18, 30, supplemented by 5, 10, 22, 25). In these, mixed acids of a wide range of composition were allowed to act at 35° upon nitrobenzene, which was usually added to the acid in quantity equivalent to the total nitric acid present; and the mixtures were shaken at 35° for periods varying up to 24 hours. Actually the reactions were reduced to very low speeds within the first few hours. The quantity of every component, inorganic and organic, was determined before and after reaction. (Isomeric dinitro-compounds were not differentiated.) The compositions of the acids before nitration are shown by crosses, those at the end of the reaction by circles. The compositions plotted are those of the aggregate inorganic contents, irrespectively of their distribution in layers, which will be discussed later.

Examination of the diagram will show that under these conditions any nitrating acid containing initially (and therefore at every other stage also) over 50 mols. % of sulphuric acid will allow all its nitric acid to be consumed; *i.e.*, if there is at least enough sulphuric acid present to form the monohydrate H_2SO_4,H_2O with the water initially present *plus* the water formed chemically, the nitric acid is all available for this nitration. Otherwise the consumption of nitric acid goes only as far as the curve shown. Thus an acid of initial composition shown at X will nitrate nitrobenzene until its composition, moving along the parallel XY, reaches Y, when it will practically cease to react. Subject to minor differences indicated in the next paragraph, the same arrest point Y will be reached by any other nitrating acid whose initial composition lies between U and Y. The yield of dinitrobenzene from acid X, expressed as mols. per g.-mol. of the mixed acid, is given by XZ, since XZ measures the nitric acid consumed. We shall refer to the compositions shown along the curve of Fig. 1 as the " end-points " or " limiting compositions "—recognising these points rather as apparent end-points than as points of absolute cessation.

It was found that the presence of previously-added *m*-dinitrobenzene, representing the main product of the reaction itself, made little difference in the limiting composition attained (Expts. 13, 14), unless the nitrating acid was one containing relatively little sulphuric acid (Expts. 25—28) : here the added dinitrobenzene had a slight inhibiting effect. It is to be borne in mind that the addition of dinitrobenzene to a mixed acid, before nitration, simulates a nitration of mononitrobenzene which had begun with an acid of the same sulphuric content but with proportionately less water.

FIG. 1.

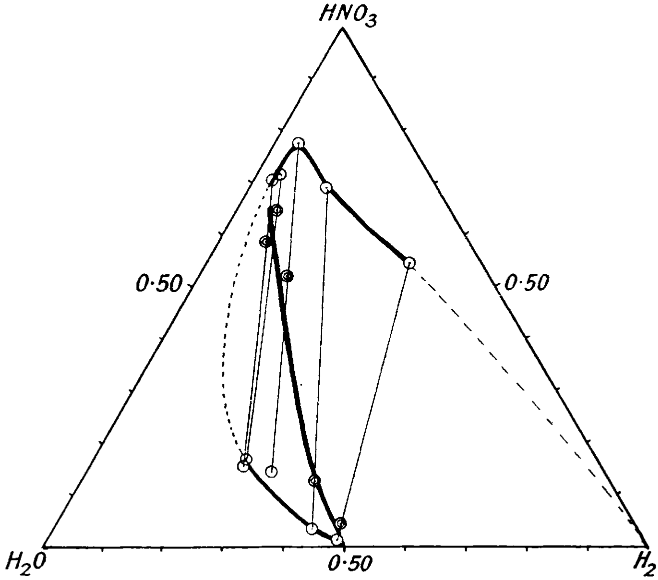


Showing change in molecular composition (mol fractions) of acids during nitration, and the curve of limiting compositions attained.

The end-point is definitely affected by superfluous mononitrobenzene, in the sense that the whole nitration goes more slowly and appears to cease at an earlier stage. For evidence of this, compare Expts. 2, 3, 4 with one another, and with 6 and 5; and the same is shown on comparing 7 with 9 (and 8, 10, which were more prolonged); 12 with 15; 16 with 13; and 26, 27, 28, 25 together. These experiments show that the line which is the limiting curve of Fig. 1 would be drawn rather as a crescent-shaped band, if we had to show the end-points of nitration not only with all conceivable acids but also with all proportions of excess nitrobenzene.

A question which arises is, how far is the inhibition of nitration connected with the formation of two phases in the nitration vessel? It can at once be said that heterogeneity is not what prevents the reaction going with " theoretical " completeness. As an extreme instance, a fairly concentrated, fuming nitric acid will dissolve much more than its chemical equivalent of nitrobenzene but nitrates none of it; and indeed, speaking generally, it happens that the mixtures best able to nitrate nitrobenzene are, approximately, those least able to dissolve it. Nevertheless, the formation of an "organic layer" does lessen the speed of arrival at the eventual end-point, however vigorously the layers are mixed; and we find two reasons for this. The physical excess of nitro-compound extracts from the acid a large quantity of nitric acid, and with it some sulphuric acid and water. One result is to lower the concentration of nitric acid in the inorganic layer and to reduce accordingly the speed of reaction in that layer. But further, we find that the extracted ternary acid contained in the organic layer, although it has a composition that would allow it easily to nitrate nitrobenzene, if it were synthetically made up afresh and mixed with its own equivalent of nitrobenzene or less, actually fails to react when dissolved in excess of that medium. In one experiment we interrupted a nitration which was still going on steadily, and separated the organic layer, with its dissolved acid, from the acid layer; and then, by direct trial and analyses, we found that the ability to nitrate more nitrobenzene was confined to the acid in the acid layer alone.

FIG. 2.



Molecular compositions of acid present in the organic layer (uppermost curve), in the acid layer (lowest curve), and in the aggregate (middle curve). The tie-lines show the conjunct layers.

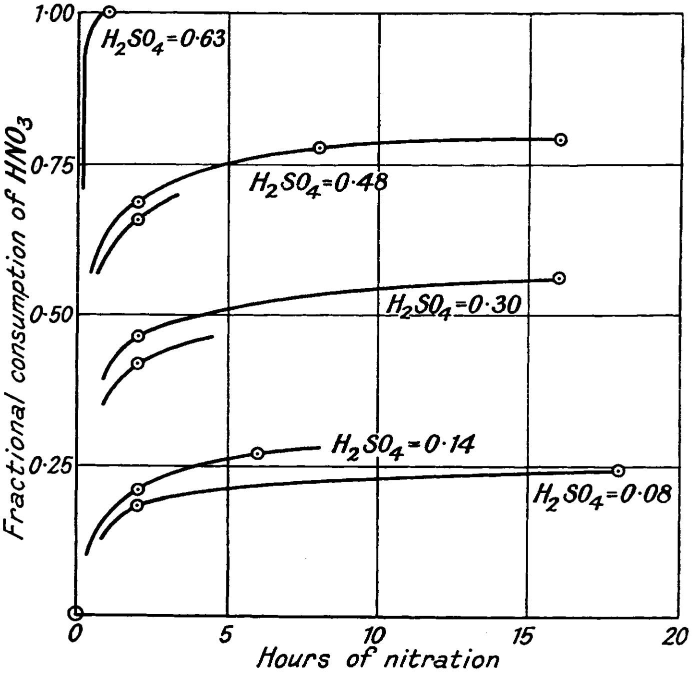
Evidently the reaction velocity in the organic medium is very small. Corresponding with this is the fact already mentioned, that excess of unused nitrobenzene, even when it is all in solution in the acid, both retards the reaction and sets back the end-point that is finally reached. A reason for these facts is discussed later; meanwhile, they show how it is better in this nitration to add the organic compound to the acid rather than vice versa.

Much of the evidence for the foregoing paragraphs is presented in Fig. 2. This shows the results of a series of distribution experiments (marked in the table by the letter D before their serial numbers), in which nitrating acids of various compositions were made up and shaken each with its "theoretical" stoicheiometric equivalent of nitrobenzene for 2 hours at 35°. (For strict comparison with the data of Fig. 1, a longer time of nitration would have been preferred, but was not practicable.) The two layers were then separated and analysed; and the compositions of the inorganic constituents of the two layers at the end of nitration are given in Fig. 2.

In this isothermal system of five components, two liquid phases and one vapour, the compositions of the acid in each liquid phase at the end of chemical reaction must necessarily depend upon the relative quantities of the two phases. Quantities other than those used here will furnish other distribution curves, and we duly observed this when carrying out the " interrupted " nitration mentioned on p. 108.

Among the partition experiments, one result is especially to be noted : nitrobenzene, shaken with aqueous sulphuric acid of composition H_2SO_4,H_2O (or slightly more aqueous) and not containing any nitric acid, dissolves only to a small extent in the acid but makes it weaker, by extracting apparently anhydrous sulphuric acid. In one of the two tests of this point, an acid of composition initially 0·490 mol. H_2SO_4 to 0·510 mol. H_2O was left as 0·441 H_2SO_4 to 0·559 H_2O when it was shaken with about twenty times its weight of nitrobenzene, while the nitrobenzene layer contained no measurable water but all the missing sulphuric acid. In another test, in which the acid and the nitro-compound were mixed in about equal weights, the molar fraction of sulphuric acid was reduced from 0·487 to 0·480, the change here being naturally less. The bearing of these facts is referred to later; it led to other work which proved the formation of the compound $PhNO_2,H_2SO_4$ (Masson, J., 1931, 3200).

FIG. 3.



Speed of consumption of nitric acid in certain nitrating acids with the molar fractions of H_2SO_4 *shown.*

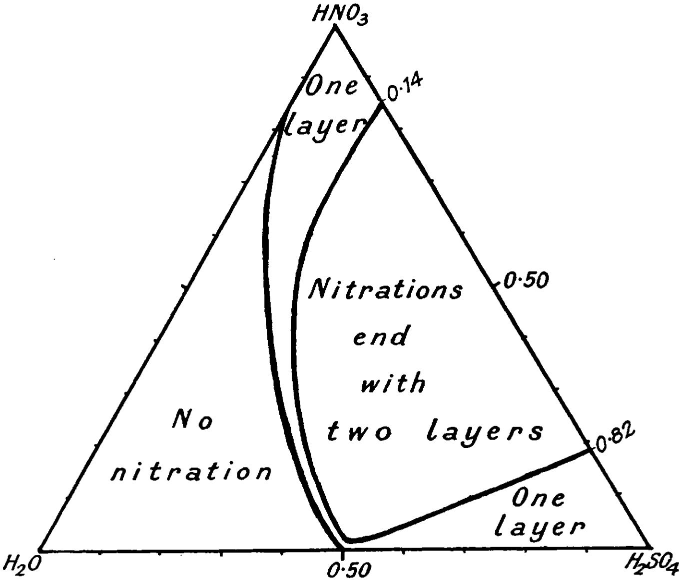
Velocities.—In the course of this work, we have analysed a number of nitrations which lasted for 2 hours, as well as others which were carried on for such times as 6, 8, or more hours (see experimental table); and the data thus afford approximate curves showing the relative speeds of nitration with different acids. Naturally, no velocity constant is to be expected from any ordinary nitration, owing to the great change in the medium as the reaction proceeds; but Fig. 3 shows the fractional consumption of nitric acid plotted against time, each point representing a separate nitration, and each curve referring to a fixed molar fraction of sulphuric acid in the acid. The chiefly notable thing is the great effect which the sulphuric acid content has upon the speed of nitration.

In this connexion it should be recalled that Martinsen (*Z. physikal. Chem.*, 1904, **50**,

385) measured the velocities of various nitrations, including that of nitrobenzene, when both the nitric acid and the organic reagent were added in quite small quantities to a large excess of sulphuric acid. This reaction followed the bimolecular law; and, unlike the nitration of phenol, it was not catalysed by nitrous acid. Martinsen's most aqueous solvent was of the composition H_2SO_4,H_2O; his strongest was a little over 100% H_2SO_4. He showed that in these two media the velocity constants were nearly equal, but that at intermediate compositions the constant rose to a maximum value about 15 to 20 times as great. The medium for fastest reaction was $0{\cdot}60H_2SO_4 + 0{\cdot}40H_2O$. Our own strongest acid happens to contain this proportion of sulphuric acid, and it gave our most rapid nitration, all the nitric acid being consumed at 35° in less than an hour from the first addition.

A study of Fig. 3 makes fairly plain the view already mentioned, *viz.*, that the self-stoppage of a nitration means that the reaction velocity has become extremely sensitive to increasing water content of the medium; or, more precisely, if k is a bimolecular velocity constant of nitration and w is the molar fraction of water in the whole medium, $-\,d^2k/dw^2$ becomes large in mixtures near the limiting curve.

FIG. 4.



Relation between final state of nitration mixture and molecular composition of initial acid.

That the influence of the water formed is too strong to be materially overcome even by the use of a higher temperature is shown in our experiments 18 and 19. These were alike except that No. 19 involved 4 hours' heating at 65—70° after they had both been carried on for 16 hours at 35°. Applying to this Martinsen's temperature coefficient of 3·5 per 10°, No. 19 had the equivalent of about 3 days' nitration at 35°, yet very little more of its nitric acid was consumed than in No. 18, which had only 16 hours (cf. table). These experiments, together with Fig. 3, give a measure of the finality of the " end-point."

Separation of Dinitrobenzene.—In order to specify more fully the physical conditions of the nitration of nitrobenzene, we determined the solubilities of dinitrobenzene in the " limiting " acids at 35° over the whole range. The results are used to make the curve of Fig. 4, in which is also drawn the limiting curve given in Fig. 1. The curved belt and wedge-shaped area marked " one layer " show the acids in which the nitration, as far as it will go, is physically homogeneous; whereas the area between the inner curve and the right-hand edge of the triangle shows acids which, when they have nitrated as far as they will, form a separate phase of dinitrobenzene. No separate organic layer is formed if the molar fraction of sulphuric acid in the nitrating acid is either greater than 0·82 or less than 0·14, whatever the nitric content of the initial acid. With compositions intermediate between 0·82 and 0·14 of sulphuric acid, homogeneity is obtained only if the initial nitric content be less than that marked by the inner curve, so as to give only a small yield before reaction ceases; but since such acids would not normally be used in practical nitration, heterogeneity is the ordinary result, as the diagram shows. When this happens, the physical excess of dinitrobenzene at 35° may appear either as a solid, or else liquefied owing to its m. p. being lowered by extracted nitric acid (together with small proportions of sulphuric acid and water). If the molar fraction of sulphuric acid in the nitrating acid is over 0·50 the dinitrobenzene is naturally formed as a solid, since there remains no unused nitric acid for it to extract. From a nitrating mixture with sulphuric acid between 0·50 and 0·14 the dinitrobenzene layer is liquid at 35° (because of extracted nitric acid) if the initial acid composition lies near and inside the inner curve; for then the yield of dinitrobenzene is necessarily small and its content of extracted nitric acid correspondingly high. If, however, the composition of the initial acid lies far inside the inner curve, as with acids likely to be used in practice, the yield of nitro-compound is greater and so the concentration of extracted nitric acid in the dinitrobenzene layer becomes too low to liquefy it at 35°. A similar condition would prevail at any other fixed temperature of nitration; but the border line between acid compositions yielding a liquid organic phase and those yielding a solid would be displaced to the right as the temperature used is higher. This border line has not been closely defined in our experiments at 35°, and is not drawn in the diagram.

The significance of Fig. 4 is that from it can be read, by inspection as indicated on p. 107, the maximum yield of dinitrobenzene obtainable from any acid, and the amounts of that product present respectively in the organic layer and in the spent acid layer at the end of the nitration at 35°. These quantities are expressed in mols. of dinitrobenzene per mol. of mixed (or of spent) acid; and it is assumed that only so much nitrobenzene is added as the acid will actually nitrate, a quantity defined by the limiting curve.

Theoretical Conclusions and Further Experiments.—The chief notable fact is the critical nature of acids in which the molar fraction of sulphuric acid is 0·5. In any acid poorer in sulphuric acid than this (cf. Fig. 1), the nitric acid is only partly available for the nitration; in this and any mixture richer in sulphuric acid, all the nitric acid readily nitrates nitrobenzene. We have made some experiments also in which *o*-nitrotoluene was nitrated to dinitrotoluene. The reaction, which is rather more rapid than with nitrobenzene, appears to be characterised by exactly the same type of end-point curve, starting at or very near the sulphuric monohydrate point and running up almost parallel with the curve of Fig. 1. It seems, then, that the sulphuric acid monohydrate point is not peculiar to the case of nitrobenzene.

The compound H_2SO_4,H_2O is well recognised; *e.g.*, it melts fairly sharply at 8·6°. Nitric acid forms two crystalline hydrates, $HNO_3,3H_2O$ and HNO_3,H_2O, melting respectively at — 18° and (with partial decomposition) at — 37°.

Our results accordingly entitle us to represent the primary condition for nitration to proceed at an appreciable rate as being controlled by the equilibrium

$$H_2SO_4 + HNO_3,H_2O \rightleftharpoons H_2SO_4,H_2O + HNO_3;$$

or, preferably adopting a more modern formulation,

$$H_2SO_4 + (H_3O)^{\cdot}(NO_3)' \rightleftharpoons (H_3O)^{\cdot}(HSO_4)' + HNO_3.$$

Further, as an outcome of this work, one of us has proved the formation of a stable complex, electrolytic in nature, between nitrobenzene and sulphuric acid (Masson, *loc. cit.*). Besides this, the high mutual miscibility of nitric acid and nitrobenzene (without any nitration occurring) suggests that these two can form a similar complex. This would be analogous to Hantzsch's " nitronium nitrate." Gibby's work in this laboratory (J., 1932, 1540) has shown the conditions under which the nitrobenzene–sulphuric acid complex freezes out in the presence of water; and the extent of its stability in solution in the presence of water is indicated in the partition experiments described on p. 109 of the present communication. There is clearly an equilibrium

$$(PhNO_2{\cdot}H)^{\cdot} + H_2O \rightleftharpoons PhNO_2 + (H_3O)^{\cdot}.$$

It was suggested (Masson, *loc. cit.*) that in the meta-nitration of nitrobenzene the immediate organic reagent is not molecular nitrobenzene, but the cation $(PhNO_2{\cdot}H)^{\cdot}$ of this complex. On this view, it is rather the group $(\text{–}NO_2H)^{\cdot}$ than the simple nitro-group which is responsible for the ensuing meta-substitutions in acid media.

Bringing together the foregoing observations, we have as antecedents to the nitration of nitrobenzene at least four interconnected equilibria, which may be formulated together :

$$\begin{aligned}
&\text{(i)}\ H_2SO_4 + (H_3O)^{\cdot}(NO_3)' \rightleftharpoons (H_3O)^{\cdot}(HSO_4)' + HNO_3\\
&\text{(ii)}\ H_2SO_4 + PhNO_2 \rightleftharpoons (PhNO_2{\cdot}H)^{\cdot}(HSO_4)'\\
&\text{(iii)}\ HNO_3 + PhNO_2 \rightleftharpoons (PhNO_2{\cdot}H)^{\cdot}(NO_3)'\\
&\text{(iv)}\ (PhNO_2{\cdot}H)^{\cdot} + H_2O \rightleftharpoons PhNO_2 + (H_3O)^{\cdot}
\end{aligned}$$

The ensuing bimolecular irreversible nitration itself will then take the course

$$\text{(v)}\ (PhNO_2{\cdot}H)^{\cdot} + HNO_3 \rightrightarrows C_6H_4(NO_2)_2 + (H_3O)^{\cdot}$$

That the nitrate ion could be the nitrating agent, instead of the anhydrous nitric acid molecule, appears to be excluded by the fact that fuming nitric acid, though it is rich in nitrate ions, will not appreciably nitrate nitrobenzene dissolved in it. As to the nature of the anhydrous nitric acid molecules, the present work furnishes no evidence.

The inhibiting effect of excess of mononitrobenzene is evidently due to its forcing equilibrium (ii) towards the right-hand side; this, by using up sulphuric acid, displaces (i) towards the left-hand side, with consequent lowering in the concentration of anhydrous nitric acid. The very strongly inhibiting effect of water is due, not only to its hydrating the acids, but also to reaction (iv), in which it decomposes the organic cation formed by nitrobenzene with the unhydrated acids, and thus removes what is held to be the immediately nitratable material (reaction v).

EXPERIMENTAL.

The nitrations were ordinarily carried out so as to treat 100—350 g. of nitrobenzene each, in loosely-closed long-necked flasks, specially altered to allow of quantitative siphoning of the reaction products. The wts. of all materials were measured to the nearest 0·01 g. For separating the products, after the mixture had been diluted with a weighed amount of H_2O, a weighed amount of $PhNO_2$ was added when it was necessary to liquefy the org. product for better separation and for the subsequent analysis. The resulting layers were then taken off with a capillary siphon and were weighed and analysed separately. With practice, transfer losses normally amounted to about 0·25 g. in a total mass of 500—1000 g.

The composition of all acids was found by using the nitrometer for HNO_3, combined with vol. determinations of total acidity. These were checked in some expts. by the direct grav. determination of H_2SO_4 as $BaSO_4$, with satisfactory concordance. HNO_2 was estimated with $KMnO_4$, but was never formed in significant quantity.

The $PhNO_2$ was made from a stock of the commercial material, for the gift of which we wish to thank the British Dyestuffs Corporation. This stock arrived partially frozen (Dec., 1929); the crystals were drained, melted, and again partly frozen at 0° and drained. The pale brown-yellow solid was melted and was dried over $Ca(NO_3)_2$ (which was insol. in it). It then had $d_{4°}^{15°}$ 1·209, and a setting point of 5·2°. It was tested for amino-compounds by diazotising and coupling with β-naphthol, and gave only a trace of azo-dye.

For analysing the org. nitration-product, the mixtures obtained were well washed (the washings being analysed with the acids) and were dried over $Ca(NO_3)_2$; their densities were then compared with those of synthetic mixtures of the $PhNO_2$ with $C_6H_4(NO_2)_2$, by means of a Westphal balance at 15°. The proportion of the latter in the former can in this way be determined within about 0·1%; the accuracy would be less if the proportion of isomerides varied materially. As a rule, the yield of dinitrobenzene found in this way agreed closely with the consumption of HNO_3; the only marked discrepancies occurred with acids of low H_2SO_4 content (see table).

The whole procedure was invariably checked by drawing up an analytical balance-sheet for all the constituents of each expt.; and for all except the preliminary series it was found on the whole very satisfactory. The table of data shows some evident errors, as when the final H_2SO_4 content and the initial are not equal (*e.g.*, Expts. 11, 19, 20), or when the HNO_3 consumption differs from the dinitrobenzene formed (*e.g.*, Expts. 22, 23, 29). Some of these were distribution expts., in which errors are doubled; and in prolonged expts., slight losses by fuming were inevitable. It may be recalled that the H_2O content, determined by diff., is the figure chiefly liable to error, and that this necessarily becomes magnified on being translated into molar fractions owing to the low mol. wt. of H_2O compared with the other compounds. The degree of fidelity of the analyses may be illustrated by quoting the molecular balance-sheet of quantities in one of the better expts. and in one of those only moderately satisfactory.

	Quantities in g.-mols.					
	Nitration 4.			Nitration 25.		
	Before.	After.		Before.	After.	
H_2SO_4	0·580	0·580		0·120	0·116	
HNO_3	0·434	0·078		1·147	0·901	
H_2O	0·203	0·556		0·249	0·558	
$PhNO_2$	1·737	1·385	1·738	0·381	0·122	0·368
$C_6H_4(NO_2)_2$ formed	—	0·353		—	0·246	
HNO_3 used	—	0·356		—	0·246	
H_2O formed	—	0·353		—	0·309	

Nitrations of Mononitrobenzene.

Relative molecular quantities.

		Initial reagents.					Final products.					
				Initial acid.			Spent acid.					
No.	Hours at 35°.	D.N.B. added.	M.N.B. added.	H_2SO_4.	HNO_3.	H_2O.	H_2SO_4.	HNO_3.	H_2O.	M.N.B. at end.	D.N.B. formed.	HNO_3 used.
1	1	—	18·8	62·9	18·8	18·3	62·9	0·0	37·1	0·0	18·8	18·8
2	2	—	35·6	47·6	35·6	16·8	48·8	2·0	49·2	2·2	33·4	33·4
D 3	2	—	78·3	47·2	35·7	17·1	47·2	4·4	48·3	49·5	28·8	31·2
4	2	—	142·8	47·6	35·6	16·8	47·8	6·4	45·8	113·8	29·0	29·2
5	16	—	104·5	47·6	35·6	16·8	47·9	2·4	49·7	72·0	32·5	33·2
6	30	—	1·5	46·9	1·3	51·8	46·5	0·0	53·5	0·2	1·2	1·3
7	2	—	42·5	40·8	42·5	16·7	41·0	13·4	45·6	14·0	28·5	29·1
8	8	—	42·5	40·8	42·5	16·7	41·0	9·5	49·5	10·3	32·2	33·0
9	2	—	169·9	40·8	42·5	16·7	41·2	14·6	44·2	141·9	28·0	27·9
10	16	—	104·2	40·8	42·5	16·7	41·1	8·8	50·1	71·5	32·7	33·6
D 11	2	—	40·4	40·3	40·4	19·3	38·9	12·9	48·2	12·8	27·6	27·5
12	2	—	55·5	29·8	55·5	14·7	29·8	29·8	40·4	30·0	25·5	25·7
13	16	—	55·5	29·8	55·5	14·7	29·0	24·1	46·9	25·0	30·5	31·3
14	13	24·1	30·7	29·0	50·3	20·7	29·8	22·0	48·2	3·3	27·4	28·3
15	2	—	133·0	29·8	55·5	14·7	29·9	32·3	37·8	110·3	22·7	23·2
16	9	—	3·6	27·9	25·5	46·6	27·6	20·5	51·9	0·3	3·3	5·0
17	9	—	6·5	28·1	21·1	50·8	28·4	18·1	53·5	3·7	2·8	3·0
18	16	—	58·2	24·8	58·2	16·9	25·1	30·5	44·3	31·0	27·2	27·7
19	(70)	—	58·2	24·8	58·2	16·9	25·6	27·7	46·7	28·9	29·3	30·5
D 20	2	—	65·4	16·1	65·6	18·3	14·7	51·9	33·4	52·5	12·9	13·7
21	2	—	210·2	14·4	70·0	15·6	14·4	55·3	30·3	197·2	13·0	14·6
22	6	—	162·0	14·4	70·0	15·6	13·4	51·1	35·5	147·8	14·2	18·9
D 23	2	—	73·8	8·5	73·5	18·0	7·8	58·6	33·5	64·9	8·9	14·9
24	2	—	103·3	7·9	75·7	16·4	7·1	62·1	30·8	93·9	9·4	13·7
25	18	—	25·1	7·9	75·7	16·4	7·4	57·2	35·4	8·9	16·2	18·5
26	19	—	5·8	7·0	57·9	35·1	7·0	50·2	42·9	0·6	5·2	7·7
27	21	18·1	17·0	7·0	57·9	35·1	7·4	54·8	37·8	14·8	2·2	3·1
28	20	24·6	17·0	6·8	68·4	24·8	7·0	58·1	34·9	9·6	7·4	10·3
D 29	2	—	74·9	6·9	74·9	18·2	6·6	64·7	28·7	67·6	7·3	10·2
30	24	—	82·8	—	83·3	16·7	—	82·8	17·2	80·6	2·2	0·4
31	5½	—	3·6	—	50·7	49·3	—	50·7	49·3	3·6	0·0	0·0

SUMMARY.

Systematic nitrations of nitrobenzene to dinitrobenzene, with full analyses, were made with a wide range of mixtures of sulphuric and nitric acids and water. Special application of triangular plotting is made to the results. The reaction is found to come to a standstill

before all the nitrobenzene and nitric acid are exhausted, unless there is enough sulphuric acid present to form H_2SO_4,H_2O with the water initially present *plus* that chemically formed. The same appeared to hold in nitrations with nitrotoluene. Whilst water is the chief inhibitor of the nitration of nitrobenzene, dissolved nitrobenzene itself acts in the same direction.

The conditions under which two layers are formed in the nitration are defined experimentally and plotted. Distribution measurements, and others, prove that the seat of reaction in a two-phase nitration is the acid layer; not the organic layer, despite the considerable concentrations of strong acids dissolved in it.

The promoting action of sulphuric acid, the inhibiting action of water, and the inhibiting action of nitrobenzene are traced to the reversible hydration of the two acids concerned and to competition between nitrobenzene and water for union with sulphuric acid (cf. Masson, J., 1931, 3200). The suggestion is renewed that the real organic agent in meta-nitration is the complex cation $Ph{\cdot}NO{\cdot}OH^+$ rather than molecular $PhNO_2$; and the results as a whole point to the equilibria formulated on p. 112 as essential to this nitration.

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