160. *The Kinetics of Aromatic Halogen Substitution. Part VII. Nitrosobenzene and Azobenzene.*

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The reaction between bromine and nitrosobenzene in carbon tetrachloride shows a period of induction, and in the presence of hydrogen bromide proceeds at a rate 10^{10} times as fast as the bromination of benzene under the same conditions. Hydrogen bromide is consumed in the process, and is also found to react with nitrosobenzene in carbon tetrachloride by a very fast reaction. A mechanism is proposed involving, as the first stage, the formation of the compound PhNBr·OH, which after rearrangement further reacts with bromine to form the various products. Azobenzene gives a measurable reaction with bromine in acetic acid at 35° only in the presence of hydrogen bromide, and here also the first stage appears to involve the preliminary addition of hydrogen bromide. Water decelerates this reaction to an unmeasurable rate in 20% aqueous acetic acid, and in the same mixed solvent chlorine reacts with azobenzene at a slow rate, five times as fast as with benzene.

Nitrosobenzene on bromination in carbon disulphide readily forms *p*-bromonitrosobenzene to the extent of as much as 40%, together with other compounds, of which *pp'*-dibromoazoxybenzene is present in the greatest amount (Ingold, *J.*, 1925, 513); likewise in benzene solution there is rapid formation of *p*-bromonitrosobenzene (Le Fèvre, *J.*, 1931, 810). This easy *para*-bromination of nitrosobenzene is unexpected, as the nitroso-group, although it can exert a $+T$ effect, has $-T$, $-I$ characteristics also; its dipole moment (3·2 D., directed away from the benzene ring) is greater than that of a *tert.*-alkyl nitroso-compound, a condition that usually determines *meta*-substitution and a slow rate of reaction. It has been suggested that the reaction taking place is the bromination of a dimer (Hammick *et al.*, *J.*, 1934, 29). We find from light-absorption measurements that there is very little difference in the intensity of colour of solutions of nitrosobenzene in acetic acid (in which the solute is unimolecular), carbon disulphide, and carbon tetrachloride, over the concentration range, M/40—M/160, at 16°. It seems probable that the concentration of the dimer in these solutions is too small to cause the rapid reactions that are observed, even if it should have a constitution favourable for *op*-substitution.

Nitrosobenzene reacts with bromine in carbon tetrachloride at a variable rate, and on examination of the solutions in a dim light a period of induction may sometimes be observed, the start of the reaction being indicated by a cloudiness spreading through the liquid. With added hydrogen bromide, there is no period of induction, and the reaction becomes moderately reproducible, a reaction mixture containing nitrosobenzene (M/80), bromine, (M/80), and hydrogen bromide (M/400) having a half-reaction time of three minutes at 17°; rising bimolecular coefficients indicate the autocatalytic nature of the process.

% bromine absorption (x)	20	30	40	50	60	70
k_2 (min.$^{-1}$ g.-mol.$^{-1}$ l.)	20	23	25	27	30	35

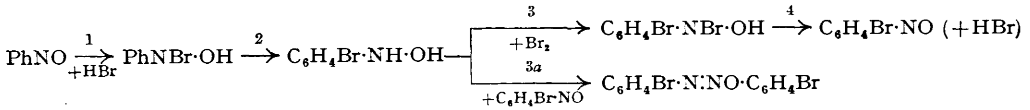
In these experiments, the reaction was stopped by shaking the solution with aqueous potassium iodide, and it was established that iodine which entered the organic phase during the titration was not acting as a catalyst, though the opposite is usually found for bromination in carbon tetrachloride.

It is instructive to compare the rates of bromination of nitrosobenzene and mesitylene. The latter has been shown to halogenate about 10^8 times faster than benzene (*J.*, 1943, 276), and therefore about 10^9 times faster than chlorobenzene (*J.*, 1948, 100). Catalysis by hydrobromic acid of its bromination (reactants, M/40, in carbon tetrachloride at 25°) results in only a threefold increase of rate with M/10-catalyst, the initial rate under these conditions being given by $k_2(x = 10) = 0{\cdot}3$. Thus nitrosobenzene, which brominates only slowly in the absence of a catalyst, reacts with bromine some 100 times as rapidly as mesitylene (and hence perhaps 10^{10} times as rapidly as benzene), when hydrobromic acid is added, despite the expected deactivation of the aromatic ring by the nitroso-group. These facts indicate that the bromination of nitrosobenzene proceeds by some mechanism other than that of normal electrophilic substitution. An atom-chain mechanism appears to be excluded as the rate of reaction is insensitive to light, and is the same in a nitrogen atmosphere as in the presence of air, the oxygen of which might oxidise the hydrogen bromide and initiate chains.

In another series of experiments in carbon tetrachloride the rates were measured by stopping the reaction with a dilute solution of sodium peroxide, and titrating the bromide ion produced. Part of the total bromine could not be accounted for, owing to the fact that some of the bromine of the hydrogen bromide formed had entered the benzene ring. The reaction, measured in this way, was found to proceed at a similar fast rate, and with M/80- (and also M/40-) reactants the disappearance of hydrogen bromide amounted to about 45% of that which should have been produced by substitution.

The reaction between nitrosobenzene and hydrogen bromide was examined kinetically. With M/80-reactants in carbon tetrachloride at 17°, the reaction proceeded rapidly to 50% absorption (0·7 minute), and stopped with about 70% absorption of the hydrogen bromide. The products of this reaction were found by Bamberger *et al.* (*Ber.*, 1899, **32**, 210) to be *p*-bromophenylhydroxylamine, *pp'*-dibromoazoxybenzene, *p*-bromoaniline, and 2 : 4-dibromoaniline. As *p*-bromophenylhydroxylamine is an intermediate product, we have also studied the reaction between phenylhydroxylamine and bromine. With M/40-reactants in carbon tetrachloride at 17°, 80% of the bromine was absorbed in about 0·7 minute, and a further 5% more slowly. The products of this reaction included a dark, slightly soluble material, and *p*-bromonitrosobenzene.

The results of these various rate-measurements, and the experiments by Ingold and by Bamberger, provide evidence for establishing a probable mechanism for the bromination of nitrosobenzene. The reaction begins by the addition of hydrogen bromide to the nitrosobenzene, and then proceeds as now indicated, all the changes being rapid ones.

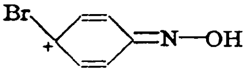


$$\begin{tikzcd} PhNO \arrow[r, "1", "+HBr"'] & PhNBr\cdot OH \arrow[r, "2"] & C_6H_4Br\cdot NH\cdot OH \arrow[r, "3", "+Br_2"'] \arrow[dr, "3a", "+C_6H_4BrNO"'] & C_6H_4Br\cdot NBr\cdot OH \arrow[r, "4"] & C_6H_4Br\cdot NO\ (+HBr) \\ & & & C_6H_4Br\cdot N{:}NO\cdot C_6H_4Br & \end{tikzcd}$$

Stage 2 in this scheme is analogous to the conversion of *N*-bromoacetanilide into the *p*-bromo-derivative; stages 3 and 4 are to be expected as a similar change takes place on the bromination of phenylhydroxylamine, and stage 3*a* takes place by condensation of the *p*-bromophenylhydroxylamine with *p*-bromonitrosobenzene. An alternative side-reaction proceeding to a limited degree appears to be, $C_6H_4Br{\cdot}NH{\cdot}OH \longrightarrow C_6H_3Br(OH){\cdot}NH_2 \longrightarrow C_6H_3Br(OH){\cdot}N{:}N{\cdot}C_6H_4Br$, as we have found that on treating the reaction product with aqueous alkali a yellow solution is obtained. This is consistent with the intermediate formation of *p*-bromophenylhydroxylamine, as its change to 4-bromo-2-hydroxyphenylhydroxylamine is known to take place.

With equimolecular amounts of nitrosobenzene and bromine about 10% of the bromine remains unconsumed, and since about 45 molecules % of hydrogen bromide are used in proceeding by route 3*a*, about one quarter of the total bromine must take part in the formation of more highly substituted products. As, according to Bamberger, *p*-bromoaniline is produced by the action of hydrogen bromide on nitrosobenzene, this would be brominated to form tribromoaniline. Another change requiring more bromine is, $C_6H_4Br{\cdot}NBr{\cdot}OH \longrightarrow C_6H_3Br_2{\cdot}NH{\cdot}OH \longrightarrow C_6H_3Br_2{\cdot}NO{\cdot}N{\cdot}C_6H_4Br$, and tribromoazoxybenzene has been identified as a product (Hammick *et al.*, *loc. cit.*).

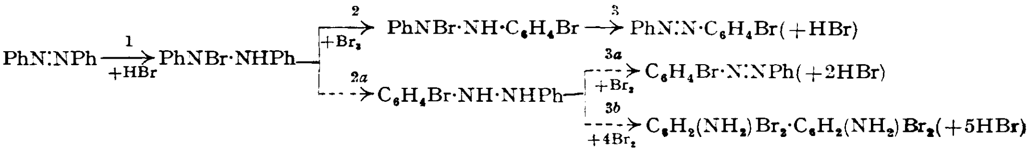
The reactivity of the bromine in *p*-bromonitrosobenzene has been discussed in connexion with the anomalous bromination of nitrosobenzene. This bromo-compound reacts with silver nitrate in acetic acid solution not only more rapidly than *p*-bromonitrobenzene but even more rapidly than picryl bromide (Le Fèvre, *loc. cit.*). Here also a reaction involving initial addition to the nitroso-group is not excluded, or it may be possible that the reactive molecule is



Azobenzene, on monobromination in acetic acid, forms *p*-bromoazobenzene (Janovsky and Erb, *Ber.*, 1886, **19**, 2156; 1887, **20**, 357; Burns, McCombie, and Scarborough, *J.*, 1928, 2928). We have now made a kinetic study of this reaction. A freshly prepared solution of M/40-bromine in acetic acid did not react with M/40-azobenzene (at 35°) during 16 hours. If this bromine solution is kept a fortnight or illuminated for several hours (both of which procedures have been found to cause the formation of a small amount of hydrogen bromide), or if hydrogen bromide is added, the reaction then proceeds. In the presence of sodium acetate or water, the reaction is inhibited. The bromination of azobenzene can be examined only with small amounts of hydrogen bromide, as this causes the formation of an insoluble salt, $PhN{:}NPh,HBr_3$, and for this same reason the reaction can be followed kinetically only during the initial stages under the selected experimental conditions. The rates determined with M/40-azobenzene and M/40-bromine at 35°, in acetic acid solution which contained (*ca.* M/1000-) hydrogen bromide and varying amounts of added water, are:

H_2O (%)	0	10	25
k_2 ($x = 5$)	0·05	0·0040	~0

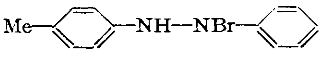
The effect of water on normal electrophilic substitution is to cause a considerable increase in the rate of reaction. It is evident that in the bromination of azobenzene a special mechanism operates involving the participation of hydrogen bromide. It was further found that hydrogen bromide very slowly added to azobenzene, giving a product in which the bromine no longer reacted with silver nitrate. It is therefore proposed that the first stage in the bromination of azobenzene proceeds by the addition of hydrogen bromide:

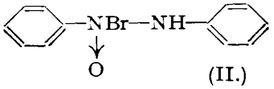


$$\begin{tikzcd} PhN{:}NPh \arrow[r, "1", "+HBr"'] & PhNBr\cdot NHPh \arrow[r, "2", "+Br_2"'] \arrow[dr, dashed, "2a"] & PhNBr\cdot NH\cdot C_6H_4Br \arrow[r, "3"] & PhN{:}N\cdot C_6H_4Br(+HBr) \\ & & C_6H_4Br\cdot NH\cdot NHPh \arrow[r, dashed, "3a", "+Br_2"'] \arrow[dr, dashed, "3b", "+4Br_2"'] & C_6H_4Br\cdot N{:}NPh(+2HBr) \\ & & & C_6H_2(NH_2)Br_2\cdot C_6H_2(NH_2)Br_2(+5HBr) \end{tikzcd}$$

As the bromination of azobenzene is very considerably faster than its reaction with hydrogen bromide, the change is considered to proceed chiefly by stages 2 and 3. Route 2*a* appears to be followed to some extent, however, and it is possible that tetrabromobenzidine, identified as a product by Mills (*J.*, 1894, 54), arises in this way, *via* a benzidine change and subsequent bromination (route 3*b*).

The theory involving the prior addition of hydrogen bromide in the bromination of azobenzene explains also the behaviour of related compounds. Under the conditions in which azobenzene is brominated, *p*-methylazobenzene does not react (Burns *et al.*, *loc. cit.*); the difference in the electronegativity of the nitrogen atoms in this compound causes the formation of the addition product (I), which, according to the scheme proposed, is unreactive, since the position *para*- to the amino-group is blocked.

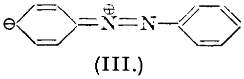

(I.)


(II.)

Azoxybenzene, which, like azobenzene, reacts with bromine in acetic acid only in the presence of hydrogen bromide, would give preferably the addition compound (II) and this would be substituted in the benzene ring not attached to the NO group, as is found experimentally.

The chlorination of azobenzene, like its bromination, does not proceed with a freshly prepared solution of chlorine in acetic acid, but only when hydrogen chloride is present. Water added to the acetic acid solution causes the rate to increase towards the true electrophilic rate. Such a reaction was not observed with bromine because the substitution is slower by several powers of ten than chlorination, and becomes unmeasurable. The rate of chlorination of azobenzene in 20% aqueous acetic acid at 25° ($k_2 = 0{\cdot}055$) is about five times that for benzene ($k_2 = 0{\cdot}012$) under the same conditions.

Although azobenzene, like nitrosobenzene, has lone pairs of electrons on the nitrogen atoms capable of conjugation with the aromatic ring (structures III, IV, V), such conjugation appears not to be favoured, since the C–N and N–N bond lengths in azomethane and azobenzene are almost identical (Brockway, *Rev. Modern Physics*, 1936, **8**, 231; Hampson and Robertson, *J.*, 1941, 409). Such structures apparently contribute to an extremely limited extent to the polarisability of the molecule, since it has now been shown that azobenzene reacts with chlorine only a little faster than benzene, and, correspondingly, the apparently fast bromination of nitrosobenzene involves a special mechanism. The relative unreactivity of these compounds to electrophilic halogenation should be contrasted with the great reactivity of acetanilide and aniline; the former compound brominates about as rapidly as mesitylene (Part I, *J.*, 1943, 276), and therefore some 10^8 times faster than benzene.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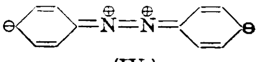
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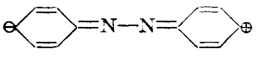
(V.)

EXPERIMENTAL.

The nitrosobenzene was prepared as required and was kept in a refrigerator before use; the different samples melted at 67°.

Typical rate measurements of bromine absorption are: M/80-PhNO + M/80-Br_2 + M/400-HBr; 8 ml. in CCl_4 at 17°; 20 ml. of KI + 20 ml. of N/80-$Na_2S_2O_3$ added; 8 ml. of this aqueous solution titrated with N/200-I_2.

Time (mins.)	0	2	5	10	12	1	3	6·5	8
Titre (ml.; average)	2·0	4·2	7·8	8·7	9·0	3·25	5·6	8·7	9·1
Bromine absorption (%)	0	27	73	84	88	15	45	83	89

These values give a smooth curve, as did other values obtained in experiments under nitrogen and under air.

A rate measurement in which bromine and hydrogen bromide were determined gave the following results:

M/80-PhNO + M/80-Br_2 + M/400-HBr; 8 ml. in CCl_4 at 17°; 10 ml. of dilute Na_2O_2 soln. were added, and 4 ml. of aqueous soln. were removed, acidified with acetic acid, and titrated with N/20-$AgNO_3$ (eosin):

Time (mins.)	0	1	2	4	6	10	20
Titre (ml.; average)	3·44	2·78	2·50	1·78	1·46	1·28	1·16
Br_2 + HBr absorption (%)	0	42	60	106	127	139	147

Other runs gave similar results, and the average of 10 runs, with reaction times 20 to 60 minutes, showed 145% absorption.

M/40-PhNO + M/40-HBr; 8 ml. in CCl_4 at 17°; titrations as in the experiment just described :

Time (mins.)	0	3	7	20
Titre (ml.)	3·1	1·2	1·1	0·9
HBr absorption (%)	0	61	65	70

M/40-PhNH·OH + M/40-Br_2; in CCl_4 at 17°.

Time (mins.)	0·7	2	8
Bromine absorption (%)	84	87	87

Azobenzene, m. p. 66—67°, and azoxybenzene, m. p. 34—35°, were used for the following measurements: M/40-Azobenzene + M/40-Br_2 + approximately M/1000-HBr at 35° in acetic acid; $x = 5, t = 42$; $x = 10, t = 100$ (at about $x = 10\%$ absorption of bromine, solid began to be deposited); in acetic acid containing 10% water, $x = 5$, $t = 500$. Other measurements, with bromine and an unknown amount of hydrobromic acid, similarly showed slower rates in aqueous than in glacial acetic acid, and also were subject to considerable retardation by added sodium acetate. M/40-Azoxybenzene + M/40-Br_2 + approximately M/1000-HBr; $x = 5$, $t = 100$. Both water and sodium acetate also reduced the rate of bromination of this compound. M/40-Azobenzene + M/40-Cl_2 in acetic acid containing 20% water at 25°, $x = 10$, $t = 80$.

The relative absorption by nitrosobenzene in different solvents was compared by use of a photoelectric colorimeter, for the red light of a mercury-vapour lamp. The following percentage transmissions were recorded at 16°: M/40-solution, in CCl_4, 38; in acetic acid, 36; in CS_2, 37; M/80-solution, in CCl_4, 52·5; in acetic acid, 52·5; in CS_2, 53·5.

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