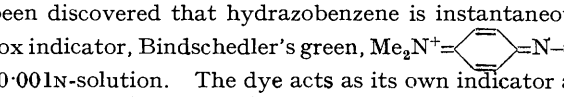
160. *The Kinetics of Some Benzidine Rearrangements, and a Note on the Mechanism of Aromatic Substitution.*

By M. J. S. Dewar.

Hydrazobenzenes can be estimated in presence of their rearrangement products by titration with Bindschedler's green. In this way the rates of rearrangement at 0° and 22·7° of hydrazobenzene, *o*-hydrazoanisole, m-*hydrazoanisole*, and *p*-hydrazotoluene have been determined, and activation energies calculated. The reactions were unimolecular. Only the salts appeared to rearrange. The results support the new mechanism recently put forward (Dewar, *Nature*, 1945, **176**, 784; this vol., p. 406) and are at variance with other electronic mechanisms that have been suggested. The theory of π-electron sharing is extended to cover aromatic substitution; certain anomalies in the older theories may thus be avoided.

It was suggested recently (Dewar, *loc. cit.*) that various rearrangements of the benzidine type could be readily interpreted in terms of a new concept—that of a bond formed by sharing of π-electrons between aromatic systems and not by localised electron-pairs shared between definite atoms. This theory also explains various other reactions of aromatic and olefinic compounds, and it was therefore desirable that definite evidence for it should be sought; the present paper describes experiments carried out with that object. These have centred on the benzidine rearrangement itself, since, in spite of its inherent interest and importance, it has been little investigated in recent years. The rates of several such rearrangements have now been determined and the results do indeed appear to support the new theory.

The only kinetic investigation of benzidine rearrangements that has been previously reported was that of Biilmann and Blom (*J.*, 1924, **125**, 1719), who followed the rearrangements of *m*- and *p*-hydrazoaniline by an ingenious potentiometric method. Unfortunately, their procedure was neither convenient nor theoretically satisfactory, and their results were somewhat inconsistent; nor did they extend their measurements to simpler cases where the data might have been more easily interpreted.

It is difficult to follow these rearrangements quantitatively, since the products are so complex: in addition to derivatives of diphenyl and diphenylamine, azo-compounds and amines are always formed by a disproportionation (see Ingold and Kidd, *J.*, 1933, 984). It is not easy to estimate hydrazobenzene in the presence of these substances, and the authors cited found iodine titration and estimation with Fehling's solution inadequate for the purpose. It has now been discovered that hydrazobenzene is instantaneously and quantitatively oxidised to azobenzene by the redox indicator, Bindschedler's green,  , and can be titrated with the dye even in 0·001N-solution. The dye acts as its own indicator and the products of the rearrangements do not interfere with the estimation. In this way the rearrangements of hydrazobenzene, *o*-hydrazoanisole and m-*hydrazoanisole*, and also the semidine rearrangement of *p*-hydrazotoluene, have been investigated at 0° and 22·7°; in the last case the velocity constants are less reliable, since the semidine was attacked by the oxidising agent.

Experimental.

Materials.—Hydrazobenzene, *o*-hydrazoanisole, and *p*-hydrazotoluene were prepared by standard methods and crystallised several times from alcohol; their properties agreed with those given in the literature. No details for the preparation of Bindschedler's green were available; the following procedure was satisfactory. Zinc dust was added to a solution of *p*-nitrosodimethylaniline hydrochloride (18·7 g.; 0·1 g.-mol.) in hydrochloric acid (200 c.c. of 20%), the temperature being kept below 30°. When the solution was no longer yellow, the zinc was filtered off and washed with a little water. The combined filtrates were mixed with a solution of dimethylaniline (12·1 g., 0·1 g.-mol.) in hydrochloric acid (100 c.c. of 20%), cooled to 0°, and a saturated solution of potassium dichromate (19·2 g.) in water added with stirring. After 20 minutes the zincichloride of the dye was collected, washed with ice-water, alcohol, and ether, and dried in an oven. This material (28—30 g.) was pure enough for the present purpose (98·6% by titration with titanous sulphate).

m-*Hydrazoanisole.*—A mixture of *m*-nitroanisole (62·5 g.), methanol (250 c.c.), sodium hydroxide (70 g.), and water (50 c.c.) was heated under reflux and stirred mechanically while zinc dust (135 g.) was gradually added, and heating was then continued till the solution was colourless (2 hours). When it was cold, chloroform (750 c.c.) was added, the zinc filtered off and washed with chloroform, and the combined chloroform extracts evaporated under reduced pressure. The resulting m-*hydrazoanisole* crystallised on scratching with light petroleum and was then recrystallised from carbon tetrachloride, forming large, pale yellow, rectangular tablets, m. p. 59—60° [Found: C, 68·5, 68·6; H, 6·5, 6·8; N, 11·3; OMe, 25·2. $C_{12}H_{10}N_2(O{\cdot}CH_3)_2$ requires C, 68·8; H, 6·6; N, 11·5; OMe, 25·4%).

m-*Azoanisole.*—Prepared from the hydrazine by iodine oxidation, m-*azoanisole* crystallised from methanol in large, orange-brown plates, m. p. 78—79° (Found: C, 69·0; H, 5·9. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%).

Procedure.—Equal volumes of hydrazobenzene solution (*ca.* 0·02N) and catalyst solution (0·2N) were mixed in an inert atmosphere, and at intervals portions were removed for analysis. In the more rapid reactions a batch method was necessary. The estimations of hydrazobenzene and its methoxyl derivatives were effected by addition to excess of standard Bindschedler's green solution and back-titration with titanous sulphate (both *ca.* 0·01N). This method was not suitable for *p*-hydrazotoluene, since the semidine formed by rearrangement was attacked by the dye; consistent results were, however, obtained by direct titration with the dye, provided that this was carried out rapidly and that the concentration of semidine was not too great. The dye solutions were somewhat unstable; they were standardised at half-hour intervals and always used within four hours of preparation. During rearrangement, the catalyst is removed by salt formation with the basic products; with the concentrations used the resulting decrease in rate was not appreciable.

Table I.

o-*Hydrazoanisole*; 0·1M-$H{\cdot}CO_2H$; 0·1M-$H{\cdot}CO_2Na$; 80% EtOH; 22·7°.

t, mins.	*x*, obs.	*x*, calc.	$10^4\times$ 0·4343*k*.	*x*, obs.	*x*, calc.	$10^4\times$ 0·4343*k*.	*t*, mins.	*x*, obs.	*x*, calc.	$10^4\times$ 0·4343*k*.	*x*, obs.	*x*, calc.	$10^4\times$ 0·4343*k*.
0	24·4	—	—	21·1	—	—	28	15·4	15·3	1·19	$13{\cdot}0_5$	13·2	1·24
8	21·3	21·3	1·23	$18{\cdot}4_5$	18·5	1·21	32	$14{\cdot}4_5$	14·3	1·18	12·4	12·4	1·20
12	$19{\cdot}9_5$	20·0	1·21	$17{\cdot}2_5$	17·3	1·22	36	13·6	13·4	1·18	$11{\cdot}5_5$	11·6	1·21
16	18·7	18·7	1·20	16·1	16·2	1·22	40	12·6	12·5	1·20	$10{\cdot}7_5$	10·8	1·22
20	17·4	17·5	1·22	15·0	15·1	1·23	44	$11{\cdot}8_5$	11·7	1·19	10·0	10·1	1·23
24	16·4	16·4	1·20	$14{\cdot}1_5$	$14{\cdot}1_5$	1·21	48	11·1	11·0	1·19	—	—	—
							52	$10{\cdot}3_5$	10·2	1·18	—	—	—

Table II.

	Catalyst.	Solvent.	10^5k. (0°).	10^4k (22·7°).	Frequency factor.	*E*, cals.
Hydrazobenzene	HCl	EtOH	271 ±3	322 ±11·5	$2{\cdot}8\times10^{11}$	17,610
Hydrazobenzene	HCl	75% EtOH	3·55 ±0·07	4·05 ±0·05	$2{\cdot}1\times10^{9}$	17,320
o-Hydrazoanisole	$H{\cdot}CO_2H$–$H{\cdot}CO_2Na$	80% EtOH	4·57 ±0·04	2·77 ±0·03	$7{\cdot}2\times10^{5}$	12,820
m-Hydrazoanisole ...	HCl	75% EtOH	6·82 ±0·03	10·85 ±0·16	$3{\cdot}1\times10^{11}$	19,680
p-Hydrazotoluene ...	$CH_2Cl{\cdot}CO_2H$–$CH_2Cl{\cdot}CO_2Na$	75% EtOH	4·10 ±0·14	2·20 ±0·10	$1{\cdot}3\times10^{5}$	11,950
Hydrazobenzene	$CCl_3{\cdot}CO_2H$	75% EtOH	—	0·788 ±0·019	—	—

Results.—Preliminary experiments established the following points. The rearrangements were unimolecular (cf. Bülmann and Blom, *loc. cit.*). Rearrangement in alcoholic hydrogen chloride at room temperature was extraordinarily fast; that of *o*-hydrazoanisole was virtually instantaneous. On the other hand, hydrazobenzene was little affected by 0·1N-alcoholic trichloroacetic acid (*ca.* 3% conversion in 6 hours at 22·7°). In anhydrous formic acid rearrangement was extremely rapid, in glacial acetic acid very slow. Azo-compounds were formed in all cases as by-products (cf. Ingold and Kidd, *loc. cit.*).

Accurate measurements of rate were carried out at 0° in a bath of melting ice and at 22·7°±0·02° in a thermostat. In Table I two typical experiments are given in full to illustrate the consistency and reproducibility of the results. All the calculated values of x (the titre at time t) were derived from the same mean unimolecular rate constant($2{\cdot}77 \times 10^{-4}$). In Table II are given mean unimolecular rate constants and mean deviations, together with activation energies and frequency factors calculated from them. Unfortunately, no suitable thermostat was available for further measurements at a higher temperature, but it is thought unlikely that the activation energies are in error by as much as 400 cals.

Discussion.

The rearrangement of hydrazobenzene, when catalysed by hydrogen chloride, is much faster in alcohol than in aqueous alcohol, but with trichloroacetic acid as catalyst the reverse is true. The ratio of the rates in alcohol is very great. These results suggest strongly that rapid and reversible salt formation precedes rearrangement, and that the reaction therefore exhibits specific catalysis by oxonium ions. The rate depends on the concentration of salt present in equilibrium. Trichloroacetic acid is a weak acid in absolute alcohol; therefore in alcoholic trichloroacetic acid little of the hydrazobenzene is present as its salt, and rearrangement is slower than in aqueous alcohol where the acid is more highly dissociated. With hydrochloric acid as catalyst, on the other hand, the rate is greater in alcohol, since hydrochloric acid is a strong acid in both solvents and the ethyloxonium cation is more strongly acidic than oxonium. In this case salt formation is more complete in the absence of water.

The activation energies of the hydrochloric acid-catalysed rearrangements in alcohol and in aqueous alcohol were the same within the limits of experimental error, the difference in rates being due mainly to a change in the frequency factor; this is easily understandable if the rate-determining step is not the formation but the rearrangement of the salt. It was fortunate that the activation energies were apparently independent of the conditions used. The range of velocities observed was much too great for study under any one set of conditions.

It had appeared extremely unlikely for other reasons that salt formation could be the rate-determining step in these rearrangements. Hydrazobenzene and its derivatives are appreciably basic, forming salts in aprotic solvents (Orelkin, Rysskaltschuk, and Aisikowitsch, *J. Gen. Chem. U.S.S.R.*, **1931**, **1**, 696). Analogy with aniline, diphenylamine, and phenylhydrazine, where the introduction of each phenyl group raises the basic pK by about 4 units, suggests that hydrazobenzene should have a pK of *ca.* 14. Slow proton transfer to a nitrogen atom with this order of basicity is extremely improbable.

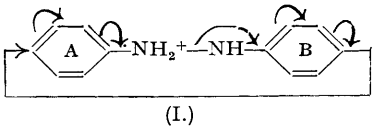
If we correct the frequency factors for the benzidine rearrangements in Table II for the varying concentrations of hydrazobenzene salt present under the operative conditions, assuming that acids have similar dissociation constants in water and in aqueous alcohol, the corrected frequency factors vary little and the variations may well be due to small differences in basicity. The entropies of activation of all these rearrangements must then be similar, and the activation energies are a true measure of the potential energy of activation. The order of decreasing ease of rearrangement is then *o*-hydrazoanisole $\gg$ hydrazobenzene $>$ *m*-hydrazoanisole. The corrected frequency factors were, moreover, normal for unimolecular reactions.

The semidine rearrangement of *p*-hydrazotoluene was abnormal, however, being evidently a "slow" reaction; the low frequency factor cannot be ascribed to a basicity effect, since hydrazotoluene must be at least as strong a base as hydrazobenzene. Here the entropy of activation must be abnormally small.

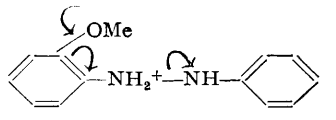
The mechanism proposed by Ingold and Kidd (*loc. cit.*; see Hughes and Ingold, *J.*, **1941**, 691) differs mainly from that of Robinson (*J.*, **1941**, 220) in supposing that salt-formation accompanies rearrangement. As we have seen, the evidence does not support this idea; salt formation appears to precede rearrangement.

The mechanism proposed by Robinson involves the electronic processes (I). The detailed theory involves a concept of electronic oscillations, which has been criticised, but an equivalent quantum-mechanical interpretation can be given. Hughes and Ingold also objected to this mechanism on the grounds that it requires electrons to recede from a positive centre. Certainly such a displacement could only be possible if appreciable bonding between the *p*-positions preceded fission of the N–N bond. In the transition state for such a process, however, the rings could not approach much closer than 4 A.; even in molecular complexes the interannular distance is 3·5 A. (Powell, Huse, and Cooke, *J.*, **1943**, 153). It is difficult to believe that a C–C link 4 A. long and distorted at both ends could have appreciable strength, and the N–N bond would have been stretched out of existence before the carbon atoms approached within that distance.

The present work provides definite evidence against such bonding. Since it would involve anionoid attack by the *p*-position of ring B on the *p*-position of ring A, it should be facilitated by methoxyl in the position *meta* to nitrogen in ring B. A *m*-methoxyl in ring A should have little influence, its electromeric effect not being



(I.)



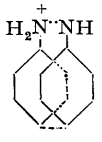
(II.)

called into play. Therefore this theory would require *m*-hydrazoanisole to be rearranged much more readily than hydrazobenzene. On the other hand, *m*-methoxyl is a cationoid group as shown by its effect on the dissociation constants of acids and bases and on the rates of various reactions; therefore in *o*-hydrazoanisole the methoxyls should deactivate both rings, and rearrangement should be less facile than that of hydrazobenzene. The order of rates so predicted is diametrically opposite to that observed.

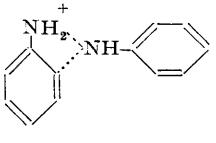
Hammick and Mason (this vol., p. 638) have recently proposed an ingenious modification of Robinson's theory which avoids its stereochemical difficulties; they suppose that ring A in the Robinson mechanism reacts in a buckled quinonoid form which allows the *p*-positions to approach within bonding distance before the N–N bond is broken. Unfortunately, this theory demands the complete destruction of the resonance of ring A in the transition state and the activation energies here reported are far too low for this to be possible. Moreover, these authors require that the semidine and other related intramolecular rearrangements should have a different and unspecified mechanism.

The evidence suggests rather strongly that the rate-determining step is fission of the N–N bond; this will be facilitated by methoxyl in the *o*-positions, and diminished by methoxyl in the *m*-positions, by the mechanism (II). But since the rearrangements are intramolecular (cf. Ingold and Kidd, *loc. cit.*), some bond must hold the halves of the molecule together after the N–N link has parted and before the C–C bond has formed; such a bond would moreover have to be little affected by the orientation of substituents. If so, the theory of π-electron sharing receives strong support, for it requires an intermediate phase in the reaction where the rings are held together in just this manner.

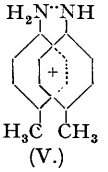
Two further pieces of evidence may be cited. The semidine rearrangement of *p*-hydrazotoluene is a " slow " reaction and must therefore have an abnormally low entropy of activation. Now the Ingold–Kidd and the Robinson theory require transition states of the types (III) and (IV) in the benzidine and the semidine rearrangement, and we should expect the latter to be not less rigid than the former; the low entropy of activation is therefore not easily explained. But the present theory requires a transition state of the type (V) for the



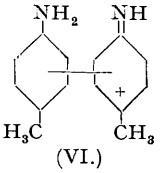
(III.)



(IV.)



(V.)



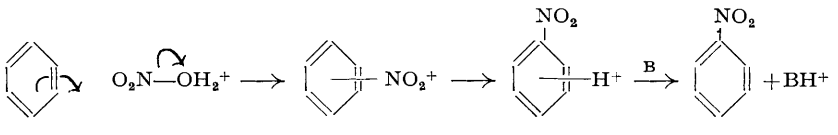
(VI.)

conversion of *p*-hydrazotoluene into the intermediate π-complex (VI); in (V) the methyl groups should mutually interfere and their rotation should be hindered. Since the entropy of free rotation of a group is large (~10 cals./°c.), the low entropy of activation is easy to understand.

Secondly, the salts formed by hydrazobenzenes in aprotic solvents, which have already been mentioned, have properties which are difficult to explain on current theory; they have intense colours, quite unlike those of the rearrangement products, and on hydrolysis they give mainly those products with only a little of the unchanged parent base. This is strange, because the rearrangements of the salts in aqueous solution are by no means instantaneous, if the present work has been rightly interpreted. If, however, these salts are actually equilibrium mixtures of the salt of the parent hydrazobenzene and of all the π-complexes formed from it by rearrangement, their properties are easily intelligible. Normally such π-complexes react further, but in the absence of adequate proton acceptors they may well be stable; on hydrolysis a mixture of the products of further reaction is obtained. Incidentally the evidence suggests that, as would be expected, more diphenyline than usual is then formed; normally the π-complex has not time to reach equilibrium (and therefore the benzidine is favoured). The colour of the salts finds analogy in the colour of solutions of aromatic hydrocarbons in anhydrous hydrogen fluoride; this has already (Dewar, *loc. cit.*) been ascribed to π-complex formation.

The Mechanism of Aromatic Substution.

The present results raise an interesting point, *viz.*, the effect that a *m*-methoxyl group has on the rate of ordinary cationoid substitution of aromatic compounds. According to current electronic theory its effect should be cationoid and it should therefore diminish the rate; this is because methoxyl has opposed inductive and electromeric effects, and in the *m*-position only the inductive effect is operative. It is well known to organic chemists, however, that a *m*-methoxyl group actually facilitates substitution; for instance, veratrole, unlike anisole, is rapidly nitrated by cold dilute nitric acid (Cardwell and Robinson, *J.*, 1915, **107**, 256), and guaiacol reacts more easily than phenol with *N*-chloromethylphthalimide (D.R.P. 442,774; " Friedländer," **15**, 1700). This anomaly can be explained if the anionoid reactivity of the nucleus in substitution is due to its π-electrons, which are analogous to the unshared pair in tervalent nitrogen (cf. the former paper). Such reactions would then proceed *via* π-complex intermediates; for example, nitration by the ion $O_2N{\cdot}OH_2^+$ might be represented as



The complexity of the kinetics of some such reactions may be due to a possible reversibility of the first step; in any case, further investigation, particularly of *o*-disubstituted benzene derivatives, would be of interest.

Current theory does not well explain why aniline and phenol couple exclusively *para* but nitrate, chlorinate, etc., *ortho* and *para*. In the previous paper it was argued that the ability of a positive ion to form a π-complex should vary inversely as its stability, and that the intermolecular character of the aminoazobenzene rearrangement could be ascribed to the stability of the benzenediazonium cation. The same argument then leads us to suppose that aromatic substitution should occur by two distinct mechanisms: a single-step mechanism of classical type when the attack is by stable cations (*e.g.*, diazonium salts), and a two-step mechanism involving a π-complex intermediate when attack is by an unstable cation or potential cation (*e.g.*, NO_2^+, Br^+). If so aromatic substitution is, like aliphatic substitution, a dual process.

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