566. *The Kinetics of the Rearrangement and Oxidation of Hydrazobenzene in Solution. Part I. The Rearrangement and Spontaneous Oxidation.*

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In acid solution, hydrazobenzene undergoes rearrangement to a mixture of benzidine and diphenyline. In alkaline solution containing oxygen, two hydrogen atoms are lost and azobenzene is formed. The two reactions are complementary in that rearrangement involves protonation while oxidation proceeds by deprotonation.

The rearrangement is of the first order with respect to hydrazobenzene and of the second order with respect to acid. This is interpreted in terms of a rate-determining transformation, caused by the approach of a second proton, of a monoprotonated species.

The oxidation of hydrazobenzene by dissolved molecular oxygen in catalyst-free solutions is a spontaneous reaction of the first order with respect to hydrazobenzene. The rate of reaction, in contrast with that of the rearrangement, decreases as the hydrion concentration increases. It is independent of the oxygen concentration once a certain critical value has been exceeded. These facts lead to a mechanism having as its rate-determining stage the second ionisation of hydrazobenzene to give a doubly charged negative ion, readily oxidised.

In acid solutions hydrazobenzene undergoes rearrangement to a mixture of benzidine and (in small proportion) diphenyline: in alkaline solutions containing oxygen it is oxidised to azobenzene. The two reactions are complementary in that they represent the consequences of protonation and deprotonation respectively. One proton may be gained or one may be lost in a reversible manner, after which, on the one hand, the approach of a second proton to the monoprotonated species causes rearrangement, or on the other, the loss of a second proton is thought possibly to yield a highly reactive ion, rapidly oxidised. The character of both reactions is controlled by the interplay of the typical aromatic transmission of charges, and the ion-forming tendencies of the $^-NH{\cdot}NH^-$ group. Both reactions, it is suggested, manifest the tendency of organic molecules to avoid states of high charge density and when such states are produced or are liable to be produced chemical reaction occurs.

The isomerisation has been previously studied, especially by Carlin, Nelb, and Odioso,[1] who concluded that the rate was proportional to the square of the hydrogen-ion concentration. Further measurements have now been made, partly to provide data strictly comparable with those obtained on the oxidation reaction, and partly to determine more fully the influence of anions which might conceivably have played a part in accepting protons from the *para*-position in the isomerisation. The oxidation by molecular oxygen seemed to offer a useful field of study especially in view of the contrast referred to above.

Experimental

Hydrazobenzene was prepared by reduction of azobenzene with zinc dust in alkaline aqueous methanol and purified by repeated recrystallisation from light petroleum (b. p. 80—100°). The white crystals (m. p. 128—130°) were stored dry and out of contact with air. A sample of pure *trans*-azobenzene was prepared by Hartley's [2] method.

The rate of the rearrangement was measured in aqueous ethanol, 44% or 93% ethanol by weight (*i.e.* at 25°, 50 ml. of ethanol + 50 ml. of water or 95 ml. of ethanol + 5 ml. of water). The rate of the oxidation was measured in the 44% ethanol only. Reaction mixtures of the

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[1] Carlin, Nelb, and Odioso, *J. Amer. Chem. Soc.*, 1951, **73**, 1002.

[2] Hartley, *J.*, 1938, 633.

appropriate nominal pH were prepared on the assumption that in all cases the autoprotolysis constant was 10^{-14}. This would not be numerically accurate but the simplification does not affect the interpretation of the results. In any case in alcoholic solutions even measured pH values are at best convenient reference numbers of no fundamental significance.[3] In general, the reaction mixtures contained either hydrochloric acid or sodium hydroxide and also inorganic. salts, but a simple boric acid buffer was used to provide pH values from 8 to 10 in the study of the oxidation. All the components of a reaction mixture with the exception of a small volume of alcohol and the hydrazobenzene were placed in a thermostat at 25° ± 0·05° for 30 min. before the start of an experiment. The total volume of each reaction mixture was 200 ml. at 25° and the run was started by addition of the alcoholic hydrazobenzene.

The rate of rearrangement was measured under nitrogen, the reaction vessel being such that liquids could be added or withdrawn without admission of air. Samples were blown out by applying a suitable pressure of nitrogen to the surface of the mixture and were immediately quenched in a small known excess of alkali. Reaction mixtures were all 10^{-3} molar in hydrazobenzene and samples were diluted 25-fold for spectrophotometric analysis in a "Unicam" S.P. 500 spectrophotometer. Carlin, Nelb, and Odioso [1] noted the optical density at three different wavelengths, *viz.* 245 mμ, 270 mμ, and 285 mμ, and these values were used to calculate the amount of hydrazobenzene, benzidine, and diphenyline in each sample, the appropriate extinction coefficients being known. In the present work the amount of hydrazobenzene present was calculated from the data at each wavelength separately. The products of rearrangement were treated collectively as a single component and a linear calibration graph made for each wavelength, the limits of each corresponding to the optical density of a solution of pure hydrazobenzene and that of the final mixed products at that wavelength. The shapes of the absorption curves for hydrazobenzene, azobenzene, and the final product are such that absorption measurements at 245 mμ provide a good check on the absence of azobenzene in significant amounts. This linear calibration method would be invalidated by any mutual interaction of reactant and products or by the formation of products in a continuously varying ratio, but these effects were shown to be absent, and the results yielded excellent first-order plots from which a pseudo-first-order rate constant, k, was calculated for each run.

The experiments on the oxidation reaction were made with blackened vessels. The solutions were kept saturated with air free from carbon dioxide or a mixture of pure oxygen and pure nitrogen in known amounts passed through calibrated capillary flow meters into the reaction mixture through a sintered-glass disc, which produced a vigorous frothing. The mixture of gases was bubbled through the reaction mixture in the thermostat for 30 min. before the start of the run. The efficiency of the saturating device was tested by experiment. Samples for analysis were withdrawn at suitable times and analysed by measurement of the optical density at 435 mμ with a "Unicam" S.P. 600 spectrophotometer. Samples were unquenched and undiluted since solutions initially 10^{-3} molar with respect to hydrazobenzene were suitable for spectrophotometric analysis. *trans*-Azobenzene was the only product of the oxidation, and end-points were obtained by preparing solutions of the appropriate pH containing this substance at a concentration identical with that of hydrazobenzene used. Linear calibration graphs were prepared and from the results the reaction was shown to be very nearly of the first order with respect to hydrazobenzene although the constants showed a slight tendency to fall with time and, in general, initial rates were recorded.

The Rearrangement Reaction.—The reproducibility in the pseudo-first-order rate constant k was generally better than 10%, and variation of initial concentration confirmed the first-order character of the reaction. The rate of reaction increases with the acidity of the medium and at a given acidity it is faster in the more aqueous medium. It was measured over a five-fold range of acid concentrations at an ionic strength maintained constant by the use of several alternative salts. The results are shown in the Table and in Fig. 1 $-\log k$ is plotted against $-\log [\mathrm{HCl}]$. The fact that all the results tend to fall on a straight line of slope 2 is evidence that the anions are not specifically concerned in the mechanism of the rearrangement process which proceeds at a rate depending on the square of the acid concentration.

The Oxidation by Molecular Oxygen.—The rate of the oxidation of hydrazobenzene in alkaline solutions containing a constant supply of oxygen depends on the pH. Variation of initial concentration showed the reaction to be of the first order with respect to hydrazobenzene. The reproducibility of results was on the whole good but under given experimental conditions the

[3] Bates, "Electrometric pH Determination," John Wiley and Sons, Inc., New York, 1954, p. 150.

rate did vary somewhat from one batch of alcohol to another. This variation, which might amount to 10 or 15%, was the first indication that the reaction might be susceptible to catalysis and inhibition.

Variation of rate of rearrangement with acidity at constant ionic strength in 44% ethanol at 25°.

HCl [N]	Salt (M)		10^3k (min.$^{-1}$)
0·015	NH_4Cl	0·235	7·60
0·015	$NaNO_3$	0·235	7·35
0·025	NH_4Cl	0·225	19·9
0·025	$NaNO_3$	0·225	18·5
0·040	$NaNO_3$	0·210	51·3
0·040	$PhSO_3Na$	0·210	45·8
0·040	$NaClO_4$	0·210	59·2
0·050	NH_4Cl	0·200	79·7
0·075	NH_4Cl	0·175	173
0·075	$NaNO_3$	0·175	186

With a constant solvent the dependence of the rate of the reaction on pH in solutions saturated with air was measured with results shown in Fig. 2 where a negative salt effect is also discernible. The ionic strength of Set II was higher than that of Set I.

FIG. 1.

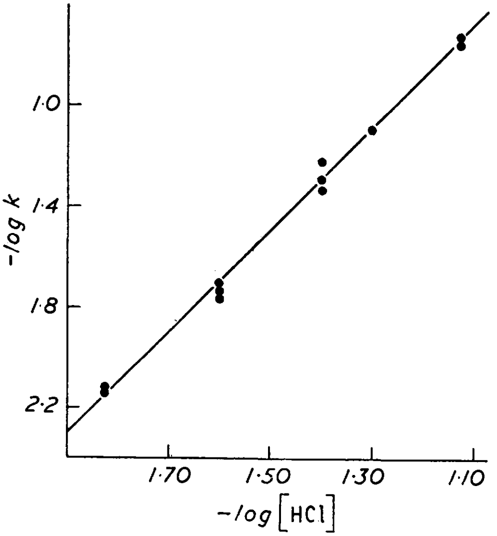
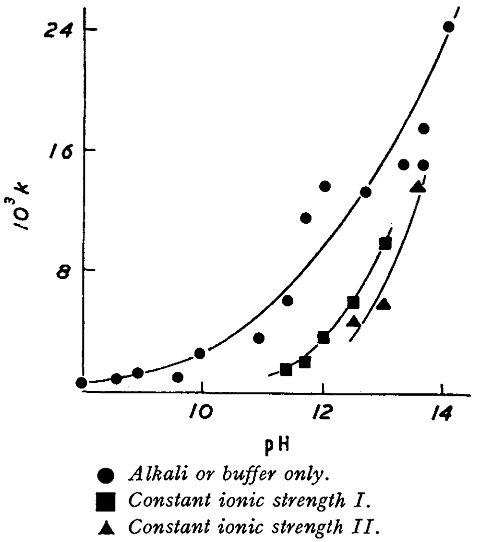


FIG. 2.



The variation of rate with oxygen concentration is shown in Fig. 3, where the abcissa gives the % of oxygen in the gas stream to which the concentration in solution is proportional. At pH 10 and at pH 13 the rate becomes independent of the oxygen concentration when a certain low value has been exceeded.

Two major questions are (*a*) whether or not the reaction is truly spontaneous and (*b*) if so whether or not chain processes are involved. *trans*-Azobenzene added at the start of a run had no effect on the rate of the reaction. Neither did this depend on the length of the saturation period immediately preceding the run. A group of antioxidants altered the rate of the reaction to so small an extent as to render very improbable the idea of long chains capable of being broken by the antioxidants which were *N*-phenyl-2-naphthylamine, 2 : 4-dimethyl-6-2′-methyl*cyclo*hexylphenol, and bis-(2-hydroxy-5-methyl-3-2′-methyl*cyclo*hexylphenyl)methane. By analogy with the oxidation of ascorbic acid to ascorbone[4, 5] and other processes the oxidation of hydrazobenzene might be catalysed by small amounts of metal ions and this idea proved to be true. A survey of the catalytic effect of small amounts of the ions of the more common metals (see Part II) showed that under the conditions of the experiments cupric ions were about nine times more effective than the ions of any other metal. It became clear that the oxidation taking place in solutions to which catalyst had not been

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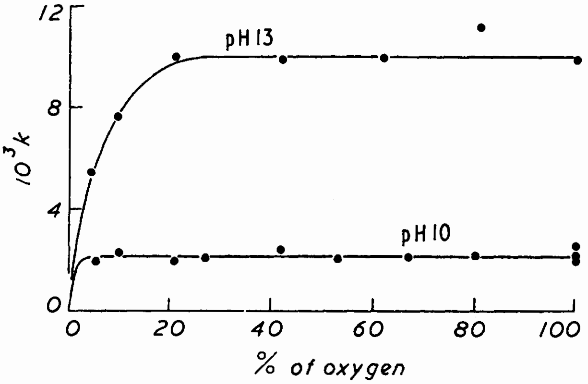
[4] Barron, De Meio, and Klemperer, *J. Biol. Chem.*, 1936, **112**, 625.

[5] Weissberger, LuValle, and Thomas, *J. Amer. Chem. Soc.*, 1944, **66**, 700.

deliberately added could hardly be due to the presence of some adventitious metal-ion catalyst since, with the possible exception of cupric and ferric ions an impossibly large amount would be required to explain the observed reaction velocities. A careful search for the ions of copper and iron in the reaction system was then made. The reagents used were di*cyclo*hexanone oxalyldihydrazone and *o*-phenanthroline, respectively.[6] These reagents are sufficiently sensitive to detect the small amounts of metal ions which, had they been present, could have accounted for the apparently spontaneous reaction. A general test for metal ions in the distilled water used throughout the experiments was provided by Zeo-Karb 225. This material removes ions from solvents but the rate of the reaction was not reduced by filtering the water through a column of the resin. Ethylenediaminetetra-acetic acid (edta) binds the ions of many metals, and experiments with edta and cupric ions showed that the catalytic effect of the metal ions is much reduced and one would therefore suppose that the rate of a reaction brought about by an adventitious metal-ion catalyst would be reduced by the addition of edta. This was not observed. Nor was the rate of oxidation increased when the residues from the ignition of a large quantity of hydrazobenzene were incorporated in a typical reaction mixture, indicating that the compound itself was free from catalytic ions. The reaction was found to be slowed by small amounts of acetaldehyde and thiophen which could possibly find their way in traces into the alcohol and which would explain the variation in rate from one batch of alcohol to the next. The possibility remained that the alcohol of the solvent was itself oxidised in some way and that this oxidation brought about the oxidation of the hydrazobenzene. Experiments of long duration, designed to show up any oxidation of the alcohol, however small, yielded negative results.

FIG. 3.



DISCUSSION

The two reactions here described are complementary in the sense that both of them involve the same reaction site and they seem to be initiated by simple protonation or deprotonation, respectively.

It has been shown beyond doubt, particularly by Smith, Wheland, and Schwartz,[7] that the rearrangement of hydrazobenzene is intramolecular. There is now a large body of kinetic results indicating that the rate of the reaction is proportional to the square of the acid concentration and it is also known that the products are formed in a fixed ratio.[3,8,9] The anions present seem to play no specific part. If the dependence of rate on acid concentration is interpreted in terms of either the rate-determining formation or the rate-determining rearrangement of a diprotonated species then a difficulty arises in drawing satisfactory structures for the intermediate.

[6] "Organic Reagents for Metals," Hopkin and Williams Ltd., 5th Edn., 1955, pp. 31, 124.

[7] Wheland, Schwartz, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 2282.

[8] Hammond and Shine, *J. Amer. Chem. Soc.*, 1950, **72**, 220.

[9] Croce and Gettler, *ibid.*, 1953, **75**, 874.

It is here suggested that the rearrangement of hydrazobenzene depends on the second power of the acid concentration because the monoprotonated species is made to rearrange itself by the approach of a second proton in the rate-determining step. The stoicheiometry of the process is as shown :

$$\text{monoprotonated species} + H^+ \longrightarrow \text{molecule of product} + 2H^+$$

The protons released come from the original *para*-positions when the new linkage is established and the second proton goes to complete the second amino-group. The important point is that the second proton should be thought of as bonding itself to the distorted ion produced by its own approach only after the transition state is passed, rather than to the species still describable as monoprotonated hydrazobenzene. In other words, rearrangement is the preferred alternative to diprotonation of hydrazobenzene.

Steps (1) and (2)

$$(1)\quad \text{PhNH·NHPh} + H^+ \rightleftharpoons \text{PhNH}_2^+\text{·NHPh} \quad . \quad . \quad K_1 = k_1/k_{-1}$$

$$(2)\quad \text{PhNH}_2^+\text{·NHPh} + H^+ \longrightarrow \text{products} \quad . \quad . \quad . \quad . \quad . \quad . \quad k_2$$

lead to the rate expression

$$-\text{d[PhNH·NHPh]}/\text{d}t = k_2K_1\text{[PhNH·NHPh]}[H^+]^2$$

Now, although with hydrazobenzene itself it appears that the monoprotonated species will rearrange only when stimulated by the approach of a second proton, this need not be true of substituted hydrazobenzenes. Carlin and Odioso [10] found that *o*-hydrazotoluene undergoes rearrangement at a rate depending on the acid concentration to a power of 1·6. This could be explained in terms of a significant contribution to the observed rate by the spontaneous rearrangement of the monoprotonated species, assumed in the early theories of the hydrazobenzene rearrangement before kinetic data became available. This spontaneous rearrangement would require the introduction of a new equation

$$(3)\quad \text{PhNH}_2^+\text{·NHPh} \longrightarrow \text{products} \quad . \quad . \quad . \quad . \quad . \quad . \quad k_3$$

Steps (1), (2), and (3) give the following expression which can explain an observed order of acid dependence anywhere between 1 and 2. With hydrazobenzene itself, k_3 is apparently negligible.

$$-\text{d[PhNH·NHPh]}/\text{d}t = K_1\text{[PhNH·NHPh]}[H^+]\{k_2[H^+] + k_3\}$$

The positive salt effect reported on several occasions is in the expected sense for a rate-determining step involving ions of like sign.

The picture of the transition state is simplified by the idea of a monoprotonated species rearranging itself under the influence of a second proton. The structures suggested by Hammick and Mason [11] are stereochemically plausible and the energy of activation contains as a major term the increase in energy when the monoprotonated species is forced into the transition state by the approach of a second proton. Dewar [12] has postulated the π-complex to dispose of the stereochemical difficulties and explain the intramolecular character of the reaction, but kinetic evidence does not help in deciding whether or not it is strictly necessary to posulate an intermediate of unusual bond structure.

The oxidation of hydrazobenzene in alkaline solutions containing oxygen is of the first order with respect to hydrazobenzene and can apparently take place in reaction mixtures which do not contain a metal-ion catalyst of the type described in the following paper. The rate of reaction increases rapidly with increasing alkalinity but becomes independent of the oxygen once a small concentration has been exceeded.

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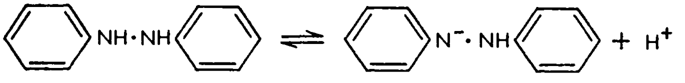
[10] Carlin and Odioso, *J. Amer. Chem. Soc.*, 1954, **76**, 100.

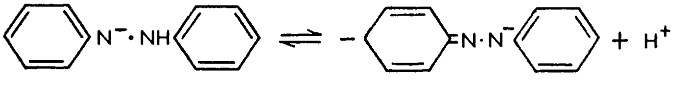
[11] Hammick and Mason, *J.*, 1946, 638.

[12] Dewar, *Nature*, 1945, **156**, 784; *J.*, 1946, 406, 777.

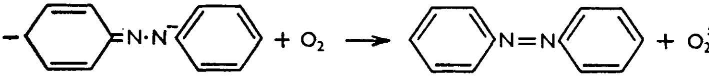
These facts lead to the formulation of a simple non-chain mechanism, the rate-determining stage of which does not involve oxygen except at very low oxygen concentrations where a different stage controls the rate. The working assumption is made that the first (acid) dissociation of hydrazobenzene is rapidly reversible whereas the second ionisation, involving a redistribution of charge, is slow. The second ionisation can take place when the negative charge on the first ion is as far away as possible from the neighbourhood of the second proton due to be lost. The doubly charged ion is so reactive that it suffers either protonation or complete oxidation by electron transfer almost at once. The reaction sequence may be set down as follows :



$K_1 = k_1/k_{-1}$. (1)



$K_2 = k_2/k_{-2}$. (2)



k_3 . . . . (3)

The concentration of the highly reactive doubly-charged ion reaches a small stationary value and the following expression is obtained for the rate of the reaction

$$-\frac{\mathrm{d}[\mathrm{PhNH{\cdot}NHPh}]}{\mathrm{d}t} = \frac{k_2k_3K_1[\mathrm{PhNH{\cdot}NHPh}][\mathrm{O_2}]/[\mathrm{H^+}]}{k_{-2}[\mathrm{H^+}] + k_3[\mathrm{O_2}]} \quad . . . \quad (4)$$

There are obviously two limiting cases of this expression which show it to be in harmony with the kinetic results

(i) $k_{-2}[\mathrm{H^+}] \gg k_3[\mathrm{O_2}]$

$$-\frac{\mathrm{d}[\mathrm{PhNH{\cdot}NHPh}]}{\mathrm{d}t} = \frac{k_2k_3K_1[\mathrm{PhNH{\cdot}NHPh}][\mathrm{O_2}]}{k_{-2}[\mathrm{H^+}]^2} \quad . . . . \quad (5)$$

(ii) $k_{-2}[\mathrm{H^+}] \ll k_3[\mathrm{O_2}]$

$$-\mathrm{d}[\mathrm{PhNH{\cdot}NHPh}]/\mathrm{d}t = k_2K_1[\mathrm{PhNH{\cdot}NHPh}]/[\mathrm{H^+}] \quad . . . . \quad (6)$$

There is some evidence for a rather slow oxidation involving undissociated hydrazobenzene and although this makes but a small contribution to the observed oxidation in alkaline solutions it is probably responsible for the rather troublesome oxidation which still tends to occur when the rate of rearrangement of hydrazobenzene is measured in acid solution.

A certain symmetry is discernible in the reactions of hydrazobenzene here discussed. Chemical transformation follows any attempt to create a doubly charged hydrazobenzene ion either by protonation of the monoprotonated species or by further dissociation of the first anion.

$$\text{Rearrangement products} \xleftarrow{\mathrm{H^+}} \mathrm{PhNH_2{}^+{\cdot}NHPh} \rightleftharpoons \mathrm{PhNH{\cdot}NHPh} \rightleftharpoons \mathrm{PhN^-{\cdot}NHPh} \xrightarrow{-\mathrm{H^+}} \text{Oxidation reaction}$$

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