[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Mechanism of the Benzidine Rearrangement. I. The Effect of Acid Concentration on Rate

BY GEORGE S. HAMMOND* AND HENRY J. SHINE

Considerable interest has been expressed recently in the elucidation of the mechanism of the benzidine rearrangement.[1–4] Since Ingold and Kidd[5] have established that the rearrangement of typical hydrazobenzenes to the corresponding benzidines and related compounds is probably an intramolecular reaction it seems likely that the two halves of the molecule are continuously bonded during the whole course of the reaction. This has led to much interesting speculation as to the geometry of the transition state and the nature of the bonds involved in it. Dewar[4c] has reported kinetic evidence in support of a novel mechanism in which a π-complex is formed as a high energy intermediate. However, Dewar's qualitative interpretation of certain of his results is not entirely satisfactory. In particular, he has assumed that the reaction is first order in oxonium ion without establishing the fact experimentally. We have, therefore, undertaken a reinvestigation of the kinetics of the rearrangement of hydrazobenzene itself in experiments in which the concentration of acid is varied.

Experimental

Materials.—**Bindschedler's Green** was prepared by the method of Wieland,[6] which was found to give a more satisfactory product than Dewar's[4c] procedure. The dye was obtained as a green, crystalline solid. When weighed amounts from several preparations were titrated with standard titanous chloride solution a value of 250 ± 5 was found for the equivalent weight as an oxidant. It therefore appears that the dye, as obtained by us, does not have the composition $C_{32}H_{40}N_6ZnCl_4$ reported by Wieland. The calculated amount of a standard solution of the dye was reduced by a weighed sample of hydrazobenzene.

Titanous Chloride Solution.—An approximately 0.01 N solution was prepared, standardized and stored under carbon dioxide.

Hydrazobenzene was prepared according to Hickinbottom.[7] The product was recrystallized from ethanol until it was nearly colorless; m. p. 124.5–125.5° (uncor.).

Alcohol Solutions.—Anhydrous ethanol was prepared by distillation from sodium ethoxide and diethyl phthalate.[8] A stock solution of hydrogen chloride was prepared by passing the dry gas into anhydrous ethanol. The solution was standardized against standard aqueous sodium hydroxide. The anhydrous alcohol and the acid solution were stored in bottles protected by drying tubes and drawn as required by means of automatic burets.

Procedure.—The procedure followed was essentially that outlined by Dewar.[4c] For each run the calculated weight of hydrazobenzene was dissolved in 75 ml. of anhydrous ethanol and diluted to 100 ml. with distilled water. One hundred ml. of a second solution was prepared by adding alcohol to the required volume of acid solution to bring the total to 75 ml. The required weight of sodium perchlorate was then added and the solution diluted to 100 ml. with distilled water. Both solutions were kept in an ice-bath for at least one hour before mixing. They were then mixed and 10-ml. aliquots were removed at intervals and pipeted into 25 ml. of a solution approximately 0.02 N in Bindschedler's Green and the excess dye was back titrated under a stream of nitrogen with the standard titanous solution. Since the oxidizing titer of solutions of the dye decreased at an appreciable rate blanks were titrated at thirty-minute intervals. The values of the blank were plotted against time and the value at the time of back titration of the samples was then read off the graph. In the more rapid runs there may be a slight error due to oxidation during the transfer of samples. The normality of the acid in the reaction mixture was checked by titration of an aliquot with standard base at the end of the runs.

Discussion of Results

The kinetic data are summarized in Table I. Column 4 gives the average calculated values of the pseudo first order rate constants. The first analytical point was taken as zero time since appreciable reaction occurred during the time of mixing in the faster runs.

TABLE I

RATE OF REARRANGEMENT OF HYDRAZOBENZENE AT ZERO DEGREES IN 75% ETHANOL

Hydrazobenzene = 0.0100 M except where noted

Run	HCl, moles/liter	NaClO$_4$, moles/liter	$k \times 10^3$ min.$^{-1}$	Probable error in $k \times 10^3$	Av. dev. of $k \times 10^3$	$k \times 10^5$/[HCl]^2
5	0.196	...	14.9	0.3	1.4	3.78
6	.392	...	107.1	2.6	7.0	6.95
7	.196	0.200	27.0	0.1	1.9	7.02
8	.0953	.300	5.25	.2	0.60	5.80
9	.0987	.300	5.48	.1	0.31	5.73
10	.292	.100	63.8	1.5	4.4	7.48
11[a]	.0986	.300	6.50	0.2	0.61	6.67

[a] Hydrazobenzene, 0.0050 M.

It appears that the rearrangement of hydrazobenzene is second order in hydrogen ion as is shown by the constancy of $k/[\mathrm{HCl}]^2$ for the various runs in which ionic strength was kept constant. There is a slight decrease in rate in the later stages of the runs, and the average values of $k/[\mathrm{HCl}]^2$ are significantly low in runs 8 and 9, in which the total acid concentration was lowest. Both these phenomena are attributed to the fact that the products of the rearrangement are probably stronger bases than hydrazobenzene. If this is true a slight decrease in the hydrogen

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* Harvard University Ph.D., 1947.

(1) Robinson, *J. Chem. Soc.*, 220 (1941).

(2) Hughes and Ingold, *ibid.*, 606 (1941).

(3) Hammick and Mason, *ibid.*, 638 (1946).

(4) (a) Dewar, *Nature*, **176**, 784 (1945); (b) *J. Chem. Soc.*, 406 (1946); (c) *ibid.*, 777 (1946).

(5) Ingold and Kidd, *ibid.*, 894 (1933).

(6) Wieland, *Ber.*, **48**, 1087 (1915)

(7) Hickinbottom, "Reactions of Organic Compounds," 2nd ed., Longmans, Green and Co., London, 1948, p. 352.

(8) Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 359.

ion activity of the medium should take place during a run. Partial confirmation of this hypothesis is furnished by the more consistent result of run 11, in which the acid concentration and ionic strength were the same as those of runs 8 and 9, but in which the concentration of hydrazobenzene was decreased. Comparison of runs 5 and 7 shows that the rate of reaction is subject to a positive salt effect. Further comparison is available from Dewar's data. This worker reported a constant of 2.7×10^{-3} reciprocal minute for a run carried out in the same solvent with 0.1 *N* acid and no added salt. From the three constants it appears that doubling the ionic strength at constant hydrogen chloride concentration results in about a twofold increase in the rate of reaction.

The new information indicates that it is the second conjugate acid of hydrazobenzene which undergoes rearrangement. The reactions involved may be formulated as

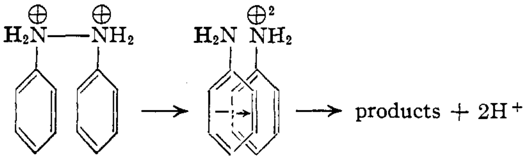
$$(1)\quad C_6H_5NHNHC_6H_5 + \overset{+}{H} \overset{k_1}{\rightleftarrows} C_6H_5\overset{+}{N}H_2NHC_6H_5$$

$$(2)\quad C_6H_5\overset{+}{N}H_2NHC_6H_5 + \overset{+}{H} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5$$

$$(3)\quad C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 \xrightarrow{k_3} H_2NC_6H_4C_6H_4NH_2 + 2\overset{+}{H}$$

It is impossible to determine from our data whether (2) or (3) is the rate-determining step of the reaction. If the second acid is formed reversibly it is to be expected that the equilibrium constant, k_2/k_{-2}, will increase with increasing ionic strength because of the charge type of the reaction.[9] Since reaction (3) involves conversion of a doubly charged ion to a transition state in which the same charge is dispersed over a larger volume, only a relatively small negative salt effect on k_3 would be expected and the principal effect of ionic strength will be that of increasing the concentration of the unstable species. If reaction (2) is rate determining similar considerations would also lead one to expect the observed results. The latter case would be somewhat exceptional in that it would be an example of a reaction in which the addition of a proton to a basic nitrogen controls the rate. This possibility cannot be excluded as the juxtaposition of two positive charges in the second acid might make its rate of formation measurably slow. If such is the case, the reaction may be subject to general acid catalysis.[10] This possibility will be the subject of further investigation in these laboratories. It is worthy of note that Dewar's evidence that the reaction is subject to specific oxonium ion catalysis is not convincing, because he never actually varied the total concentration of acidic species while maintaining constant hydrogen ion activity.

Dewar proposed that the first conjugate acid is converted to a π-complex which subsequently undergoes further rearrangement to give the observed products of the reaction. The attractive feature of this formulation is that the dissymmetry of the molecule allows for strong π-bonding between an electron-rich aniline molecule and an electron-poor positive ion, with an opportunity for dispersing charge at the same time. This general type of formulation does not seem as plausible when applied to the symmetrical second acid. The sequence is not considered to be likely



since it involves increased charge concentration in the π-complex. On the other hand, breaking the nitrogen–nitrogen bond symmetrically would give two similar electron-deficient ion radicals which would be expected to react with the solvent or neutral organic substances rather than with each other. It is, however, conceivable that two such ion radicals might recombine while still in the solvent cage without the agency of any special type of complex formation.

It is our opinion that the new bonds of the products of the rearrangement are partially formed before the old bond is broken in a manner similar to that suggested by Robinson[1] and Hughes and Ingold.[2] However, the designation of the direction of electronic shifts during the reaction as has been attempted by these authors, becomes meaningless in the symmetrical system. The geometrical difficulty of bringing nuclear carbon atoms close to each other in the transition state would be decreased by the stretching of the old bond due to electrostatic repulsion between the two positively charged nitrogen atoms.

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Summary

The dependence of the rate of the rearrangement of hydrazobenzene in 75% alcohol on acid concentration has been investigated. The reaction is second order in acid and the rate is subject to a positive salt effect. Some implications of the results in the formulation of the mechanism of the reaction are discussed.

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(9) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 90.

(10) Hammett, *ibid.*, p. 215.