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Kinetics of Fischer–Hepp Rearrangement

B. T. Baliga

UNIROYAL Research Laboratories,
Guelph, Ontario, Canada

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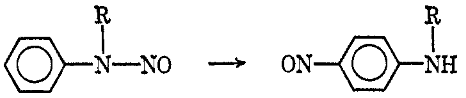
The rearrangement of aromatic nitrosamines on treatment with acids, particularly HCl and HBr, to give ring-substituted isomerides is known as the Fischer–Hepp rearrangement.[1] Although at one time this reaction was believed to be truly intramolecular, considerable evidence accumulated in later years proved this to be untrue. Thus, when the rearrangement was carried out in the presence of urea, no C-nitroso isomeride was produced but only the secondary amine;[2] also, when the rearrangement occurs in the presence of more active foreign aromatic molecules, major transfers of the nitroso group to this molecule have been observed.[3,4] It has been found[3] that the conversion by HX occurs through the liberation of NOX, and with HCl and HBr the NO group is quantitatively removed. With sulfuric acid the yields are low, and with nitric acid no rearrangement occurs. The subsequent reaction of NOCl with the formed secondary amine to give C-nitroso compound was found to be very fast. To gain further insight into the mechanism of this reaction, a kinetic study seemed desirable, and the present work describes such a study on the hydrogen chloride catalyzed rearrangement of N-nitrosodiphenylamine to *p*-nitrosodiphenylamine.



Experimental Section

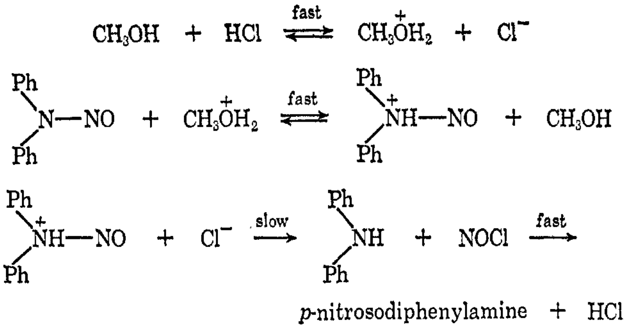
Eastman Kodak White Label compounds N-nitrosodiphenylamine and *p*-nitrosodiphenylamine were used. Analytical grade methanol and redistilled toluene were used as solvents. The solvent mixture was made up by volume. The stock solution of HCl (made by passing dry HCl into the solvent) in the desired solvent was variously diluted as required for the kinetic runs. The solution containing N-nitrosamine was mixed with the solution containing HCl in a volumetric flask thermostated at the desired temperature controlled within ±0.03°. Aliquots withdrawn at various times were quenched with methanolic sodium hydroxide, suitably diluted in methanol, and the absorbance at 430 mμ was measured in a 1-cm quartz cell on a Carl Zeiss (Models PMQ II and M4Q III) spectrophotometer to an accuracy of about 0.2%. The ultraviolet and visible spectra for both amines in methanol have been found to be similar to those reported in ethanol.[5] It has been established that the absorbance of *p*-nitrosodiphenylamine at this wavelength is linear with concentration (ϵ 16.74×10^3) in methanol in accordance with the Beer–Lambert law.

Results and Discussion

The rate of the reaction was found to be first order in nitrosamine and first order in hydrogen chloride at a given temperature and with a given solvent

$$\frac{-d[\text{N-nitrosamine}]}{dt} = \frac{d[\text{C-nitrosamine}]}{dt} = k_2[\text{N-nitrosamine}][\text{HCl}]$$

where k_2 is the second-order rate constant given in the last column of Table I. Arrhenius plots of log k against $1/T$ in the two solvents (not shown) are linear in the temperature range 30–50°, and the various activation parameters obtained from these plots are given in Table II.



A stepwise mechanism with a slow step involving the nucleophilic attack of chloride ion on the protonated N-nitrosamine requires third-order kinetics which are

$$\text{rate} = k_3[\text{N-nitrosamine}][\text{H}^+][\text{Cl}^-]$$

first order in each, nitrosamine, hydrogen ion, and chloride ion. Since the dependence of the rate on the concentration of chloride ion is indistinguishable from the stoichiometric concentration of molecular HCl, it seemed desirable to verify this mechanism by adding chloride ion. The results are shown in Table III where it can be seen that first-order dependence on chloride ion was not observed. The rate is still first

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(1) O. Fischer and E. Hepp, *Ber.*, **19**, 2291 (1886).

(2) W. Macmillen and T. H. Reade, *J. Chem. Soc.*, 585 (1929).

(3) P. W. Neber and H. Rauscher, *Ann.*, **550**, 182 (1942).

(4) J. Glazer, E. D. Hughes, C. K. Ingold, A. T. James, G. T. Jones, and E. Roberts, *J. Chem. Soc.*, 2657 (1950).

(5) W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, *Anal. Chem.*, **23**, 1740 (1951).

TABLE I

RATE CONSTANTS FOR THE HYDROGEN CHLORIDE CATALYZED REARRANGEMENT OF N-NITROSODIPHENYLAMINE TO *p*-NITROSODIPHENYLAMINE

Temp, °C	Solvent	[N-nitrosamine], mol l.$^{-1}$	[HCl], mol l.$^{-1}$	$-d$[N-nitrosamine]/dt 10^6 mol l.$^{-1}$ sec^{-1} [a]	10^4k_2,[b] l. mol^{-1} sec^{-1}
30.00	Methanol	0.1033	0.169	1.76	1.03
		0.0517	0.169	0.881	1.04
	Toluene + methanol (3:1 v/v)	0.0507	0.148	2.70	3.60
		0.0254	0.074	7.00	3.73
40.18	Methanol	0.1033	0.194	5.02	2.79
		0.0517	0.194	2.58	2.80
		0.0310	0.194	1.55	2.86
		0.0826	0.213	4.33	2.78
		0.1022	0.115	3.07	2.81
		0.1022	0.229	5.85	2.79
		0.1022	0.0687	1.85	2.81
		0.1022	0.183	4.72	2.78
	Toluene + methanol (3:1 v/v)	0.0507	0.231	5.55	5.91
		0.0254	0.116	1.50	5.81
		0.0152	0.185	1.32	5.77
50.00	Methanol	0.031	0.0537	1.02	6.89
		0.01033	0.0716	0.433	6.72
	Toluene + methanol (3:1 v/v)	0.0254	0.083	1.58	8.95
		0.0254	0.083	1.60	9.15

[a] The absorbance of *p*-nitrosodiphenylamine at 430 mμ under acidic conditions was found to decrease slowly over a period of time, perhaps owing to some change in molecular structure. This being the case, the rate constants were obtained from initial rates by plotting [N-nitrosamine] against t. The quantity in this column represents the slope of this plot at $t = 0$. [b] In evaluating this constant, the concentrations in columns 3 and 4 have been corrected for thermal expansion of the solvent. For each run, the concentration of N-nitrosamine at $t = 0$ used to evaluate k_2 is slightly lower than that shown in column 3 since some of the N-nitrosamine will already have been converted to C-nitrosamine when the first reading was taken.

order with respect to HCl for different concentrations in the presence of added chloride ion. The slight increase in rate by chloride ion can reasonably be attributed to a salt effect. A stepwise mechanism, therefore, seems unlikely for this rearrangement.

TABLE II

ACTIVATION PARAMETERS FOR THE HYDROGEN CHLORIDE CATALYZED REARRANGEMENT OF N-NITROSODIPHENYLAMINE TO *p*-NITROSODIPHENYLAMINE

Solvent	log A, l. mol^{-1} sec^{-1}	E_A, cal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
Methanol	9.1	18,140 ± ~600	−19.0 ± ~2.0
Toluene + methanol (3:1 v/v)	2.9	8,750 ± ~600	−47.0 ± ~2.0

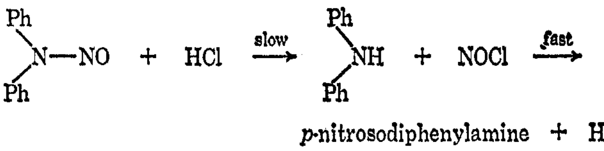
TABLE III

EFFECT OF LITHIUM CHLORIDE ADDITION ON RATE CONSTANTS FOR THE HYDROGEN CHLORIDE CATALYZED REARRANGEMENT OF N-NITROSODIPHENYLAMINE TO *p*-NITROSODIPHENYLAMINE IN METHANOL AT 50.00°[a]

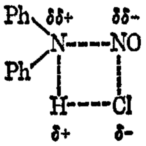
[HCl], mol l.$^{-1}$	[LiCl], mol l.$^{-1}$	$-d$[N-nitrosamine]/dt, 10^6 mol l.$^{-1}$ sec^{-1}	10^4k_2, l. mol^{-1} sec^{-1}
0.175	0	2.25	6.94
0.154	0.113	2.32	8.10
0.0765	0.113	1.19	8.24
0.154	0.225	2.70	9.37
0.0765	0.225	1.35	9.35
0.162	0.338	3.27	10.8
0.176	0.450	4.03	12.3
0.0306	0.450	0.708	12.1

[a] [N-nitrosamine] = 0.02075 mol l.$^{-1}$ for all runs. Footnotes of Table I apply to columns 3 and 4.

The results can be accommodated by a concerted mechanism



with a cagelike transition state for the slow step.



Since a cyclic transition state is formed from noncyclic reactants, a negative $\Delta S^{\ddagger}$ is to be expected due to the restricted free rotation about the single bonds in this transition state. In addition, there may be contribution arising from charge separation whose value depends strongly on the solvent. The observed $\Delta S^{\ddagger}$ in methanol, −19.0 cal deg^{-1} mol^{-1}, and its considerable decrease to −47.0 cal deg^{-1} mol^{-1} in toluene + methanol are consistent with this picture. The slight increase in rate with added chloride ion might arise from a salt effect similar to that known for a reaction between neutral molecules forming a dipolar transition state.[6] The specificity of HCl and HBr in the Fischer–Hepp rearrangement, unlike other acids, can be attributed to the facile elimination of the NO group as NOX from a cagelike transition state.

Registry No.—N-Nitrosodiphenylamine, 86-30-6.

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(6) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 186.