[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, SIR JOHN CASS COLLEGE]

A Kinetic Study of the Hydrolysis of Some Substituted *p*-Nitroso-dialkylanilines

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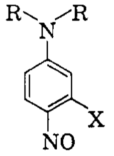
A preliminary kinetic study of the hydrolysis of some *p*-nitroso-N,N-dialkylanilines by aqueous sodium hydroxide indicates that the reaction is of the S_N2 type, and that the results conform to Hammett's equation. The values of both specific rate constant and activation energy for the hydrolysis of *p*-nitroso-N,N-di-*n*-propylaniline are significantly lower than for the corresponding methyl and ethyl compounds; this effect is interpreted in terms of a greater degree of rigidity in the transition state for the former case.

The hydrolysis of *p*-nitroso-dialkylanilines by aqueous alkali and by sodium bisulfite has long been used as a preparative method for secondary amines and *p*-nitrosophenols[2]; but apart from a paper by Miller and Adams[3] there is no record of any kinetic studies on this system. Indeed, studies of the activating influence of the nitroso group in nucleophilic substitution reactions have in general been rather neglected by kineticists. The very comprehensive review of nucleophilic substitutions[4,5] contains only general statements on the activating influence of the nitroso group; but a qualitative comparison by Le Fevre[6] and others[7] of the activating effects of nitroso and nitro groups in nucleophilic hydrolysis reactions indicates that the former is much stronger.

This result is rather unexpected, since it is generally accepted that the nitro and nitroso groups are at least equally electronegative, a conclusion supported by studies of electrophilic substitution reactions,[8] measurements of dipole moments[9] and dissociation constants of *p*-nitroso and *p*-nitro dialkylanilines. Results obtained from the study of the kinetics of the hydrolysis of some substituted nitroso-dialkylanilines of the general type I are now presented in this paper.

I 

X = H, CH_3, Cl, OEt, OH
R = Me, Et, *n*-Pr

The progress of the hydrolysis reaction was followed by spectrophotometric analysis using the pronounced absorption peaks produced by the nitroso grouping in reactant and product. The stoichiometry of the reaction also was checked by a second method in which the secondary amine produced in the reaction was estimated volumetrically by absorption in standard acid and back titration with alkali.

Experimental

1. **Materials.**—*p*-Nitroso-N,N-dimethylaniline (m.p. 85°, lit.[10] 85–87°) and *p*-nitroso-N,N-diethylaniline (m.p. 83°, lit.[11] 84°) were recrystallised from technical grade materials to constant melting point and absorption spectra.

Standard nitrosation methods using sodium nitrite were modified as necessary for the preparation of these needed materials: *p*-nitroso-N,N-di-*n*-propylaniline (m.p. 40°, lit.[12] 42°), *p*-nitroso-*n*-methyl-N,N-dimethylaniline (m.p. 92°, lit.[13] 92°), *p*-nitroso-*m*-chloro-N,N-dimethylaniline (m.p. 130° dec., lit.[14] 130°, *p*-nitroso-*m*-hydroxy-N,N-diethylaniline hydrochloride (m.p. 170° dec., lit.[15] 170° dec.), *p*-nitroso-*m*-ethoxy-N,N-diethylaniline hydrochloride (m.p. 154° dec.), *p*-nitrosophenol (m.p. 125–126°, lit.[16] 124–128°), *p*-nitroso-*m*-cresol (m.p. 155° dec., lit.[17] 145–150° dec.). In all cases cleaner products were obtained by carrying out the nitrosation in an atmosphere of nitrogen. *m*-Chloro-N,N-dimethylaniline was prepared from *m*-chloroaniline by methylation following the method of Gilman and Banner.[18] For *p*-nitroso-resorcinol (m.p. 170–173° dec.) it was necessary to nitrosate very slowly with isoamyl nitrite at 0° under nitrogen.

p-Nitroso-*m*-ethoxyphenol and *p*-nitroso-*m*-chlorophenol, for which the nitrosation reaction was unsatisfactory, were prepared by hydrolysis of *p*-nitroso-*m*-ethoxy-N,N-diethylaniline and *p*-nitroso-*m*-chloro-N,N-dimethylaniline, respectively.

2. **Analytical Methods.** (a) **Spectrophotometric Analysis.**—The concentration of the *p*-nitroso dialkylaniline was determined by measurement of the absorption spectra of samples from the reaction mixture. Since one of the reaction products also absorbs light in the same spectral region, it was necessary to take absorption readings at two wave lengths, and in separate measurements to determine the extinction coefficients at the same wave lengths for the pure components of the mixture. For such a mixture of independently absorbing substances which obey Beers' law, the extinction coefficient of the mixture is equal to the sum of the coefficients of the components and from the measured data the concentration of either component may be calculated, *i.e.*

$$C_B = \frac{\alpha_1}{|D|} \times x_2 - \frac{\alpha_2}{|D|} \times x_1$$

where

C_B = concentration of component B
$|D|$ = $\alpha_1\beta_2 - \alpha_2\beta_1$
α_1,β_1 = extinction coefficients of pure A and B at wave length λ_1
α_2,β_2 = extinction coefficient of pure A and B at wave length λ_2
x_1 = measured optical density of mixture at λ_1
x_2 = measured optical density of mixture at λ_2

Trials showed that optimum resolution of the absorption peaks was obtained when the spectra were measured in

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[1] Material taken from a thesis by F. H. Kendall in partial fulfillment of the degree of Ph.D., London.

[2] A. Baeyer and H. Caro, *Ber.*, **7**, 964 (1874); R. Munch, G. T. Thannhauser and D. L. Cottle, THIS JOURNAL, **68**, 1297 (1946).

[3] F. M. Miller and M. L. Adams, THIS JOURNAL, **75**, 4599 (1953).

[4] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[5] J. F. Bunnett, *Quart. Revs.*, **12**, No. 1, 1 (1958).

[6] J. R. Le Fevre, *J. Chem. Soc.*, 810 (1931).

[7] V. Merz and W. Weith (A. Weber), *Ber.*, **10**, 761 (1877); P. Van Romburg, *Rec. trav. chim.*, **2**, 105 (1883); D. S. Pratt and C. O. Young, THIS JOURNAL, **40**, 1428 (1918).

[8] D. Hammick, R. G. A. New and L. E. Sutton, *J. Chem. Soc.*, 742 (1932).

[9] C. E. Ingham and G. C. Hampson, *ibid.*, 981 (1939); J. W. Le Fevre and J. W. Smith, *ibid.*, 2239 (1932).

[10] C. Wurster and L. Roser, *Ber.*, **12**, 523 (1823); C. Matignon and Deligny, *Compt. rend. acad. sci.*, **125**, 1104 (1897).

[11] A. Kopp, *Ber.*, **8**, 621 (1875).

[12] "Beilstein," Vol. XII, p. 685.

[13] W. J. Hickinbottom, *J. Chem. Soc.*, 1797 (1933).

[14] H. H. Hodgson and J. S. Wignall, *ibid.*, 1144 (1927).

[15] R. Mohlau, *Ber.*, **25**, 1060 (1892).

[16] J. L. Bridge, *Ann.*, **277**, 85 (1893); E. Bamberger, *Ber.*, **33**, 1955 (1900).

[17] C. Wurster and L. Roser, *Ber.*, **12**, 1799 (1879).

[18] H. Gilman and I. Banner, THIS JOURNAL, **62**, 344 (1940).

aqueous acid solution and unless otherwise stated all optical densities were measured in aqueous 0.005 *N* hydrochloric acid. In every case the optical density was compared with a blank solution containing identical quantities of hydrochloric acid and dissolved salts.

Conformity to Beer's law was established for each *p*-nitrosodialkylaniline and for each reaction product, *i.e.*, the corresponding *p*-nitrosophenol.

Measurements were made in 1-cm. quartz cells using a Unicam SP 500 spectrophotometer.

The wave length of peak absorption used in the calculation of concentration is shown in Table I.

It was shown separately that the second reaction product, a secondary aliphatic amine which would always be present in the system, had negligible absorption in the wave length range considered, so that the reaction mixture could be correctly treated as a two-component system.

It also was necessary to show that the *p*-nitrosophenol formed in the reaction was stable at the elevated temperatures used to study the reaction. Thermal stability up to 80° was established for all the phenols encountered.

TABLE I

	λ, mμ
p-Nitroso-N,N-dimethylaniline	350
p-Nitroso-N,N-diethylaniline	350
p-Nitroso-N,N-di-*n*-propylaniline	355
p-Nitroso-*m*-methyl-N,N-dimethylaniline	340
p-Nitroso-*m*-chloro-N,N-dimethylaniline	345
p-Nitroso-*m*-ethoxy-N,N-diethylaniline	330
p-Nitroso-*m*-hydroxy-N,N-diethylaniline	327
p-Nitroso-*m*-methylphenol	300
p-Nitroso-*m*-chlorophenol	304
p-Nitroso-*m*-ethoxyphenol	295
p-Nitroso-*m*-hydroxyphenol	295
p-Nitrosophenol	300

(b) **Volumetric Analysis of Aliphatic Amine.**—For each molecule of *p*-nitroso dialkylaniline hydrolyzed one molecule of dialkylamine is evolved. By removing the liberated amine in a stream of nitrogen gas and then absorption in standardized hydrochloric acid it was possible to check the stoichiometry of the reaction by a method quite independent of the spectrophotometric procedure. In a typical estimation, *p*-nitroso-N,N-dimethylaniline (0.18 g.) was dissolved in 50 ml. of 0.2 *N* sodium hydroxide in a 100-ml. kjeldahl flask equipped with a nitrogen gas inlet tube reaching to the bottom of the flask. A splash head with a narrow bore outlet was connected to two conical flasks in series, each containing 25 ml. of dilute standard hydrochloric acid. The kjeldahl flask was heated to 83° for two hours with nitrogen gas passing continuously. At the end of this period the absorption flasks were disconnected and their contents titrated against 0.10 *N* sodium hydroxide.

Using this procedure it was shown that with a sufficiently long aspiration period it was possible to determine quantitatively all the dimethylamine present in the kjeldahl flask, and that good agreement was obtained between this method and the spectrophotometric procedure. However, when the hydrolysis reaction was studied in non-aqueous media such as ethyl or butyl alcohol–water mixtures, the reaction did not conform to the simple stoichiometric equation and the results indicated that other simultaneous side reactions occurred.

The aspiration method also was used in the preparation of derivatives required to establish the products of the reaction between aqueous sodium hydroxide and *p*-nitroso-*m*-hydroxy-N,N-diethylaniline.

3. **Rate Measurements.**—With the exception of *p*-nitroso-*m*-hydroxy-N,N-diethylaniline all rate measurements were made in the apparatus illustrated in Fig. 1. The vessel was designed to facilitate the mixing of two reactants after pre-heating to a constant temperature in a thermostated liquid bath, and to allow samples to be removed by a pipet maintained at the temperature of the reactants. The bulb A is connected by a looped capillary tube T to the vessel B; the tops of the vessels A and B are connected by a bridge fitted with a stopcock C; P is a constant volume pipet sealed into a stopper; this fills automatically when immersed in the solution in A, or alternatively it can be filled quite safely by mouth suction. The pipet volume was determined at the required temperatures by calculation from the weights of dilute standard sodium hydroxide delivered under standardized conditions. The density of the sodium hydroxide at the required temperatures was calculated from data given in the "International Critical Tables." From 16 replicate deliveries the variation in delivered volume was less than 0.75% measured on the pipet volume of 2.26 ml. at 60°. In a separate experiment it was established that under the conditions used for kinetic measurements there was no detectable interaction between the glass vessel and the sodium hydroxide solution used.

The general procedure adopted for determination of a specific rate constant was: the required volume of *p*-nitrosodialkylaniline solution was measured from a buret into compartment A and sodium hydroxide introduced from a bulb pipet into B. With the side-arm B stoppered and the pipet P closed with a screw clip, attached at S, the tap C was opened to maintain equal pressure in the two vessels and the apparatus immersed up to the tap C in a water-bath which could be thermostatically controlled to better than ±0.1°. In all cases a pre-heat period of one hour was allowed to establish thermal equilibrium.

At the required time the two solutions were mixed by closing tap C and blowing gently through the tube into B (with the pipet raised slightly) until the whole of the sodium hydroxide had been transferred to vessel A. Tube B was rinsed by twice sucking back part of the reaction mixture before finally transferring it to A. Gently blowing through B ensured thorough mixing of the reactants. On removal of the screw clip the pipet filled automatically, but the first filling was always returned to A so that the pipet was rinsed with the reactants before sampling. Samples were removed at timed intervals and discharged into hydrochloric acid contained in volumetric flasks, the pipet being returned immediately to vessel A. The volumetric flasks were filled to correct volume, shaken, and the contents analyzed on the same day by the spectrophotometric method already described.

The determination of the specific rate constants for the hydrolysis of *p*-nitroso-*m*-hydroxy-N,N-diethylaniline required apparatus which was capable of attaining higher temperatures than those possible in a water-bath. The kinetic measurements in this case were carried out in glass stoppered Pyrex tubes immersed in a vapor bath thermostat.[19]

TABLE II

Time, min.	Opt. density x_1 (300 mμ)	Opt. density x_2 (350 mμ)	Concn. (C_t) of *p*-NO-di-Me-aniline millimoles/l.	$k' = (1/t)2.3 \log (C_0/Ct)$, min.$^{-1}$	$k = k'/B_0$, min.$^{-1}$ l. moles^{-1}	$(1/t)[(1/c_t) - (1/c_0)]$ min.$^{-1}$ l. moles^{-1}
			Run 1			
0	0.240	0 524	$5.254 = C_0$			
2.5	.287	.437	4.147	0.0958	1.451	20.3
5	.325	.365	3.233	.0983	1.490	23.8
10	.380	.269	2.003	.0976	1.479	30.9
15	.407	.209	1.254	.0966	1 464	40.5
30	.446	.134	0.3037	.0961	1.457	103.4
60	.455	.111	0203	0938	1 422	816 8
			Run 2			
0	0.311	0.672	$6.730 = C_0$			
2.5	.373	.557	5.266	0.099	1.418	20.5
5	.425	.459	4.022	.105	1.494	20.0
10	.488	.334	2.443	.103	1.465	26.1
15	.527	.259	1.493	.102	1.451	34.7
37	.582	.155	0.173	.102	1.431	152.7
60.5	.590	.144	0.027	.092	1.320	609.7

4. **Order of Reaction and Activation Energies.**—A full investigation of kinetic order has not yet been completed, but preliminary studies using the integration method suggest that the rate data for over 90% of the reaction conform more to a second- than to a first-order rate equation; this is shown in Fig. 2 where typical data are plotted as first- and second-order functions.

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(19) W. E. Silberman and T. Henshall, THIS JOURNAL, **79**, 4107 (1957).

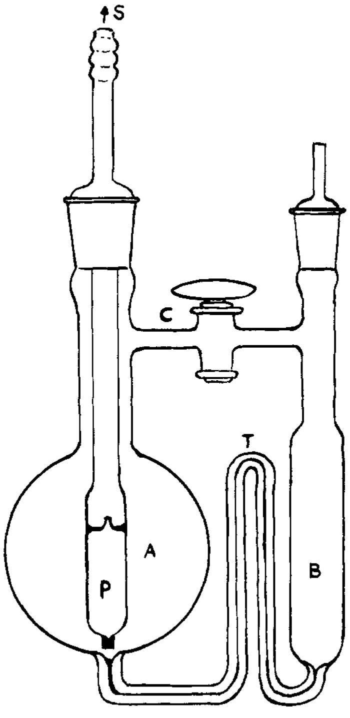


Fig. 1.—The reaction cell.

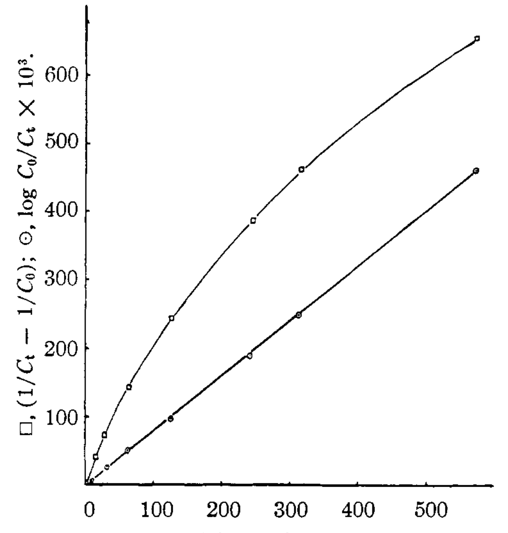


Fig. 2.—Kinetic order.

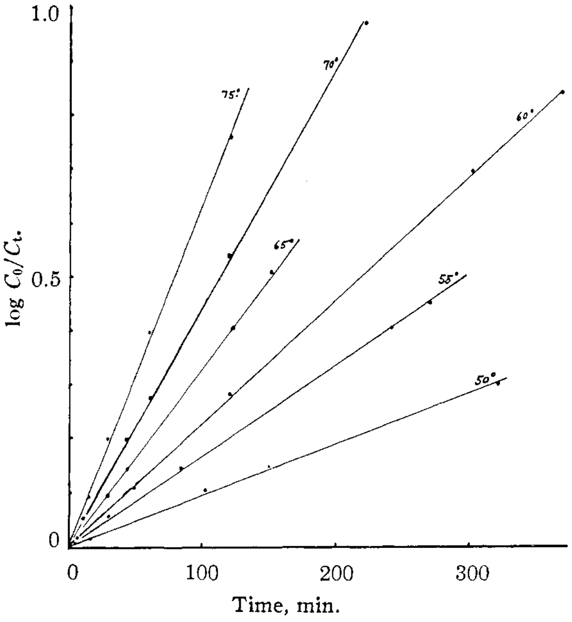


Fig. 3.—First-order rate plots for the hydrolysis of *p*-nitroso-*m*-ethoxy-N,N-diethylaniline.

TABLE III

Substance, aniline	Temp. T, °A.	k, l. moles^{-1} min.$^{-1}$	E_A, kcal.	log PZ
p-Nitroso-N,N-dimethyl-	303	0.172		9.20
	313	.345		9.18
	323	.666		9.17
(1)	333.15	1.332	13.8	9.23
p-Nitroso-N,N-diethyl-	313	0.103		8.52
	323	.191		8.49
	333.15	.439		8.57
	338.1	.512		8.51
(2)	343	.698	13.6	8.52
p-Nitroso-N,N-di-*n*-propyl-	323.1	.141		6.05
	336	.252		6.04
	338	.272		6.04
	343	.351		6.05
(3)	353.5	.557	10.2	6.06
p-Nitroso-*m*-methyl-N,N-dimethyl-	303	.087		9.84
	313	192		9.84
	323	.419		9.85
(4)	333	.813	15.1	9.83
p-Nitroso-*m*-chloro-N,N-dimethyl-	312.6	.450		10.43
	323.3	1.221		10.51
	333	1.960		10.41
(5)	343	4.201	15.4	10 44
p-Nitroso-*m*-ethoxy-N,N-diethyl-	323	0.047		9.64
	328.3	.077		9.68
	333	.107		9.67
	338.15	.155		9.67
	343.1	.206		9.66
(6)	348	.295	16.2	9.65
p-Nitroso-*m*-hydroxy-N,N-diethyl-	359.6	.0001		10.00
	369.8	.00027		10.00
	373	.00033		10.00
(7)	378.5	.00078	23.0	10.05

In separate experiments the order with respect to *p*-nitroso-N,N-dimethylaniline was investigated by the isolation method using a large excess of sodium hydroxide. Typical results shown in Table II indicate that under these conditions the data closely fit a first-order but not a second-order equation.

Concn. of sodium hydroxide (B_0): run 1, 0.066 molar: run 2, 0.070 molar: temperature of reaction 60° ±0.1°; extent of reaction followed 99.8%; x_1 = opt. density at 300 mμ, x_2 = opt. density at 350 mμ.

For the other *p*-nitroso-N,N-dialkylanilines investigated, the rate constants were obtained by the isolation method using a constant excess of sodium hydroxide. In all cases rate constants were calculated from large scale plots of log C_0/C_t against time, in which very satisfactory linearity was obtained for up to 90% of the total reaction. Typical results are shown in Fig. 3 for *p*-nitroso-*m*-ethoxy-N,N-diethylaniline.

Activation energies were computed from large scale plots of log k against $1/T$ in which the rate constant k was determined at four or more different temperatures.

A summary of rate constants, activation energies and the derived probability term log PZ are given in Table III.

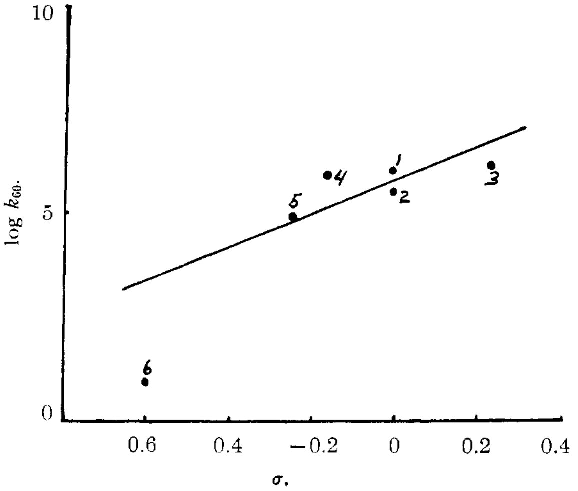
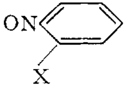


Fig. 4.—A plot of log k_{60} against Hammett's σ-constants in



ON–C$_6$H$_3$(X)–NR$_2$: 1, R = Me, X = H; 2, R = Et, X = H; 3, R = Me, X = Cl; 4, R = Me, X = Me; 5, R = Et, X = OEt; 6, R = Et, X = OH.

5. **Dissociation Constants.**—The pK_B values for *p*-nitrosodimethyl, diethyl- and di-*n*-propylanilines were determined from the equation

$$pK_B = 14 - pH - \log \times \frac{C_{BH^+}}{C_B} + \frac{0.5\sqrt{\mu}}{1 + \sqrt{\mu}}$$

The ratio C_{BH^+}/C_B for the above three substances was measured by spectrophotometric estimation of undissociated base (C_B) and conjugate acid (C_{BH^+}) in 5% alcoholic solution containing suitable buffers. The ionic strength was calculated from the known molarities of the buffer solutions. *p*H values were measured with a glass electrode and a silver/silver chloride reference electrode using a Cambridge *p*H meter.

For comparative purposes the pK_B value of *p*-nitrodimethylaniline was determined by a method similar to that described by Flexer, *et al.*[20] Since *p*-nitrodimethylaniline has very weak basic properties it was necessary to use strong hydrochloric acid to form the conjugate acid.

Aniline	Mean pK_B
p-Nitroso-N,N-dimethyl-	10.03
p-Nitroso-N,N-diethyl-	9.89
p-Nitroso-N,N-di-*n*-propyl-	9.83
p-Nitro-N,N-dimethyl-	13.40

Discussion

Application of currently accepted theories of nucleophilic substitutions[4,5,21] to the results obtained indicates that the hydrolysis of *p*-nitroso-N,N-dialkylanilines is of the S_N2 type, a conclusion that is based on observations that are strongly suggestive of over-all second-order kinetics, being separately of first order in each reactant, and on the increase in activation energy caused by the introduction of electron-releasing groups into the benzene ring. This is further supported by the previous observations of Miller and Adams on the hydrolysis of the parent compound *p*-nitroso-N,N-dimethylaniline for which over-all second-order kinetics were reported.[3]

Since the introduction of substituents in the aromatic ring influenced the reaction rate, it is appropriate to consider whether or not the Hammett substituent constants are valid for this reaction. The near constancy of the log *PZ* values for the *m*-substituted compounds shown in Table III indicates that the reaction rate in this series is controlled almost entirely by the activation energy term E_A, and under these sufficient conditions the Hammett equation may be applied.[22]

Although the second substituent is *meta* to the site of reaction it seems probable that it is most likely to exert its influence by interaction with the nitroso group in the *o*-position and Fig. 4 shows the relationship between log k_{60} and the Hammett *ortho* constant (σ^0). In those cases where σ^0 is not available σ_p has been used as being in near equality.[23] In Fig. 4 the σ-value of −0.6 for the OH group is that reported by Berliner and Monack[24] where partial conversion to the phenoxide ion was expected.

In the strongly alkaline media used in this work almost complete conversion to phenoxide ion ($R\text{–}O^-$) is to be expected and consequently a value of $\sigma = -1.5$ which is obtained from Fig. 4 by extrapolation, does not seem unreasonable.

The ρ-value derived from Fig. 4 is +3.6 which is higher than most values reported for side chain reactions; on the other hand, it is somewhat less than the value of +4.95 found for the nucleophilic reaction between substituted nitrobromobenzene and piperidine.[24]

Thus from the limited data available it seems reasonable to conclude that the Hammett constants may be applied in a general way to this reaction, although it is likely that a set of σ-values specially adjusted to the requirements of nucleophilic substitution reactions would give better agreement between observed and predicted effects of substituents.

Entropy of Activation—Whereas nuclear substituents appear to influence the reaction rate mainly by changing the reaction activation energy, there is evidence from the limited data obtained to suggest that a change of groups on the anilinium nitrogen influences the reaction by quite a different mechanism. Thus the kinetic data for *p*-nitroso-N,N-di-*n*-propylaniline (Table III) shows that in addition to a drop in activation energy there is also a marked decrease in activation probability when compared with the data for *p*-nitroso-N,N-dimethylaniline.

The significance of this is further emphasized by consideration of the entropy of activation. This has been calculated from the equation[25]

$$\Delta S^* = 2.303R\left(\log PZ - \log \frac{\bar{k}T}{h}\right) - R$$

These values were obtained:

Aniline	E_A, kcal.	k_{60}	$-\Delta S^*$, cal. deg.$^{-1}$
p-Nitroso-N,N-dimethyl-	13.8	1.31	18.7
p-Nitroso-N,N-diethyl-	13.6	0.412	21.8
p-Nitroso-N,N-di-*n*-propyl-	10.2	0.222	33.1

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[20] L. A. Flexer, *et al.*, THIS JOURNAL, **57**, 2103 (1935).

[21] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[22] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 120.

[23] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," Ed. M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 593.

[24] E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1574 (1952).

[25] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y.

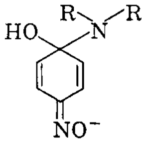
Thus as the groups attached to the anilinium nitrogen are changed from methyl through ethyl to *n*-propyl, the entropy of activation increases sharply; and application of the transition state theory rate equation

$$k = e \times \frac{\bar{k}T}{h} e^{-E_A/RT} \times e^{\Delta S^*/R}$$

shows that the reaction rate of these compounds is strongly controlled by the entropy changes.

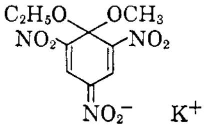
Reaction Mechanism.—While the data at present available are too limited to allow any firm conclusion to be drawn about the most probable reaction mechanism, it is useful to consider some possibilities.

In this discussion it is accepted that there is no valid transition state model for aromatic substitution in which benzenoid resonance is maintained,[4] and the pentadienate anion is considered to be the most probable form. In the compounds under investigation the pentadienate structure II will be stabilized if the nitroso group can act as an electron sink, thus



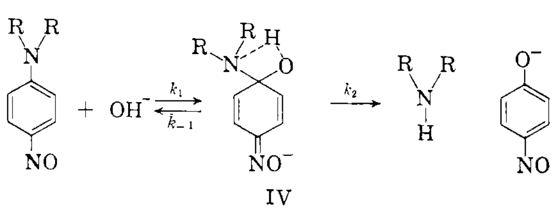
II

Such structures have been suggested[4,26] for addition complexes in which nitro-groups are present in the ring, *e.g.*, III



III

The existence of these complexes has given rise to the suggestion that nitro-activated substitution reactions may proceed through an intermediate of this type,[27,28] and Bunnett[5] cites recent evidence in powerful support of the intermediate-complex mechanism for nuclear substitution. Using the pentadienate system as a *transition* state, it is possible to formulate the hydrolysis of the *p*-nitrosodialkylanilines in this way, IV[29]



IV

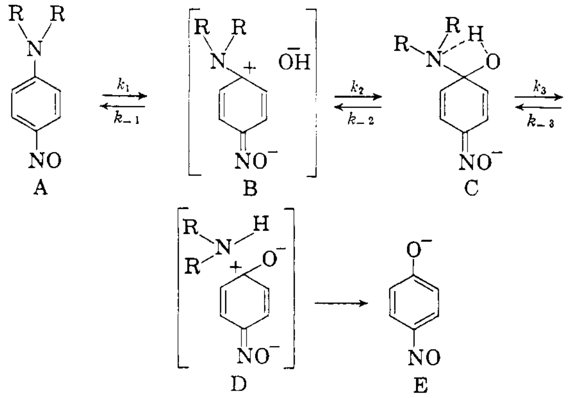
From simple kinetic data it is not possible to determine whether the rate-controlling step is the formation of the new bond (k_1) or the breaking of the carbon–nitrogen bond (k_2). It is, however· quite clear that if the transition state is stabilized by the nitroso group acting as an electron sink, then the presence of electron-releasing groups such as –OEt and –OH in the ring will, by cross conjugation with the nitroso group, destabilize the pentadienate structure and so cause the rise in activation energy which is found experimentally.

However, this simple reaction scheme is not wholly adequate since it cannot account for the observed decrease in rate constant when the anilinium nitrogen substituents are changed from methyl through ethyl to propyl. It is apparent from the discussion of activation entropy that the reaction rate for these three compounds is controlled mainly by the entropy term; but it is difficult to account for this and for the significant drop in activation energy of the *n*-propyl compound in terms of the pentadienate transition state IV.

It seems possible that the alkyl groups might influence the reaction by hyperconjugative electron release through the nitrogen atom to the site of substitution; in this case the methyl group might be expected to have the greatest effect. Another possibility is that the propyl groups might cause some steric inhibition of resonance between the nitrogen atom and the aromatic system; although if this is so, it would almost certainly lead to an increase rather than the observed decrease in activation energy.

If either of these effects is in fact operative, it seems likely that it would also influence the basicity of the anilinium nitrogen. Electron release from the nitrogen substituents should increase basicity, *i.e.*, di-*n*-propyl < diethyl < dimethyl; whilst steric inhibition of resonance would decrease the delocalization of the unshared electron pair on the nitrogen atom, thus increasing basicity in the order dimethyl < diethyl < di-*n*-propyl. Experimental measurements of pK_B values for the three compounds showed that the latter order of basicity prevailed, but that the differences are very small and not likely to account for the differences in kinetic constants.

An alternative approach to the problem of mechanism is based upon the reaction sequence V involving the pentadienate structure as a true intermediate as distinct from a transition state



V

In this sequence, the intermediate C is by definition considered to have a real though short exist

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(29) The authors wish to acknowledge helpful suggestions by the referee concerning the reaction scheme.

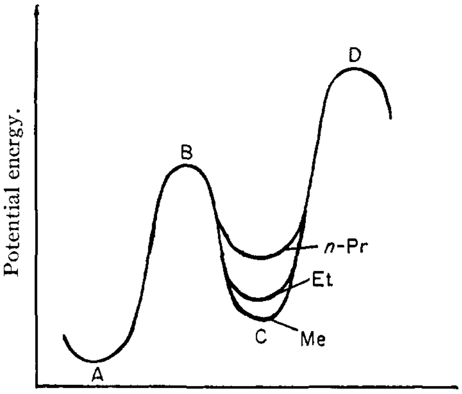

Fig. 5.—Schematic potential energy diagram.

ence; B and D are the two transition states representing its formation and decay. It is emphasised that no evidence is yet available for the occurrence of such an intermediate in this reaction, but by analogy with the nitro-stabilized intermediate already mentioned, the suggestion appears plausible.

Since the pK_B values for the three *p*-nitrosodialkylanilines were shown to be very similar it seems that change of R from methyl to propyl does not materially affect the general electronic distribution in the reactant molecule. Hence the energy of stage A in the above sequence will be largely independent of the changes in R.

However in the intermediate C, and transition states B and D, the carbon atom in position 1 will be approximately tetrahedral; and with two bonds fixed in the pentadienate structure the possibility of steric crowding becomes real. Examination of molecular models shows that the crowding of atoms prevents free rotation about many single bonds in the amine groups, and that this crowding increases considerably as R is changed from methyl to *n*-propyl. Thus the intermediate C and related transition states become more rigid as the size of R increases; this would explain the greater negative entropy of activation observed for the larger alkyl groups.

Such atomic crowding will also influence the stability of the complex C, so that its potential energy will be less for R = methyl, than for R = ethyl or *n*-propyl. A further degree of stability in the former case may also arise from the greater electron release of the methyl groups with the production of a higher C–N bond-order.

It now remains to consider the relative potential energies of the transition states B and D, and hence also the relative magnitudes of the rate constants k_{-1} and k_3. Consideration both of the alternative modes of cleavage of the intermediate C, and of the structures of the related transition states of which B clearly has the greater over-all conjugation, would suggest that the mode of decomposition to *p*-nitrosophenol is less energetically favorable. Hence the over-all rate of reaction will be governed by k_3 and the equilibrium concentration of intermediate C which will be greatest for the case R = methyl. These factors are summarized in a potential energy diagram for the system shown in Fig. 5.

A mechanism of this form may also account for the failure of *p*-nitro-N,N-dimethylaniline to undergo facile hydrolysis. Certainly something more than the creation of positive charge at the site of substitution in the reactant molecule seems to be required, since the nitro group undoubtedly exerts a powerful inductive electron attraction on the remainder of the molecule. This is confirmed by the measured pK_B value of 13.40 for *p*-nitro-N,N-dimethylaniline compared with only 10.03 for the *p*-nitroso-N,N-dimethylaniline, and which suggests that the initial polarization is greater in the nitro than in the nitroso compounds.

Hence it is suggested that stabilization of the pentadienate transition or intermediate states is of greater significance than initial polarization. Highest stability will be conferred by those substituents which can efficiently conjugate or overlap with the aromatic system and at the same time act as an electron sink. In this connection Bunnett and Zahler[4] have pointed out that the most powerful nucleophilic activating group $-N_2^+$ which facilitates replacement of nitro, methoxy and halogen by hydroxyl even at room temperature can, by becoming neutral in the transition state, accommodate a unit electronic charge. On the other hand, the trimethylammonio group $-\overset{+}{N}(CH_3)_3$ which also contains a positive charge to produce initial polarization, is *not* a particularly strong activating group, possibly because it cannot become neutral in the transition state by rearrangement of electrons, for the covalency maximum of nitrogen is 4 and this is already reached in the original group. Le Fevre[30] concluded from a study of dipole moments of nitroso compounds that "The nitroso group has an unusually large capacity for producing polarization of aromatic systems which is restricted only by the limitation of the remainder of the molecule to act as an electron source." Thus in the pentadienate anion where a complete negative charge is available it is possible that the nitroso group can produce a greater polarization than the nitro group. The required conditions for the efficient conjugation with the aromatic system may well be more favorable for the nitroso group which contains an unshared pair of *p*-π-type electrons than for the nitro group.

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