dissolved completely in the liquid, forming a complex which could be heated above the boiling point of bromine. The excess of bromine (including that contained in the hydrobromic acid) is necessary because a certain loss of bromine is unavoidable on a laboratory scale. It is carried away by the rapid current of hydrochloric acid (and CO_2) formed in the reaction.

The contents of the flask was heated to 65° and 96 g. of furfural added at such a rate that the steady flow through the capillary took about 2 to 2.5 hours. The furfural reacts exothermically with the bromine. The temperature was allowed to reach 75° and the bromine started to reflux. As soon as the deep red color of the liquid became lighter, a fast current of chlorine was passed through the liquid. The flow of furfural and chlorine has to be adjusted in a ratio of 1:3 by weight. The temperature was kept between 75 and 85° by external cooling. When about $^2/_5$ of the furfural had been added, the evolution of large quantities of hydrogen chloride began. Almost no cooling was then needed to keep the temperature at 80–85°. After all of the furfural was in, the temperature was raised to 95° and the chlorine flow cut in half. Chlorine was then added until the whole usage was about 290 g. (90–94% of the theoretical 4.5 mole equivalents). There remained in the flask a pale yellow liquid which on cooling formed a stiff slurry of almost white crystals. This crude product was purified by crystallization from hot water. The yield was 90–94% of theory; m.p. of the purified compound, 122.5°. Titration with caustic showed a molecular weight of 212 (theory, 213).

Anal. Calcd. for $C_4H_2O_3BrCl$: C, 22.5; H, 0.95; Br + Cl, 54.07. Found: C, 22.7; H, 1.02; Br + Cl, 53.7.

Acknowledgments.—We are indebted to Dr. R. J. Vander Wal for suggesting the use of 3,4-dichloro-2-furoic acid to make Hill's 4-chloro-2-furoic acid and for his kindness in supplying a copy of his thesis. We wish to thank Dr. D. N. Kendall for making and interpreting the infrared absorption curves, and O. E. Sundberg for the microanalysis.

CHEMICAL RESEARCH DEPT.
CALCO CHEMICAL DIVISION
AMERICAN CYANAMID CO.
BOUND BROOK, N. J.

Kinetics of the Hydrolysis of *p*-Nitrosodimethylaniline[1]

BY F. M. MILLER AND MARTHA L. ADAMS

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The cleavage of *p*-nitrosodialkylanilines by base, a classical preparative method for dialkylamines, has often been considered to be a typical aromatic nucleophilic displacement reaction.[2] There has been, however, beyond gross similarities, no available evidence to support this contention. Further, since this is one of the few known examples of a reaction in which the group displaced is activated by a nitroso group, it was of interest to examine the reaction kinetically.

$$p\text{-ON—}C_6H_4N(CH_3)_2 + NaOH \longrightarrow p\text{-ON—}C_6H_4ONa + (CH_3)_2NH$$

Experimental

Materials.—*p*-Nitrosodimethylaniline was prepared by nitrosation of dimethylaniline,[3] and obtained as green crystals from ligroin with a melting point of 86°.[4] *p*-Nitrosophenol was obtained by hydrolysis of the nitrosoaniline,[5] and purified by recrystallization from water to a constant melting point of 124–128°.[6]

Method.—It was found from the absorption spectra of *p*-nitrosodimethylaniline in 50% alcohol–water and of *p*-nitrosophenol in the same solvent, which was also approximately 0.2 *M* in sodium hydroxide, that at a wave length of 675 mμ there is a maximum absorption due to *p*-nitrosodimethylaniline and a corresponding minimum in the curve for *p*-nitrosophenol. Using a Coleman spectrophotometer, the optical densities of various mixtures of *p*-nitrosodimethylaniline and *p*-nitrosophenol were determined, and a standard curve drawn.

One-tenth molar solutions of *p*-nitrosodimethylaniline in 50% alcohol–water were prepared frequently by weighing out the calculated amount of the substance. In carrying out an experimental run, definite quantities of this 0.100 *M* *p*-nitrosodimethylaniline solution were measured into the reaction flask by means of a buret. A calculated amount of potassium chloride was added to maintain a constant ionic strength of 0.203. The flask and contents were allowed to reach bath temperature and a calculated quantity of standard sodium hydroxide, also at bath temperature, added with stirring from a pipet. At convenient intervals samples of the reaction mixture were withdrawn by means of a pipet and diluted to give a concentration of approximately 0.01 *M* or less. The extent of dilution nearly stopped the reaction. The diluted samples were immediately transferred to the spectrophotometer cuvettes and readings of the optical density taken at 675 mμ. The concentrations of *p*-nitrosodimethylaniline were then determined from the standard curve, and the concentration of the withdrawn sample calculated using the appropriate dilution factor. Runs were made at 30 and 50 ± 0.05°.

Results and Discussion

Typical data for reactions at 30 and 50° are listed in Tables I and II, respectively, and plots of these data are given in Fig. 1. The results of several runs at various concentrations are given in Tables III and IV. From the average values of the rate constants at the two temperatures the energy of activation was calculated to be 13 kcal. and log *PZ* to be 6.

TABLE I

TYPICAL DATA FOR A REACTION AT 30°

Time, sec.	Optical density	$(b - x)$ (p-$ONC_6H_4N(CH_3)_2$)	$(a - x)$ (NaOH)	$\log \frac{a - x}{b - x}$
0	...	0.0750	0.203	0.432
360	0.511	.0599	.188	.497
615	.495	.0572	.185	.510
1065	.471	.0535	.181	.529
1515	.460	.0517	.180	.542
1810	.450	.0505	.178	.548
2340	.430	.0476	.176	.568
2595	.420	.0455	.173	.580

TABLE II

TYPICAL DATA FOR A REACTION AT 50°

Time, sec.	Optical density	$(b - x)$ (p-$ONC_6H_4N(CH_3)_2$)	$(a - x)$ (NaOH)	$\log \frac{a - x}{b - x}$
0	...	0.0500	0.199	0.600
135	0.520	.0413	.190	.663
380	.479	.0365	.186	.707
610	.440	.0325	.182	.748
945	.400	.0282	.177	.798
1880	.310	.0187	.168	.954

The second-order character of the rate constants, and the values of the Arrhenius parameters are in

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[1] Abstracted from the thesis presented by M. L. Adams to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science.

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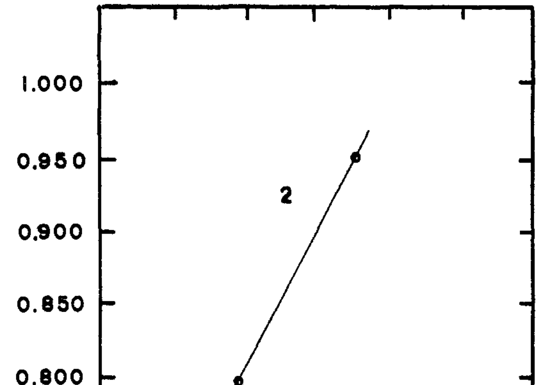

Fig. 1.—Rate curves for the hydrolysis of *p*-nitrosodimethylaniline: 1, at 30°; 2, at 50°.

TABLE III

VALUES OF THE SPECIFIC REACTION RATE AT 30°

NaOH	*p*-ONC$_6$H$_4$N-(CH$_3$)$_2$	$k \times 10^3$ (l. mole^{-1} sec.$^{-1}$)
0.203	0.100	5.96
.203	.075	6.23
.102	.095	7.27
.143	.085	7.51
.203	.050	7.16
	Av.	6.4 ± 0.7

TABLE IV

VALUES OF THE SPECIFIC REACTION RATE AT 50°

NaOH	*p*-ONC$_6$H$_4$N-(CH$_3$)$_2$	$k \times 10^3$, (l. mole^{-1} sec.$^{-1}$
0.075	0.075	2.46
.203	.050	2.82
.199	.050	2.58
.203	.070	2.20
.199	.090	2.10
	Av.	2.4 ± 0.4

agreement with similar data for known aromatic nucleophilic displacement reactions.[2c] Therefore, the cleavage of *p*-nitrosodimethylaniline may now be considered as an example of this reaction type, and the mechanism of the reaction may be thought of as that of a typical aromatic nucleophilic displacement reaction,[2] although, as pointed out by Berliner,[7] it is not yet possible to decide whether the formation or decomposition of the transition complex is the rate determining step. It is noteworthy that the values of the activation energy and log *PZ* for this reaction, in comparison with those for other reactions of this type, substantiate the statement of LeFevre[8] that one nitroso group will activate a group toward displacement roughly to the same extent as two nitro groups.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
BALTIMORE 1, MARYLAND

Copolymerization of Anthracene with 1,3-Butadiene[1]

BY C. S. MARVEL AND W. S. ANDERSON

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Recently Stockmayer and Peebles demonstrated the ability of benzene to copolymerize with vinyl acetate.[2] This prompts us to record the copolymerization of another aromatic hydrocarbon, anthracene, with 1,3-butadiene.

Copolymers prepared from butadiene (95 pts.) and anthracene (5 pts.) in the Mutual recipe[3] showed an intense ultraviolet absorption with maxima at 2575, 2645 and 2720 Å. which were not altered by repeated solution and reprecipitation of the copolymer. These absorption peaks resemble very closely those reported for 9,10-dihydroanthracene[4a] and for 9,10-dimethyl-9,10-dihydroanthracene,[4b] which indicates that the copolymerization involves the 9,10-positions in the anthracene molecule. Using the extinction coefficients for 9,10-dihydroanthracene for comparison, it is calculated that approximately 5% by weight of anthracene has been incorporated in a copolymer prepared to 25% conversion.

Agitation of anthracene with polybutadiene latex does not produce a polymer with these absorption maxima; hence the anthracene is not introduced by an addition to the polybutadiene.

Benzene was employed as a mutual solvent for butadiene and anthracene in these emulsion polymerizations. There were no absorption maxima which indicated incorporation of benzene units in the copolymer when anthracene was present or absent during such polymerizations.

That anthracene does give free-radical reactions has been demonstrated before. 2-Methylanthracene has been shown to copolymerize with styrene.[5] Anthracene itself inhibits the autoxidation of benzaldehyde.[6] The photodimerization of anthracene is well known,[7] and recently[8] the addition of free radicals to anthracene, both with and without con-

(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

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