Kinetics of the Reaction of N-Arylpyridinium Chloride with Anilines

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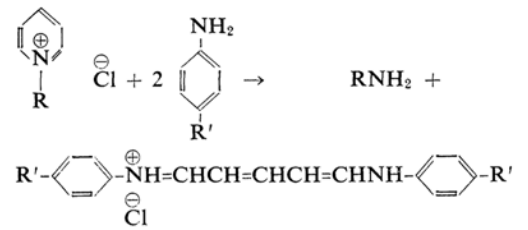
(Received September 22, 1962)

It is known that some *N*-arylpyridinium salts react with aniline to give glutacondialdehydedianil hydrochloride (I)[1,2]:



(Here R stands for 2, 4-dinitrophenyl or other electron-withdrawal groups.) Since the mechanism of the reaction had scarcely been studied, for the present paper the rates of the reaction with various R′ and R were measured by the estimation of the dianil produced in order to obtain some information on the mechanism.

Results and Discussion

The rate of the reaction is expressed in terms of the third-order equation:

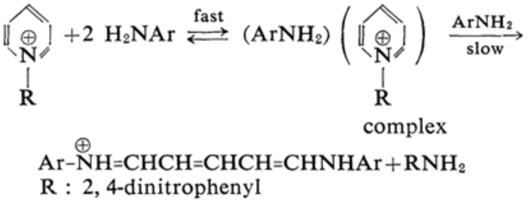
$$\mathrm{d}x/\mathrm{d}t=k(a-2x)^2(b-x)$$

or

$$k=\frac{2.30}{t(a-2b)^2}\log\frac{b(a-2x)}{a(b-x)}+\frac{1}{t(a-2b)}\cdot\left\{\frac{1}{a-2x}-\frac{1}{a}\right\}$$

Here, *a* is the initial concentration of aniline, *b*, that of pyridinium salts, and *x*, the concentration of dianil at time *t*. As an example, a typical run with aniline is shown in Table I. The second-order equation does not agree with the results. The third-order constants for substituted anilines are listed in Table II, which shows the effect of substituents in aniline.

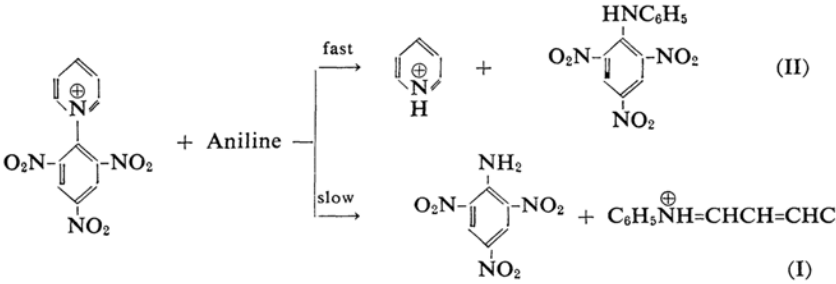
The Hammett plot of σ: $\log(k/k_0)$ gives a straight line (Fig. 1) which affords the ρ-value of -4.50. This fact suggest a mechanism involving a nucleophilic attack of aniline on the pyridine-aniline complex and a transition state consisting of two molecules of aniline and a molecule of the pyridinium ion:



The equilibrium for the formation of complex as well as the rate of the nucleophilic attack of aniline should be suppressed by the decreased electrophilicity of the pyridinium salt, i. e., by the smaller electron-withdrawal group. This expectation is supported by the fact that *p*-nitrophenylpyridinium salt (lower electrophilicity) failed to react with aniline.

TABLE I. TYPICAL THIRD-ORDER RATE CONSTANTS FOR THE REACTION OF ANILINE WITH 2, 4-DINITROPHENYLPYRIDINIUM CHLORIDE

Time min.	Conversion %	$k\times10^{-2}$ l. mol^{-2} sec^{-2}
2	2.77	1.89
10	13.1	1.77
20	24.1	1.75
40	39.5	1.77
60	43.5	1.50



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[1] T. Zincke, G. Heuser and W. Möller, *Ann.*, 333, 296 (1904).

[2] G. E. Ficken and J. D. Kendall, *J. Chem. Soc.*, 1959, 3988.

TABLE II. THE EFFECT OF SUBSTITUENTS IN ANILINE ON THE RATE

R′	a, M	b, M	k (l^2 mol^{-2} sec^{-1})	
			at 30°C	at 50°C
p-OCH$_3$	$0.266\times2/5$	$0.0888\times2/5$	3.43×10^{-1}	
p-OC$_2$H$_5$	$0.266\times2/5$	$0.0888\times2/5$	2.38×10^{-1}	
m-CH$_3$	$0.266\times2/3$	$0.0888\times2/3$	4.76×10^{-2}	
H	0.266	0.0888	1.75×10^{-2}	2.20×10^{-1}
p-Cl	$0.266\times5/2$	$0.0888\times5/2$	7.80×10^{-4}	
p-NO$_2$	no reaction			

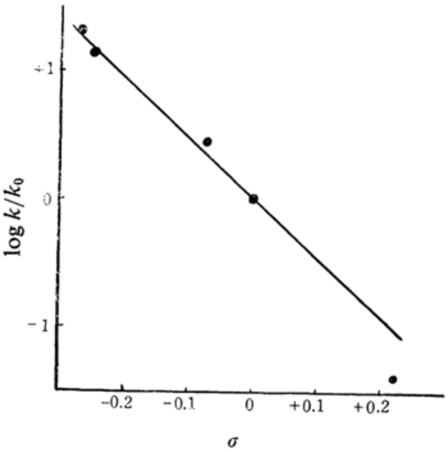

Fig. 1. Hammett's plot of the reaction of pyridinium salt with anilines.

2, 4, 6-Trinitrophenylpyridinium salt reacted very rapidly with aniline, yielding a considerable amount of picrylphenylamine (II) as well as a smaller amount of dianil I.

Experimental

Materials.—2, 4-Dinitrophenylpyridinium chloride was prepared by the reaction of 2, 4-dinitrochlorobenzene and pyridine[1]. p-Nitrophenylpyridinium chloride was prepared by the reaction of p-nitroaniline, pyridine and cyanogen bromide[2]. 2, 4, 6-Trinitrophenylpyridinium chloride was prepared by the reaction of picryl chloride[2]. The melting points of all these materials agree with those in the literature.

The Rate Measurements.—2, 4-Dinitrophenylpyridinium chloride (2.50 g.) was dissolved in methanol (90 ml.) and 9 ml. of the solution was introduced into test tubes dipped in a thermostat maintained at 30°C. Ten milliliters of a methanolic solution of aniline (2.48 g.) was kept at the same temperature until the temperature equilibrium was reached. One milliliter of the aniline solution was then pipetted out and poured into the pyridinium solution to start the reaction. At appropriate time intervals, the contents of the test tubes were poured into an ice-cooled mixture of acetone (15 ml.) and concentrated hydrochloric acid (15 ml.) to stop the reaction, and the mixture was allowed to stand for about 30 min. while being shaken. The red precipitate, glutacondialdehyde-dianil, was filtered with a glass filter, washed with a small amount of acetone and water, dried at 80∼100°C, and weighed. From the amount of the dried product, the third-order rate constant was calculated. Another product, 2, 4-dinitraniline, is soluble in acetone, but is only with difficulty soluble in water, while the dianil is soluble in water, but far less soluble in acetone. From blank tests under the kinetic conditions, the ratios of the produced amount of dianil after a long reaction time vs. the calculated amount were found to be as follows: p-anisidine, 1.00; aniline, 1.02; p-phenetidine, 1.04; p-chloraniline, 1.10; p-toluidine, 1.02 and p-nitraniline, no reaction. The amount of the obtained precipitate was corrected by the above ratio.

The Reaction of 2, 4, 6-Trinitrophenylpyridinium Chloride.—In a methanolic solution, 2, 4, 6-trinitrophenylpyridinium chloride (0.29 g.) was reacted with aniline (0.248 g.) at 30°C for 5 min. The solution immediately turned red. After filtration of the precipitate of 2, 4, 6-trinitrodiphenylamine (m. p. and mixed m. p. 178°C), diluted aqueous hydrochloric acid was added to the solution. The resulting precipitate, after being filtered and washed with boiling acetone, gave the dianil; 0.011 g. (4.3%); m. p. and mixed m. p., 143°C. 2, 4, 6-Trinitrodiphenylamine was recovered from the acetone solution. The combined yield of this product was 0.213 g. (81%).

Summary

The rates of the reaction of 2, 4-dinitrophenylpyridinium chloride with ring-substituted anilines in methanol have been estimated by the gravimetry of the produced glutacondialdehyde dianil. The rates have been found to be second-order with aniline and first-order with pyridinium salt. The electron-withdrawal groups in pyridine accelerate the reaction. These facts suggest a mechanism involving a nucleophilic attack of the molecules of aniline on a complex consisting of 2 molecules of aniline and a pyridinium ion. The products of the reaction of 2, 4, 6-trinitrophenylpyridinium chloride with aniline were 2, 4, 6-trinitrodiphenylamine and the dianil.

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