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The Activating Effects of Amino Groups in Diazo-coupling Reactions

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Synopsis. The rates of the reactions of various aromatic amines with diazotized sulfanilic acid have been studied. It was found that, among the *N,N*-disubstituted anilines, the activating effect of amino groups is roughly proportional to their pK_a values.

The kinetics of diazo-coupling reactions have been studied extensively in order to elucidate the reaction mechanism and the structural effects of the reactions on the reactivity.[1] As to the structural effect of the azo components on the reactivity, studies of phenols[2-4] and active methylene compounds[5] have been reported. However, much less work has been done on the reactions of aromatic amines; quantitative studies of the effects of amino groups in the electrophilic aromatic substitution have not been extensively undertaken, probably because of their basic properties and powerful substituent effects.[6]

This paper will report the quantitative results of the reactions of various aromatic amines with diazotized sulfanilic acid.

Experimental

Materials. *N,N*-Di-*iso*-propylaniline and *N*-ethyl-*N*-methylaniline were prepared by alkylating aniline and *N*-methylaniline with the corresponding alkyl iodides.[7] 9-Aminoanthracene was synthesized by the method of Kaufler.[8] The other aromatic amines were of commercal origin and were purified by distillation under reduced pressure. Their purities were confirmed by means of their physical constants and by vaporphase chromatography.

Kinetic Measurements. The diazo-coupling reaction of aromatic amines is known to be expressed by Eq. (1):[1]

$$\text{Rate} = k_2(\text{Ar-}\overset{+}{\text{N}}_2)(\text{Ar}'\text{-NH}_2) \quad (1)$$

In our experiment, the rate measurements were carried out spectrophotometrically in the presence of a large excess of amine in an aqueous buffer solution at a constant ionic strength of 0.04 at 20 °C. Then, the apparent rate constant (k') was calculated from Eq. (2):

$$k't = \ln\frac{E_\infty}{E_\infty - E_t} \quad (2)$$

where E_t and E_∞ represent the concentrations of the dyestuff formed at time t, and at an infinite time, respectively. The second-order rate constant (k_2) was obtained by dividing the k' value by the concentration of free amine, which can be calculated from the pK_a value, the concentration of amine, and the pH value of the medium. The buffering agents were of conventional CH_3COONa–CH_3COOH or CH_3COONa–HCl systems.

pK_a *Measurements.* The pK_a values of amines were determined spectrophotometrically under conditions identical with those of the kinetic experiments (20 °C, μ: 0.04, Table 1). As can be seen from Table 1, excepting the results for *N,N*-di-*n*-propylaniline, there is no serious disagreement between the present results and the published values; the slight disagreement may be ascribed to the differences in temperature and ionic strength.

Results and Discussion

The kinetic results are summarized in Table 1. As is shown in Table 1, the structural change of amine does not affect the reaction rate to any marked degree.

From the results (No. 1—3), it can be seen that the reactivity increases in the order of; primary<secondary <tertiary amine. This reactivity order is essentially the same as that obtained for alkylation;[9] it may be explained by an increased resonance donation of the lone pair of electrons of the amino nitrogen atom due to the alkyl group in the amino substituent.[6]

TABLE 1. RATE CONSTANTS OF THE REACTION OF DIAZOTIZED SULFANILIC ACID WITH AROMATIC AMINES AT 20 °C

No.	Amine	pK_a	k_2 (l/mol·min)
1	*m*-Toluidine	4.84(4.70)[a]	1.65×10^3
2	*N*-Methyl-*m*-toluidine	4.94	1.24×10^4
3	*N,N*-Dimethyl-*m*-toluidine	5.47(5.24)[b]	1.54×10^4
4	*N,N*-Dimethylaniline	5.17(5.06)[b]	7.34×10^2
5	*N*-Ethyl-*N*-methylaniline	5.98(5.98)[b]	1.72×10^3
6	*N,N*-Diethylaniline	6.72(6.56)[b]	3.92×10^3
7	*N,N*-Di-*n*-propylaniline	6.69(5.59)[b]	1.27×10^4
8	*N,N*-Di-iso-propylaniline	7.50(7.37)[c]	3.71×10^3
9	*N,N*-Di-*n*-butylaniline	6.37(6.21)[c]	7.71×10^3
10	*N*-Benzyl-*N*-ethylaniline	5.75	1.96×10^3
11	*N*-(2-Hydroxyethyl)-*N*-ethylaniline	5.86	1.84×10^3
12	*N,N*-Di-(2-hydroxyethyl)-aniline	4.31	2.67×10^2
13	*N*-(2-Cyanoethyl)-*N*-ethylaniline	3.47	3.49×10^1
14	*N*-(2-Cyanoethyl)-*N*-(2-hydroxyethyl)aniline	2.71	1.86×10^1
15	*N,N*-Dimethyl-*o*-toluidine	6.04(6.11)[d]	2.73×10^1
16	*N,N*-Diethyl-*o*-toluidine	7.64	2.90×10^2
17	1-Naphthylamine	4.09(3.92)[a]	7.09×10^4
17′	1-Naphthylamine	(3.70	1.53×10^5)[e]
18	*N,N*-Dimethyl-1-naphthylamine	4.76	1.12×10^3
19	2-Naphthylamine	4.11(4.16)[a]	4.16×10^4
20	9-Aminoanthracene	(3.25	3.29×10^5)[e]

a) A. Bryson, *J. Amer. Chem. Soc.*, **82**, 4858 (1960). b) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932). c) G. Girault-Vexlearschi, *Bull. Soc. Chim. Fr.* **1956**, 589. d) B. M. Wepster, *Rec. Trav. Chim.*, **76**, 357 (1957). e) Data in 50% methanolic solution.

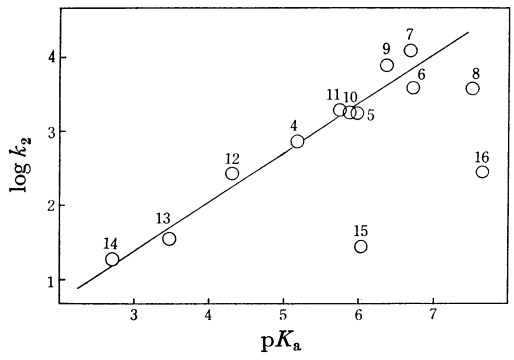

Fig. 1. Relationship between pK_a-value and rate constant. Figures refer to compounds in Table 1.

From the results of *N,N*-disubstitued anilines (No. 4—14), it was found that, among the di-*n*-alkyl-substituted amines (No. 4—7, 9), the activating effect of the amino group increases in the following order: NMe_2< NMe(Et)≈NEt_2<N-*n*-Pr_2≈N-*n*-Bu_2. This order is in accord with that of the inductive effect of the alkyl group, which may be explained on the basis of the effect of the alkyl group on the electron density at the amino nitrogen atom. On the other hand, the replacement of the hydrogen atom in the amino alkyl group by such an electron-attracting group as a hydroxy or cyano group (NO. 12—14) lowered the reactivity of dialkylaniline considerably.

Thus, it may be expected that a parallel correlation holds between the basicities of amines and the activating effects of their amino groups, since the electron-donating abilities of amino groups are considered generally proportional to their electron densities at the amino nitrogen atom. The relation between the basicity and the activating effect of a series of *N,N*-disubstituted anilines (No. 4—14) is shown in Fig. 1. From Fig. 1, it can be seen that a linear correlation holds between the basicities and the activating effects; an increase in the pK_a value by three units results in an increase in the reactivity by a factor of about 100.

The results (No. 15, 16) in Table 1 show that the introduction of methyl group into the ortho position leads to an increase in the basicity, but decreases the rate constant of *N,N*-dialkylaniline by a factor of about ten. The increase in the basicity may be ascribed mainly to the steric inhibition of the resonance; a departure from the coplanarity of the dialkylamino group with an aromatic ring as a result of the presence of an ortho methyl group should result a decrease in the electron donating ability of the amino group and is, therefore, base-strengthening. Consequently, although the methyl group s electrondonating, a methyl group in the ortho position of dialkylaniline lowers the reactivity of amine; thus, the plots of *o*-methyl-dialkylamines deviated markedly from the pK_a—log k line, as is shown in Fig. 1. In this sense, a linear relation between the basicities and the reactivities of the amines is considered to hold when the coplanarities of the amines are not hindered.

In the cases of 1-naphthylamine (No. 17) and 9-aminoanthracene (No. 20), the hydrogen atom at the peri position in the former, and the two hydrogen atoms the 1,8-positions in the latter, are considered to inhibit the interaction between the amino group and the aromatic ring to some extent. This inhibition is expected to become significant in the cases of secondary and tertiary amines. This estimation can easily be seen in the case of *N,N*-dimethyl-1-naphthylamine (No. 18), in which the reactivity is lower than that of 1-naphthylamine (No. 17), unlike the cases of the aniline series. Generally, it is well known that, in the electrophilic aromatic substitution, the reactivities of fused aromatic ring systems are much higher than those of monocyclic aromatic systems; there is a tendency for the reactivity to increase with an increase in the number of the condensed ring.[10] However, it can be seen from a comparison of the results of (No. 17′) and (No. 20) that the reactivities of 1-naphthylamine and 9-aminoanthracene are of the same order, suggesting that the steric inhibition by the hydrogen atom is larger in the latter than in the former.

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