The Salt Effect in the Aniline-Formaldehyde Condensation

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In our previous paper the kinetic study of the aniline-formaldehyde condensation in aqueous hydrochloric acid media has been reported.(1) The rate has been found to be second-order with respect to the initial concentration of aniline and first-order with respect to the sum of the concentrations of formaldehyde and methylene-anilines present. The purpose of the present investigation is to find the effect of inorganic salts on the rate of this reaction in aqueous hydrochloric or sulfuric acid media. The results show that the catalytic action of the salts is explicable in terms of the primary and secondary salt effects.(2)

Experimental

Materials and General Procedures are substantially the same as those in the previous paper.(1)

Experimental Results are shown in Fig. 1 and Table 1. Fig. 1 shows the effect of pH on the

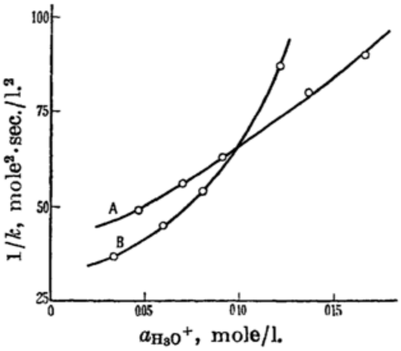

Fig. 1.—Relationship between $1/k$ and $a_{H_3O^+}$: A, 0.10 M $C_6H_5NH_2$+0.10 M CH_2O+0.15~0.30 M HCl; B, 0.10 M $C_6H_5NH_2$+0.10 M CH_2O+0.10~0.30 M H_2SO_4.

Table 1

The Effect of Various Salts on the Rate of the Aniline-Formaldehyde Condensation (25.0±0.1°C)

(A) Concentrations of reactants in original solutions:
Aniline 0.1 M, HCl 0.2 M, Formaldehyde 0.1 M.

Added salt	M	pH	$a_{H_3O^+}M$	$k_f \times 10^4$ (1/sec.)	$1/k_e$ (mole^2·sec./l.^{2})	$1/k_c$ (mole^2·sec./l.^{2})	μ_e	μ_c	β
None		1.05	0.090	1.57	64		0.20		
NaCl	0.50	0.99	0.105	1.88	53	67	0.70	0.22	0.6
〃	1.00	0.93	0.120	2.12	47	75	1.20	0.23	0.7
〃	2.00	0.79	0.160	2.66	38	89	2.20	0.30	0.9
KCl	1.00	0.96	0.110	2.32	43	71	1.20	0.22	0.8
$MgCl_2$	0.50	0.92	0.120	2.61	38	75	1.70	0.23	0.8
KBr	1.00	0.97	0.110	2.49	40	71	1.20	0.22	1.0
Na_2SO_4	0.10	1.40	0.040	2.78	36	46	0.50	0.15	0.9
K_2SO_4	0.10	1.42	0.038	2.82	35	45	0.50	0.15	0.9

(B) Concentrations of reactants in original solutions:
Aniline 0.1 M, H_2SO_4 0.1 M, Formaldehyde 0.1 M.

Added salt	M	pH	$a_{H_3O^+}M$	$k_f \times 10^4$ (1/sec.)	$1/k_e$ (mole^2·sec./l.^{2})	$1/k_c$ (mole^2·sec./l.^{2})	μ_e	μ_c	β
None		1.48	0.033	2.67	37		0.30		
Na_2SO_4	0.10	1.64	0.023	3.87	26	34	0.60	0.26	1.1
〃	0.20	1.79	0.016	4.81	21	33	0.90	0.22	1.0
〃	0.30	1.84	0.014	5.63	18	32	1.20	0.22	0.9
K_2SO_4	0.10	1.65	0.023	3.84	26	34	0.60	0.26	1.1
$MgSO_4$	0.10	1.56	0.028	3.81	26	34	0.70	0.28	1.0
KBr	1.00	1.28	0.053	3.52	29	42	1.30	0.41	0.6
KCl	1.00	1.29	0.051	3.38	29	42	1.30	0.41	0.6

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(1) Ogata, Okano and Sugawara, *J. Am. Chem. Soc.*, **73**, 1715 (1951).

(2) La Mer, *Chem. Rev.*, **10**, 179 (1932); Moelwyn-Hughes, "Kinetics of Reactions in Solution," Clarendon Press, Oxford, 1933, pp. 184.

rate with constant stoichiometric initial concentrations of aniline (0.1M) and formaldehyde (0.1M). In the figure, k is equal to k_f/a^2, where a is the initial concentration of aniline and k_f, the pseudo-first-order constant with respect to formaldehyde present. Table 1 tabulates the effect of the addition of several salts. Here, k_e corresponds to k described above and μ_e is the ionic strength of the solution; the definitions of k_c, μ_c and β will be given in the next paragraph. The salts employed are those alone which afford homogeneous solutions during rate measurements and do not interfere with titrimetric analyses.

Discussion of Results

Fig. 1 suggests that in sulfuric acid solution more attention should be paid to the concentration of free arylamino group together with undissociated arylammonium sulfate upon the rate than in hydrochloric acid solution. In order to derive the generalized rate equation in which undissociated aniline hydrochloride is taken into account as in dimethylaniline-formaldehyde condensation,(3) equilibria

$$ArNH_2 + HCl \rightleftharpoons ArNH_3Cl \quad (a) \quad K_a$$
$$ArNH_3Cl \rightleftharpoons ArNH_3^+ + Cl^- \quad (b) \quad K_b$$

should be considered. Here, K_a is the average equilibrium constant of the formation of hydrochlorides of aniline and its condensate; K_b, that of their ionization. Consequently, the initial concentration of aniline is expressed as

$$a \doteqdot \sum[ArNH_2] + \sum[ArNH_3Cl] + \sum[ArNH_3^+]$$

or

$$\sum[ArNH_2] = a/\{(K_A/K_W)(1+[a_{Cl^-}/K_b])+1\}$$

in which K_A is the average ionization constant of aniline and its condensate, $ArNH_2$, and K_W is the ion product of water. Introduction of this value into the rate equation previously given,(1) *i. e.*,

$$dx/dt = K\,a_{H_3O^+}(\sum[ArNH_2])^2(f-x)$$
$$(K\text{: a constant})$$

leads to

$$dx/dt = \frac{K\,a_{H_3O^+}a^2(f-x)}{\left\{1+\frac{K_A}{K_W}\left(1+\frac{a_{Cl^-}}{K_b}\right)a_{H_3O^+}\right\}^2} = k_f(f-x) \qquad (1)$$

in which $a_{H_3O^+}$ etc. are the activities of the subscripted substances, H_3O^+ etc. Hence, the relation between a^2/k_f and $a_{H_3O^+}$ is given by

$$\frac{1}{k} = \frac{a^2}{k_f} = \frac{1}{K\,a_{H_3O^+}} + \frac{2K_A}{KK_W}\left(1+\frac{a_{Cl^-}}{K_b}\right) + \frac{K_A^2}{KK_W^2}\left(1+\frac{a_{Cl^-}}{K_b}\right)^2 a_{H_3O^+} \qquad (2)$$

The plot of $1/k$ against $a_{H_3O^+}$ expressed in two curves in Fig. 1 should be consistent with this equation (2). If the equation is compared with equation (18) in the previous paper, it is apparent that the added terms $1/Ka_{H_3O^+}$ and a_{Cl^-}/K_b are related with free aniline and undissociated aniline hydrochloride, respectively. In hydrochloric acid media, a_{Cl^-}/K_b shows the ratio $[ArNH_3Cl]/[ArNH_3^+]$, and $1/K\,a_{H_3O^+}$ may be negligible in comparison with the other terms. In sulfuric acid media, however, the latter term should probably not be eliminated.

The dissociation of excess hydrochloric acid and that of hydrochlorides of aniline together with its condensate will be affected by adding salt. Although pH increases generally by adding inorganic salt into aqueous acid, the present results show that the pH decreases and therefore the concentration of hydrochloric acid ($HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$) as well as free aniline seems to increase as the amount of salt increases. Surely this change in pH will give rise to the change in the rate, *i. e.*, "secondary salt effect". The variation of k with pH was estimated from the curves in Fig. 1, while the effect of an increase in ionic strength on the rate will be considered later. These presumptive values of rate constant k_c and ionic strength μ_c in Table 1, where no inorganic salt is contained in the solution at the same pH's as shown in the third column of the same line, were measured by employing these curves. On the other hand, the change of the dissociation of arylammonium hydrochlorides seems to be difficult to evaluate, but probably it is reasonable to suppose that the value of $1/k$ decreases as the mean value of K_b increases by the addition of chloride in aniline sulfate solution. (See equation (2).)

The effect of salts on activity coefficients of reactants, so-called "primary salt effect," is expressed as equation (3) for the reaction between a neutral molecule and an ion at relatively high concentration.(4)

$$k = k_0(1+\mu\beta) \qquad (3)$$

where k is a rate constant with ionic strength μ, k_0, that with the ionic strength zero, and β, a constant. In hydrochloric acid medeia, the above values of k_c together with those of

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(3) Ogata and Okano, *J. Am. Chem. Soc.*, **72**, 1459 (1950).

(4) Glasstone, "Text-book of Physical Chemistry", D. Van Nostrand Company, New York, 1940, pp. 1115.

k_e, *i. e.*, the values of experimentally found, are expressed as

$$1/k_0=(1+\mu_c\beta)/k_c \qquad (4)$$

$$1/k_0=(1+\mu_e\beta)/k_e \qquad (5)$$

Therefore, β can be calculated by means of an equation

$$\beta=\{(1/k_c)-(1/k_e)\}/\{(\mu_e/k_e)-(\mu_c/k_c)\} \qquad (6)$$

As shown in Table 1, β holds good constancy. In hydrochloric acid media, average value of β is equal to 0.8 and in sulfuric acid media, β, 1.0. Using these values of β and those of k at appropriate oxonium ion activity (*e. g.*, pH$=1.5$) in Fig. 1, k_0 may be calculated by means of equation (3). The values of k_0 calculated independently by using the data in hydrochloric and sulfuric acid solutions are in agreement; *i. e.*, $k_0=2.09\times10^{-2}$ and 2.11×10^{-2} (l^2./mole.$^2\cdot$sec.), respectively. Abnormal values of β were obtained when either bromide or chloride was added into sulfuric acid media. These facts may be explained by assuming that the mean values of K_b are increased under these conditions. This catalytic effect of anions of salts may be ascribed to the acceleration of the rate-determining attack of carbonium ion $ArNHCH_2^+$ on the carbon atom of the benzene nucleus by attracting proton of the nucleus to the anion. A similar concerted mechanism has been suggested by Swain in other nucleophilic reactions.⑸

Summary

In the hydrochloric or sulfuric acid-catalyzed condensation of aniline with formaldehyde, it was found that the addition of inorganic salt, *e. g.*, sodium chloride or potassium sulfate, increases the rate and this fact is ascribed to the so-called primary and secondary salt effects.

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(5) Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948); **72**, 2794 (1950).