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The Catalytic Effect of Acid on the $O \rightarrow N$ Migration of the *s*-Triazinyl Group of *O*-(*s*-Triazinyl)-2-aminophenols

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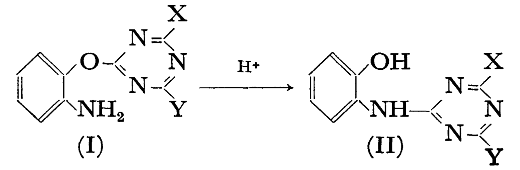
In a previous paper[1] we have reported that *O*-(*s*-triazinyl)-2-aminophenols (I) rearrange readily in the presence of acid to give *N*-(*s*-triazinyl)-2-aminophenols. However, the details of the rearrangement in the presence of acid have not yet been given. This paper will report the quantitative results on the influence of acid on the rearrangement of *O*-(*s*-triazinyl)-2-aminophenols.



a: $X=OCH_3$ $Y=N(CH_3)_2$
b: $X=Y=N(CH_3)_2$

Experimental

Materials. The *O*-(*s*-triazinyl)-2-aminophenols were synthesized by the method described in a previous paper.[2] The *O*-(2,4-dinitrophenyl)-2-aminophenol (III) was prepared by the method of Roberts.[3]

Kinetic Measurements. The kinetic measurements were carried out in a manner similar to that described in a previous paper[2] in buffer solutions of a constant ionic strength of 0.1 at 25 °C; the apparent first-order rate constants were calculated using Eq. (1);

$$k' = -2.303/t \log \{D_\infty - (D_t)/(D_\infty) - D_0\} \qquad (1)$$

where D_0, D_∞, and D_t denote the optical densities of a solution at an appropriate wavelength observed at initial and infinite times, and at time *t*. The measurements were carried out in aqueous solutions in the cases of the compounds (I) and in a 50% (vol) methanolic solution in the case of compound (III).

Results and Discussion

The effect of the pH of the solution on the apparent rate constants (k') for the rearrangement of Ia, Ib, and III were investigated; compound (III) was used in order to elucidate the function of the *s*-triazine nucleus by means of a comparison of the results of I and III. The results are shown in Fig. 1.

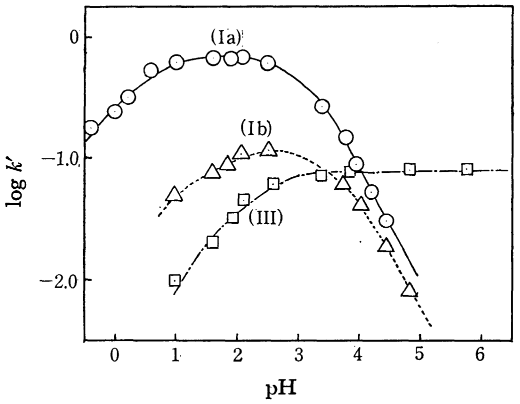
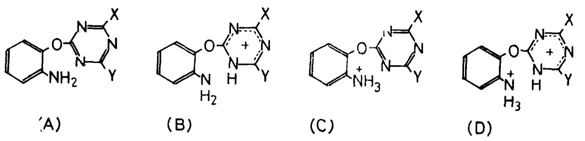


Fig. 1. pH dependence of the apparent rate constants for the rearrangement reactions of compounds (Ia, Ib, and III). (unit of k' is min^{-1})

In the case of III, the apparent rate constant decreased with an increase in the acidity of the solution; the result is considered to be due to a decrease in the concentration of III by protonation at the amino group.

On the contrary, in the case of Ia or Ib, no simple relation between $\log k'$ and pH value was observed. With an increase in the acidity of the solution, the apparent rate constant increased in the pH region above 3; however, it decreased in the pH region below 2. In these cases, the presence of two kinds of basic groups, *i.e.*, the amino and *s*-triazinyl groups, is considered to be the reason for the complexity. Under the present experimental conditions, the four species indicated by (A)—(D) may be assumed to be present in the solutions:



Among these, B is expected to be the most reactive species, for in this case an intramolecular nucleophilic attack by the amino group is considered to take place most readily by lowering the electron density of the ring-carbon atoms of the *s*-triazine nucleus. In the pH region above 3, the fact that the rate constant increased with an increase in the acidity of the medium can be explained by assuming that the concentration of B increases with the increase in the acidity by a preferential protonation at the ring-nitrogen atom of the *s*-triazine nucleus.[4,5] On the other hand, in the pH region below 2, it is assumed that the apparent rate constant decreased because of a decrease in the concentration of B as a result of further protonation at the amino group to give D.

If we assume that the protonation (expressed by Eq.

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[1] T. Harayama, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 981 (1970).

[2] N. Maeno, T. Itagaki, S. Uno, and K. Matsui, This Bulletin, **45**, 3133 (1972).

[3] K. C. Roberts, C. G. M. deWorms, and H. B. Clark, *J. Chem. Soc.*, **1935**, 196.

[4] G. Morimoto, *Nippon Kagaku Zasshi*, **87**, 790 (1966).

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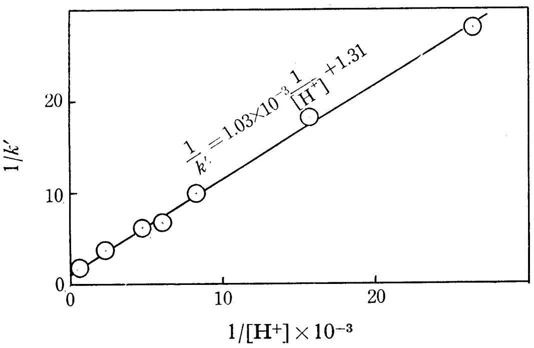

Fig. 2. Plots of $1/k'$ against $1/[H^+]$ for the rearrangement of compound (Ia) in the pH range of 4.42 to 2.50.

(2)) proceeds much faster than the rearrangement (Eq. (3)), and that B is the only reactive species, the apparent rate constant may be expressed by Eq. (4):[6]

$$(A) + H^+ \overset{K_a}{\rightleftarrows} (B) \qquad (2)$$

$$(B) \xrightarrow{k} (II) \qquad (3)$$

$$1/k' = 1/k + 1/kK[H^+] \qquad (4)$$

K_a: equilibrium constant

Table 1. Rate constants and dissociation constants (pK_a)

Compound	pK_a(TH$^+$)[a]	pK_a (NH$_3^+$)	k (min^{-1})
Ia	3.11	0.33	7.63×10^{-1}
Ib	3.64	0.886	1.32×10^{-1}
III		1.99	7.50×10^{-2}

a) TH$^+$ denote the species (B).

From Eq. (4), the plots of $1/k'$ against $1/[H^+]$ may be expected to give a straight line. Indeed, a linear relation was observed, as is shown in Fig. 2 in the case of (Ia).

From the intercepts and slopes of the lines, the rate constants of the reactive species (B) and the equilibrium constants were calculated; they are listed in Table 1. From the data obtained in the pH region below 2, the equilibrium constants attributable to the amino group were also obtained. Using these values, the relations between $\log k'$ and pH values can be calculated; they are shown in Fig. 1 by full, dotted, and dashed lines. It can be seen that the corresponding experimental results (expressed by circles, squares, and triangles respectively) lie close to the calculated lines. This finding supports the assumptions that the basicity of the *s*-triazine nucleus is stronger than that of the amino group and that the reactive species in the presence of acid is the protonated product at the ring nitrogen of the *s*-triazine nucleus (B), which rearranges faster by a factor of 4 orders or more than the neutral molecule.[2]

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[6] From Eq. (2) and (3), the rate of the rearrangement of B is expressed by Eq. (5):

$$v = k[B] = kK[A] \times [H^+] \qquad (5)$$

Since the apparent rate constant was calculated in the manner described in the Experimental section, the rate of the rearrangement in the presence of acid can be written by Eq. (6):

$$\begin{aligned} v &= k'([A]+[B]) \\ &= k'[A](1+K[H^+]) \qquad (6) \end{aligned}$$

From the assumption presented above, Eq. (4) is obtained by putting Eqs. (5) and (6) as equal.