A Kinetic Study of Alkaline Hydrolysis of 1-Arylamino-3-arylimino-1-butene

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Alkaline hydrolysis of 1-arylamino-3-arylimino-1-butene (1) was studied kinetically. The reaction proceeded in two ways; by hydrolysis at the 1-position of 1 to give β-arylaminocrotonaldehyde (2) and arylamine (pathway A), and by hydrolysis at the 3-position of 1 to give 4-arylamino-3-buten-2-one (3) and arylamine (pathway B), of which the former predominated. In the first step of pathway A, 1-position of 1 is attacked by hydroxide ion to give a tetrahedral intermediate which is then transformed into 2 and arylamine in the second step. Plots of the rate constants of pathway A, k_A, *vs.* [OH$^-$] were concave downward because the rates of the two steps are of similar order of magnitude. We were able to calculate the hydroxide ion-catalyzed rate constant (k_I^{OH}) of the first step of pathway A for 4 substrates, 1a—d. The k_I^{OH}'s decreased with increasing electron-withdrawing effect of the aryl substituents. The reaction mechanism is discussed.

Keywords alkaline hydrolysis; kinetic study; 1-arylamino-3-arylimino-1-butene; reaction mechanism; isotope effect

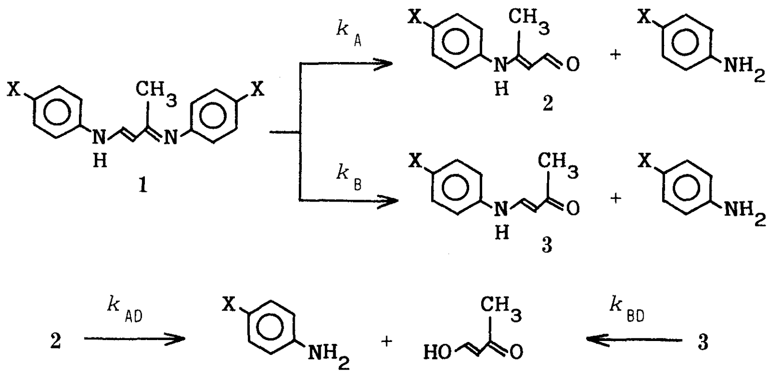
In a previous paper[1] we reported alkaline hydrolysis of 1-arylamino-3-arylimino-1-butene (**1**) in aqueous EtOH solution. The reaction proceeded mainly at the 1-position of **1** to give β-arylaminocrotonaldehyde (**2**) and arylamine (pathway A), and a small amount of 4-arylamino-3-buten-2-one (**3**), a product of hydrolysis at the 3-position of **1** (pathway B), was detected in the reaction mixture. There was no evidence for alcoholysis in the alkaline hydrolysis of **1** in aqueous EtOH solution while in the presence of AcOH and AcONa, a small amount of 4,4-diethoxy-2-butanone was formed in aqueous EtOH solution.

In this paper we will report a kinetic study of the alkaline hydrolysis of **1** in 40% EtOH–H$_2$O solution at 25 °C. The reaction sequence is shown in Chart 1. The reaction of pathway A proceeds *via* a tetrahedral intermediate (Chart 2).

In a previous paper[2] we reported a kinetic study of the acid-catalyzed hydrolysis of β-arylaminoacrolein. The reaction involved two steps, and we showed that the rate coefficient of the second step, k_{II}, can be subdivided into catalytic terms. The rate constant of pathway A, k_A, is represented by Eq. 1 on substitution of $k_2(k_1/k_{-1})$ by k_{II}.

$$k_A = \frac{k_I k_{II}}{k_I + k_{II}} = \frac{(k_I^0 + k_I^{OH}[OH^-])(k_{II}^0 + k_{II}^{OH}[OH^-])}{k_I^0 + k_I^{OH}[OH^-] + k_{II}^0 + k_{II}^{OH}[OH^-]} \qquad (1)$$

Plots of k_A *vs.* [OH$^-$] are concave downward (Fig. 1) suggesting that k_I and k_{II} are of similar order of magnitude for all substrates examined (**1a**—**d**) under the experimental conditions used. The k_I^{OH}'s obtained indicate that k_I^{OH} decreases with increasing electron-withdrawing effect of substituents on the aryl group. The attack of hydroxide ion at the 1-position of **1** is assisted by water as a general acid catalyst.



X: a, CH$_3$O; b, CH$_3$; c, H; d, Cl

Chart 1

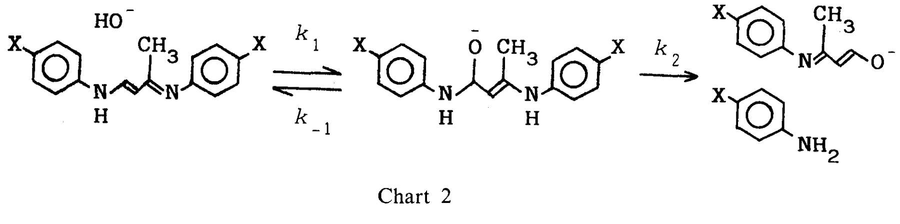


Chart 2

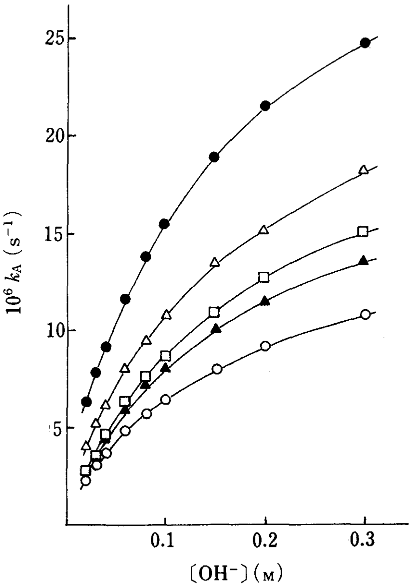


Fig. 1. Plots of Rate Constants, k_A, of Alkaline Hydrolysis of **1b** in 40% $EtOH-H_2O$ *vs.* [OH^-] at 25°C

Ionic strength 0.50. ●, **1a**; △, **1b**; ▲, **1c**; ○, **1d**; □, **1b** in 40% $EtOD-D_2O$.

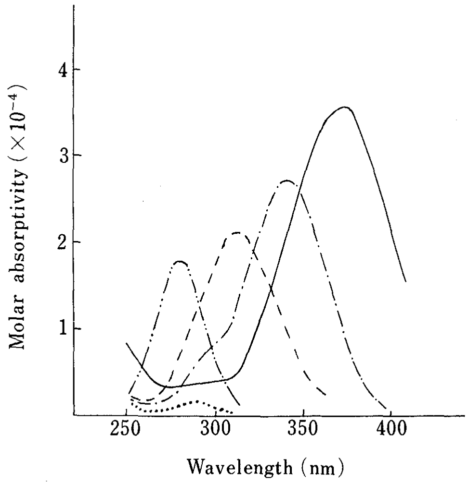


Fig. 2. Absorption Spectra of **1b**, **2b**, **3b**, *p*-Toluidine and Formylacetone in 40% $EtOH-H_2O$ in the Presence of 0.50 M AcONa

——, **1b**; ----, **1b**; —·—, **3b**; ····, *p*-toluidine; —··—, formylacetone.

Experimental

Absorption spectra were measured on Hitachi spectrophotometer, model 139, and proton nuclear magnetic resonance (^1H-NMR) spectra were recorded on JNM-PMX 60 and JNM-GX 400 NMR spectrometers with Me_4Si as an internal standard.

The ionic strength of the reaction solution was maintained at 0.50 by the addition of NaCl. The kinetic runs were carried out at 25 °C.

Materials Compounds **1d**, **2b**, **2c**, **2d** and **3d** were prepared according to the previous paper[1] and compounds **1b**,[3] **1c**,[4] **3b**[3] and **3c**[5] were prepared according to the cited references.

1-(*p*-Methoxyphenylamino)-3-(*p*-methoxyphenylimino)-1-butene (1a) Hydrochloride A solution of 10.45 g (0.10 mol) of *β*-chlorocrotonaldehyde[4] in 50 ml of a mixture of benzene–EtOH (2 : 1) was added slowly to a solution of 24.63 g (0.20 mol) of *p*-anisidine in 150 ml of the same solvent under ice cooling. The mixture was allowed to stand in a refrigerator for 2 d. The precipitates were collected to give 27.27 g (82%) of the HCl salt of **1a**. mp 197 °C. *Anal.* Calcd for $C_{18}H_{20}N_2O_2 \cdot HCl$: C, 64.96; H, 6.36; N, 8.42. Found: C, 64.80; H, 6.44; N, 8.23. ^1H-NMR (400 MHz, CD_3SOCD_3): 2.62 (3H, s, CH_3), 3.76 and 3.81 (each 3H, s, CH_3O), 5.84 (1H, d, $J = 12$ Hz, 2-position), 6.98, 7.08, 7.27 and 7.41 (each 2H, d, $J = 8.5$ Hz, Ar), 8.51 (1H, br s, 1-position), 11.63 and 11.72 (each 1H, br s, NH). On addition of D_2O, the signal of the 1-position was observed at δ 8.49 as a doublet ($J = 12$ Hz).

***β*-(*p*-Methoxyphenylamino)crotonaldehyde (2a)** A solution of NaOH (2.40 g) in 36 ml of H_2O was added to a solution of 6.66 g (0.02 mol) of the hydrochloride of **1a** in 144 ml of EtOH. The mixture was heated at 80 °C for 1 h on a water bath, and 500 ml of 7% $NaHCO_3$ was added to the mixture. The whole was distilled under reduced pressure, and the distillate was treated as usual to give 0.16 g of *p*-anisidine. The remaining liquid was extracted with ether. The ether layer was dried over K_2CO_3, and concentrated under reduced pressure. The residue was subjected to column chromatography (100 g of Al_2O_3, 250 ml of benzene) to give 3.75 g of oil. The oil was taken up in 8 ml of EtOH and 2 ml of concentrated HCl and the mixture was allowed to stand overnight at room temperature. The precipitates were collected to give 3.12 g of the hydrochloride of **1a**. A solution of excess NaOEt in EtOH was added to the mother liquor and the mixture was concentrated under reduced pressure. Then 200 ml of ether was added to the residue and the whole was allowed to stand for 3 h. The precipitates were collected to give a mixture of Na salt of **2a** and NaCl. The precipitates were treated as usual and the resulting raw product was subjected to preparative thin layer chromatography (PTLC) (silica-gel, benzene–AcOEt) to give 0.23 g of crude **2a**. Recrystallization of the crude product from petroleum-benzin gave 0.15 g of pure **2a**. mp 75 °C. *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found C, 69.01; H, 6.88; N, 7.57. MS *m/z*: 191 (M^+, 89%), 176 (28), 162 (9), 108 (100). ^1H-NMR (60 MHz, $CDCl_3$): 1.93 (3H, s, CH_3), 3.80 (3H, s, CH_3O), 5.09 (1H, d, $J = 3$ Hz, α-position), 6.75 and 7.13 (each 2H, d, $J = 9$ Hz, Ar), 9.03 (1H, d, $J = 3$ Hz, CHO), 12.25 (1H, br s, NH). ^1H-NMR showed that **2a** is in the *s-cis* form in $CDCl_3$.

4-(*p*-Methoxyphenylamino)-3-buten-2-one (3a) Compound **3a** was prepared from *p*-anisidine hydrochloride and the Na salt of formylacetone according to Thielepape.[5] mp 68 °C. *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found C, 69.05; H, 6.88; N, 7.36. Duguay *et al.*[6] reported the preparation and ^1H-NMR of **3a**, but they did not present analytical data or the melting point.

Kinetic Runs The description of kinetic runs is exemplified by the case of *p*-methyl derivatives.

Hydrolysis of 1b An EtOH solution (1 ml, 2.67×10^{-3} M) of **1b** was added to NaOH solution (0.02—0.30 M) in 40% $EtOH-H_2O$ in a 100 ml volumetric flask, and the sample was diluted to the mark with the same $EtOH-H_2O$ solution. For the spectrophotometric measurement of the reaction rates, the reaction solution was neutralized with AcOH to avoid complexity owing to the partial ionization of **2b**: 1 ml of 40% $EtOH-H_2O$ solution of AcOH, a concentration representing a tenfold excess over NaOH in each reaction solution, was put in a 10 ml volumetric flask and the solution was diluted with the reaction solution to the mark. The absorbance of the solution was measured at 310, 315, 335, 340, 370 and 375 nm, and the concentrations of **1b**, **2b** and **3b** were evaluated by the least-squares method (Fig. 2).

Hydrolysis of 2b and 3b The reaction solution was prepared in a similar manner to the hydrolysis of **1b**. The absorbance of the reaction solution was measured at 315 nm for **2b** and 340 nm for **3b**. The rate constants, k_{AD} and k_{BD}, were evaluated by applying the equation, $kt = \ln A_0/A$. The results were as follows. [OH^-], $10^6 k_{AD}$ (s^{-1}), $10^6 k_{BD}$ (s^{-1}): 0.02, 2.80, 0.67; 0.03, 3.73, 1.06; 0.04, 4.46, 1.37; 0.06, 5.64, 1.93; 0.08, 6.57, 2.79; 0.10, 7.30, 3.53; 0.15, 8.58, 4.87; 0.20, 9.68, 6.41; 0.30, 10.6, 9.21.

Hydrolysis of 1b in $EtOD-D_2O$ Solution H–D exchange proceeded gradually at the 2- and 4-position of **1b** in alkaline $EtOD-D_2O$ solution. To avoid this complexity, the substrate was deuterated before use: a solution of **1b** in MeOD containing some MeONa was warmed at 55 °C for 30 min, and saturated with CO_2. The mixture was filtered, and the filtrate was concentrated under reduced pressure to give *N*,2,4,4,4-pentadeuterio-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-butene. The completion of deuteration was ascertained by measurement of the ^1H-NMR ($CDCl_3$). The kinetic runs were carried out in the same manner as described in the section on hydrolysis of **1b**.

Hydrolysis of 2b and 3b in $EtOD-D_2O$ Solution The deuteration of the substrates was carried out in the same manner as described in the preceding section. The kinetic runs of hydrolysis of the resulting *N*,*α*,*γ*,*γ*,*γ*-pentadeuterio-*β*-(*p*-methylphenylamino)crotonaldehyde and *N*,1,1,1,3-pentadeuterio-4-(*p*-methylphenylamino)-3-buten-2-one were carried out in the same manner as described in the section on hydrolysis of **2b** and **3b**. The results were as follows. [OD^-], $10^6 k_{AD}$ (s^{-1}), $10^6 k_{BD}$ (s^{-1}): 0.02, 2.94, 0.69; 0.03, 3.41, 0.90; 0.04, 3.98, 1.18; 0.06, 4.90, 1.69; 0.08, 5.42, 2.17; 0.10, 5.87, 2.62; 0.15, 6.66, 3.67; 0.20, 7.30, 4.64; 0.30, 7.53, 6.23.

Results and Discussion

Mathematical Treatment of Experimental Data The proportions of **1**, x, of **2**, y, and of **3**, z, in the reaction solution are represented by Eqs. 2—4, respectively.

$$x=\exp\{-(k_A+k_B)t\} \tag{2}$$

$$y=\frac{k_A}{k_A+k_B-k_{AD}}[\exp(-k_{AD}t)-\exp\{-(k_A+k_B)t\}] \tag{3}$$

$$z=\frac{k_B}{k_A+k_B-k_{BD}}[\exp(-k_{BD}t)-\exp\{-(k_A+k_B)t\}] \tag{4}$$

k_{AD} and k_{BD} were evaluated separately from kinetic experiments on the hydrolysis of **2** and of **3** under the same conditions as used for the hydrolysis of **1**. The values of (k_A+k_B) were obtained from Eq. 2. The proportions of **1**, **2** and **3** were determined at 8 time points for each kinetic run. Initial approximate values for k_A and for k_B were estimated as average values of $(k_A+k_B)y/(y+z)$ and of $(k_A+k_B)z/(y+z)$ for the first 3 points, respectively. The values were corrected by means of the non-linear least-squares method. The method was carried out on the assumption that the approximate Eqs. 5—7 are valid,

$$x-x_c=\Delta k_A\frac{\delta x}{\delta k_A}+\Delta k_B\frac{\delta x}{\delta k_B} \tag{5}$$

$$y-y_c=\Delta k_A\frac{\delta y}{\delta k_A}+\Delta k_B\frac{\delta y}{\delta k_B} \tag{6}$$

$$z-z_c=\Delta k_A\frac{\delta z}{\delta k_A}+\Delta k_B\frac{\delta z}{\delta k_B} \tag{7}$$

where x_c, y_c and z_c are proportions calculated from Eqs. 2—4, and $k_A+\Delta k_A$ and $k_B+\Delta k_B$ are corrected values for k_A and k_B, respectively. The k_A and k_B values for alkaline hydrolysis of **1b** in EtOH–H_2O and in EtOD–D_2O are shown in Table I. As can be seen in Table I, k_B's were always smaller than k_A's under the conditions examined without any significant change with increasing $[OH^-]$.

Plots of k_A *vs.* $[OH^-]$ showed a gradually decreasing slope (Fig. 1). This is because k_I and k_II are of similar order of magnitude but not because the substrates are converted partially to their unreactive conjugate bases (see Appendix).

The reaction proceeds *via* the tetrahedral intermediate (Chart 2). The first step of the reaction is an attack of hydroxide ion at the 1-position of **1**, and therefore the rate of the first step is expected to increase steeply with increasing $[OH^-]$. The second step is departure of the arylamino group from the negatively charged intermediate, probably assisted by water as a general acid catalyst. The rate of the second step is, therefore, expected to be less dependent on $[OH^-]$. Consequently, the rate of the reaction is mainly dependent on that of the second step at high $[OH^-]$.

We developed a mathematical method to obtain the catalytic constants from the non-linear relations between the rate constants and concentrations of the catalyst (in acetate buffer) in a kinetic study of the hydrolysis of β-arylaminoacrolein under acidic conditions.[2] In that case, while the relation was non-linear in acetate buffer, it was linear under more acidic conditions (in the presence of HCl and of AcOH), in which the second step is rate-limiting. Thus, the catalytic constants for the second step can be obtained by the usual method.

Table I. Rate Constants (s^{-1}) of Alkaline Hydrolysis of **1b** in 40% EtOH–H_2O and in 40% EtOD–D_2O Solutions at 25 °C. Ionic Strength 0.50[a]

$[OH^-]$	EtOH–H_2O 10^6k_A	EtOH–H_2O 10^6k_B	$[OD^-]$	EtOD–D_2O 10^6k_A	EtOD–D_2O 10^6k_B
0.02	3.96 (0.029)	1.60 (0.009)	0.02	2.79 (0.003)	1.14 (0.003)
0.03	5.14 (0.014)	1.62 (0.011)	0.03	3.54 (0.013)	1.00 (0.011)
0.04	6.07 (0.019)	1.63 (0.015)	0.04	4.53 (0.030)	1.17 (0.024)
0.06	7.98 (0.034)	1.58 (0.027)	0.06	6.34 (0.023)	1.09 (0.018)
0.08	9.37 (0.048)	1.68 (0.038)	0.08	7.56 (0.026)	1.11 (0.019)
0.10	10.9 (0.09)	1.58 (0.069)	0.10	8.52 (0.034)	1.21 (0.027)
0.15	13.3 (0.09)	1.64 (0.071)	0.15	10.8 (0.04)	1.09 (0.031)
0.20	15.1 (0.05)	1.35 (0.042)	0.20	12.7 (0.06)	1.02 (0.045)
0.30	18.2 (0.08)	1.27 (0.062)	0.30	15.1 (0.12)	1.29 (0.089)

a) Standard deviations are shown in parentheses.

In the alkaline hydrolysis of **1**, relations between the rate constants and $[OH^-]$ were not linear under any of the conditions examined. In this work, we devised a general method to obtain catalytic constants of each step from the non-linear relationships.

Preliminary approximate values for k_I^O and k_I^OH were calculated by the least-squares method from Eq. 8 using k_A's at $[OH^-]=0.02$, 0.03, 0.04 and 0.06 on the assumption that k_II equals k_A at $[OH^-]=0.30$.

$$k_\mathrm{I}=k_\mathrm{I}^\mathrm{O}+k_\mathrm{I}^\mathrm{OH}[OH^-]=\frac{k_\mathrm{II}k_A}{k_\mathrm{II}-k_A} \tag{8}$$

The approximate values for k_II^O and $k_\mathrm{II}^\mathrm{OH}$ were calculated by the least-squares method from Eq. 9 using k_A's at $[OH^-]=$ 0.15, 0.20 and 0.30 and the approximate values for k_I^O and k_I^OH

$$k_\mathrm{II}=k_\mathrm{II}^\mathrm{O}+k_\mathrm{II}^\mathrm{OH}[OH^-]=\frac{k_\mathrm{I}k_A}{k_\mathrm{I}-k_A} \tag{9}$$

Improved approximate values for k_I^O and k_I^OH were obtained from Eq. 8 using the approximate values for k_II^O and $k_\mathrm{II}^\mathrm{OH}$. This procedure was repeated until k_I became close to $2k_A$ at $[OH^-]=(k_\mathrm{II}^\mathrm{O}-k_\mathrm{I}^\mathrm{O})/(k_\mathrm{I}^\mathrm{OH}-k_\mathrm{II}^\mathrm{OH})$ (about 5 repetitions were required). Finally, k_I^O, k_I^OH, k_II^O and $k_\mathrm{II}^\mathrm{OH}$ obtained by the above procedure were corrected by means of the non-linear least-squares method. The method was carried out on the assumption that the approximate Eq. 10 is valid,

$$k_A-k_A^c=\Delta k_\mathrm{I}^\mathrm{O}\frac{\delta k_A}{\delta k_\mathrm{I}^\mathrm{O}}+\Delta k_\mathrm{I}^\mathrm{OH}\frac{\delta k_A}{\delta k_\mathrm{I}^\mathrm{OH}}+\Delta k_\mathrm{II}^\mathrm{O}\frac{\delta k_A}{\delta k_\mathrm{II}^\mathrm{O}}+\Delta k_\mathrm{II}^\mathrm{OH}\frac{\delta k_A}{\delta k_\mathrm{II}^\mathrm{OH}} \tag{10}$$

where k_A^c is the calculated rate constant from Eq. 1, and $k_\mathrm{I}^\mathrm{O}+\Delta k_\mathrm{I}^\mathrm{O}$, $k_\mathrm{I}^\mathrm{OH}+\Delta k_\mathrm{I}^\mathrm{OH}$, $k_\mathrm{II}^\mathrm{O}+\Delta k_\mathrm{II}^\mathrm{O}$ and $k_\mathrm{II}^\mathrm{OH}+\Delta k_\mathrm{II}^\mathrm{OH}$ are corrected values for k_I^O, k_I^OH, k_II^O and $k_\mathrm{II}^\mathrm{OH}$, respectively (Table II).

While reliable values were obtained for k_I^OH, the other catalytic constants are variable with large standard deviations, as shown in Table II. This is probably because the reaction rate is mainly decided by the rate of the first step, and k_I^O makes only a small contribution to the overall reaction rate.

Discussion of the Mechanism The value of k_I^OH decreased with increasing electron-withdrawing effect of aryl substituents, indicating that the attack of hydroxide ion at the 1-position of **1** is assisted by water as a general acid catalyst. Electron-withdrawing substituents diminish the

Table II. Catalytic Constants of Alkaline Hydrolysis of **1** in 40% EtOH–H_2O and in 40% EtOD–D_2O Solutions at 25 °C. Ionic Strength 0.50[a]

	k_{I}^{0} (s^{-1})	$k_{\mathrm{I}}^{\mathrm{OH}}$ ($M^{-1}s^{-1}$)	k_{II}^{0} (s^{-1})	$k_{\mathrm{II}}^{\mathrm{OH}}$ ($M^{-1}s^{-1}$)
EtOH–H_2O				
1a	2.31×10^{-6} (2.94×10^{-4})	2.72×10^{-4} (1.17×10^{-6})	3.08×10^{-5} (1.44×10^{-4})	1.34×10^{-5} (4.67×10^{-5})
1b	1.08×10^{-6} (2.35×10^{-4})	1.76×10^{-4} (4.73×10^{-6})	2.44×10^{-5} (1.88×10^{-4})	1.03×10^{-5} (6.35×10^{-5})
1c	2.41×10^{-7} (2.61×10^{-4})	1.37×10^{-4} (3.02×10^{-6})	1.91×10^{-5} (2.52×10^{-4})	2.88×10^{-6} (8.09×10^{-5})
1d	2.62×10^{-7} (6.34×10^{-4})	1.19×10^{-4} (3.80×10^{-6})	1.28×10^{-5} (2.49×10^{-4})	8.66×10^{-6} (9.78×10^{-5})
EtOD–D_2O				
1b	3.68×10^{-7} (2.82×10^{-4})	1.36×10^{-4} (3.81×10^{-6})	2.21×10^{-5} (3.53×10^{-4})	5.51×10^{-6} (1.14×10^{-4})

[a] Standard deviations are shown in parentheses.

basicity of the arylamino nitrogen and so reduce the catalytic effectiveness of water (Chart 3). Compound **1** exists as a tautomeric mixture of **1** and 3-arylamino-1-arylimino-2-butene (**1′**) so that ambiguity exists in assigning the site of catalysis by water (Chart 3).

The ratio k_H/k_D was 0.84 for the first step of alkaline hydrolysis of *β*-(*p*-methylphenylamino)acrolein, indicating that the first step involves an attack of hydroxide ion and the participation of water as a general acid catalyst is not significant.[7)]

In the present study, k_H/k_D was 1.3 for $k_{\mathrm{I}}^{\mathrm{OH}}$ of pathway A of hydrolysis of **1b**. Thus, the isotope effect on the nucleophilicity of hydroxide ion is more than offset by the inverse effect on the proton-transfer in the transition state. Cordes and Jencks[8)] reported that k_H/k_D is 1.13—1.20 and 1.65 for hydrated proton and for acetic acid, respectively, in general acid-catalyzed semicarbazone formation.

Alkaline hydrolysis of amide follows higher than first-order kinetics in hydroxide ion due to the poor leaving ability of the amino group.[7,9)] In the present reaction, there was no evidence for a second order term in hydroxide ion. Probably the amino group is more easily expelled from the tetrahedral intermediate with the aid of the electron-releasing power of the second nitrogen atom and methyl group.

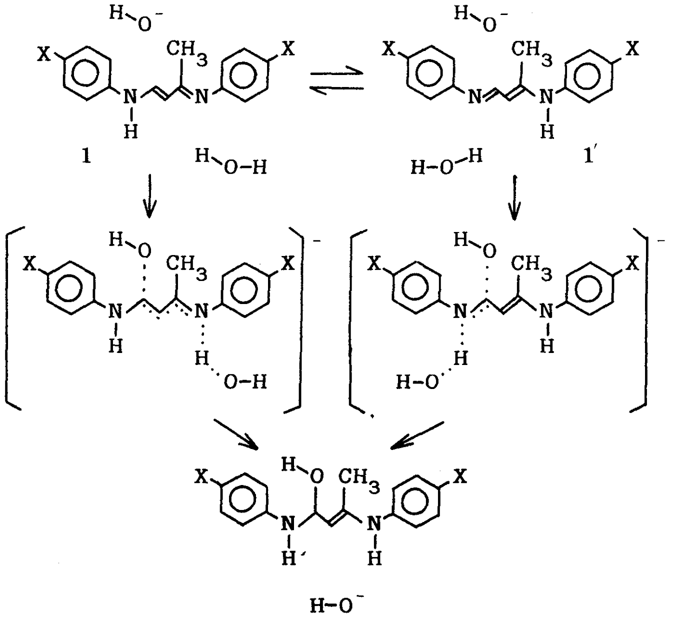


Chart 3

The values of k_B did not change much with increasing $[OH^-]$. These results indicate that the second step is rate-limiting for the reaction of pathway B. The ratio k_H/k_D was 1.4 for k_B of the reaction of **1b** (Table II) suggesting that the departure of the arylamino group from the tetrahedral intermediate is assisted by water as a general acid catalyst. The adjacent methyl group hinders the approach of a water molecule to the leaving nitrogen atom. The predominance of pathway A over B is mainly decided by the difference in the rates of their second steps, and we cannot tell anything about the regioselectivity of the attacking hydroxide ion.

Appendix

DeWolfe[10)] studied the alkaline hydrolysis of symmetrically substituted N^1,N^2-diarylformamidines. He found that plots of k_{obs} *vs.* $[OH^-]$ are concave downward, and attributed this non-linear relation to the partial conversion of the substrates to their unreactive conjugate bases. He determined the dissociation constants of *p*-nitro, *m*-nitro and 3,4-dichloro derivatives spectrophotometrically. He derived the rate equation on the assumption that the second step of the reaction is rate-limiting:

$$BH + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} B^- + H_2O$$

$$BH + H_2O \overset{K_2}{\rightleftharpoons} BHOH_2$$

$$BHOH_2 + OH^- \xrightarrow{k_3} \text{products}$$

$$k_{obs} = k_3K_2[OH^-]/(1 + K_1[OH^-]) \qquad (11)$$

From linear relations obtained by plotting $1/k_{obs}$ against $1/[OH^-]$, he

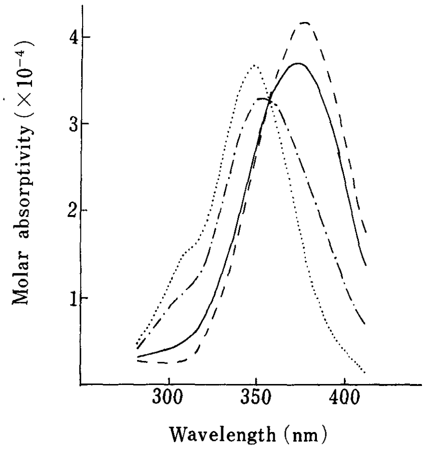


Fig. 3. Absorption Spectra of **1d** in 40% EtOH–H_2O. (——), in the Presence of 0.30 M AcOH; (– – – –), in the Presence of 0.30 M AcONa; (—·—), in the Presence of 0.02 M NaOH; (· · · ·)

Absorption spectra of **1d** in the presence of 0.30 M HCl and 0.30 M NaOH are not shown because they are identical with those in the presence of 0.30 M AcOH and 0.02 M NaOH, respectively. In all cases, ionic strength was maintained at 0.50 by the addition of NaCl.

calculated k_3K_2 and K_1. He showed that the calculated dissociation constant, K_1, for the *p*-nitro derivative was in good agreement with that determined spectrophotometrically.

Using the rate data in DeWofe's paper, we calculated K_1 for the *m*-chloro derivative to be $0.86\,\mathrm{M}^{-1}$ from Eq. 11. This value is large enough to allow spectrophotometric determination of the dissociation constant. DeWolfe did not, however, report the spectrophotometric analysis of the *m*-chloro derivative.

Assuming that $k_\mathrm{I}^\mathrm{O} \ll k_\mathrm{I}^\mathrm{OH}[\mathrm{OH}^-]$ and $k_\mathrm{II}^\mathrm{O} \gg k_\mathrm{II}^\mathrm{OH}[\mathrm{OH}^-]$, Eq. 1 is transformed into

$$k_\mathrm{A} = k_\mathrm{II}^\mathrm{O} k_\mathrm{I}^\mathrm{OH}[\mathrm{OH}^-]/(k_\mathrm{II}^\mathrm{O} + k_\mathrm{I}^\mathrm{OH}[\mathrm{OH}^-]) \qquad (12)$$

Eq. 12 is apparently indistinguishable from Eq. 11.

Calculation of our kinetic data on the basis of Eq. 11 gave values of K_1 (M^{-1}) which decrease as the expected acidity of the substrates increases: **1a**, 14.3 ± 1.21; **1b**, 11.5 ± 0.96; **1c**, 8.64 ± 0.78; **1d**, 9.62 ± 0.43. This is apparently contradictory.

The ultraviolet (UV) spectra of **1d** under various conditions indicate that **1d** is converted into its conjugate acid in acidic solutions, whereas it remains as the non-charged free base in alkaline solutions (Fig. 3).

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