Hydrolysis of α-Cyanobenzylideneanilines. Part 2.[1] Kinetic Studies in Basic Media

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The base-catalysed hydrolysis of α-cyanobenzylideneanilines (I) was studied in aqueous dioxan (40 and 50% v/v) at 30 °C. The rate of hydrolysis was first-order with respect to hydroxide ion. The plot of the logarithm of second-order rate constants for (I) with substituents on the *C*-phenyl ring against the σ value was linear (ρ 2.10), whereas that for (I) with substituents on the *N*-phenyl ring was concave. These results were compared with those for the reaction of (I) with ethoxide ion, where similar substituent effects were observed. These results were interpreted in terms of a mechanism involving tetrahedral addition intermediate, where the attack of hydroxide ion on the substrate is probably rate-determining. The curved Hammett plot cannot be ascribed to a change in mechanism, but seems to result from some other factors.

The hydrolysis of α-cyanobenzylideneanilines (I) gives different products depending upon the nature of the medium; benzanilides in alkaline solution,[2,3] benzoyl cyanides in strongly acidic solution,[4] and benzoic acids and anilines in slightly and/or moderately acidic solution, where benzoic acids are formed *via* benzoyl cyanides.[1] Kinetic studies in acidic media suggested that in the hydrolysis of (I) unstable tetrahedral addition intermediates are formed and anilines are expelled only from the zwitterionic form of the intermediates.[1] In strong acid solution the proportion of the zwitterionic form is reduced and the rate of hydrolysis decreases. The products and the rate-determining step of the hydrolysis will depend on the form of the tetrahedral intermediates in the particular medium as observed in the hydrolysis of imidate esters.[5]

$$XC_6H_4{\cdot}C(CN){=}N{\cdot}C_6H_4Y$$
(I)

Recently reactions of (I; X = H) with amines in acetonitrile and with alkoxides in alcohols have been studied kinetically and effects of substituents (Y) have been explained in terms of mechanisms involving tetrahedral addition intermediates.[6] However, in the reactions with alkoxides the rate-determining step was not demonstrated explicitly, though a rate-determining decomposition of a tetrahedral intermediate was suggested to be preferable. Preliminary experiments on the hydrolysis of (I) in basic solution showed more complex effects of substituents on the *N*-phenyl ring (Y) than those observed [6] in the reactions with alkoxides. It is expected, therefore, that the examination of the substituent effects (Y) together with those of the *C*-phenyl ring (X) will give information on the nature of the rate-determining step. This paper reports kinetic studies on the hydrolysis and ethanolysis of (I) in basic media, and the results are discussed in the light of findings reported by Ta-Shma and Rappoport.[6]

RESULTS

Hydrolysis of (I) in basic aqueous dioxan (40% v/v) solution (NaOH 0.01—0.5M) gave the corresponding benzanilide (II) almost quantitatively. In a run with a high concentration of (Ia) small amounts (0.6%) of benzoic acid and aniline were formed. The hydrolysis of (IIa) was negligible under the conditions (see Experimental section). The reaction of (I) with ethoxide ion in ethanol–dioxan (1 : 1 v/v) gave the corresponding imidate (III) as reported previously.[6]

$$(I) \xrightarrow{HO^-} XC_6H_4{-}CO{-}NH{-}C_6H_4Y \qquad (II)$$

a; X = Y = H
b; X = *p*-CN, Y = H
c; X = *p*-Cl, Y = H
d; X = *p*-Me, Y = H
e; X = *p*-MeO, Y = H
f; X = *p*-Me$_2$N, Y = H
g; X = H, Y = *p*-CN
h; X = H, Y = *m*-Cl
i; X = H, Y = *p*-Cl
j; X = H, Y = *p*-Me
k; X = H, Y = *p*-MeO
l; X = H, Y = *p*-Me$_2$N

$$XC_6H_4{-}C(OEt){=}N{-}C_6H_4Y$$
(III)

The observed pseudo-first-order rate constant k_{obs} for the hydrolysis of (Ia) in 40% aqueous dioxan (μ = 0.5 with KCl) increased linearly with the concentration of sodium hydroxide in the range 0.01—0.1M, but levelled off at higher concentrations (Figure 1). Similar results were obtained

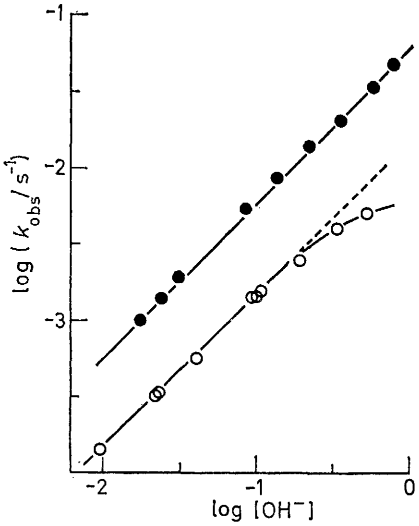

FIGURE 1 Plot of the observed pseudo-first-order rate constant for the hydrolysis of (Ia) against hydroxide ion concentration in 40% aqueous dioxan at 30 °C: ○, NaOH–KCl, μ = 0.5; ●, TEAOH–TEACl, μ = 1.0

with (Ii) and (Ik). When tetraethylammonium hydroxide (TEAOH) and tetraethylammonium chloride (TEACl) were used in the place of NaOH–KCl, the plot of log k_{obs} against log [TEAOH] gave a straight line with a slope equal to unity over the entire range of base concentration employed (Figure 1). The second-order rate constant k_{OH} obtained according to equation (1) was independent of the concentration of sodium hydroxide ([NaOH] < 0.11M), indicating that the spontaneous hydrolysis is negligible under the

$$k_{obs} = k_{OH}[OH^-] \qquad (1)$$

experimental conditions. Essentially the same results were obtained in 50% aqueous dioxan. The values of k_{OH} are summarized in Table 1.

TABLE 1

Second-order rate constants [a] for the hydrolysis and for the reaction of (I) with ethoxide ion at 30 °C

Compound (I)	X	Y	10^3k_{OH} [b]	10^3k_{OH} [c]	10^3k_{OH} [d]	10^3k_{EtO} [e]
a	H	H	14.1	14.1	59.0	8.12
b	*p*-CN	H	253	339		269
c	*p*-Cl	H	34.5	39.8		32.6
d	*p*-Me	H	6.05	6.17		3.42
e	*p*-MeO	H	3.54	3.63		1.69
f	*p*-Me_2N	H	0.345	0.251		0.110
g	H	*p*-CN	1 430	1 950		13 700
h	H	*m*-Cl		123		255
i	H	*p*-Cl	65.3	79.4	322	98.2
j	H	*p*-Me	5.65	5.62		2.44
k	H	*p*-MeO	3.95	3.98	17.3	1.02
l	H	*p*-Me_2N	0.731	0.490		0.0886

[a] l mol^{-1} s^{-1}. [b] In 40% aqueous dioxan; NaOH–KCl, $\mu = 0.5$. [c] In 50% aqueous dioxan; NaOH–KCl, $\mu = 0.1$. [d] In 40% aqueous dioxan; TEAOH–TEACl, $\mu = 1.0$. [e] In ethanol–dioxan (1 : 1 v/v).

TABLE 2

Effects of salts on the hydrolysis of (I) in 40% aqueous dioxan at 30 °C

Compound	[NaOH]/ M	[KCl]/ M	[NaCN]/ M	10^2k_{OH}/ l mol^{-1} s^{-1}
(Ia)	0.0240	0.08		1.91
	0.0235	0.48		1.44
	0.0231	0.98		1.03
	0.0095	0.09		1.97
	0.0095		0.09	1.92
(Ii)	0.0095	0.09		9.74
	0.0095		0.09	9.60
(Ik)	0.0095	0.09		0.637
	0.0095		0.09	0.629

The effects of ionic strength and cyanide ion were examined, and the results are shown in Table 2. The k_{OH} value for (Ia) decreased with an increase in the concentration of potassium chloride. Replacement of potassium chloride by sodium cyanide did not cause an appreciable rate depression.

The observed pseudo-first-order rate constant k^E_{obs} for the reaction of (I) with ethoxide ion in ethanol–dioxan

$$k^E_{obs} = k_0 + k_{EtO}[EtO^-] \qquad (2)$$

(1 : 1) (EtONa 0.02—0.1M) was analysed by equation (2), which was employed to correlate the rate of the same reaction in pure ethanol.[6] In the present solvent system, however, the value of k_0 was negligible compared to that of the base catalysed term except for (Il; Y = *p*-Me_2N), that is, $k^E_{obs}/[EtO^-]$ was essentially constant over the range of ethoxide ion concentration examined.* For (Il) $k_0 = 1.7 \times 10^{-6}$ s^{-1} and $k_{EtO} = 8.86 \times 10^{-5}$ l mol^{-1} s^{-1}. The values of k_{EtO} are also summarized in Table 1. The effects of substituents on the rate of hydrolysis and on the rate of reaction of (I) with ethoxide ion are shown in Figures 2 and 3. The rate constants for (I) with substituents on the *C*-phenyl ring [(I)-X] were well correlated by the σ constants, with ρ values of 2.10 (r = 1.000) and 2.30 (r = 0.999) for the hydrolysis and for the reaction with ethoxide ion, respectively (Figure 2). On the other hand, the Hammett plots for both the reactions of (I) with substituents on the *N*-phenyl ring [(I)-Y] did not give straight lines, but obviously displayed upward curvature (Figure 3). In the reaction of (I)-Y with ethoxide ion in pure ethanol,[6] however, a linear Hammett plot was demonstrated for (Ia, h, i, and k) with a ρ value of 3.8.† The rate constants for the reaction of (Ia) and (Ih—k) with ethoxide ion in the present study (ethanol–dioxan, 1 : 1) could be linearly correlated by the σ constants (ρ = 3.8, r = 0.997). A linear correlation could also be obtained for the hydrolysis of (Ia) and (Ih—k) (ρ = 2.5, r = 0.993). Thus the Hammett plots for the reactions of (I)-Y can be regarded as either both curved or both linear with the points for (Ig; Y = *p*-CN) and (Il; Y = *p*-Me_2N) deviating upwards.‡ When log k_{OH} for (I)-Y was plotted against the correspond-

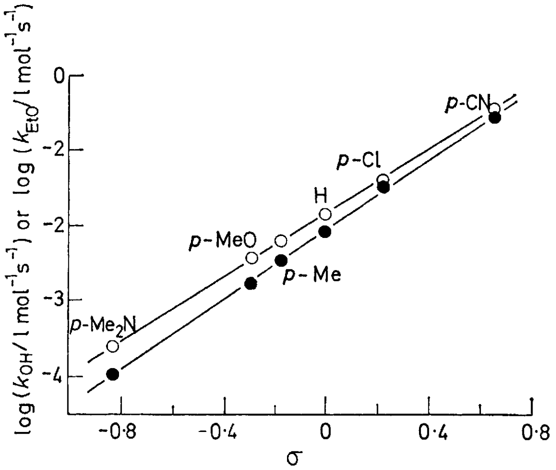

FIGURE 2 Logarithm of the second-order rate constants for the hydrolysis and for the ethanolysis of (I) with substituents on the *C*-phenyl ring (X) against the σ constants at 30 °C; ○, k_{OH} in 50% aqueous dioxan (NaOH–KCl, $\mu = 0.1$); ●, k_{EtO} in ethanol–dioxan (1 : 1 v/v)

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* These results are not incompatible with the results in pure ethanol,[6] in which a k_0 value larger than 2% of the corresponding k_{EtO} value was observed only for Ik (Il was not used in the study).

† In ref. 6 (Ia, h, i, k) and α-cyanobenzylidene-*p*-nitroaniline (I; Y = *p*-NO_2) were used for study, but (Il) was not.

‡ The rate constant (k_{EtO}) for the reaction of (Il) with ethoxide ion expected from the linear plot constructed by (Ia) and (Ih—k) is almost 1/100 of the rate constant (k_{OH}) obtained for the hydrolysis of the same compound. Since the ethanol and the dioxan used in the study were purified by conventional methods (see Experimental section), a possibility of rate enhancement due to a small amount of water contaminating the medium was considered. However, the value of k_{EtO} for (Il) was essentially constant even when the initial concentration of the substrate was varied in the range of 4×10^{-5} to 1×10^{-3}M. The absorption spectra of the reaction mixtures after 10 half-lives were those expected for (IIIl) (imidate ester) except for the run carried out with the lowest initial concentration of (Il) (4×10^{-5}M), where the spectrum was that expected for (III) (anilide).

ing log k_{EtO}, a straight line was obtained ($r = 0.998$, Figures not shown).

The rate of hydrolysis of (I) was slower in H_2O-OH^- system than in D_2O-OD^- system. The value of k_{OH}/k_{OD} (*ca.* 0.7) did not change appreciably with substituents. These results are summarized in Table 3 together with the activation parameters for the hydrolysis.

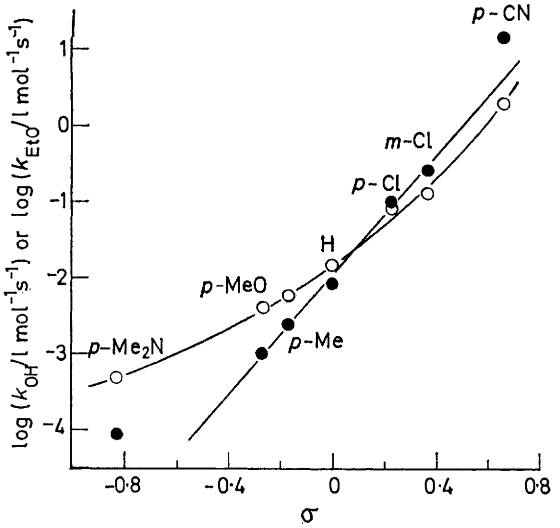


FIGURE 3 Logarithm of the second-order rate constants for the hydrolysis and for the ethanolysis of (I) with substituents on the *N*-phenyl ring (Y) against the σ constants at 30 °C: ○, k_{OH} in 50% aqueous dioxan (NaOH–KCl, $\mu = 0.1$); ●, k_{EtO} in ethanol–dioxan (1 : 1 v/v)

TABLE 3

Solvent deuterium isotope effects[a] and activation parameters[b] for the hydrolysis of (I) in aqueous dioxan ($\mu = 0.5$)

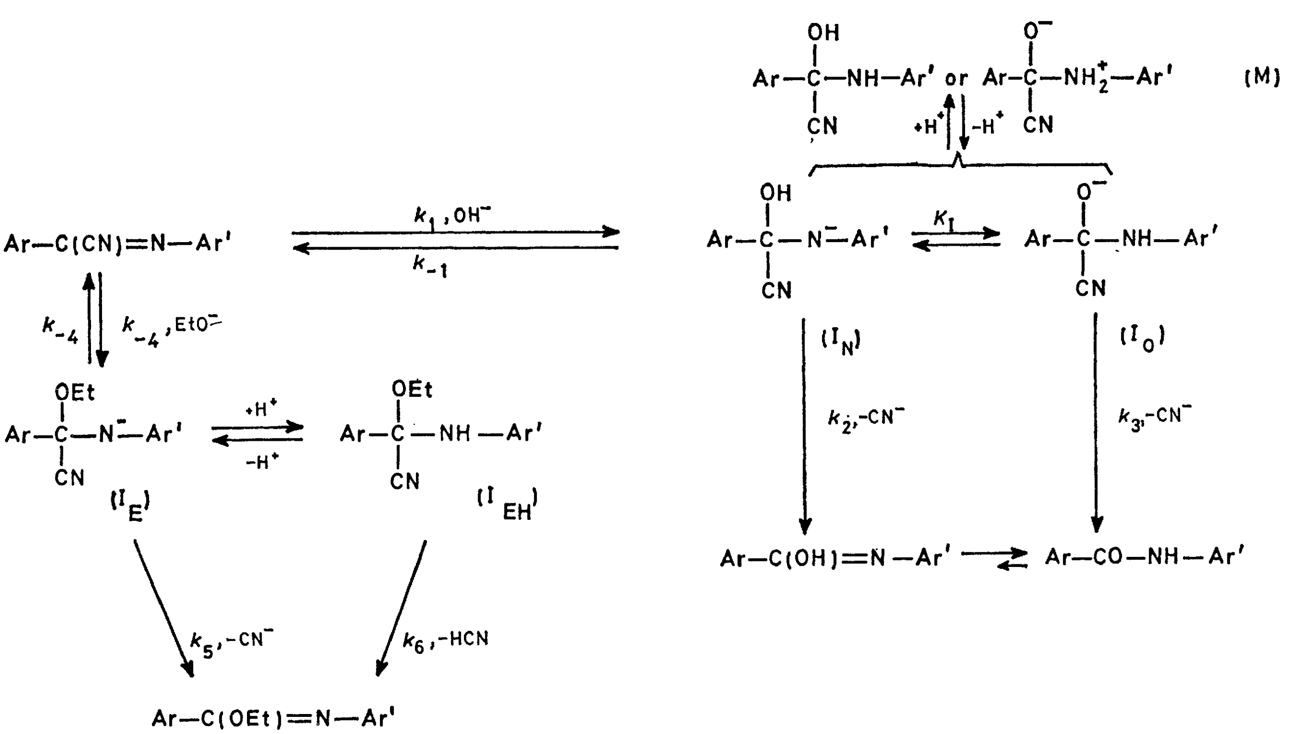
Compound X	Compound Y	E_a/ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}	k_{OH}/k_{OD}
H	H	11.4	−32	0.72
p-Cl	H	12.4	−26	0.72
p-MeO	H	14.9	−23	0.72
p-Me₂N	H	15.8	−24	0.75
H	*p*-Cl	12.2	−26	0.73
H	*p*-MeO	14.3	−24	0.71
H	*p*-Me₂N	15.0	−25	0.76

[a] At 30 °C. [b] The values were evaluated from the second-order rate constants obtained at 20, 30, and 40 °C.

DISCUSSION

The hydrolysis of (I) in basic media seems to be best represented by a mechanism involving tetrahedral addition intermediates. In the reaction of (I) with ethoxide ion in pure ethanol,[6] the reaction was shown to proceed through a tetrahedral addition intermediate. An alternative process involving prior cleavage of C–CN bond to form an ion-pair or a free nitrilium ion was discarded for several reasons,[6] although similar ionization mechanisms had been suggested in the solvolysis,[7,8] and aminolysis [9] of α-chlorobenzylideneanilines.

The ionization mechanism for the hydrolysis of (I) is excluded for the following reasons. In the mechanism, the observed second-order kinetics—first-order with respect to (I) and hydroxide ion—require a rate-determining attack of hydroxide ion either on the ion-



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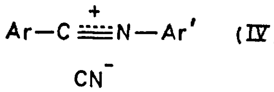
pair (IV) or on the free nitrilium ion (V) formed in a pre-equilibrium step. Negligible common-ion rate retardation (Table 2) eliminates the reaction path through (V).



$$\underset{\mathrm{CN^-}}{\mathrm{Ar{-}\overset{+}{C}{\equiv}N{-}Ar'}}$$

(IV)

$$\mathrm{Ar{-}\overset{+}{C}{\equiv}N{-}Ar'}$$

(V)

The large positive ρ value (2.1) for (I)-X is not compatible with the ion-pair mechanism. A negative or at most a small positive ρ value will be expected for a rate-determining attack of hydroxide ion on (IV) because substituent effects on the equilibrium formation of (IV) ($\rho < 0$) will overcome the effects on the attack of hydroxide ion on (IV) ($\rho > 0$). A large negative ρ values ($\rho < -2$) were reported for the ionization of α-chlorobenzylideneanilines.[7,9]

Another plausible mechanism might be a one-step substitution of the cyanide group by hydroxide ion. Although the present results alone do not exclude such a possibility, the two-step mechanism involving tetrahedral addition intermediates is preferred because the hydrolysis of (I) in acidic media was well accounted for by a similar two-step mechanism.[1] Two-step mechanisms have been well established in the hydrolysis of imidate esters,[5] where the effects of pH on the nature of the hydrolysis products are similar to those in the hydrolysis of (I). Thus the reaction steps as shown in the Scheme are plausible for the reaction of (I) in the present study.

The levelling of the hydrolysis rate of (I) at high concentrations of sodium hydroxide (Figure 1) can be ascribed mainly to ion-pairing of hydroxide ion, or agglomeration.[10] With the TEAOH–TEACl system such ion-pairing will be negligible, and the rate increased linearly with the concentration of TEAOH over the entire range of the base concentration examined. Although no quantitative explanation can be given for the negative salt effect of potassium chloride on the hydrolysis of (I) in the NaOH–KCl system (Table 2) and for the rate enhancement produced by replacing alkali-metal cations by a quaternary ammonium cation (Figure 1), these effects are similar to the salt effects observed in the alkaline hydrolysis of methyl 1-naphthoate in 50% aqueous dioxan, where alkali-metal salts produce small and nearly colligative rate retardation, whereas quaternary ammonium cations form loose van der Waals complexes with the ester and facilitate the attack of hydroxide ion electrostatically.[11]

A change in mechanism, or competition of two reaction pathways, is demonstrated when a Hammett-type plot is concave up.[12] The non-linear Hammett plot observed in the hydrolysis of (I)-Y (Figure 3) could be explained in terms of competition of the two mechanisms involving the ion-pair (IV) and the tetrahedral intermediates (I_N and I_O), respectively, where the ion-pair mechanism prevails in the hydrolysis of (I) with electron-donating Y, as reported in the substitution of α-chlorobenzylideneanilines by amines in benzene.[13] However, in the latter reaction, electron-donating substituents on the *C*-phenyl ring also caused a similar change in mechanism and gave a non-linear Hammett plot, whereas in the present study the hydrolysis of (I)-X afforded a linear correlation (Figure 2). The values of activation parameters and the kinetic isotope effects for (I)-Y are almost identical with those for the corresponding (I)-X as shown in Table 3, where both electron-donating and electron-withdrawing substituents are included. Since (I)-X gave a linear Hammett plot (Figure 2), it seems hard to believe that the reaction of (I) with electron-donating Y proceeds by a different mechanism.

As to the rate-determining step of the reaction, the present results seem to be explained by a rate-determining attack of hydroxide ion on the substrate as well as by a rate-determining decomposition of the tetrahedral addition intermediates. One might *a priori* prefer the rate-determining attack of hydroxide ion because cyanide ion is a weaker base than hydroxide ion (or alkoxide ion) and hence may be a better leaving group, that is, k_2 or $k_3 > k_{-1}$. In alkene-forming eliminations, however, cyanide ion has been shown to be a poorer leaving group than methoxide ion.[14] Relative leaving abilities of potential leaving groups will not be determined solely by the basicity of the groups, but seems to depend on the type of the particular reaction, solvent system, *etc.*[14]

In the Scheme, the equilibrium between I_N and I_O may lie exclusively on the side of I_O, as judged from the pK_a values of methanol[15] (*ca.* 15) and aniline[16] (*ca.* 27). Since hydroxide ion will not be expelled from I_O, the above equilibrium will make the departure of hydroxide ion from the tetrahedral addition intermediates unfavourable. Cyanide ion, on the other hand, would be expelled from both I_N and I_O with similar facility. Another form of the intermediate, M, may be considered. However, contribution of M to the overall reaction should be negligible because anilines alone are expelled[1] from M and only a small amount of anilines were formed in the present study.

In the reaction of (I) with ethoxide ion, the equilibrium between I_E and I_{EH} may also lie largely on the side of I_{EH} under the experimental conditions ($[\mathrm{EtO^-}] < 0.1\mathrm{M}$). A rate-determining departure of cyanide ion from I_{EH} would give kinetics zero-order with respect to ethoxide ion as well as a rate-determining attack of ethanol on (I). However, contribution of such a process to the overall reaction will be small because the uncatalysed term (k_0) was negligible compared to the base-catalysed term (k_{EtO}) except for (Il). The rate-determining step of the reaction will then depend on the relative magnitude of k_{-4} and k_5, that is, the relative leaving abilities of ethoxide ion and cyanide ion from I_E under the conditions.

As mentioned above, the rate-determining steps for the hydrolysis and ethanolysis of (I) in the present study are not decided unambiguously. However, the following considerations prefer a rate-determining attck of hydroxide or ethoxide ion on the substrate. By assuming the equilibrium between I_N and I_O is rapid and both the intermediates are in the steady-state, the second-order rate constant for the hydrolysis is given by equation (3) with the rate constants as defined in the

$$k_{\mathrm{OH}} = k_1(k_2 + k_3K_{\mathrm{I}})/(k_{-1} + k_2 + k_3K_{\mathrm{I}}) \qquad (3)$$

Scheme and $K_{\mathrm{I}} = [\mathrm{I_O}]/[\mathrm{I_N}]$. Similarly the second-order rate constant for the ethanolysis is given in equation (4).

$$k_{\mathrm{EtO}} = k_4k_5/(k_{-4} + k_5) \qquad (4)$$

The values of k_1 and k_4; k_{-1} and k_{-4}; k_2, k_3, and k_5 can be regarded as similar in magnitude, respectively. Since $K_{\mathrm{I}} \gg 1$ is reasonable, equation (3) can be reduced to equation (5). It seems hard to explain the similar

$$k_{\mathrm{OH}} = k_1k_3K_{\mathrm{I}}/(k_{-1} + k_3K_{\mathrm{I}}) \qquad (5)$$

values of k_{OH} and k_{EtO} for (Ia; X = Y = H), and the similar substituent effects for the hydrolysis and ethanolysis in terms of different rate-determining steps for both reactions. If the departure of cyanide ion from the tetrahedral addition intermediate is rate-determining, equations (4) and (5) would be reduced to (6) and (7),

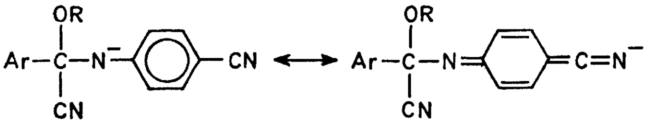
$$k_{\mathrm{EtO}} = k_4k_5/k_{-4} \qquad (6)$$

$$k_{\mathrm{OH}} = k_1k_3K_{\mathrm{I}}/k_{-1} \qquad (7)$$

respectively. From the above considerations for the relative magnitude of rate constants, equations (6) and (7) do not predict similar values for k_{OH} and k_{EtO}, but k_{OH} considerably larger than k_{EtO} because $K_{\mathrm{I}} \gg 1$. Another possibility is to treat the reaction directly by equations (5) and (4). The effects of substituents on k_{OH} and k_{EtO} (Figures 2 and 3) must mainly result from those effects on k_1 and k_4, respectively, because negative ρ values are expected for k_{-1}, k_3, k_{-4}, and k_5. This is consistent with larger ρ values for (I)-Y than for (I)-X especially in the ethanolysis. Similar relations in the ρ values have been observed for the equilibrium addition of methoxide ion[17] and the attack of hydroxide ion[18] to benzylideneanilines. In the hydrolysis, the value of K_{I} will not vary appreciably with X, since both negative charges on $\mathrm{I_N}$ and $\mathrm{I_O}$ are separated from the *C*-phenyl ring by one carbon atom. Thus the ρ value for k_{OH} with change in X would be almost the same as that for k_{EtO} (Figure 2). On the other hand, a negative ρ value for K_{I} will be expected with change in Y. This factor, which is absent in the ethanolysis, would result in the lower sensitivity of k_{OH} to change in Y than that of k_{EtO} (Figure 3). These considerations seem to explain satisfactorily the relative magnitude of the substituent effects between the hydrolysis and ethanolysis, though they oppose the assumption that $k_3K_{\mathrm{I}} \gg k_5$.

The activation parameters and the kinetic isotope effects (Table 3) are not inconsistent with the mechanistic possibilities described above. The values of $k_{\mathrm{OH}}/k_{\mathrm{OD}}$ are in the range expected for nucleophilic attack of hydroxide ion on the substrate.[19]

As described above, the curved Hammett plots (Figure 3) can be regarded as straight lines with the points for (Ig) and (II) deviating upwards. A positive deviation of α-cyanobenzylidene-*p*-nitroaniline (I; Y = *p*-$\mathrm{NO_2}$) in the Hammett plot for the ethanolysis of (I) in pure ethanol has been ascribed to the strong resonance of the nitro-group with the negative charge on $\mathrm{I_E}$, and a $\sigma_{p\text{-}\mathrm{NO_2}}$ value of 1.00 was suggested.[6] The deviation of (Ig) may be explained in the same way. Thus de-



R = H, or Et

(VI)

localization of the negative charge by the cyano group such as (VI) will add an extra stability to the intermediate or the transition state leading to it. A $\sigma_{p\text{-}\mathrm{CN}}$ value of 0.84, required to fit the points for (Ig) on the correlation lines, seems not unreasonable.

The positive deviation of (II) cannot be ascribed to some specific interaction of the dimethylamino-group with the medium because the group on the *C*-phenyl ring behaves normally (Figure 2). Some other factors which are common to both the hydrolysis and ethanolysis must be responsible. The effects of substituents on the electronic spectra of (I) in ethanol suggested that the conjugation of the two phenyl rings in (I) is enhanced with an electron-withdrawing substituent on the *C*-phenyl ring and an electron-donating substituent on the *N*-phenyl ring;[20] the electronic spectra of (II) suggested that the compound has an almost coplanar structure[20] as in the case of *p*-nitrobenzylidene-*p*′-dimethylaminoaniline.[21] This change in molecular conformation might be responsible for the positive deviation of (II), though no reasoning can be given for it at the present stage.

EXPERIMENTAL

Materials.–α-Cyanobenzylideneanilines were prepared by known methods,[22] and gave the expected analytical values. Dioxan was distilled first from sodium metal and then from calcium hydride. Ethanol was distilled from sodium metal. Other chemicals were of reagent grade and were used without further purification.

Product Analysis.—Typical examples are described.

(a) *Benzanilide*. α-Cyanobenzylideneaniline (Ia) (2.125 mg) was subjected to hydrolysis in aqueous dioxan (50% v/v; 10 ml) containing 0.022M-NaOH (μ = 0.1 with KCl) at 30 °C. After 10 half-lives, the reaction mixture was subjected to h.p.l.c. to determine benzanilide using a Waters 6000-A solvent delivery system with a U6K universal injector and a JASCO UVIDEC-1 spectrophotometer. The conditions were as follows: Bondapack $\mathrm{C_{18}}$-Corasil (37—50 μm); 1/8 in × 2 ft column; water–methanol (3 : 2 v/v), 1 ml $\mathrm{min^{-1}}$; at 266 nm. The yield was 95%.

(b) *Aniline and benzoic acid*. Compound (Ia) (218 mg) was subjected to hydrolysis in aqueous dioxan (200 ml) containing 0.03M-NaOH at 30 °C. After 10 half-lives, water (300 ml) was added and the solution was extracted with chloroform (3 × 50 ml). The chloroform layer was dried ($\mathrm{Na_2SO_3}$) and evaporated to dryness under reduced pressure. The residue was dissolved in benzene (50 ml), and the solution was extracted with 1M-phosphate buffer of pH 1.7 (3 × 15 ml). The extract was submitted to colorimetric determination of aniline[23] after adjustment of the volume to 50.0 ml with water in a volumetric flask. Aniline was found in 0.6% yield. The initial water layer was neutralized with aqueous HCl and extracted with chloroform (3 × 50 ml). The chloroform layer was concentrated to a small amount and adjusted to 10.0 ml. The resulting solution was subjected to h.p.l.c. as described previously,[24] to determine the yield of benzoic acid; it was 0.6%. Benzanilide gave neligible amounts of aniline (<0.05%) and benzoic acid (<0.1%) under the same conditions.

(c) *α-Ethoxybenzylideneaniline*. Compound (Ia) (3 g) was allowed to react in ethanol–dioxan [1 : 1 (v/v); 100 ml] containing 1M-NaOEt at 30 °C until no starting material was detected by t.l.c. Water (200 ml) was added and the solution was extracted with chloroform (3 × 50 ml). The chloroform extract was dried and the chloroform was removed under reduced pressure. The residue was distilled to give α-ethoxybenzylideneaniline (2 g), b.p. 125—127 °C at 3 mmHg.

Similar results as for (a) and (c) were obtained with other α-cyanobenzylideneanilines used in the present study.

Kinetic Measurements.—Kinetic measurements were made spectrophotometrically by following the disappearance of (I) at 30 ± 0.1 °C in aqueous dioxan (40 and 50% v/v) and ethanol–dioxan (1 : 1 v/v). The procedures were essentially the same as described previously.[1] U.v. data for (I) used in the present study have been reported.[20] The stock solutions of the bases were standardized before each set of kinetic runs with standard hydrochloric acid solution. Good first-order kinetics were obtained for up to 80% reaction in every run. In the hydrolysis or in the ethanolysis of (I), the absorption spectrum of the reaction mixture after 10 half-lives coincided with that of the corresponding anilide or imidate, respectively.

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