[Chem. Pharm. Bull.
29(10)2753—2761(1981)]

Hydrolysis of Electrophilic Olefins. II.[1] Kinetic Studies on the Hydrolysis of *m*- or *p*-Substituted α-Benzoylcinnamonitriles

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(Received December 22, 1980)

The hydrolysis of *m*- or *p*-substituted α-benzoylcinnamonitriles (I) was studied kinetically in 30% (v/v) ethanol (pH 2—13) at 25°C. The pH-rate profile showed a maximum at nearly neutral pH and an inflection point at weakly acidic pH. The pH-rate profile and substituent effect suggested that the rate-determining step is the carbon-carbon bond fission of an addition intermediate in the strongly acidic range, and is the nucleophilic attack of water on the carbon-carbon double bond of I in the weakly acidic range. It was also suggested that the hydrolysis of I, except for the compounds with strongly electron-withdrawing substituents, CN and NO_2, involves appreciable carbon-carbon bond fission of the addition intermediate at the transition state of breakdown of the intermediate on the basis of the large negative ρ values observed in the alkaline range. Deviation in the cases of the above substituents from the Hammett plots and the enthalpy-entropy relationships appears to show that in these compounds the processes of carbon-carbon bond fission are concerted with deprotonation of the alcoholic hydroxy group of the intermediate.

Keywords——α-benzoylcinnamonitrile; electrophilic olefin; kinetics; pH-rate profile; substituent effect; Hammett relationship; enthalpy-entropy relationship; transition state, two-wavelength method

A number of studies on nucleophilic addition to the carbon-carbon double bonds of activated electrophilic olefins XYC=CHAr (X, Y: electron-withdrawing groups) have been described.[2] In the preceding paper,[1] it was suggested that the pK_a values[1] of the *p*-dimethylaminobenzylidene derivatives of active methylene compounds $XYCH_2$ are useful parameters to evaluate the relative ability of the activating groups, X and Y, to support the attack of nucleophiles on the electrophilic olefins.

On the other hand, substituent effects on nucleophilic attacks at the double bonds of aryl-substituted electrophilic olefins have been analyzed.[3] However, few papers appear to have described the effects of substituents on the phenyl ring upon the rate of the carbon-carbon bond fission of an addition intermediate. Calmon *et al.*[4] evaluated the substituent effect in the hydrolysis of a series of substituted benzylideneacetylacetones to be small; electron-withdrawing substituents slightly accelerated the reaction.

In this work, the kinetics and mechanism of hydrolysis of *m*- or *p*-substituted α-benzoylcinnamonitriles, I, are examined. The proposed hydrolysis mechanism accounts well for the substituent effects of the benzylidene moiety of I, not only on the attack of water or hydroxide ion at the carbon-carbon double bonds of I, but also on the carbon-carbon bond fission of the uncharged addition intermediate of I.

Results and Discussion

The rates of hydrolysis of I in the range of pH 2—13 were measured in 30% (v/v) ethanol at 25°C and ionic strength 0.7. The final products of hydrolysis of I were benzoylacetonitrile and substituted benzaldehyde.

Fig. 1 shows a typical example of the dependence on pH of the pseudo first-order rate constants, k_0, extrapolated to zero buffer concentration; a rate maximum is found at nearly neutral pH with a small inflection at weakly acidic pH.

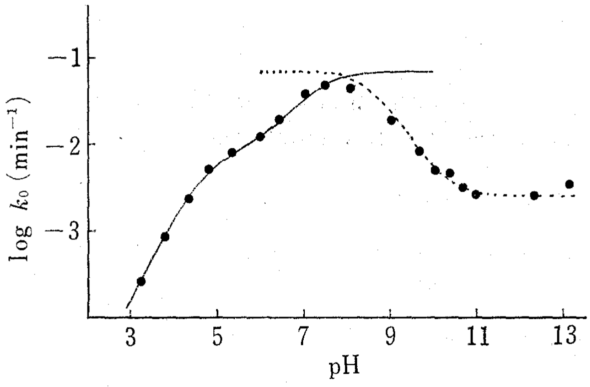


Fig. 1. pH-rate Profile for the Hydrolysis of α-Benzoylcinnamonitrile

The solid line is calculated from Eq. (4) and the dotted line from Eq. (1).

In the alkaline range, faster disappearance of I was followed by slower appearance of the products. The same kinetic behavior was observed for the alkaline hydrolysis of the *p*-dimethylamino derivative of I.[1)] Thus, there must be accumulation of a carbanion intermediate in the hydrolysis of I in the alkaline range. Acidification of the alkaline reaction mixture of I gave partial recovery of I, which decreased with progress of the hydrolysis. Under the same conditions, I was not produced in a mixture of benzoylacetonitrile and the corresponding substituted benzaldehyde. This result also appears to support the accumulation of an addition intermediate, as indicated for the alkaline hydrolysis of 4-hydroxy-3-methoxy-β-nitrostyrene.[5)]

The rates of alkaline hydrolysis of I, except for the *p*-dimethylamino derivative, decreased markedly with increase of pH in the range of pH 8—10 and approached a limiting value in the more strongly alkaline range. The rates of alkaline hydrolysis of the *p*-dimethylamino derivative of I increased with increase of pH and approached a limiting value in the strongly alkaline range as described previously.[1)] Electron-donating groups accelerated the alkaline hydrolysis of I.

In the acidic and neutral ranges, an isosbestic point was observed and the rates of disappearance of I were equal to those of appearance of the products. No intermediate could be detected in the acidic and neutral reaction mixtures of I. The rate constants (k_0) increased markedly with increase of pH in the range of pH 2—5 and reached a maximum at nearly neutral pH through a small inflection point. In the acidic and neutral ranges, electron-withdrawing groups accelerated the reaction.

The kinetics of hydrolysis of I in 30% ethanol is consistent with the following reaction pathway through the carbanion intermediate II and its protonated intermediate III.[6)]

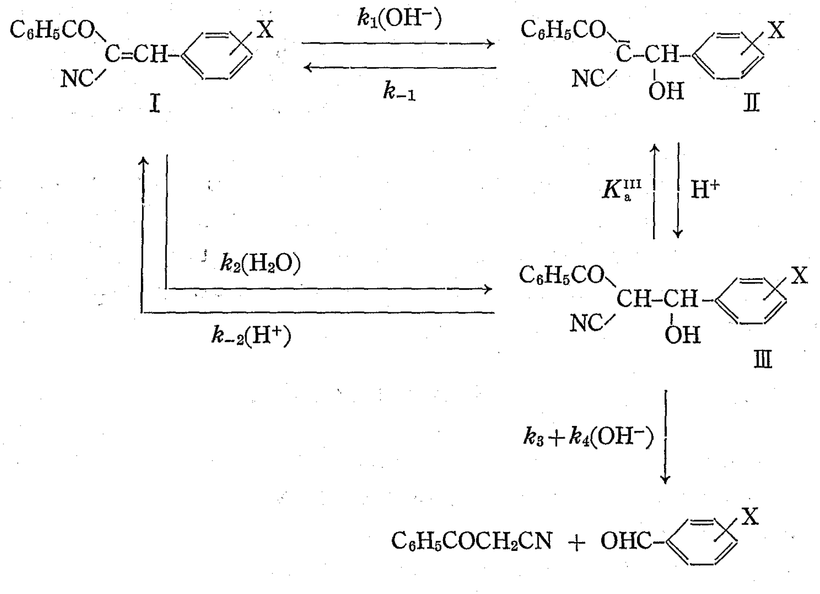


Chart 1

On alkaline hydrolysis of I, the intermediate, II, must be accumulated significantly as described above. The dissociation constants ($K_a^{\rm III}$) of the intermediate, III, are expected to be higher than that ($K_a^{\rm AM}$) of benzoylacetonitrile as described previously.[1] Thus, the assumption, $K_a^{\rm III} \gg a_{\rm H^+}$, will be valid in the range of pH 8—13 from the p$K_a^{\rm AM}$ value of 7.96,[1] where $a_{\rm H^+}$ is the activity of a hydronium ion. Assuming that k_2 is negligible in comparison with $k_1 a_{\rm OH^-}$ in the above pH range, k_o is given by Eq. (1), where K_w is the ionic product of the water in the mixed solvent and $a_{\rm OH^-}$ is the activity of a hydroxide ion. If $k_1 a_{\rm OH^-} \gg k_{-1}$ in the above pH range, Eq. (1) is reduced to Eq. (2).

$$k_o = \frac{k_1 K_w (k_3 + k_4 a_{\rm OH^-}) / K_a^{\rm III}}{k_1 a_{\rm OH^-} + k_{-1}} \tag{1}$$

$$k_o = k_3 a_{\rm H^+} / K_a^{\rm III} + k_4 K_w / K_a^{\rm III} \tag{2}$$

Eq. (2) can explain well the pH-rate profile observed in the alkaline range. The linear relationship of Eq. (2) between k_0 and $a_{\rm H^+}$ gives $k_3/K_a^{\rm III}$ as the slope and $k_4 K_w / K_a^{\rm III}$ as the intercept. These rate parameters are shown in Table I.

If $k_{-1} \gg k_1 a_{\rm OH^-}$ in the above pH range, Eq. (1) is reduced to Eq. (3) and the accumulation of II is not explicable.

$$k_o = k_1 K_w (k_3 + k_4 a_{\rm OH^-}) / k_{-1} K_a^{\rm III} \tag{3}$$

Eq. (3) also could not account for the pH-rate profile in Fig. 1, while Eq. (3) was in good accord with the kinetic behavior during the hydrolysis of the *p*-dimethylamino derivative of I in a weakly alkaline solution,[1] though k_3 was neglected there.

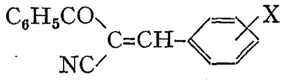
In the acidic and neutral ranges, the rates of disappearance of I coincided well with those of appearance of the products. Assuming that the intermediates II and III are in a steady state, and that $k_3 \gg k_4 a_{\rm OH^-}$ in the above ranges, k_0 is given by Eq. (4). Furthermore, if $k_2 \gg k_1 a_{\rm OH^-}$ and $k_{-2}(a_{\rm H^+})^2 + k_3 a_{\rm H^+} \gg k_{-1} K_a^{\rm III}$ in the acidic range, Eq. (4) can be simplified to Eq. (5). Eq. (5) explains well the acidic part of the observed pH-rate profile.

$$k_o = \frac{(k_1 a_{\rm OH^-} + k_2) k_3 a_{\rm H^+}}{k_{-1} K_a^{\rm III} + k_{-2}(a_{\rm H^+})^2 + k_3 a_{\rm H^+}} \tag{4}$$

$$k_o = k_2 k_3 / (k_{-2} a_{\rm H^+} + k_3) \tag{5}$$

From Eq. (5), inverse plots of k_0 against $a_{\rm H^+}$ give a linear relationship with a slope of $k_{-2}/k_2 k_3$ and an intercept of $1/k_2$. Table I summarizes the parameters, $k_2 k_3 / k_{-2}$ and k_2, together with $k_3 / K_a^{\rm III}$ and $k_4 K_w / K_a^{\rm III}$. Eq. (5) shows that the rate-determining step is the carbon-carbon

TABLE I. Rate Parameters for the Hydrolysis of I

	$10^2\ k_2$ (min^{-1})	$10^7\ k_2 k_3 / k_{-2}$ (min^{-1} M)	$10^{-7}\ k_3 / K_a^{\rm III}$ (min^{-1} M^{-1})	$10^3\ k_4 K_w / K_a^{\rm III}$ (min^{-1})
p-N(CH$_3$)$_2$				55[a]
p-OCH$_3$	0.11	0.24	11	8.6
p-CH$_3$	0.31	0.50	5.6	4.5
m-CH$_3$	0.50	1.2	3.9	3.5
H	0.82	1.5	3.5	2.5
m-OCH$_3$	2.0	2.2	2.1	1.8
p-Cl	3.0	4.0	1.1	1.5
m-Cl	7.6	10	0.60	0.90
m-CN	23	50	0.18	0.37
p-CN	23	48	0.26	0.40
m-NO$_2$	32	59	0.15	0.32
p-NO$_2$	38	71	0.17	0.33

a) see reference 1).

bond fission of III in the strongly acidic range and the nucleophilic attack of water in the weakly acidic range which is near the inflection point on the pH-rate profile.

The values of k_1 and k_{-1} were estimated to fit Eq. (4) in the weakly acidic to neutral ranges by the use of the parameters, k_2, k_2k_3/k_{-2}, and k_3/K_a^{III}, listed in Table I. The k_1 and k_{-1} values were $1.6 \times 10^6\,\text{min}^{-1}\text{M}^{-1}$ and $2.8\,\text{min}^{-1}$, respectively, for the unsubstituted derivative of I. For the hydrolysis rates of the unsubstituted derivative of I, the solid line in Fig. 1 was calculated from Eq. (4), and the dotted line from Eq. (1) by using the k_1 and k_{-1} values with the rate parameters listed in Table I. These calculated lines agree well with the observed rate constants. However, such k_1 and k_{-1} values could not be obtained for most derivatives of I.[7]

As shown in Fig. 2, Hammett plots of log k_2 against σ gave a straight line with a slope of 2.77 (ρ_1) except for the strongly electron-withdrawing substituents, CN and NO_2, which formed a curved line. This curvature may be due to cross conjugation, as proposed to explain the rates of attack of amines on aryl-substituted electrophilic olefins.[8]

Plots of $\log(k_2k_3/k_{-2})$ against σ also gave a linear relationship with a slope of 2.38 (ρ_2), as shown in Fig. 2. Comparison of the ρ_1 and ρ_2 values suggests that the substituent effect on the term, k_3/k_{-2}, is small. Because the k_3 process is expected to contain appreciable carbon-carbon bond fission at the transition state, as discussed below, the k_{-2} process must also contain appreciable carbon-oxygen bond fission where δ_+ charge is formed on the β-carbon of III at the transition state.

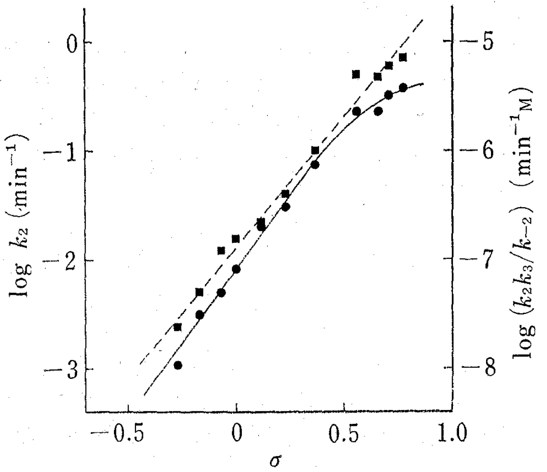


Fig. 2. Hammett Plots of log k_2 or $\log(k_2k_3/k_{-2})$ against σ

●——●: log k_2 vs. σ, ■——■: log (k_2k_3/k_{-2}) vs. σ.

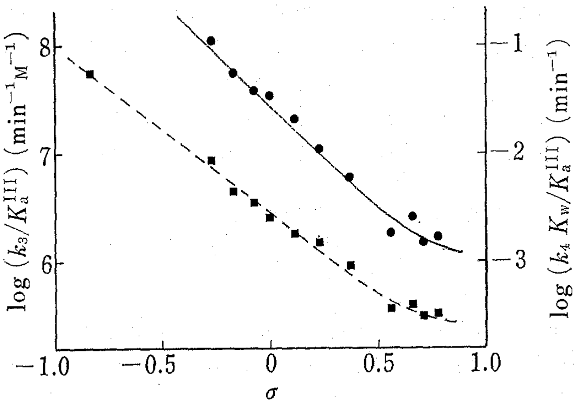


Fig. 3. Hammett Plots of log (k_3/K_a^{III}) or $\log(k_4K_w/K_a^{III})$ against σ

●——●: log (k_3/K_a^{III}) vs. σ, ■——■: log (k_4K_w/K_a^{III}) vs. σ.

As shown in Fig. 3, plots of $\log(k_3/K_a^{III})$ or $\log(k_4K_w/K_a^{III})$ against σ gave a good linear correlation except for the strongly electron-withdrawing substituents (CN and NO_2). The substituent effect on K_a^{III} is suggested to be small because there is a hydroxymethylene group between the α-carbon and phenyl ring of III; Calmon *et al.*[4] estimated a small positive ρ value for the substituent effect on the dissociation constants of an addition intermediate such as III. A small positive ρ value for K_a^{III} is also likely and may be partly responsible for the negative ρ values for k_3/K_a^{III} and k_4K_w/K_a^{III} shown in Table II, together with the ρ_1 and ρ_2 values. However, the large negative ρ values for k_3/K_a^{III} and k_4K_w/K_a^{III} suggest that appreciable carbon-carbon bond fission occurs at the transition states of both the k_3 and k_4 processes where δ_+ charge is formed on the β-carbon of III. The rate-determining carbon-carbon bond fission mechanism in the alkaline hydrolysis of I is similar to that of the *p*-dimethylaminobenzylidene derivatives of active methylene compounds described in the preceding paper.[1]

Table II. Hammett ρ Values for the Rate Parameters, k_2, k_2k_3/k_{-2}, k_3/K_a^{III}, and k_4K_w/K_a^{III}

Rate parameters	$\rho \pm s_\rho$	n	r
k_2	$\rho_1 = 2.77 \pm 0.14$	7	0.994
k_2k_3/k_{-2}	$\rho_2 = 2.38 \pm 0.09$	11	0.993
k_3/K_a^{III}	$\rho_3 = -1.89 \pm 0.09$	7	0.994
k_4K_w/K_a^{III}	$\rho_4 = -1.50 \pm 0.06$	8	0.995

Different results have been reported for the substituent effect on carbon-carbon bond fissions such as the k_4 process in the hydrolysis of a series of substituted benzylideneacetylacetones; a slightly positive ρ value has been evaluated.[4] In the previous paper,[1] the rates of carbon-carbon bond fission of addition intermediates such as III were correlated with the stability of the carbanion ($ArCO\bar{C}HCN$) formed in the hydrolysis of α-(substituted benzoyl)-*p*-dimethylaminocinnamonitriles. If such a correlation is also applied to the hydrolysis of benzylideneacetylacetones and α-benzoylcinnamonitriles, the former rates are appreciably slower than the latter.[9] Thus, the former transition states are presumed to involve smaller extents of carbon-carbon bond fission than the latter.[10] The ρ value for the substituent effect on the former rates is evaluated to be less negative than that for the latter, though a slightly positive value has been estimated instead.[4]

The deviation of the strongly electron-withdrawing substituents, CN and NO_2, from the linear Hammett relationships for k_3/K_a^{III} and k_4K_w/K_a^{III} can be explained by the following enthalpy-entropy relationships.

Table III. Activation Parameters for the Hydrolysis of I

Substituent (X)	$\Delta H^{\ddagger}$ (kcal/mol) at 25°C	$\Delta S^{\ddagger}$ (e.u.) at 25°C
p-$N(CH_3)_2$	20.88	−2.73
p-OCH_3	23.75	4.33
p-CH_3	23.23	1.29
m-CH_3	24.21	3.70
H	25.89	9.06
m-OCH_3	25.95	8.42
p-Cl	26.42	9.89
m-Cl	27.30	11.22
m-CN	23.32	−3.48
p-CN	23.53	−2.93
m-NO_2	22.76	−6.13
p-NO_2	23.79	−2.25

Table III shows the activation parameters for the alkaline hydrolysis of I at pH 13, where the observed first-order rate constant approximate closely to their limiting values. Enthalpy-entropy relationships[11] seem to form two lines (not shown); one for substituents other than *m*- or *p*-CN and *m*- or *p*-NO_2, and the other for the above four strongly electron-withdrawing substituents. These relationships, assuming that the relation for K_a^{III} is linear for all the compounds I, appear to show that there are smaller carbon-carbon bond fissions of III and larger interactions between hydroxide ion and the alcoholic hydroxy group of III at the transition state of the k_4 processes for the above four compounds than for the other compounds I. It is likely that the carbon-carbon bond fission at the transition states of the k_3 and k_4 processes for the former compounds is more synchronously concerted with the deprotonation of the alcoholic hydroxy group of III.[12] Thus, the δ_+ charge formed on the β-carbon of III at both transition states must be much smaller. This conclusion is consistent with the result that the strongly electron-withdrawing substituents deviate from the linear lines shown in Fig. 3.

Deviation of the above four substituents from the linear Hammett relationships in Fig. 3 and from the enthalpy-entropy relationships suggests a difference of transition-state structures at the k_3 and k_4 processes between these substituents and the others of I. The More O'Ferrall-Jencks reaction coordinate diagram[13] shown in Fig. 4 illustrates such a difference of the transition-state structures, with a more concerted transition state for the former (diagonal reaction coordinate), and a more unbalanced transition state for the latter (curved reaction coordinate). It is likely that in the curved reaction coordinate, the deprotonation of the alcoholic hydroxy group of III lags behind the carbon-carbon bond fission because of the stability of the forming carbanion, $PhCO\overset{-}{C}HCN$, and carbonium ion, $\overset{+}{C}H(OH)Ar$.[14] A decrease of stability of the carbonium ion could possibly cause the shift from the curved to the diagonal reaction coordinate on changing from the latter substituents to the former.

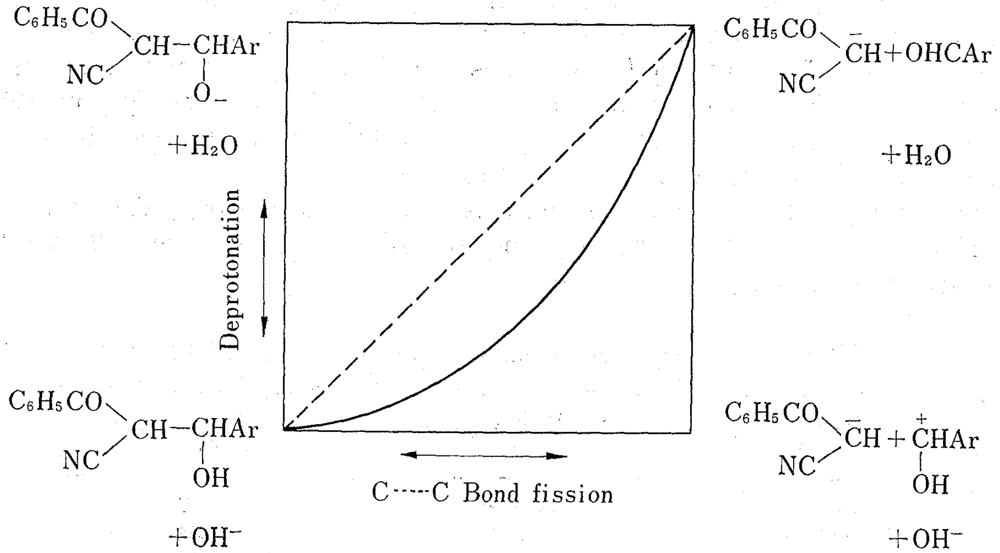


Fig. 4. Schematic Reaction Coordinate Diagram for the k_4 Process

The horizontal and vertical axes represent the amount of carbon-carbon bond fission of III and that of deprotonation of the alcoholic hydroxy group of III, respectively. The diagonal and curved lines show the reaction coordinate for the strongly electron-withdrawing substituents and that for the other compounds I, respectively. The energy contour lines are omitted.

Hammett plots of $\log(k_2k_3/k_{-2})$ and $\log(k_3/K_a^{III})$ against σ gave ρ values of 2.38 and -1.89, respectively, as shown in Table II. Thus, the plots of $\log(k_2/k_{-2})$ against σ give the ρ value of 4.27, neglecting the substituent effect on K_a^{III} as discussed earlier. This large ρ value of 4.27 is comparable to that (4.18) reported for the equilibrium constants of the addition of a hydroxide ion to benzylidene Meldrum's acid derivatives with electron-donating substituents.[15] A large ρ value can also be expected for k_1/k_{-1}. Such a large ρ value for k_1/k_{-1} appears to explain the difference of pH-rate profile between the *p*-dimethylamino derivative and the other compounds I. The equilibrium of nucleophilic addition of a hydroxide ion in the former hydrolysis in weakly alkaline solution lies on the side of formation of the carbon-carbon double bond of the former[1]; $k_{-1} \gg k_1a_{OH^-}$. Thus, the hydrolysis rate constants of the former increase with increase of pH in this alkaline range. On the other hand, the addition equilibrium for the latter lies on the side of the nucleophilic attack of a hydroxide ion even in the above alkaline range; $k_1a_{OH^-} \gg k_{-1}$. Thus, the hydrolysis rate constants of the latter decrease with increase of pH in the weakly alkaline range as shown in Fig. 1.

The normalized[16] $\alpha^n(k_2)$ value calculated from the ρ values for k_2 and k_2/k_{-2} is 0.66, neglecting the substituent effect on K_a^{III} as discussed above. This α^n value is larger than that (0.36) observed for the nucleophilic attack of a hydroxide ion on α-(substituted benzoyl)-*p*-dimethylaminocinnamonitriles,[1] and is slightly larger than those reported for the addition of amines to substituted benzylidene Meldrum's acid derivatives.[16] Some reasons for the difference between the α^n value, $\alpha^n(k_1)$, reported previously[1] and that, $\alpha^n(k_2)$, studied here may be as follows.

1) The Difference of Substituents on the Benzylidene Moiety: The most strongly electrondonating substituent, *p*-$N(CH_3)_2$, was used in the previous paper.[1] If the substituent effect on the benzylidene moiety shows loss of conjugation,[16] it is probable that the $\alpha^n(k_1)$ value is lower than the $\alpha^n(k_2)$ value.

2) The Difference of Nucleophiles: A hydroxide ion attacks the carbon-carbon double bonds of *p*-dimethylaminocinnamonitriles.[1] The difference of nucleophilicity between hydroxide ion and water may also explain the lower $\alpha^n(k_1)$ value, although a very low β_{nuc} value (0.08) was reported.[16]

3) The Difference of Substituent Effects: The substituent effect on the benzoyl group was discussed in the previous paper.[1] The $\alpha^n(k_1)$ value was expected to show a measure of negative charge formation on the α-carbon at the transition state.[1] However, the substituent effect on the benzylidene moiety studied here may be a measure of a) the loss of conjugation, b) the progress of rehybridization of the benzylic β-carbon, or c) the negative chargelocalized on the benzylic β-carbon (or delocalized into the phenyl ring), in the transition state.[16] Accordingly, more complex evaluation would be required for the substituent effect on the benzylidene moiety than for that on the benzoyl group.[17]

In conclusion, the hydrolysis mechanism presented here can account well for the substituent effects on the carbon-carbon bond fission of III as well as on the nucleophilic addition to the carbon-carbon double bonds of I. It is also concluded that deviation of the strongly electron-withdrawing substituents from the linear Hammett relationships and the enthalpy-entropy relationships observed in the alkaline range implies a difference of the transition-state structures at breakdown of the uncharged addition intermediate between these substituents and the other compounds I.

Experimental

Materials——*m*- or *p*-Substituted α-benzoylcinnamonitriles (I) were prepared by the method of Kauffmann.[18] Table IV summarizes the melting points and analytical results of I. Reagent-grade benzoylacetonitrile was purified by recrystallization. Substituted benzaldehydes were purified by recrystallization or distillation. Ethanol was purified as described previously.[1] Glass-distilled water was used throughout. Other chemicals were of reagent-grade and were used without further purification.

Apparatus——Spectroscopic measurements were carried out with a Hitachi 356 dual-wavelength double-beam spectrophotometer. The pH measurement system and the high performance liquid chromatography (HPLC) system were described previously.[1]

pH Determination——In 30% (v/v) ethanol, it was considered that pH = meter reading -0.10 at 25°C as described previously.[1] The pK_w value of 14.47 was used for calculation of the activity of a hydroxide ion as described previously.[1]

Product Analysis——A typical example is described. α-Benzoylcinnamonitrile was subjected to hydrolysis in 30% ethanol (pH 4.3, 7.1, or 10.4) at 25°C. Its initial concentration in the mixture was 4.58×10^{-5} M. After 10 half-lives, the reaction mixture was subjected to HPLC to determine benzoylacetonitrile and benzaldehyde. The HPLC conditions were the same as described in the previous paper.[1] No peak other than those of the above two components could be detected. All of the yields on hydrolysis were more than 95% for both products.

Kinetic Measurements——Kinetic measurements were made spectrophotometrically by following the appearance of the products in 30% ethanol at 25.0 ± 0.1°C. The ionic strength of the reaction mixture was maintained at 0.7 with potassium chloride. The initial concentrations of I were in the range of 1×10^{-5} to 1×10^{-4} M. The reactions were initiated by the addition of 5 ml of the stock solution (ethanol) of I equilibrated thermally at 25°C to a volumetric flask (100 ml) preequilibrated at 25°C in a water bath and containing 70 ml of aqueous buffer solution and 25 ml of ethanol. The mixture was quickly shaken and then stored in the bath. At appropriate intervals, 5 ml of the solution was pipetted into a test-tube containing 3 ml of

Table IV. Melting Points and Analytical Results of I, and Wavelength Pairs for Measurement of the Products

Substituent (X)	mp, °C (lit.)	Analysis, % Found (Calcd) C	H	N	λ_1, nm	λ_2, nm
p-OCH$_3$	100.0—101.5	77.83	4.89	5.27	282	404
	(101.2—101.8)$^{a)}$	(77.55	4.98	5.32)		
p-CH$_3$	89.0—90.0	82.60	5.40	5.74	253	375
	(88.0—89.0)$^{a)}$	(82.57	5.30	5.66)		
m-CH$_3$	75.0—76.0	82.46	5.27	5.74	250	360
		(82.57	5.30	5.66)		
H	83.5—85.5	82.39	4.82	5.99	248	354
	(83.0—84.0)$^{a)}$	(82.38	4.75	6.01)		
m-OCH$_3$	91.0—92.5	77.73	4.96	5.34	250	358
	(90.0—90.8)$^{a)}$	(77.55	4.98	5.32)		
p-Cl	102.0—103.8	71.97	3.82	4.96	253	365
	(102.8—103.8)$^{a)}$	(71.78	3.77	5.23)		
m-Cl	127.5—128.5	71.95	3.74	5.21	247	342
		(71.78	3.77	5.23)		
m-CN	130.0—131.0	79.19	3.87	10.56	245	325
		(79.06	3.90	10.84)		
p-CN	127.0—128.0	79.31	4.04	11.02	250	341
		(79.06	3.90	10.84)		
m-NO$_2$	121.0—123.0	69.17	3.67	9.92	237	323
		(69.06	3.62	10.07)		
p-NO$_2$	143.0—144.5	69.07	3.69	9.82	252	349
	(140)$^{b)}$	(69.06	3.62	10.07)		

a) D.J. Currie and H.L. Holmes, *Can. J. Chem.*, **47**, 863 (1969); the actual data are taken from the Depository of Unpublished Data, National Research Council, Ottawa, Canada.
b) see reference 18).

30% ethanol (0.1 or 1.0 N HCl)[19] and then the absorbance due to the reaction products was measured by the two-wavelength method. The values of the wavelength pairs, λ_1 and λ_2, are also listed in Table IV. The λ_1 value was selected as the wavelength of maximum absorption of an equimolar solution of benzoylacetonitrile and substituted benzaldehyde in 30% ethanol (0.1 N HCl) and the λ_2 value was selected as the wavelength at which the absorbance of I in 30% ethanol (0.1 N HCl) was equal to that at the λ_1 value. The observed pseudo first-order rate constants were calculated from the least-squares plots of $\ln(A_\infty - A_t)$ against time. All runs were linear for at least 2 half-lives.

Acknowledgment The authors are grateful to Professor M. Masui and Dr. H. Ohmori of Osaka University for valuable discussions and suggestions during this work.

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6) The pathway proceeding from I to III through the k_2 process in Chart 1 may represent kinetically indistinguishable water-catalyzed attack of water on I followed by protonation of the resulting carbanion intermediate II.
7) It was difficult to estimate such k_1 and k_{-1} values for I with more strongly electron-withdrawing substituents than p-Cl, since the inflection points of the pH-rate profiles appeared at near the corresponding rate maxima. As their maximum rate constants are expected to approximate to $k_1k_3K_w/k_{-1}K_a^{III}$ from Eq. (1) and (4), their k_2 values are probably comparable to $k_1k_3K_w/k_{-1}K_a^{III}$.
8) C.E. Lough and D.J. Currie, *Can. J. Chem.*, **44**, 1563 (1966).
9) The dissociation constant, K_a^{AM}, of acetylacetone is lower (*ca.* 1.2 log units) than that of benzoylacetonitrile as described in the preceding paper: see reference 1).

10) It is also likely that the carbon-carbon bond fission at the former transition states is concerted with the deprotonation of the alcoholic hydroxy group of an addition intermediate such as III, as suggested by Calmon *et al.*: see reference 4).

11) The significance of these relationships has been recognized by Leffler[a] and their statistical validity has been examined by Exner[b] and Wold[c]: *a)* J.E. Leffler, *J. Org. Chem.*, **31**, 533 (1966), and references therein; *b)* O. Exner and V. Beránek, *Collect. Czech. Chem. Commun.*, **38**, 781 (1973), and references therein; *c)* S. Would, *Chem. Scr.*, **2**, 145 (1972).

12) These transition states may also be similar to those in the hydrolysis of the benzylideneacetylacetones: see reference 4) and note 10).

13) *a)* R.A. More O'Ferrall, *J. Chem. Soc (B)*, **1970**, 274; *b)* W.P. Jencks, *Chem. Rev.*, **72**, 705 (1972).

14) This interpretation of the transition state also explains the large negative ρ values for k_3/K_a^{III} and k_4K_w/K_a^{III}.

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