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NOTE

Cinnamoyl Azide와 *p*-Nitrophenyl Cinnamate의 알칼리 가수분해반응에 대한 아실치환기의 효과

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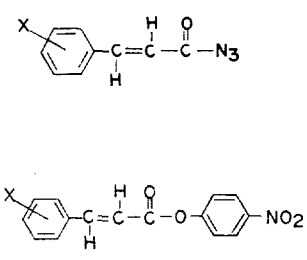
Acyl Substituent Effects in the Alkaline Hydrolysis of Cinnamoyl Azide and *p*-Nitrophenyl Cinnamates

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Acyl transfer reactions of acyl azides have rarely been studied because they usually undergo Curtius rearrangement.[2] We have found that the derivatives of cinnamoyl azide (**1a**) are stable against the rearrangement. In the previous study,[3] we investigated the reactivity of aryl-substituted phenyl cinnamates and **1a**. Thus, we found that **1a** was much more stable toward the aminolysis by quinuclidine derivatives and the alkaline hydrolysis than the ester analog containing a phenolate leaving group whose basicity was similar to that of azide ion. Besides, the leaving ability of azide ion from the tetrahedral intermediate relative to phenolates or quinuclidine derivatives was reported.[3]

In order to obtain further information on the electronic requirement for the reaction of acyl azides, we have studied the structure-reactivity relationships for the alkaline hydrolysis of acyl-substituted cinnamoyl azides(**1a**∼**1d**) and acyl-substituted *p*-nitrophenyl cinnamates (**2a**∼**2d**). In this article, the Hammett plots for these reactions are described.



1a: X = H
1b: X = p-Cl
1c: X = 3,4-diCH$_3$O
1d: X = p-NO$_2$

2a: X = H
2b: X = p-Cl
2c: X = 3,4-diCH$_3$O
2d: X = p-NO$_2$

EXPERIMENTAL

The acyl-substituted cinnamoyl azides were prepared by reacting the corresponding cinnamoyl chlorides with sodium azide either in aqueous acetone[4] or in dry ether[5]. The acyl azides prepared are: **1a**, 85∼86 °C (*lit.*[4] 86 °C) from hexane; **1b**, 84∼85 °C (*lit.*[5] 84 °C) from 1 : 2 toluene-hexane; **1c**, 101∼103 °C (*lit.*[5] 103 °C) from ether-hexane; **1d**, 121∼123 °C (*lit.*[6] 123 °C) from acetone.

The acyl-substituted *p*-nitrophenyl cinnamates were prepared with the aid of N, N′-dicyclohexylcarbodiimide in acetone. The esters obtained are: **2a**, 145∼147 °C(*lit.*[7] 146.5∼147.5 °C) from acetone-hexane: **2b**, 147.5∼148 °C

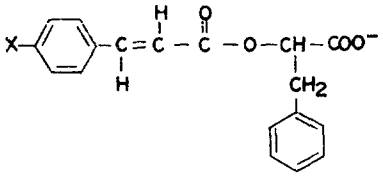
from ether–hexane; **2c**, 135~137 °C from ether–hexane; **2d**, 188~190 °C from ether.

Other experimental details including the kinetic measurements have been reported previously.[3]

RESULTS AND DISCUSSION

The alkaline hydrolysis of **1a**~**1d** was studied in water containing 0.8 % (v/v) acetonitrile or in 1 : 1 (v/v) acetone–water mixtures at 25 °C and ionic strength 1.0. The alkaline hydrolysis of **2a**~**2d** was studied only in 1 : 1 (v/v) acetone–water mixtures because of the limited solubilities of the esters in water.

The pseudo first-order rate constants for the substrates were proportional to the concentration of hydroxide ion, and the second-order rate constants, k_{OH^-}, are summarized in *Table* 1. In *Fig.* 1, the Hammett plots for the alkaline hydrolyses are illustrated. The σ values employed were those of Jaffé[8,9]. The ρ values calculated from the linear lines of *Fig.* 1 are summarized in *Table* 2. Also included in *Table* 2 is the ρ value[10] for the alkaline hydrolysis of acyl-substituted *O*-cinnamoyl-*L*-β-phenyllactates (**3**) measured in water at 25 °C and ionic strength 0.55.



3

The results summarized in *Table* 2 disclose almost identical ρ values for the alkaline hydrolysis of **1a**~**1d** and that of **2a**~**2d** in spite of the large structural differences in leaving group. Besides, Kirsch and co-workers observed that the ρ values for the alkaline hydrolysis of various acyl-substituted phenyl benzoates were virtually the same when the phenyl portions were changed as *p*-methylphenol, phenol, *p*-chlorophenol, *m*-chlorophenol, and *p*-nitrophenol.[11] Furthermore, the ρ value measured for the alkaline hydrolysis of the derivatives of **3** in water at 25 °C and ionic strength 0.55 falls within the error limit of that for **1a**~**1d** measured in water containing a trace of acetonitrile

Table 1. Rate data for the alkaline hydrolysis of acyl-substituted cinnamoyl azides and *p*-nitrophenyl cinnamates at 25 °C and ionic strength 1.0.

Compound	Solvent[a]	OH^- (m*M*)	wavelength followed (nm)	k_{OH^-} ($M^{-1}sec^{-1}$)
1a	W	3~30	270	2.61±0.04
1b	W	3~20	270	4.17±0.05
1c	W	3~20	330	1.77±0.05
1d	W	1.5~13	330	14.8 ±0.9
1a	A/W	5~30	330	0.99±0.01
1b	A/W	5~35	330	1.55±0.05
1c	A/W	10~25	330	0.47±0.01
1d	A/W	2.5~15	330	8.26±0.15
2a	A/W	8~20	400	0.42±0.01
2b	A/W	5~25	400	0.90±0.03
2c	A/W	6~25	400	0.20±0.01
2d	A/W	2.5~20	400	3.52±0.04

[a]W stands for water containing 0.8% (v/v) acetonitrile and A/W for 1 : 1 (v/v) acetone–water.

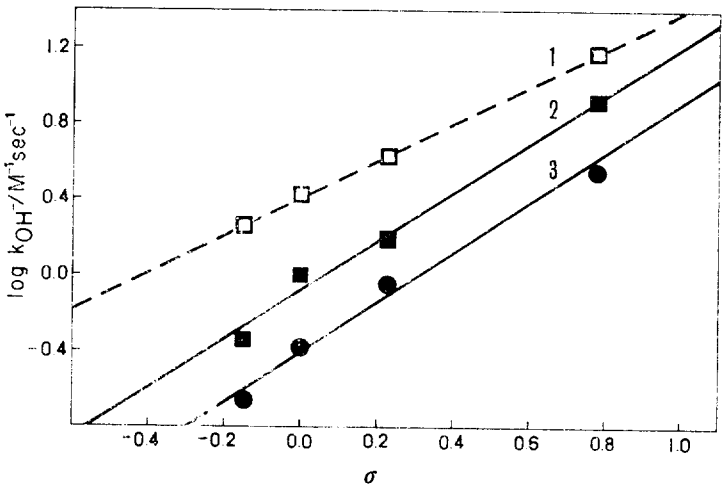


Fig. 1. The Hammett plots for the alkaline hydrolysis of **1a**~**1d** in water containing 0.8 % (v/v) acetonitrile (line 1), **1a**~**1d** in 1 : 1 (v/v) acetone-water (line 2), and **2a**~**2d** in 1 : 1 (v/v) acetone-water (line 3) at 25 °C and ionic strength 1.0.

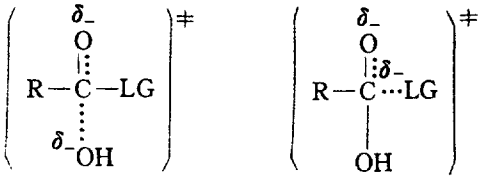
Table 2. Hammett reaction coefficients for the alkaline hydrolysis reactions.[a]

Compound	Solvent[b]	ρ[d]	Correlation coefficient
1a~**1d**	W	0.98±0.01	0.999
1a~**1d**	A/W	1.29±0.07	0.994
2a~**2d**	A/W	1.27±0.07	0.994
3	*c*	0.92±0.07[e]	0.991

[a]At 25 °C. Ionic strength 1.0 for **1a**~**1d** and **2a**~**2d** and 0.55 for **3**. [b]See footnote *a* of *Table* 1. [c]Water without any added organic solvent. [d]σ values used are 0.23 for *p*-Cl, 0.78 for *p*-NO_2, and −0.15 for 3.4-diCH_3O. [e]Data taken from ref. 10.

at 25 °C and ionic strength 1.0. Thus, the ρ values for the alkaline hydrolysis of the acyl azides, phenyl esters, and alkyl esters are almost the same. The leaving groups discussed here include various phenolates, an alkoxide, and azide ion. These vary widely in their basicity and contain different leaving elements (N and O).

The virtually same ρ values observed in the present investigation can be explained by examining the structures of the transition states for the rate-determining steps. One can expect that the free energy of the transition state is much closer to that of the corresponding tetrahedral intermediate than that of the corresponding ground state or product. According to the Hammond's postulate[12], the transition state would resemble the corresponding tetrahedral intermediate, and consequently, the distance between the reaction center and the nucleophilic atom (oxygen of hydroxide ion) or the leaving atom in the transition state would not deviate greatly from the normal bond length of C-O or C-N. Thus, the electronic effect exerted by the acyl-substituents can be transmitted almost fully to the nucleophilic atom and the leaving atom in the transition state. The transition state that determines the magnitude of the ρ value is either structure **A** or structure **B** depending on the nature of the rate determining step.



A **B**

Since the amount of negative charges around

reaction center in the rate-determining transition state is -1 and that in the ground state is zero regardless of the nature of the leaving group, the virtually same ρ values obtained in the present study are expected.[13]

On the other hand, the ρ value for the alkaline hydrolysis of **1a**~**1d** is affected appreciably by the change in solvent. The ρ value is greater in 1 : 1(v/v) acetone-water than in water. One may expect that solvation of the negative charges around the reaction center is more extensive in water than in 1 : 1 (v/v) acetone-water. Stabilization of the transition state by the electron attracting acyl-substituents would be smaller in water because of the greater dispersion of the negative charges by solvation in water. Thus, the solvent effect on the ρ value observed in the present study is related to the solvation of the negative charges in the transition state.

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