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Solvolysis of Phenylacetyl Chlorides in Methanol-Acetonitrile Mixtures

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The methanolysis reactions of phenylacetyl chlorides have been investigated in methanol-acetonitrile mixtures at temperatures ranging -15.0—0.0°C. Substituent and solvent effects on the rate supported an associative S_N2 mechanism for the solvolysis. Activation parameters indicated that the reaction is entropy controlled, while the ρ values of the Taft's solvatochromic correlation proved to be remarkably constant with a typical value of 0.50 that is consistent for the reactions proceeding by a typical S_N2 path.

Introduction

The reactions of acyl chlorides, $RCOCl$, have been studied extensively partly because they are the most widely used reactions in organic synthesis¹. However due to their strong reactivity, the mechanisms are not well elucidated

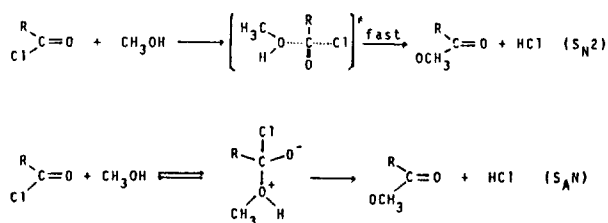
compared to the mechanisms of reactions of other carbonyl compounds. To remedy the situation, various experimental devices for the fast-rate measurement have been introduced².

Ethanolysis of aliphatic acyl chlorides³ are reported to proceed by a bimolecular synchronous displacement (S_N2)

Table 1. Pseudo-First-Order Rate Constant ($k_1 \times 10^2 \text{sec}^{-1}$) for Solvolysis of Substituted Phenylacetyl Chlorides in MeOH-MeCN. The Errors Shown are the Standard Deviations

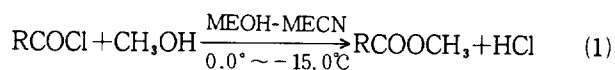
(V/V%)		0°C	5°C	-10°C	-15°C
100	Y = H	6.85 ± 0.21	4.78 ± 0.11	3.01 ± 0.01	2.08 ± 0.07
	p-Cl	7.19 ± 0.11	5.11 ± 0.09	3.33 ± 0.08	2.23 ± 0.01
	p-NO ₂	8.64 ± 0.14	6.25 ± 0.12	4.28 ± 0.03	2.98 ± 0.06
90	H	6.63 ± 0.09	4.52 ± 0.03	3.16 ± 0.05	2.10 ± 0.07
	p-Cl	7.08 ± 0.11	4.95 ± 0.02	3.43 ± 0.01	2.34 ± 0.01
	p-NO ₂	8.61 ± 0.03	6.14 ± 0.01	4.39 ± 0.05	3.02 ± 0.08
80	H	6.28 ± 0.08	4.35 ± 0.10	2.96 ± 0.08	1.95 ± 0.03
	p-Cl	6.76 ± 0.01	4.73 ± 0.01	3.31 ± 0.03	2.20 ± 0.06
	p-NO ₂	8.32 ± 0.05	5.87 ± 0.09	4.17 ± 0.05	2.81 ± 0.08
70	H	5.76 ± 0.15	3.97 ± 0.07	2.69 ± 0.06	1.78 ± 0.07
	p-Cl	6.24 ± 0.10	4.34 ± 0.01	2.97 ± 0.13	1.98 ± 0.11
	p-NO ₂	7.59 ± 0.01	5.42 ± 0.08	3.86 ± 0.05	2.56 ± 0.06
60	H	4.86 ± 0.05	3.43 ± 0.04	2.30 ± 0.05	1.56 ± 0.11
	p-Cl	5.43 ± 0.09	3.81 ± 0.03	2.56 ± 0.07	1.78 ± 0.02
	p-NO ₂	6.79 ± 0.02	4.84 ± 0.02	3.42 ± 0.05	2.41 ± 0.15
50	H	4.06 ± 0.10	2.82 ± 0.07	1.96 ± 0.07	1.30 ± 0.01
	p-Cl	4.54 ± 0.01	3.15 ± 0.00	2.21 ± 0.07	1.50 ± 0.11
	p-NO ₂	5.74 ± 0.06	4.04 ± 0.09	2.98 ± 0.13	2.08 ± 0.03
40	H	3.09 ± 0.11	2.12 ± 0.01	1.48 ± 0.03	0.989 ± 0.05
	p-Cl	3.46 ± 0.13	2.43 ± 0.07	1.71 ± 0.05	1.16 ± 0.08
	p-NO ₂	4.35 ± 0.13	3.16 ± 0.05	2.30 ± 0.09	1.59 ± 0.01
30	H	2.13 ± 0.01	1.53 ± 0.01	1.09 ± 0.04	0.768 ± 0.01
	p-Cl	2.40 ± 0.08	1.74 ± 0.05	1.26 ± 0.01	0.898 ± 0.03
	p-NO ₂	3.05 ± 0.10	2.28 ± 0.06	1.65 ± 0.05	1.21 ± 0.07

mechanism or a combination of this with an addition-elimination ($S_A N$) mechanism, (Scheme 1). Recently Bentley *et al.*⁴

**Scheme 1**

were able to dissect the solvolysis data of benzoyl chlorides into two simultaneous, distinct reaction channels of S_N2 and $S_A N$ paths by choosing appropriate substituents and solvent systems.

We report here the results of our kinetic investigation of methanolysis of phenylacetyl chlorides ($\text{R} = \text{YC}_6\text{H}_4\text{CH}_2$) in methanol-acetonitrile mixtures. (1),



$\text{R} = \text{YC}_6\text{H}_4\text{CH}_2$, with $\text{Y} = \text{H}$, $p\text{-Cl}$ or $p\text{-NO}_2$.

Table 2. Hammett ρ_Y Values^a for Reactions of Substituted Phenylacetyl Chlorides in MeOH-MeCN Mixtures at 0, -5, -10 and -15°C^b

V/V%	0°	-5°	-10°	-15°
100	0.13	0.15	0.20	0.21
90	0.15	0.17	0.19	0.20
80	0.16	0.17	0.19	0.20
70	0.15	0.17	0.20	0.20
60	0.18	0.19	0.22	0.24
50	0.19	0.20	0.23	0.26
40	0.19	0.22	0.24	0.26
30	0.20	0.22	0.23	0.25

^a Values obtained with $\text{Y} = \text{H}$, $p\text{-Cl}$ and $p\text{-NO}_2$ using normal σ Values ($p\text{-Cl} = 0.227$ and $p\text{-NO}_2 = 0.778$). ^b Correlation coefficients were better than 0.996 in all cases.

Results and Discussion

The solvolysis rate constants k_1 are summarized in Table 1. The k_1 value of $6.85 \times 10^{-2} \text{sec}^{-1}$ for $\text{Y} = \text{H}$ in 100% methanol at 0.0°C is somewhat greater than the value of $11.0 \times 10^{-2} \text{sec}^{-1}$ for the same compound in 100% ethanol at 25.0°C³ taking account of the temperature difference. The rate is seen to increase with the MeOH content of the solvent, reflecting the mass law effect of the reactant MeOH. At the low temperature of -10.0° and -15.0°C, the maximum rate behavior is exhibited at ~90% MeOH, which must reflect the maximum ionizing power, Y , and the nucleophilicity, N , of the solvent at the same composition determined with the solvolysis of 1-adamantyl tosylate⁵ for the four parameter correlation 2⁶. At -10.0°C for $\text{Y} = \text{H}$, the m and l values were 0.16 and 0.47 (corr. coeff. = 0.999) re-

$$\log(k/k_o) = mY + lN \quad (2)$$

spectively for the reaction (1); this clearly shows that the methanolysis precedes by the S_N2 pathway since the ratio of l/m is nearly 3.0, indicating that the rate is ~3 times more susceptible to the solvent nucleophilicity, N , than to the solvent ionizing power (Y)⁶. This means that bond formation is more important than bond breaking in the S_N2 transition state (TS).

The ρ_Y values obtained with only three substituents, $\text{Y} = \text{H}$, $p\text{-Cl}$ and $p\text{-NO}_2$, are given in Table 2. Positive sign of the ρ values suggest again that bond forming is ahead of bond cleavage in the TS. The relatively small magnitude of ρ is mainly due to a nonconjugating intervening, CH_2 , group between the reaction center, carbonyl carbon, and the benzene ring, which is known in general to halve the magnitude of ρ_Y ⁷. The corresponding ρ_Y values for benzoyl chlorides range 0.38–0.60 in 100%–50% MeOH mixtures at 35.0°C⁸. Thus the $|\rho_Y|$ values for phenylacetyl chloride series seem still a little smaller than those for benzoyl chloride series even allowing for the effect of an intervening CH_2 group. The ρ_Y values increase with an increase in acetonitrile content and with a decrease in temperature, which may originate mainly from a decrease in the electrophilic assistance in bond breaking due to a decrease in the hydrogen bonding ability with a decrease in the MeOH content. This provides evidence in support of a concerted bond-

Table 3. Solvatochromic Coefficients α and s and Their Ratios α/s for Solvolysis of Substituted Phenylacetyl Chloride

Y		0°	-5°	-10°	-15°
H	a	3.71	3.57	3.48	3.15
	s	7.28	6.99	6.90	6.13
	a/s	0.51	0.51	0.50	0.51
p-Cl	a	3.66	3.47	3.34	3.10
	s	7.27	6.82	6.64	6.14
	a/s	0.50	0.51	0.50	0.50
p-NO ₂	a	3.59	3.32	3.32	2.94
	s	7.20	6.58	6.66	5.81
	a/s	0.50	0.50	0.50	0.51

forming and -breaking process in the TS.

The rate data in Table 1 are subjected to the multiple linear correlation analysis⁹ using Taft's solvatochromic equation (3)¹⁰, where α , β and π^* are the hydrogen bonding-

$$\log k = \alpha\alpha + s\pi^* + b\beta \quad (3)$$

donor acidity, and -acceptor basicity and polarity parameters of solvent respectively. In this type of reaction, β term can be neglected¹⁰ so that two terms involving α and π^* were used in the analysis. Reference to Table 3 reveals a remarkable constancy in the value of the α/s ratio throughout the temperature and substituent variations. The actual magnitude, $\alpha/s = 0.50$, is well within the range of the ratio for the typical S_N2 reactions^{10,11}.

In order to assess the involvement of CH₃OH molecules in the TS, the Kivinen type plot^{1,12}, eq. 4, was attempted and the n values of nearly 1.0 were obtained^{12b}. According to the

$$\log k_1 = n \log (\text{MeOH}) + \text{const} \quad (4)$$

criteria suggested by Kivinen¹ this should indicate that the reaction proceeds by a typical S_N pathway.

The activation parameters, ΔH^\ddagger and ΔS^\ddagger , for the methanolysis of phenylacetyl chlorides are presented in Table 4. The ΔH^\ddagger values are relatively low while the $-\Delta S^\ddagger$ values are relatively high, which are both in the normal range of the values for a typical S_N2 reaction. The two parameters, $\Delta H^\ddagger = 10.7$ kcal/mol and $\Delta S^\ddagger = -27.0$ e.u., obtained for the ethanolysis of phenylacetyl chloride (Y = H) at 25.0°C³ are indeed comparable to the corresponding parameters for the methanolysis in Table 4. As indicated by the lower isokinetic temperature (β) ranging 194–199 compared to the ex-

perimental temperature ($T_{\text{exp}} \approx 280$) i.e., $\beta < T_{\text{exp}}$, the reaction is entropy controlled as usually found for solvolysis reaction¹³. Inspection of Table 4 shows that the activation enthalpy stays nearly constant as the solvent composition is varied but the activation entropy decreases steadily with the increase in the CH₃CN content, in agreement with the steady rate decrease as the CH₃CN content is increased. A slight decrease in the ΔH^\ddagger value with a more electron-withdrawing group (EWG), Y = p-NO₂, reflects the rate increase accompanied (Table 1) by a greater electron withdrawing polar effect of substituent Y which should facilitate bond forming process.

We can therefore conclude that every piece of evidence based on substituent and solvent effects on rate points to a typical S_N2 pass in which bond formation is ahead of bond breaking in the TS for the methanolysis of phenylacetyl chlorides in CH₃OH-CH₃CN mixtures.

Experiments

Materials. GR grade methanol and acetonitrile were used without further purification. Phenylacetyl chlorides were prepared by reacting Y-phenylacetic acid with thionyl chloride at -70°C for 2–5 hrs in an oil bath. The physical constants after distillation under reduced pressure or recrystallization were: C₆H₅CH₂COCl, b.p. 91–92°C/11mm (lit¹⁵, b.p. 110–111°C/23mm); p-ClC₆H₄CH₂COCl, b.p. 77–78°C/2mm (lit¹⁶, b.p. 119°C/14mm); p-NO₂C₆H₄CH₂COCl, m.p. 44–46°C (lit¹⁷, m.p. 45–46°C).

Rate Measurement. Rates were measured conductmetrically. The pseudo-first-order rate constants k , were obtained by the Guggenheim method¹⁸. The rate constants given in Table 1 are the average values of at least three determinations. Rate constants were reproducible to within $\pm 5\%$.

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Table 4. Activation Parameters for the Solvolysis of Substituted Phenylacetyl Chlorides in MeOH-MeCN Mixtures^a

V/V% MeOH	H ΔH^\ddagger (kcal/mol)	H $-\Delta S^\ddagger$ (e.u.)	p-Cl ΔH^\ddagger (kcal/mol)	p-Cl $-\Delta S^\ddagger$ (e.u.)	p-NO ₂ ΔH^\ddagger (kcal/mol)	p-NO ₂ $-\Delta S^\ddagger$ (e.u.)
100	10.8	24	10.5	25	9.4	29
90	10.1	27	9.8	28	9.2	29
80	10.4	26	9.9	28	9.5	28
70	10.4	26	10.2	27	9.5	29
60	10.1	27	10.0	28	9.1	30
50	10.1	28	9.7	29	8.8	32
40	10.0	29	9.6	30	8.8	32
30	9.0	33	8.6	34	8.1	36

^a The values of activation parameters are at 0°C with errors in ΔH^\ddagger of ± 0.3 kcal/mol and in ΔS^\ddagger of ± 1.0 e.u.

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Dehydrogenation of Ethylalcohol Catalyzed by Alcoholdehydrogenase Under High Pressure

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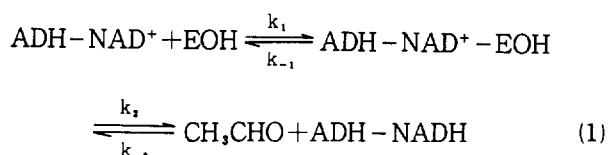
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A pressure effect of the dehydrogenation of ethylalcohol catalyzed by alcoholdehydrogenase was observed in Tris-HCl buffer, pH 8.8 from 25°C to 35°C under high pressure system by using our new theory. The theory makes it possible for us to obtain all rate and equilibrium constants for each step of all enzymatic reaction with a single intermediate. We had enthalpy and volume profiles of the dehydrogenation to suggest a detail and reasonable mechanism of the reaction. In these profiles, both enthalpy and entropy of the reaction are positive and their values decrease with enhancing pressure. It means that the first step is endothermic reaction, and its strength decrease with elevating pressure. At the same time, all activation entropies have large negative values, which prove that not only a ternary complex has a more ordered structure at transition state, but also water molecules make a iceberg close by the activated complex. In addition to this fact, the first and second step equilibrium states are controlled by enthalpy. The first step kinetic state is controlled by enthalpy but the second step kinetic state is controlled by entropy.

Introduction

The steady-state approximation provides a many convenient solutions to the kinetic equations for studying enzyme kinetics. But inherent disadvantage of the approximation is that little information about a transition of enzymatic reaction is obtained¹⁻¹⁰. To remove this weakness we have suggested a new method which were able to give all rate constants for each step of all enzymatic reactions with a single intermediate¹¹. The new method was applied to the dehydrogenation of ethylalcohol catalyzed by yeast alcoholdehydrogenase as follows;



where NAD⁺, NADH and EOH are β-nicotinamide adenine dinucleotide, its reduced form and ethylalcohol respectively.

In this paper we will study the pressure effect of Eq(1). If the total substrate concentration, [EOH], is much greater than the total concentration of holoenzyme which is a complex between ADH and NAD⁺, the value of [EOH] can be assumed to remain constant during the course of the reaction. The reaction now becomes pseudo first order and rate equation can be written, as

$$v = d[\text{NADH}]/dt = k[\text{EOH}][\text{ADH-NAD}^+] = k_o[\text{ADH-NAD}^+] \quad (2)$$

where k_o stands for an observed pseudo first order rate constant. The k_o values can be obtained from the following equation¹²⁻¹³.

$$\ln(A_\infty - A_t) = -k_o t + \ln(A_\infty - A_o) \quad (3)$$

where A's represent the UV absorbances of NADH and their