Kinetics of Elimination Reactions of 1,2-Diphenyl Ethyl Substrates in Acetonitrile: A Mechanistic Change in the Presence of a Strong Base

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ABSTRACT: Kinetics of elimination of methanesulfonic acid from 1,2-diphenylethylmethane sulfonate and its 1-*p*-methylphenyl- and 1-*p*-chlorophenyl-substituted derivatives is studied. The results show that the elimination reaction is unimolecular (E1) as reported in the case of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane. The rate of the elimination reaction in the presence of added weak base pyridine is independent of the concentration of the base, but in the presence of a strong base piperidine the rate shows a linear upward drift and this is due to the appearance of a bimolecular component along with the unimolecular pathway. The shift from the unimolecular to bimolecular process takes place independently of the nature of the leaving group and the parasubstituent in the 1,2-diphenylethyl substrate. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 481–487, 2008

INTRODUCTION

Substitution and elimination reactions often compete with each other and generally take place simultaneously in solvolytic reactions [1]. Tertiary substrates follow the ionization mechanism in solvolysis reactions, and the formed carbocation may be subjected to addition of nucleophilic species, giving substitution products $D_N + A_N$ (S_N1), or loss of a β-hydrogen, giving elimination products $D_N + A_ND_E$ (E1). As another possibility, the substrate may undergo base- or solvent-promoted bimolecular elimination reactions if one of its β-hydrogens is acidic, which is parallel to the ionization pathway [2,3]. Since the barrier for the loss of hydrogen from a highly reactive carbocation is small, the leaving group within an ion pair or the solvent molecules in the solvation shell can act as a base to effect the dehydrogenation process, which may also

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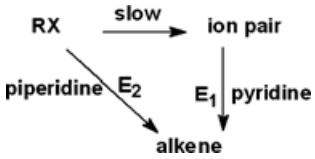

Scheme 1 Elimination reaction pathways.

be promoted by added bases. In a solvent-favoring ionization, acetonitrile, the reaction undergoes a pure E1 mechanism in the absence of a suitable nucleophile [4].

In the unimolecular dehydrochlorination of 2-chloro-2-phenylpropane (cumyl chloride) [4] and 1-chloro-1-(4-methoxyphenyl)-2-phenylethane (1-*p*-anisyl-2-phenylethyl chloride) [5] in acetonitrile, it is established that the added weak base pyridine does not enter into the rate equation. The pyridine merely abstracts the eliminated hydrogen chloride without involving in the abstraction of β-hydrogen. The possibility of substitution with a solvent [6] or base can be completely discarded [7–9] since the product analysis showed only the presence of alkene. In the pure E1 reaction, the product should be completely nonstereospecific, since the carbocation is free to adopt its most stable conformation before giving up the proton [1,5].

A strong base can not only neutralize the formed acid but also abstract the β-proton, shifting the mechanism toward E2 (Scheme 1). A change from the unimolecular to bimolecular mechanism was suggested in the presence of strong bases such as methoxide ions in methanolysis reactions [10–12]. In methanolysis [12,13] as well as in aqueous organic solvolysis reactions [14–16], the possibility of various pathways that are difficult to be distinguished by kinetic and product analysis led to controversial suggestions without confirmative results. The E1 mechanism established recently [5] in the dehydrochlorination of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane in acetonitrile, with a lone thermodynamically stable transproduct, is a promising system for the study of mechanistic changes in the presence of the added strong base.

MATERIALS AND METHODS

The 1,2-diphenylethyl alcohol and its *p*-substituted derivatives were prepared by the Grignard reaction of benzyl chloride (Thomas Baker & Co., Mumbai, India) with the corresponding parasubstituted benzaldehydes. The alcohols were extracted with suitable solvents and purified by repeated crystallization in petroleum ether, and the melting points were compared with the standard values. The purity of alcohols was confirmed by TLC, and the authenticity was established by elemental analysis, IR, and NMR spectra.

The preparation and kinetic measurements of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane is reported earlier [5]. The mesylates were prepared by the dropwise addition of methanesulfonyl chloride (3 mL) to the corresponding alcohols (5 g) in dry pyridine (25 mL) kept at 0°C. The reaction mixture was stirred for 3 h. The excess pyridine was removed by adding the reaction mixture to 100 mL cold 6 N HCl containing 75 mL ether. The water layer was extracted twice with 50 mL portions of ether. The ether fractions were combined and washed consecutively with two 50 mL portions of water, 20 mL of 10% cadmium chloride solution, and 20 mL of water. After drying over anhydrous sodium sulfate, the ether was removed at room temperature under reduced pressure (20 mmHg) and the residue was crystallized from pentane. The solid mesylates were dried under vacuum and stored at -10°C under which condition they were quite stable.

The solvent A.R. acetonitrile (BDH, Mumbai, India) was further purified by the method of Pocker and Wong [17], and the DMSO (BDH) was purified by repeated distillation under vacuum.

A Hitachi 220A double-beam spectrophotometer fitted with a thermostated cell holder and an automatic printer was used for the rate measurements. The solvents were taken in a 25-mL standard flask kept at a thermostat, having the temperature same as that of the thermostat attached to the spectrophotometer. The solution of the substrate in the concentration range of 10^{-8} M was injected by means of a Hamilton syringe into the flask, stirred well, and 3 mL of solution was transferred into the cuvettes (for solid substrate a suitable solution in ether was prepared). The rate constants were calculated from the monitored peak heights of the product peaks using the integrated first-order rate equation. The rate coefficients were also obtained by the method of least squares [18]. All runs were conducted at least in duplicate, and the mean values of the rate constants calculated by the least-square method were used for the analysis.

RESULTS AND DISCUSSION

The rate coefficients for the dehydrochlorination of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane in pure acetonitrile (Scheme 2) in the presence of different initial concentrations of added pyridine (a weak base) and piperidine (a strong base) under pseudo-first-order conditions are given in Table I. The added weak base pyridine has practically no effect on the rate of elimination, but the strong base piperidine increases the rate of elimination substantially. This finding indicates that

Scheme 2 Elimination reaction in 1,2-diphenylethyl system, when X = Cl, Y = OCH_3; X = OO_2SCH_3, Y = H, CH_3, or Cl.

Table I Effect of Added Base Pyridine and Piperidine on the Rate of Dehydrochlorination of 1-Chloro-1-(4-methoxyphenyl)-2-phenylethane in Acetonitrile at 40.0°C

[Base] (M)	Pyridine $10^{-5}k_1$ (s^{-1})[a]	Piperidine $10^{-5}k_1$ (s^{-1})[b]	$10^5\ k_2$ ($M^{-1}\ s^{-1}$)
Nil	5.42	5.42	
0.050	5.44	–	
0.10	5.46	7.47	
0.20	5.42	8.17	13.8
0.30	–	9.68	14.2
0.50	–	12.4	14.0

[Substrate] = 10^{-8} M.
Estimated uncertainty: [a]less than ±0.2%; [b]less than ±0.3%.

the increase in the rate in the presence of the added strong base piperidine is not due to any change in the ionic strength effect as in the primary salt effect. As shown in Scheme 1, there are two possible pathways to accommodate the above-mentioned observation: a complete shift in mechanism from E1 to E2, where the base piperidine abstracts β-hydrogen, limiting the ion pair formation to a minimum level, or a mixed mechanism (E1 + E2), where the base piperidine abstracts β-hydrogen along with the unimolecular dehydrohalogenation. The order with respect to piperidine is determined [18] by plotting log k_1 versus log [piperidine]. The slope of the linear plot was only 0.46 (plot c in Fig. 1), suggesting the operation of a mixed mechanism. The possibility of $A_ND_E + D_N$ (E1cB) can be discarded on the account of the mass law effect shown by this substrate. A rate enhancement in the presence of weak bases like chloride ion is expected in an E1cB mechanism, whereas a rate deceleration with a characteristic mass law constant value of 11 ($\alpha = k_{-1}/k_2$) is reported in the presence of added tetrabutyl ammonium chloride [5].

The observed rate constants in the presence of piperidine in solvent acetonitrile represent the sum of the rate constants for the pseudo-first-order reaction with piperidine (excess of piperidine in solvent acetonitrile [19]) and the unimolecular elimination reaction. The difference between the observed rate constants in the presence and absence of piperidine gives the value of the pseudo-first-order reaction with piperidine. The second-order rate coefficients for the reaction between piperidine and the substrate were obtained by dividing

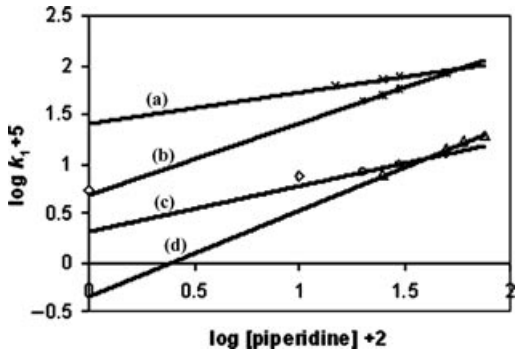

Figure 1 Determination of order of the reaction by log k_1 versus log [piperidine]. (a) 1-*p*-methylphenyl-2-phenylethylmesylate (slope = 0.32, s = 0.0048, r = .9979), (b) 1-*p*-chlorophenyl-2-phenylethylmesylate (slope = 0.73, s = 0.0028, r = .9998), (c) 1-chloro-1-(4-methoxyphenyl)-2-phenylethane (slope = 0.46, s = 0.0343, r = .9572), (d) 1,2-diphenylethylmesylate (slope = 0.87, s = 0.0084, r = .9993), where s is standard deviation and r is correlation coefficient.

the pseudo-first-order rate coefficients with the corresponding concentrations of piperidine.

$$k_2 = \frac{k_1 - k_0}{[\text{Base}]} \tag{1}$$

where k_1 is the observed rate constant in the presence of added base piperidine and k_0 is the first-order rate constant in the absence of base.

The constancy of the values of the second-order rate coefficients for all the initial concentrations of piperidine suggests the operation of a mixed mechanism (E1 + E2) for the elimination reaction in the presence of piperidine (Table I).

Mixed mechanisms of unimolecular and bimolecular processes obey a rate law [20].

$$\text{Rate} = k_1[\text{S}] + k_2[\text{B}][\text{S}] \tag{2}$$

where k_1 and k_2 are the specific rate constants for unimolecular and bimolecular processes and [S] and [B] are concentrations of substrate and base, respectively.

$$\frac{\text{Rate}}{[\text{S}]} = k_1 + k_2[\text{B}] \tag{3}$$

A plot of the rate constant values against concentrations of a base gave a straight line with slope, which is

Table II Kinetic Data for the Elimination of Hydrogen Chloride from 1-Chloro-1-(4-methoxyphenyl)-2-phenylethane in Acetonitrile

				[Substrate] $= 10^{-8}$ M		
Added Base	Temperature (°C)	$10^5 k_1$ (s^{-1})[a]	$10^5 k_1$ (s^{-1})[a] at 298 K	$\Delta H^{\neq}$ 298 K (kJ mol^{-1})	$-\Delta S^{\neq}$ 298 K (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ 298 K (kJ mol^{-1})
	24.0	1.08				
	35.0	3.39				
Nil[b]	40.0	5.42	1.22	74.2 ± 0.2	90.5 ± 0.6	101.1 ± 0.2
	50.0	13.1				
Piperidine	19.0	1.37				
(0.10 M)[c]	24.0	2.16				
	35.0	5.12	2.30	58.6 ± 0.1	137.4 ± 0.8	99.6 ± 0.2
	40.0	7.47				
		$10^5 k_2$ M^{-1} s^{-1} (using Eq. (1))				
	24.0	1.08				
	35.0	1.73	1.13	28.8 ± 0.1	243.2 ± 0.9	101.3 ± 0.2
	40.0	2.05				

[a] Estimated uncertainty is less than ±2%.
[b] Data reported earlier in [5].
[c] The observed rate constants are used for the calculation of activation parameters.

equal to k_2 and the intercept k_1. The values of k_2 and k_1 obtained were 13.6×10^{-5} M^{-1} s^{-1} and 5.66×10^{-5} s^{-1}, respectively. There is a close agreement of these values with those obtained by the subtraction method (Table I).

The activation parameters for the elimination reaction calculated using the observed rate constants of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane in the presence of 0.10 M piperidine (Table II) show that there is a substantial decrease in enthalpy of activation (15 kJ mol^{-1}) and entropy of activation (47 J K^{-1} mol^{-1}). In a bimolecular reaction, two initial state particles may join together to form one transition-state particle, the translational and rotational entropies of the two particles become reduced to those of one, and there is small additional entropy of vibration but not enough to compensate for the loss of entropy. These changes constitute a negative contribution to entropy in the bimolecular process in comparison to the unimolecular process of the same molecule. The suggestion of Long et al. [21] that bimolecular reactions should generally possess small positive or greater negative entropies of activation than most nearly analogous unimolecular reaction supports the E2 component in this reaction. The activation parameters for the bimolecular components of the reaction can be calculated from the calculated values of k_2 using Eq. (1) at different temperatures and are given in Table II. For the bimolecular component of the reaction, the enthalpy of activation is 29 kJ mol^{-1} and entropy of activation is -244 J K^{-1} mol^{-1}. There is a very large drop in the energy of activation (from 74 to 29 kJ mol^{-1}) and entropy of activation (from -137 to -243 J K^{-1} mol^{-1}) as suggested by Long et al.

1-Chloro-1-(4-methoxyphenyl)-2-phenylethane is stabilized by electron donation of the *p*-methoxy group and an extended system of conjugation throughout the benzene rings. The stability of carbocation intermediate is well understood from the observed mass law and special salt effect in acetonitrile [5,22]. The secondary aralkyl halides have a tendency to undergo solvolysis by a borderline mechanism, and it is a matter of controversy among physical organic chemists for a long time [23]. The unsubstituted compound, i.e. 1,2-diphenylethyl chloride, is a better choice to study these aspects, especially when the steric factors influence the stability–yield relationship of S_N1–E1 process in aqueous organic solvents [24,25], but too slow in solvent acetonitrile. A better nucleofuge mesylate, which is 10^4 times faster than chloride in 1-phenylneopentyl system in aqueous acetone [26], is selected for the study.

The rate of elimination of methane sulfonic acid from 1,2-diphenyl methane sulfonate and its 1-*p*-methylphenyl- and 1-*p*-chlorophenyl-substituted derivatives is given in Table III. The rate of elimination of 1,2-diphenyl methane sulfonate in DMSO solvent and its solvolysis rate in 90% acetonitrile are given for comparison. In DMSO, the elimination rate

Table III Kinetic Data for the Elimination of Methane Sulfonic Acid from 1,2-Diphenylethyl Methane Sulfonate in Acetonitrile

				[Substrate] $= 10^{-8}$ M		
Substituent	Temperature (°C)	$10^5 k_1$ (s^{-1})[a]	$10^5 k_1$ (s^{-1})[a] at 298 K	$\Delta H^{\neq}$298 K (kJ mol^{-1})	$-\Delta S^{\neq}$ 298 K (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ 298 K (kJ mol^{-1})
	40.0	1.40				
	65.0	17.3				
H	75.0	49.7	0.240	88.0 ± 0.2	57.7 ± 0.9	105.2 ± 0.2
	85.0	106				
	19.0	5.48				
	24.0	9.03				
CH_3	35.0	26.1	10.0	70.0 ± 0.1	87.1 ± 0.4	96.0 ± 0.1
	40.0	40.2				
	75.0	13.1				
	85.0	34.8				
Cl	95.0	76.5	0.0575	91.6 ± 0.5	57.5 ± 2.0	108.7 ± 0.6
			In the presence of 0.10 M piperidine			
	33.0	2.48				
	40.0	3.96	1.23	61.2 ± 0.4	133.8 ± 1.3	101.1 ± 0.5
H	45.0	6.40				
	56.0	13.9				
			In 90% aqueous acetonitrile			
	19.0	13.9				
	24.0	23.9				
H	33.0	60.5	26.5	74.5 ± 0.5	63.9 ± 1.2	93.5 ± 0.6
	40.0	116				
			In DMSO			
	24.0	4.14				
	35.0	12.9				
H	40.0	24.1	4.50	83.3 ± 0.5	49.0 ± 1.1	97.9 ± 0.5
	50.0	66.8				

[a] Estimated uncertainty is less than ±2%.

is 20 times than that in acetonitrile (dielectric constants of acetonitrile and DMSO are 35.94 and 46.45, respectively) and is characteristic for a unimolecular mechanism [5]. In 90% aqueous acetonitrile, the rates of hydrolysis and elimination are measured by noting the absorbance due to the formation of 1,2-diphenylethyl alcohol at 265 nm and trans-stilbene at 295 nm. The same rate observed clearly indicates a common rate-determining step, i.e. the elimination is E1 and substitution is S_N1. The activation parameters in 90% acetonitrile and pure acetonitrile indicate the unimolecular mechanism [4,5]. The reduction in the rate in pure acetonitrile is due to a decrease in water content rather than a change in the nature of mechanism [4].

The rate of elimination from *p*-methyl-substituted compound is very much higher ($k_{(p\text{-}CH_3)}/k_{(p\text{-}H)} = 43$) and that for *p*-chloro-substituted compound is lower than ($k_{(p\text{-}Cl)}/k_{(p\text{-}H)} = 0.25$) the unsubstituted compound. The free energy of activation for *p*-methyl is less by 9 kJ and that of *p*-chloro is more by 4 kJ than the unsubstituted compound. Application of Brown equation, [27] $\log k/k_0 = \rho^+\sigma^+$, gave an average value of −5.30 for ρ^+. For the standard substrate cumyl chloride in 90% acetone [22,28], it is −4.54 and for the dehydrochlorination reaction in acetonitrile [4] the value is −4.73. The more negative ρ^+ value observed for the 1,2-diphenyl ethyl substrate shows more electron demand at the carbocation center, confirming the unimolecular elimination. The 1,2-diphenylethyl mesylate even though secondary undergoes the elimination reaction by the unimolecular mechanism. The change in the nucleofuge from chloride to mesylate does not cause a change in the mechanism of the reaction but only alters the rate of reaction.

The effect of added pyridine and piperidine on the rate of elimination of sulfonic acid from 1,2-diphenyl

Table IV Effect of Added Base Pyridine and Piperidine on the Rate of Elimination of Methane Sulfonic Acid from (*p*-Substituted) 1,2-Diphenylethyl Methylsulfonate in Acetonitrile at 40°C

p-Substituent	[Base] M	Pyridine[a] $10^{-5}k_1$ (s^{-1})	Piperidine[b] $10^{-5}k_1$ (s^{-1})	10^5k_2 (M^{-1} s^{-1})
	Nil	1.40	1.40	–
	0.10	1.41	3.96	25.6
	0.25	1.39	7.56	24.6
H	0.50	1.42	14.1	25.3
	0.60	1.40	16.7	25.4
	0.75	1.38	19.6	24.3
	Nil	44.8	44.8	–
	0.10	44.5	55.1	103
	0.15	44.6	60.3	103
CH_3	0.25	44.7	70.5	103
	0.30	44.8	76.0	104
	Nil	1.67	1.67	–
	0.10	1.69	2.99	13.2
	0.20	1.68	4.28	13.1
Cl	0.30	1.66	5.69	13.4
(at 54°C)	0.50	1.68	8.31	13.3

[Substrate] = 10^{-8} M.
Estimated uncertainty: [a]less than ±2%; [b]less than ±3%.

ethyl mesylate and its 1-*p*-substituted derivatives is given in Table IV. As in the case of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane, here also the weak base pyridine has no effect on the rate of elimination. In the presence of the strong base piperidine, the rate of reaction increases linearly with the concentration of added base. The fractional orders with respect to piperidine indicate the simultaneous occurrence of E1 and E2 mechanisms (Fig. 1).

The rate constant values for the bimolecular reaction with piperidine, by the graphical method using Eq. (3), are 24.4 × 10^{-5} M^{-1} s^{-1}, 104 × 10^{-5} M^{-1} s^{-1}, and 13.4 × 10^{-5} M^{-1} s^{-1} for 1,2-diphenylethylmesylate and its *p*-methyl and *p*-chloro derivatives, respectively. The values observed by the subtraction method (Table IV) correlate with those obtained by the graphical method. The enthalpy, entropy, and free energy of activation for the elimination reaction of 1,2-diphenylethyl mesylate in the presence of 0.10 M piperidine are 61 kJ mol^{-1}, 134 J K^{-1} mol^{-1}, and 101 kJ mol^{-1}, respectively. The substantial decrease in enthalpy (25 kJ mol^{-1}) and entropy of activation (77 J K^{-1} mol^{-1}) on the addition of piperidine (Table III) confirms the shift of mechanism from E1 to E1 + E2.

The rate of elimination in the presence of 0.10 M piperidine from *p*-methyl-substituted compound is higher ($k_{(p\text{-}CH_3)}/k_{(p\text{-}H)}$ = 14) and that for *p*-chloro-substituted compound is lower than ($k_{(p\text{-}Cl)}/k$(p-H) = 0.63) the unsubstituted compound. The rate enhancement by *p*-methyl in the absence of piperidine is 43, which is much higher than that in the presence of piperidine. A shift from E1 to E1 + E2 reduced the electron demand at positively charged intermediate (Scheme 1). For *p*-chloro-substituted compound, ($k_{(p\text{-}Cl)}/k_{(p\text{-}H)}$) is 0.25 in the absence of piperidine and 0.63 in the presence of piperidine. The reduced rate of retardation in the presence of piperidine reflects the less demand for electron density at the charged intermediate due to the shift in the mechanism.

1,2-Diphenylethyl mesylate and its *p*-substituted compounds undergo elimination of methane sulfonic acid in acetonitrile by the E1 mechanism. The addition of a weak base pyridine has no effect on the rate of the reaction, indicating the absence of solvent/weak base involvement in the stability of the reaction intermediate. In the presence of a strong base piperidine, all these substrates undergo elimination by a mixed E1 + E2 pathway. Thus, the change in the leaving group or parasubstituents resulted the same change of mechanism in the presence of the strong base piperidine even though the extent of changes was different as shown by the different values of fractional orders with respect to the piperidine (Fig. 1).

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