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MECHANISM OF ELIMINATION REACTIONS[1]

THE E2 REACTIONS OF SUBSTITUTED α-PHENYLETHYL BROMIDES

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Abstract—The rates of the base-catalysed elimination of a series of substituted α-phenylethyl bromides have been determined in t-BuOK-t-BuOH, t-BuOK-t-BuOH-DMSO and EtONa-EtOH systems. The Hammett ρ values obtained were, although small and not in linear correlation with σ values, positive in all cases. β-Methyl group retarded the rate in t-BuOK-t-BuOH and in t-BuOK-t-BuOH-DMSO, but enhanced it in EtONa-EtOH. β-Hydrogen kinetic isotope effects were 5·0, 3·5 and 3·4, respectively. The nature of transition states is discussed in the light of these observations.

Numerous publications concerning the nature of the transition states of E_2 reactions are known,[2] but very few systematic studies on the effect of substituents at the α-carbon atom are available.

In general, the nature of transition state for a given E2 elimination reaction is mainly determined by the structure of the substrate that undergoes the reaction, while the surrounding conditions such as solvents or bases are of minor importance in controlling the transition states of E^2 reactions. The most extensively studied is the β-phenylethyl system. DePuy *et al.*[3] indicated that the transition state in the elimination reactions of β-arylethyl halides is not affected by the nature of solvents and bases. While, Saunders, Jr., *et al.*[4] studied the effect of added DMSO in the base catalysed elimination reactions of 2-arylethyl bromides with potassium t-butoxide in t-butyl alcohol, and observed that although the rate is markedly accelerated by the addition of DMSO to the solvent, the ρ value and β-hydrogen kinetic isotope effect, k_H/k_D, remain nearly identical. We also reported that in the elimination reactions of *p*-substituted phenyl β-chloroethyl sulfones in anhydrous acetonitrile, the effect of the base strength is nearly insensitive to the change of the transition state.[5] However, the transition states of these elimination reactions hitherto examined are of either central or nearly carbanion type according to Bunnett's definitions.[2c][*] With such substrates as the title compounds which undergo facile SN1 and E1 reactions, the base-catalysed elimination may proceed via E1-like transition state and

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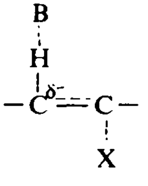
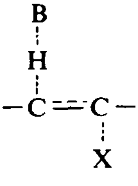
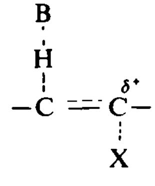
[*] In E2 reactions, three extremes are considered to exist with the relative extents of C—X and C—H bond rupture at the transition state.



nearly E1cB



(central)



nearly E1

become sensitive to the change of surrounding conditions. In order to examine this possibility and also the effects of substituents at the α-C atom in comparison with those at the β-C atom, the E2 reaction of the title compounds was carried out in t-BuOK-t-BuOH, t-BuOK-t-BuOH-DMSO and EtONa-EtOH systems.

RESULTS AND DISCUSSION

The pseudo-first order rate constants were obtained spectrophotometrically, and the E2 rate constants were calculated by dividing them by the base concentration. The results are shown in Tables 1, 2 and 3.

No solvolytic reaction was observed in t-BuOH under the reaction conditions. However, since solvolysis cannot be neglected in EtONa-EtOH system, the kinetic analysis is rather complicated. Namely, all the possible processes, i.e., SN1, SN2, E1 and E2 reactions occur simultaneously with these compounds. Therefore, the rate constants for the E2 reaction (k_{E2}) are calculated from the following equation.

$$k_{obs} = k_{E1} + k_{SN1} + (k_{SN2} + k_{E2})[OEt]$$

$$k_{E1} + k_{E2}[OEt] = k_{obs}(\text{Olefin }\%)$$

$$k_{E2} = \frac{k_{obs}(\text{Olefin }\%) - k_{E1}}{[OEt]}$$

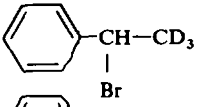
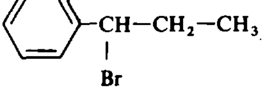
As shown in Table 3, rate constants of the E2 reaction decrease with increase of the base concentrations. This indicates that the rate is not first order with respect to the base concentration. The solvolysis of α-phenylethyl system has been generally known to proceed not only by way of SN1 mechanism alone, but also via a bimolecular process in absolute methanol and ethanol, and the rates of substitution increase considerably by the addition of lyate ion.[6] Recently, Sneen *et al.*[7] suggested an ion pair mechanism through which all the four basic processes (SN1, SN2, E1 and E2) proceed via a common ion pair intermediate in the reaction of α-phenylethyl bromide in a EtONa-EtOH system. In order to obtain a rough picture of the transition states of E2 reactions of all the substituted compounds the reactions have been carried out under the same concentration of the base.

Effects of substituents on the aryl ring

The effect of substituents on phenyl ring of α-phenylethyl system in E2 reactions has not been reported. Meanwhile, Maccoll *et al.*[8] have shown that, in the pyrolysis of substituted α-phenylethyl chlorides, the ρ value, obtained through a good correlation with Brown-Okamoto's σ^+ values, was $-1{\cdot}36$ (at 308°), and indicated that there is a general similarity between the transition state for the gas-phase elimination of α-phenylethyl halides and that for the solvolysis of the corresponding compounds in 80% aqueous acetone. This strongly suggests a moderate degree of charge separation in the transition state. In other words, this gas phase elimination reaction proceeds via El-like transition state.

The Hammett plots of our data are shown in Fig 1. Although the methoxy compound was not available, the Hammett plots did not give a straight line. However, as shown in Fig 1, the ρ values are definitely positive except for an electron-donating group, p-CH_3. That the type of conjugative effect of substituents on the phenyl ring is

TABLE 1. THE E2 RATE CONSTANTS OF SUBSTITUTED-α-PHENYLETHYL BROMIDES WITH t-BuOK IN t-BuOH AT 50°[a]

X	[Br]	[Base]	Olefin (%)	$k_{obs} \times 10^4$ (sec^{-1})	$k_{E2} \times 10^4$ (M^{-1}, sec^{-1})
H[b]	0·01802	0·2053	100 ± 0·3	1·69 ± 0·03	8·24
	0·01802	0·2874		2·42 ± 0·05	8·48
	0·01802	0·4106		3·46 ± 0·08	8·38
					av. 8·38
p-CH_3	0·01453	0·2053	85·0 ± 0·1	1·81 ± 0·05	7·51
	0·01537	0·2053		1·70 ± 0·02	7·03
					av. 7·27
p-Cl	0·01523	0·2053	95·0 ± 0·1	1·94 ± 0·02	9·02
	0·01407	0·2053		1·90 ± 0·03	8·83
					av. 8·92
m-NO_2	0·01466	0·2053	84·0 ± 0·2	5·71 ± 0·05	23·4
	0·01480	0·2043		5·63 ± 0·12	23·2
					av. 23·3
	0·01695	0·2053	89·0 ± 0·2	3·88 ± 0·05	1·68
	0·01497	0·2053		3·84 ± 0·05	1·66
					av. 1·67
	0·01447	0·2043	95·5 ± 0·1	7·46 ± 0·16	3·50

[a] Controlled within ±0·02°C 60°: 1·39 × 10^{-3}(M^{-1}, sec^{-1}) 70°: 3·38 × 10^{-3}(M^{-1}, sec^{-1})

[b] Ea; 15·0 Kcal/mole; ΔS‡ −28·7 e.u. (at 50°)

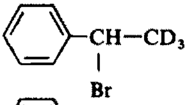
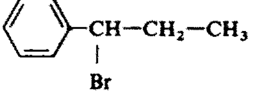
different, can be seen in SN2 reactions on the benzylic C atom in which the Hammett plots usually gives a U shape curve.[9]

β-Hydrogen kinetic isotope effect

β-Hydrogen kinetic isotope effect is a useful tool to examine the state of the C—H bond fission in the transition state.[10] The k_H/k_D values for α-phenylethyl bromide and α-phenylethyl bromide-d_3 are rather small as compared to those obtained with β-phenylethyl bromide (6·9 in t-BuOH; 6·0 in EtOH).[11] Namely, k_H/k_D, obtained for α-phenylethyl compounds are 3·5 in t-BuOH-DMSO, 5·0 in t-BuOH and 3·4 in EtOH, respectively.

To shed further light on the nature of the transition state, the effect of a β-Me group (α-phenylpropyl bromide) was examined. As Ingold *et. al.*[12] have pointed out, in the elimination reaction that gives Saytzeff type orientation of olefin distribution, a Me group at α or β-C atom accelerates the rate by the effect of hyperconjugation of Me group. In this case, the transition state is either of central or nearly E1 type. The data summarized in Table 4 show that the rate is retarded in both t-BuOH and

TABLE 2. THE RATE CONSTANTS IN t-BuOK[a]-t-BuOH-DMSO (10% v/v) AT 50°

X	[Br] × 10^3	Olefin (%)	k_{obs} × 10^4(sec^{-1})	k_{E2} × 10^2 (M^{-1}, sec^{-1})
H	1·562	93·4 ± 0·1	2·55 ± 0·07	1·30
	1·562		2·54 ± 0·06	1·30
				1·30
p-CH_3	1·407	67·8 ± 0·1	3·68 ± 0·03	1·36
	1·407		3·48 ± 0·03	1·42
				av. 1·39
p-Cl	1·185	92·4 ± 0·3	4·80 ± 0·03	2·24
	1·185		4·73 ± 0·07	2·39
				av. 2·41
p-Br	1·164	93·9 ± 0·1	5·03 ± 0·06	2·58
	1·164		5·05 ± 0·12	2·59
				av. 2·59
m-NO_2	1·105	94·0 ± 0·6	12·6 ± 0·4	6·48
	1·105		12·0 ± 0·2	6·17
				av. 6·33
 CH—CD_3 Br	1·531	84·9 ± 0·7	0·795 ± 0·017	0·368
	1·531		0·794 ± 0·010	0·368
				av. 0·368
 CH—CH_2—CH_3 Br	1·398	88·0 ± 0·3	1·62 ± 0·09	0·778
	1·398		1·62 ± 0·07	0·778
				av. 0·778

[a] The concentration of base is 1·830 × 10^{-2}M 40°; 0·597 × 10^{-2}(M^{-1}, sec^{-1}), 60°; 2·67 × 10^{-2}(M^{-1}, sec^{-1})

[b] Ea; 14·9 Kcal/mol: ΔS‡; −23·2 eu. (at 50°)

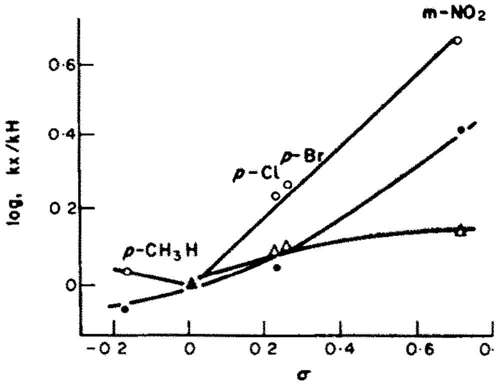
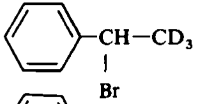
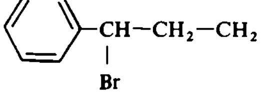


FIG. 1. The Hammett plots of the elimination of substituted α-phenylethyl bromides.

○t-BuOK-t-BuOH-DMSO, ● t-BuOK-t-BuOH, △ EtONa-EtOH

TABLE 3. RATE CONSTANTS IN EtONa-EtOH AT 50°

	[Br]	[OEt]	Olefin (%)	$k_{obs} \times 10^4$ (sec^{-1})	$k_{E1} \times 10^5$ (sec^{-1})	$k_{E2} \times 10$ (M^{-1}, sec^{-1})
H	0·02530		2·0	1·19 ± 0·05	0·24	
	0·01847	0·1432	23·8 ± 0·1	3·44 ± 0·09		5·55
	0·01487	0·1432		3·54 ± 0·07		5·72 av. 5·64
	0·02323	0·2863	28·2 ± 0·2	4·66 ± 0·13		4·51
	0·02187	0·2863		4·92 ± 0·09		4·79 av. 4·65
	0·02377	0·4295	31·2 ± 0·1	6·18 ± 0·27		4·45
	0·02181	0·4295		6·16 ± 0·13		4·42 av. 4.44
	0·02436	0·5726	32·0 ± 0·3	7·15 ± 0·03		3·94
	0·02356	0·5726		7·25 ± 0·21		4·02 av. 3·98
	0·02360	0·7158	32·6	8·53 ± 0·21		3·86
p-Cl	0·01877		1·6	0·487 ± 0·009	0·08	
	0·01948	0·2863	31·1 ± 0·0	5·49 ± 0·09		5·94
	0·02028	0·2863		5·58 ± 0·22		6·04 av. 5·99
p-Br	0·01974		1·0	0·350 ± 0·004	0·04	
	0·01715	0·2863	32·9 ± 0·1	5·44 ± 0·09		6·25
	0·01634	0·2863		5·38 ± 0·11		6·18 av. 6·22
m-NO_2	0·01646		too slow			
	0·01646	0·2863	31·6 ± 0·1	5·78 ± 0·03		6·39
	0·01648	0·2863		5·98 ± 0·03		6·60 av. 6·50
	0·02410		0·90	1·15 ± 0·30	0·10	
	0·02101	0·2863	10·6 ± 0·1	3·76 ± 0·07		1·36
				3·68 ± 0·05		1·33 av. 1·35
	0·03393			0·396 ± 0·03		
	0·02216	0·2863	65·3 ± 1·2	3·40 ± 0·05		7·75
	0·02031	0·2863		3·35 ± 0·06		7·65 av. 7·70

Activation parameters were calculated from the following E2 rate constants: $k_{E2} = 1{\cdot}83 \times 10^{-4}$(M^{-1}, sec^{-1}) at 40°, $k_{E2} = 13{\cdot}1 \times 10^{-4}$(M^{-1}, sec^{-1}) at 60°. Ea: 18 Kcal/mol: $\Delta S\ddagger = -18{\cdot}2$ e.u. (at 50°)

t-BuOH-DMSO, and is enhanced in EtOH by the substitution of methyl group on β-C atom.

The effect of substituents in the reaction with EtONa-EtOH is worthy of note. As can be seen in Table 4, the ρ value is unexpectedly positive despite the inherent positive character that develops during the reaction on the benzylic C atom. It appears that the ρ value remains positive except in E1 or Ei reactions. Another interesting point is the effect of solvent. The rate of elimination of β-phenyl bromide in t-BuOK-t-BuOH has been reported to be 7·4 times greater than that in EtONa-EtOH, while the present results indicate that the reaction of α-phenylethyl bromide in t-BuOK-t-BuOH is only 1·8 times faster than that in EtONa-EtOH. This indicates that solvation to the leaving group is quite important in the reaction of α-phenylethyl bromide in EtONa-EtOH.

The nature of transition state

Generally, the nature of the transition state of an E2 elimination reaction such as our system is disclosed by examining the Hammett ρ value, β-hydrogen kinetic isotope effect and the effect of a β-Me group. As can be seen in Fig 1, the ρ values are positive in all the cases and diminish in the following order.

t-BuOK-t-BuOH-DMSO > t-BuOK-t-BuOH > EtONa-EtOH

This indicates that carbanionic character on the β-C is well advanced in a t-BuOK-t-BuOH-DMSO system as compared with other systems.

The β-hydrogen kinetic isotope effects, as shown in Table 4, are rather small. According to the current theory,[10] a maximum value is obtained when hydrogen is half-transferred to base. The values obtained in our cases show that a proton is either transferred to the base or not sufficiently broken from the β-C atom. Meanwhile, the effect of a β-Me group is quite significant. In the EtONa-EtOH system, the rate of elimination of α-phenylpropyl bromide is 1·7 times greater than that of α-phenylethyl bromide. This suggests that the hyperconjugation of a Me group as proposed by Ingold[2a] is also operative in this case. In other words, the elimination reaction in EtONa-EtOH proceeds via E1 like transition state.

TABLE 4. SUMMARY OF THE DATA OBTAINED (AT 50°)

	t-BuOK -t-BuOH-DMSO	t-BuOK-t-BuOH	EtONa-EtOH
ρ value	most positive	more positive	positive
k_H/k_D	3·5	5·0	3·4
$k_{E2}(CH_3)/k_{E2}(H)$*	0·60	0·42	1·7
Nature of transition state	nearly carbanionic	between central and nearly carbanionic	nearly E1

* $k_{E2}(CH_3)$ and $k_{E2}(H)$ are the E2 rate constants of α-phenylpropyl bromide and α-phenylethyl bromide, respectively.

Although it has been suggested that hyperconjugative effect is in operation in order to stabilize the developing double bond, its effect appears to be called upon mainly at E1-like transition state rather than to stabilize the developing double bond.

From these observations, the nature of the transition state of the E2 reaction of α-phenylethyl system changes substantially by the surrounding conditions such as solvents and bases. Perhaps this is the first example to show that the transition state of an E2 reaction changes from carbanionic to carbonium ion character by the change of solvents and bases.

EXPERIMENTAL

Preparation of materials. The bromides used for the kinetic study were prepared from the corresponding alcohols with PBr_3 as described.[14] Purities of all the substrates used were checked by IR and NMR. Properties are listed in Table 5.

TABLE 5. PROPERTIES OF SUBSTITUTED α-PHENYLETHYL BROMIDES

	Yield (%)	b.p. or m.p.	(lit)
H	76	66·5°/3 mm	(76°/7 mm)[15]
p-CH_3	69	86°/5 mm	
p-Cl	67	96–7°/5 mm	(120–1°/8 mm)[16]
p-Br	65	99–100°/3 mm	
m-NO_2	45	42–42·5°	(41–2°)[17]
β-CH_3	73	78°/4 mm	(127–8°/40 mm)[18]
β-d_3	73	67·5°/4 mm	

* Recrystallized from n-hexane-CH_2Cl_2

Preparation of substituted styrenes. p-Substituted styrenes were prepared by dehydrating the corresponding carbinols with potassium bisulfate.[17] m-Nitrostyrene was prepared by dehydration with phosphoric acid (d; 1·74) as described.[20] β-Methylstyrene was obtained from the corresponding carbinols in the presence of a trace of sulfuric acid according to the procedure of Bruylants.[21] Purities were carefully checked by VPC, IR and NMR.

TABLE 6. PROPERTIES OF STYRENES

Substituent	B.p. (lit)	
H	41°/18 mm	(38°/15 mm)[22]
p-CH_3	61°/18 mm	(50°/13 mm)[22]
p-Cl	45°/4 mm	(38°/2·2 mm)[22]
p-Br	55°/2 mm	(84°/11 mm)[23]
m-NO_2	87–8°/2 mm	(81°/12 mm)[20]
β-CH_3	41·5–42°/3 mm	(64°/10 mm)[21]

Preparation of deuterated compounds

α-Phenylethyl bromide-β-d_3. Acetophenone (5 gr) was dissolved in 15 ml dioxan containing 5 g D_2O and 0·5 g Et_3N. The mixture was heated at 100° for 10 hr. The water was removed as dioxan azeotrope. A new mixture of dioxan, D_2O, and Et_3N was added to the residue. This procedure was repeated 4 times. The NMR spectra showed no protons in the Me group (2·59 ppm in CCl_4). The deuterated acetophenone was reduced with LAH and then the deuterated alcohol was brominated with PBr_3. The NMR spectra showed no protons in the Me group.

Olefin determination. UV absorption spectra of the freshly distilled styrenes in EtOH were determined. The optical densities at the maxima used for analysis were then carefully determined with HITACHI 124 spectrometer. Molar extinction coefficients at these maxima are listed in Table 7. Beer's law was obeyed over the concentration ranges used. Samples of the mixture at "time infinity" were appropriately diluted and optical densities were determined, from which the olefin concentrations were calculated. In the case of EtONa-EtOH, substitution products disturb the λ_{max} of styrenes. The optical densities were corrected with the following molar extinctions (substituted ether; ε, H; 131, p-Cl; 210 *p*-Br; 326, *m*-NO_2; $4\cdot95 \times 10^2$). Styrenes were stable enough to remain after more than ten half lives under these reaction conditions.

TABLE 7. UV ABSORPTION OF *p*-SUBSTITUTED STYRENES IN ABS EtOH

	λ max, mμ (lit)	Molar extinction (ε) × 10^{-4} (lit)
H	$248(248)^{21}$	$1\cdot37(1\cdot38)^{22}$
p-CH_3	$252(252)^{22}$	$1\cdot70(1\cdot69)^{22}$
p-Cl	$253(253)^{22}$	$1\cdot97(1\cdot97)^{22}$
p-Br	255	2·02
m-NO_2	239·5	2·35
β-CH_3	$250(251)^{17}$	$1\cdot72(1\cdot73)^{24}$

Ref. 21; In 95% EtOH

Kinectic measurement. An appropriate amount of an organic bromide was weighed accurately in a 25 ml volumetric flask. It was made up to 25 ml with a desired amount of the base soln and with the solvent at a fixed temp. The flask was shaken vigorously and kept in a thermostat. At appropriate time intervals, 2 ml of the soln was pippeted out and diluted with abs EtOH to a suitable concentration. In t-BuOK-t-BuOH and t-BuOK-t-BuOH-DMSO, the rate constants were obtained by following the appearance of the styrenes, and while in EtONa-EtOH, the decrease of the starting materials (H; 230 mμ, *p*-Cl; 235 mμ, *p*-Br; 240 mμ, β-d_3; 230 mμ) was followed. In the cases of *m*-NO_2 and β-Me, the absorbance of the corresponding styrenes was followed. In all cases the reactions were followed up to 40–60% completion.

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