Tetrahedron Letters No. 25, pp. 2317-2320, 1971. Pergamon Press. Printed in Great Britain.

A RE-EXAMINATION OF THE "UNIFIED" S_N2-E2 MECHANISM

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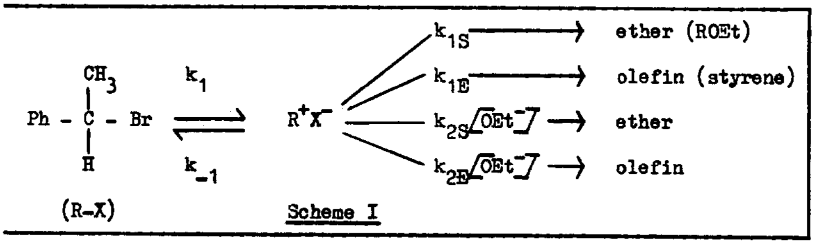
(Received in UK 11 May 1971; accepted in UK for publication 20 May 1971)

Doubt[1-3] has recently been cast on the claims of Sneen[4] to have demonstrated a "unified" S_N1-S_N2 mechanism, in which an ion-pair is involved in both the unimolecular and bimolecular steps. We now reconsider the claim that E2 and S_N2 reactions of 1-phenethyl bromide (1-PEB) with sodium ethoxide in ethanol proceed via a common ion-pair intermediate[5] (Scheme I) instead of competitively as has been previously supposed.[6]



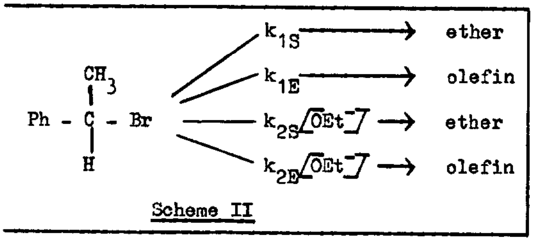
Scheme I

The two pieces of evidence cited by Sneen and Robbins[5] in favour of the mechanism in Scheme I are (i) that the observed kinetics and product ratios are in agreement with those expected for the ion-pair mechanism (which of course is not compulsive evidence) and (ii) that second-order rate "constants", k_2, for a competitive S_N2-E2 scheme as calculated from Eq. (1), are not in fact constant, as can be seen

$$k_{obs} = k_1 + k_2[OEt^-] \qquad \text{.............. (1)}$$

from Table I. In Eq.(1), k_{obs} is a pseudo first-order rate constant and $k_{obs} = k_1$ when $[OEt^-] = 0$, i.e. when the reaction is wholly solvolytic.

However, Eq.(1) does NOT represent the kinetics expected for a competitive S_N2-E2 system. The latter is shown, together with solvolytic reactions of the substrate, in Scheme II. The k_{1S} and k_{1E} steps in the Schemes are not necessarily as simple as has been illustrated. If f_E is the fraction of olefin formed in all reactions (performed under pseudo first-order conditions) consideration of the product ratio gives Eq.(2), where the rate constants pertain to Scheme II, and consideration of the rate of bromide ion production gives Eq.(3). From these equations arises the expression[7] shown in Eq.(4) for k_{2E}, the separated E2 rate constant for a competitive system. The fraction of styrene produced in neutral solvolysis is f_o.



Scheme II

$$f_E = \frac{k_{1E} + k_{2E}[OEt^-]}{k_{1E} + k_{2E}[OEt^-] + k_{1S} + k_{2S}[OEt^-]} \qquad \text{.............. (2)}$$

$$k_{obs} = k_{1E} + k_{2E}[OEt^-] + k_{1S} + k_{2S}[OEt^-] \quad \ldots\ldots\ldots\ldots (3)$$

$$k_{2E} = \frac{f_E k_{obs} - f_o k_1}{[OEt^-]} \quad \ldots\ldots\ldots\ldots (4)$$

Using rate and product data from our work and from the papers of Sneen[5] and Taylor[8], we have calculated values of k_{2E}, which are shown in Table I. Values of k_{2S}, (not shown) calculated from Eq.(5) are not constant, and their decrease with increasing $[NaOEt]$ cannot be attributed to a normal salt effect. This is hardly surprising, since the numerical value of

TABLE I

The 1-PEB/NaOEt Reaction in EtOH at 50.0°.

$[NaOEt]$ (M)	$10^4 k_{obs}$ (a)	f_E	$10^4 k_2$ (b)	$10^4 k_{2E}$ (b)	α (c)
0	1.13 (d)	*ca.* 0.03 (d)	-	-	-
0.114	3.54 (d)	0.165 (e)	21.1	4.82	0.480
0.121	3.57 (d)	0.170 (e)	20.2	4.74	0.475
0.362	5.35 (f)	0.275 (f)	11.7	4.00	0.352
0.533	6.57 (d)	0.296 (e)	10.2	3.58	0.287
0.686	7.48 (d)	0.320 (e)	9.2	3.44	0.243
0.844	8.4 (f)	0.323 (f)	8.6	3.17	0.213
1.07	9.8 (d)	0.325 (e)	8.2	2.94	0.177
1.432	12.0 (f)	0.329 (f)	7.6	2.67	-
1.714	13.5 (f)	0.331 (f)	7.2	2.58	-

[a] In $sec.^{-1}$ [b] In $M.^{-1}sec.^{-1}$ [c] Degree of dissociation of sodium ethoxide ion-pairs; see text. [d] Ref. 5. [e] Interpolated from data in Ref. 8. [f] This work; rates measured by titration for Br^-, $[styrene]$ measured spectrophotometrically.

$$k_{2S} = \frac{(1-f_E)k_{obs} - (1-f_o)k_1}{[OEt^-]} \quad \ldots\ldots\ldots\ldots (5)$$

$(1-f_o)k_1$ is important in determining k_{2S}, and it is very unlikely that k_1 is not subject to a significant salt effect. The well-known phenomenon of lyate-ion retardation[9] operating on k_1 may be responsible for some of the decrease in k_{2S}, but quantitative constancy is not easily obtained. The use of various linear relationships between k_1 and $[NaOEt]$ in conjunction with corrections to the resulting k_{2S} values for ion-pairing of NaOEt (see below) yields reasonably constant values except for the second and third entries in Table I. It is impossible to independently assess the quantitative form of the lyate ion retardation of course. This phenomenon is not important when k_{2E} values are considered since $f_o k_1$ is insignificant compared with $f_E k_{obs}$ in almost all NaOEt/EtOH systems.

Values of k_{2E} are seen to decrease also with increasing $[NaOEt]$. This does not disqualify the mechanism of Scheme II, as two lines of evidence indicate that the decrease is caused by a normal salt effect. Firstly, if k_i and k_{ip} are the respective rate constants for E2 attack of free OEt^- and the ion-pair Na^+OEt^- on 1-PEB,[3,10] consideration of Eq.(6) leads

$$k_{2E} = \alpha k_i + (1-\alpha)k_{ip} \quad \ldots\ldots\ldots\ldots (6)$$

to the conclusion that if k_{2E} is subject to an ion-pairing effect, a plot of $k_{2E}/(1-\alpha)$ *vs.*

$\alpha/(1-\alpha)$, where α is the degree of dissociation of NaOEt ion-pairs, should be linear.[11] The use of interpolated α values[10] does indeed lead to a linear plot (Fig. I) with correlation coefficient 0.999, whence $k_i = (7.95 \pm 0.07) \times 10^{-4}$ M.$^{-1}$sec.$^{-1}$ and $k_{ip} = (1.88 \pm 0.04) \times 10^{-4}$ M.$^{-1}$sec.$^{-1}$ It is noteworthy that values of k_2 calculated according to Eq.(1) do not yield a linear plot of this sort, in accordance with Sneen's observation that their decrease with increasing [NaOEt] is not a normal salt effect.[5]

Secondly, we fine that the effect of [NaOEt] on the unambiguous[12] k_{2E} values for dehydrobromination of 2-phenethyl bromide (2-PEB), where interfering solvolysis and substitution reactions can be ignored, parallels its effect on 1-PEB E2 rates. A salt effect on 2-PEB rates at 55° has been reported[12] and in Table II are shown k_{2E} values, obtained under pseudo first-order conditions and calculated from Eq.(4) with $f_E = 1.00$ and $k_1 = 0$, for the 2-PEB/NaOEt reaction at 50°. A plot of $k_{2E}/(1-\alpha)$ vs. $\alpha/(1-\alpha)$ is again linear; $k_i = (45.0 \pm 0.7) \times 10^{-4}$ M.$^{-1}$sec.$^{-1}$, $k_{ip} = (23.9 \pm 0.4) \times 10^{-4}$ M.$^{-1}$sec.$^{-1}$ and correlation coefficient = 0.999. Most importantly, a plot of k_{2E} for 1-PEB vs. k_{2E} for 2-PEB with rate constants taken at corresponding [NaOEt] values is satisfactorily linear, with correlation coefficient = 0.989 (Fig. II). The slope is not unity and neither is it expected to be so. This is not a linear free energy relationship, and the non-unit slope merely reflects the fact that the relative reactivity of OEt$^-$ vs. Na$^+$OEt$^-$ differs between 1-PEB and 2-PEB. Thus the salt effect on the undoubted second-order rate constants for 2-PEB dehydrobromination is quantitatively comparable with the salt effect that we claim is affecting the 1-PEB k_{2E} values in a competitive system. Such negative salt effects are used by Kohnstam and co-workers[1] in their counter to the proposal of the "unified" S_N1-S_N2 mechanism.

TABLE II

The 2-PEB/NaOEt Reaction in EtOH at 50.0°.[(a)]

[NaOEt] (M)	10^4k_{obs}[(b)]	10^4k_{2E}[(c)]	α[(d)]	10^4k_{2E}(1-PEB)[(c,e)]
0.1	-	34.2[(f)]	0.495	4.90
0.207	6.83	33.0	0.422	4.47
0.362	11.5	31.7	0.352	4.00
0.614	17.7	28.8	0.260	3.49
0.844	24.1	28.6	0.213	3.17
1.041	28.8	27.7	0.179	3.00

[a] Rates measured spectrophotometrically. [Styrene] = 100% in all runs. Solvolysis accounts for ca. 2% of total reaction at lowest [NaOEt] and less at other concentrations. [b] In sec.$^{-1}$ [c] In M.$^{-1}$sec.$^{-1}$ [d] Degree of dissociation of sodium ethoxide ion-pairs, from Ref. 10. [e] Calculated from data in Table I. [f] From Ref. 13.

While the present work does not remove the Sneen mechanism from consideration, it does show that in an elimination system inherently favourable to a "unified" ion-pair mechanism, the competitive S_N2-E2 scheme remains viable. A radical change of views on bimolecular elimination is not called for at this time, and prevailing ideas on transition states, stereochemistry, substituent effects etc.[14] need not be reconsidered.

ACKNOWLEDGEMENT: I thank Mr R. J. Wong for least-squares computations.

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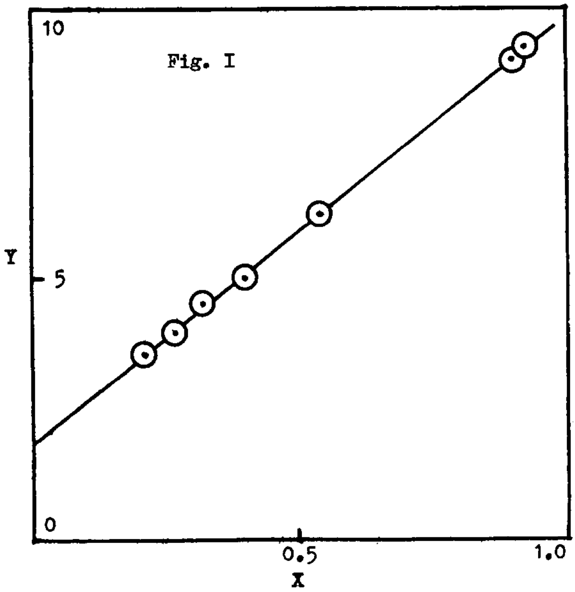

Fig. I : $Y = 10^4 k_{2E}/(1-\alpha)$
$X = \alpha/(1-\alpha)$

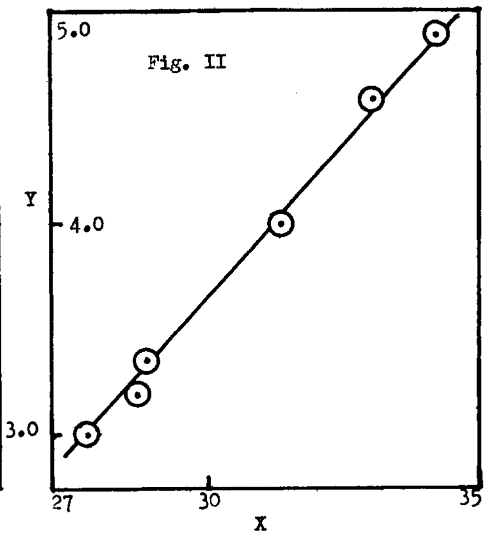

Fig. II : $Y = 10^4 k_{2E}$(1-PEB)
$X = 10^4 k_{2E}$(2-PEB)