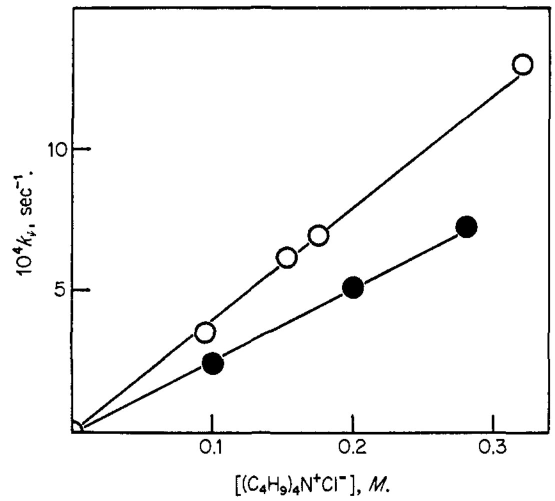

Figure 2. Pseudo-first-order rate coefficients for elimination from **2** (open circles) and from **3** (filled circles), in 1,4-dioxane at 69.9°, as functions of tetrabutylammonium chloride concentration.

The fact that rates of chloride ion induced elimination are greater for the more hindered substrate is probably also to be ascribed to steric acceleration. If the transition-state geometries for solvolysis and bimolecular elimination were the same in the vicinity of bromine (which they probably are not), and if there were no steric hindrance of chloride ion attack, **2** ought to have reacted about ten times faster than **3** in bimolecular elimination. Inasmuch as it actually reacted only about twice as fast, the extent of steric retardation caused by changing from **3** to **2** is crudely estimated as fivefold. This is reasonable if the chloride ion attacks β-H in the elimination transition state, but steric retardation should have depressed the rate by several powers of ten if covalent interaction of chloride ion with C_α were requisite.

Thus, a specific prediction of the "E2C" mechanism fails to be fulfilled. We conclude that chloride ion, as an elimination-inducing base, does not need closely to approach C_α in the transition state. Inasmuch as the "E2C" mechanism fails to meet this crucial test, and in view of the absence of compelling evidence in support of it, we feel that the notion should be discarded.

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David Eck, J. F. Bunnett
University of California
Santa Cruz, California 95060
Received February 24, 1969

Identification of an Intermediate Common to Mechanisms SN2 and E2[1]

Sir:

Historically mechanisms SN2 and E2, bimolecular nucleophilic substitution and elimination, although often observed concurrently, have been interpreted separately as distinct modes of reaction, the one initiated by nucleophilic attack on carbon and the other by attack on hydrogen. We herein report evidence that these mechanisms, as operative in the reactions of α-phenylethyl bromide with sodium ethoxide in solvent ethanol, share a common ion-pair intermediate.

Before the theory is developed it is desirable to establish that, in fact, the kinetic behavior of α-phenylethyl bromide under these conditions is extraordinary. It will later be established that the data are consistent with an ion-pair mechanism.

In particular, as is evident from Table I, the second-order rate "constant" for the reaction of α-phenylethyl bromide with ethoxide[2] decreases by a factor of greater than two on passing from 0.114 *M* to 0.533 *M* base. On the other hand the model substrate, ethyl bromide, under these conditions shows a modest decrease of only 17% over approximately the same concentration range, and this latter behavior appears to be fairly typical.[3] Thus there would appear to be something unique about the α-phenylethyl bromide system.

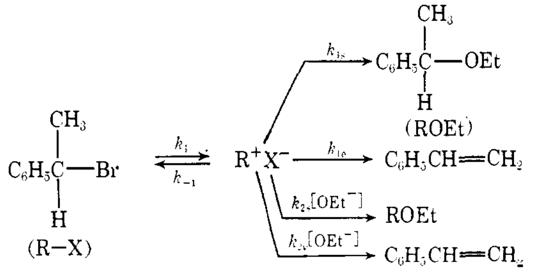
Table I. Comparison of Observed and Predicted Rate Constants in Ethanol at 50°

[NaOEt], *M*	k_{obsd_1},[a] sec^{-1} × 10^5	k_2,[b] l. mole^{-1} sec^{-1} × 10^4	k_{ip},[c] sec^{-1} × 10^5	k_{SN_2},[d] sec^{-1} × 10^5
	11.3 ± 0.3			
0.114	35.4 ± 1.0	21.1	28.8	36.2
0.121	35.7 ± 1.1	20.2	29.6	36.7
0.533	65.7 ± 1.9	10.2	59.6	123
0.686	74.8 ± 0.7	9.2	65.0	150
1.07[e]	98 ± 7	8.2	75.6	236
∞			106	∞

[a] Experimentally observed pseudo-first-order rate constant. [b] Calculated from the equation $k_{\text{obsd}} = k_1 + k_2[\text{OEt}^-]$. [c] Calculated from eq 10 with $a = 0.018$, $b = 0.500$, $y = 12.5$, and $x = 8.5$. [d] Calculated from eq 10 with $a = 0.018$, $b = 0.500$, $y = 12.5$, and $x = \infty$. [e] Average of three separate runs.

The experimental approach chosen to implicate such a common ion-pair intermediate recognizes that certain quantitative relations between rates of reaction and product distributions as a function of sodium ethoxide concentration, assuming such a mechanism, must necessarily exist. Scheme I is consistent with our experimental observations.

Scheme I



According to this scheme the ratio, *R*, of styrene to α-phenylethyl ethyl ether is given by eq 1.

$$\frac{[\text{styrene}]}{[\alpha\text{-phenylethyl ethyl ether}]} = R = \frac{k_{1e} + k_{2e}[\text{OEt}^-]}{k_{1s} + k_{2s}[\text{OEt}^-]} \quad (1)$$

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(1) Supported in part by the National Science Foundation.

(2) Calculated from the equation $k_{\text{obsd}} = k_1 + k_2[\text{OEt}^-]$.

(3) See for example, D. J. Cram, F. D. Greene, and C. H. Depuy, *J. Am. Chem. Soc.*, **78**, 790 (1956).

In the absence of base, R_{NB}, this reduces to eq 2, and

$$R_{\mathrm{NB}} = a = k_{1e}/k_{1s} \qquad (2)$$

at infinite base, $R_{\infty\mathrm{B}}$, it becomes eq 3.

$$R_{\infty\mathrm{B}} = b = k_{2e}/_{2s} \qquad (3)$$

Defining

$$y = k_{2s}/k_{1s} \qquad (4)$$

one obtains relation 5.

$$k_{2e}/k_{1s} = by \qquad (5)$$

Equation 1 can now be rewritten

$$R = \frac{a + by[\mathrm{OEt^-}]}{1 + y[\mathrm{OEt^-}]}$$

or, solving for y

$$y = \frac{R - a}{[\mathrm{OEt^-}](b - R)} \qquad (6)$$

The constants a and b can be evaluated from experimental data with the aid of eq 2 and 3, respectively ($a = 0.018$ and $b = 0.500$), and the constant, $y = k_{2s}/k_{1s}$, can then by evaluated from the remaining product data. Product data are available from this work (50°, vpc) as well as from the published data of Taylor[4] and of Hughes and Ingold[5] (55°, bromine titration of styrene). A value of $y = 12.5$ is reasonably consistent with the available data, as is evident from Figure 1; however a more accurate estimate of (the lower limit of) this constant can be evaluated kinetically (*vide infra*).

Scheme I predicts that the observed rate constant, k_{obsd}, will be given by eq 7. On division by k_{1s} and the

$$k_{\mathrm{obsd}} = \frac{k_1[k_{1s} + k_{1e} + (k_{2s} + k_{2e})[\mathrm{OEt^-}]]}{k_{-1} + k_{1s} + k_{1e} + (k_{2s} + k_{2e})[\mathrm{OEt^-}]} \qquad (7)$$

use of the definitions of a, b, and y from eq 2, 3, and 4 and with $k_{-1}/k_{1s} = x$, this can be rewritten as eq 8.

$$k_{\mathrm{obsd}} = \frac{k_1[1 + a + (1 + b)y[\mathrm{OEt^-}]]}{x + 1 + a + (1 + b)y[\mathrm{OEt^-}]} \qquad (8)$$

In the absence of base, k_{NB}, this reduces to eq 9.

$$k_{\mathrm{NB}} = \frac{k_1(1 + a)}{x + 1 + a} \qquad (9)$$

Elimination of k_1 between eq 8 and 9 gives eq 10.

$$\frac{k_{\mathrm{obsd}}}{k_{\mathrm{NB}}} = \frac{(x + 1 + a)[1 + a + (1 + b)y[\mathrm{OEt^-}]]}{(1 + a)[x + 1 + a + (1 + b)y[\mathrm{OEt^-}]]} \qquad (10)$$

The constant $x = k_{-1}/k_{1s}$, which is independent of nucleophile, has been evaluated independently; a value of $x = 8.5$ has been obtained[6] for the competitive reactions in ethanol at 50° of α-phenylethyl bromide with solvent and either azide ion or thiocyanate ion by application of the techniques described in a recent publication.[7]

It remains but to evaluate normal salt effects; to a first approximation these appear to be minimal at the levels of concentration of ethoxide used in this work.[8]

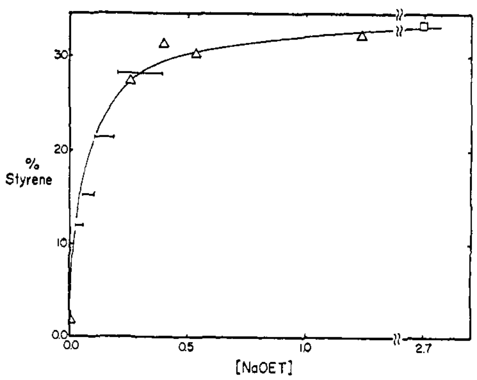

Figure 1. The solid line represents a theoretical plot of eq 6 with $a = 0.018$, $b = 0.500$, and $y = 12.5$. The triangles are from this work; the horizontal bars, with their uncertainties, are from ref 4.

In any event the deviations of kinetic behavior observed in the present studies from those predicted for "traditional" SN2 and E2 mechanisms[9] cannot reasonably be ascribed to normal salt effects. Thus k_{NB} has been assumed to be independent of ethoxide concentration.

The kinetic data are presented in Table I with $a = 0.018$, $b = 0.500$, $y = 12.5$,[10] and $x = 8.5$. It will be apparent that the ion-pair mechanism (with the constants a, b, x, and y all evaluated by independent means) correlates the kinetic data quite accurately, while deviations from bimolecular behavior are equally apparent.

The generality of this mechanism remains to be established but, since at large values of x the mechanism becomes kinetically indistinguishable from traditional E2–SN2 behavior (*i.e.*, eq 10 degenerates to the equation of ref 9), it is attractive to consider it quite universal.

The cycle is now complete. In this work a common intermediate has been shown to link mechanisms SN2 and E2. In a recent publication[7] mechanisms SN2 and SN1 were unified. Mechanisms SN1 and E1 have long been recognized as possessing a common intermediate.

Thus the four basic mechanisms, SN1, SN2, E1, and E2, at least on occasion, possess in common an ion-pair intermediate whose subsequent reactions (1) determine the nature of the product, elimination or substitution, and (2) influence the kinetic order of the reaction to be first, second, or borderline.

Richard A. Sneen, Howard M. Robbins[11]
Department of Chemistry, Purdue University
Lafayette, Indiana 47907

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[4] W. Taylor, *J. Chem. Soc.*, 1962 (1937).

[5] E. D. Hughes, C. K. Ingold, S. Materman, and B. J. McNulty, *ibid.*, 899 (1940).

[6] H. M. Robbins, unpublished work.

[7] R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, 91, 362 (1969).

[8] In these laboratories (*vide supra*) ethyl bromide was chosen as a model substrate for the evaluation of normal salt effects; thus although this substrate may well undergo elimination *via* the ion-pair mechanism, it would be expected to exhibit a large value of $k_{-1}/k_{1s} = x$, approaching traditional behavior. Other extant studies corroborate our findings.[3]

[9] Equation 10 with $x = \infty$; *i.e.*, $k_{\mathrm{obsd}}/k_{\mathrm{NB}} = [1 + a + y(1 + b)\cdot[\mathrm{OEt^-}]]/(1 + a)$.

[10] Although this value is consistent with product data, y is more accurately evaluated as necessarily equal to or greater than the value obtained from the initial slope of a plot of $k_{\mathrm{obsd}}/k_{\mathrm{NB}}$ *vs.* B assuming the equation of ref 9 (where the slope $= y(1 + b)/(1 + a)$, $y \geq 12.7$); that is, the experimentally determined value of the ratio $k_{\mathrm{obsd}}/k_{\mathrm{NB}}$ cannot be greater than that predicted by the classical SN2–E2 mechanism. Use of a larger value of y would magnify deviations from classical behavior (and, incidentally, improve the correspondence with the ion-pair picture).

[11] David Ross Fellow of the Purdue Research Foundation, 1967–1969.