

R_3Ge ,⁴³ R_3Sn ,⁴³ R_2N ,⁴⁴ $R_2C=N$,⁴⁵ and $R_2C=NO$ ⁴⁶ radicals. Its further extension to other areas of

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chemistry where reactive intermediates are involved is a foregone conclusion.

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Distinguishing between Concerted and Nonconcerted Eliminations

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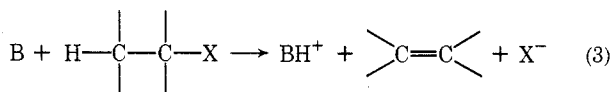
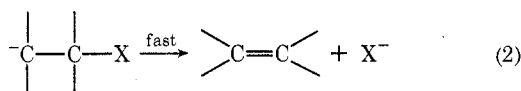
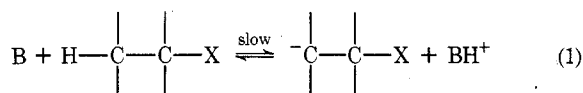
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Received March 13, 1975

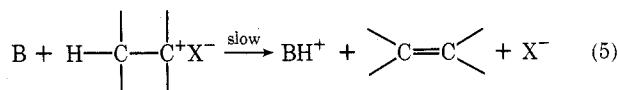
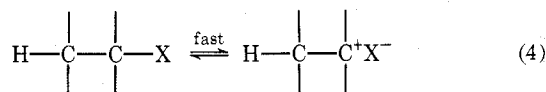
Recent articles by Bordwell have questioned the widely held view that concerted reactions in general¹ and concerted (E2) eliminations in particular² are quite common. He presents numerous examples of reactions for which there is evidence that they belong to the E1cB or ion-pair mechanisms, and then suggests that many more reactions formerly assigned to the E2 category may proceed by one of these mechanisms.

The scope of concerted processes is clearly a subject of wide interest. It is my aim in this Account to propose an operational definition of concerted elimination and to discuss evidence on the range of validity of the E2 mechanism.

Of the eight classes of elimination mechanisms cited by Bordwell,² there are three that show bimolecular kinetics and are particularly difficult to distinguish from each other: the irreversible carbanion mechanism (E1cB)_I, eq 1 and 2, the E2 mechanism, eq 3, and the (E2)_{ip} or ion-pair mechanism, eq 4-5.



E1cB and (E2)_{ip} mechanisms where the first and second steps happen to proceed at comparable rates will also show many of the characteristics of the E2 mechanism. Other types of bimolecular mechanisms are



readily distinguished from the above three. The (E1cB)_R mechanism, for example, in which the step shown in eq 1 is rapid and reversible, can be detected by isotopic exchange studies.

Before we can arrive at useful conclusions on the best ways of distinguishing the concerted E2 from the other two mechanisms, we must define precisely what we mean by the term "E2 mechanism". The basic definition, first proposed by Hanhart and Ingold in 1927,³ was a one-stage process in which base attacks the β hydrogen and removes it at the same time as the α -C-X bond is breaking and a carbon-carbon double bond is forming. These bond changes need not be precisely synchronous, and various workers have pointed out that C-X breaking may lag behind hydrogen transfer, or vice versa, at the transition state.³⁻⁸ This concept has become known as the "Variable Transition State Theory", and has been reviewed on numerous occasions, most recently by Saunders and Cockerill.⁹ Such a flexible concerted process can obviously mimic certain characteristics of the E1cB process at one extreme and the (E2)_{ip} process at the other.

Nonetheless, there is available, in principle, a clear operational distinction: for an E2 mechanism, the β

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hydrogen will be partially but not completely transferred, and the α -C-X bond partially but not completely broken, in the transition state for the rate-determining step. Note that this definition does not exclude the possibility that intermediates may occur along the reaction coordinate prior to or after this rate-determining transition state. Lowe has also pointed out that there is no inconsistency in defining as concerted a reaction with intermediates, so long as two or more bonds are undergoing covalency change in the rate-determining transition state.¹⁰

Some more or less probable intermediates that one might envision for E2 reactions include electrostatic or hydrogen-bonded complexes between base and substrate and ion pairs with partial covalent character. Such intermediates are, however, irrelevant to the kinetics or rate of the overall process. All of the characteristics of an elimination reaction which we customarily attempt to explain in terms of a mechanism, such as relative reactivities with different substrates, bases, or solvents, the competition between syn and anti elimination, and orientation effects, can be discussed without reference to possible intermediates of this sort. This conclusion is simply a consequence of the fact that rate (and relative rate) measurements can tell us only about the reactant and the rate-determining transition state, not about any species in between.¹¹ If we can show that the conditions of our operational definition are satisfied, we have established the existence of a concerted mechanism, and any intermediates which may be demonstrated by nonkinetic means, though important to discussions of mechanism, will not alter our conclusions.

Having established an operational criterion, we can now consider the type of experimental evidence needed to apply it. The primary β -deuterium or -tritium isotope effect is clearly the best means of determining the extent of β -hydrogen transfer in the transition state. For simple three-center models,¹²⁻¹⁴ and the E2 transition state as well,^{15,16} a large isotope effect ($k_H/k_D \approx 3-8$ near room temperature) demonstrates that the proton transfer is substantial but not complete. Smaller effects can result from highly unsymmetrical¹²⁻¹⁶ or nonlinear¹⁶⁻¹⁸ transition states, so there will be regions where one cannot decide unequivocally whether proton transfer is occurring in the rate-determining step. At one extreme, k_H/k_D will approach 1.0 for a very reactant-like transition state. At the other, it will approach the equilibrium isotope effect for a very product-like transition state.¹⁹ The equilibrium effect could be either normal or inverse, depending on whether motions of the hydrogens are looser or tighter in products than in reactants, and will probably be quite small. In the reac-

tion of methoxide in methanol with 2-methyl-3-phenylpropionitrile at 60°, the equilibrium value of k_H/k_D is 1.2.²⁰ An observed k_H/k_D much above 1.2 (say 1.5 or greater) can be considered as rather strong evidence for a rate-determining proton transfer. A lower effect still permits, but does not require, rate-determining proton transfer.

Other techniques that might be used to determine the extent of proton transfer are β -carbon isotope effects^{16,21} and β -substituent effects.^{7,9} Available values of the former are too few in number so far to be very useful. Many values of the latter are to be found in the literature,⁹ but the numbers depend not only on the extent of proton transfer but also on the extent of cleavage of the bond to the leaving group in the transition state.

The extent to which the bond between the α -carbon atom and the leaving group is weakened in the transition state can be most straightforwardly determined by leaving-group or α -carbon isotope effects.¹⁶ Available data are very limited for the latter, but a considerable number of sulfur isotope effects with sulfonium salts and nitrogen isotope effects with ammonium salts have been determined.⁹ A related technique is the leaving group effect, or element effect,²² where changing the leaving group is expected to have only a small inductive effect if the bond to the α carbon is not weakened in the transition state, but a much larger effect (provided the ease of cleavage of the bonds differs sufficiently) if it is. The tosylate/bromide rate ratio, though sometimes ambiguous, has been particularly widely used.²³⁻²⁵

A final, but important, difference between concerted and stepwise eliminations is driving force. For the concerted path to be utilized it should be of lower energy, and hence faster, than the possible stepwise paths. To apply this criterion experimentally, one must be able to estimate the rate of the slow step in the nonconcerted process. This estimated rate is then compared to the observed rate. To distinguish between the (E1cB)₁ and E2 processes, for example, one estimates the rate of the simple proton transfer that constitutes the slow step of the former. Ways of doing this have been reviewed recently²⁶ and will not be discussed in detail here. Suffice it to say that small driving forces are difficult to establish in this way, for there is always some uncertainty in the estimated rate. The observed rate should be at least one or two orders of magnitude greater than the estimated rate to establish a concerted process beyond reasonable doubt. Even then, one must be careful that the model used in estimation is as close as possible to the real substrate in both electronic and steric structure.

In some cases, one may be unable to decide whether a driving force operates, or evidence on driving force may be unavailable. If the reaction nonetheless shows evidence that both the β -carbon-hydrogen and the α -carbon-X bond are weakened in the transition state, how does one distinguish an E2 process from a

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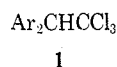
(26) Reference 9, pp 20-22.

stepwise process in which the two steps happen to be of comparable rates? This can usually be done by appropriate variation in substrate or reaction conditions, which will seldom have the same effect on both steps of a two-step process. In the E1cB reaction, for example, a stronger base will speed up the proton removal (eq 1) but not affect the carbanion decomposition (eq 2), while a poorer leaving group will slow the carbanion decomposition but have little effect on the proton removal provided the charge type is unchanged. Similarly, the proton-removal step (eq 5) of the ion-pair mechanism will be speeded up by a stronger base, but the substrate ionization (eq 4) will be unaffected.

The remainder of this paper will consider various groups of elimination reactions and the available evidence for the assignment of each group to the concerted E2 or one of the nonconcerted categories of mechanism. I will first take up cases that appear to be near the borderline between E2 and (E1cB)₁ reactions.

2,2-Diarylethyl Derivatives

DDT and related compounds (1) have two β-aryl



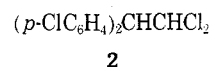
groups to activate the β hydrogen, and α-halogen substituents which are known to decrease the ease of removal of halide ion.²⁷ Both factors should favor an E1cB path, but 1 was considered for some time to follow the E2 mechanism in its elimination reactions because it was general-base promoted and failed to exchange the β hydrogen with the medium.²⁸ Furthermore, its elimination reaction with hydroxide in 92.6% ethanol has the moderate ρ value of +2.4²⁹ rather than the +4 to +5 expected for simple proton removal.⁹

More recently, however, McLennan and Wong³⁰⁻³² have presented evidence pointing to the (E1cB)₁ mechanism. They utilized the suggestion by Bell and Goodall^{33a} that the proton should be half-transferred, and $k_{\text{H}}/k_{\text{D}}$ at a maximum,^{12,13} when the substrate and the conjugate acid of the attacking base have equal pK_a values. They determined the isotope effect for the reaction of DDT with various bases in ethanol, and found a maximum for reaction with phenoxide. This suggests a pK_a of about 16 for DDT. The pK_a was then estimated by starting with the pK_a of diphenylmethane and calculating the effects of the p-Cl and -CCl₃ substituents, using the Hammett and Taft equations with reasonable ρ and ρ* values. The

result was a pK_a of 17. Thus, DDT is not significantly more acidic than would be expected if no driving force resulted from C-Cl weakening in the slow step.^{33b} In addition, DDT follows a relationship between rate of proton removal and pK_a which is based on fluorene-type hydrocarbons which cannot, of course, eliminate.^{31,32}

These observations clearly indicate little or no driving force due to C-Cl cleavage in eliminations from DDT, and strongly suggest the (E1cB)₁ mechanism. The ρ value of +2.4 is somewhat worrisome, for it is not only smaller than estimated values for carbanion processes (see above), it is also smaller than the values observed for some 2-arylethyl derivatives,⁹ for which there is a strong evidence that the E2 mechanism holds (see below). One would expect a carbanion-forming reaction to have a larger ρ value than a comparable concerted process, but McLennan and Wong argue that the nonreacting α-chlorine atoms help to dissipate part of the negative charge on the β-carbon atom.

Variation in both substrate structure and reaction conditions seem to be able to shift the mechanism from (E1cB)₁ to E2. Reactions of DDT-type compounds with weak bases in dimethylformamide have ρ values substantially smaller than the +2.4 for the (E1cB)₁ reactions,^{34a} while DDD (2) with methoxide



in methanol eliminates faster than predicted from its estimated pK_a value.^{34b} The driving force is too small (ca. 5-fold) to be definite proof that the reaction is partly or entirely E2. One can say that the DDD reactions are at least very close to the borderline, particularly in the light of the evidence cited in the next paragraph.

The reactions of the 2,2-diarylethyl benzenesulfonates with methoxide ion in Methyl Cellosolve at 50° seem to be clearly in the E2 category.³⁵ Large (>5) β-deuterium isotope effects are observed, and the ρ value for the substitution in the benzenesulfonate leaving group is +1.1, much larger than those found for reactions that probably do belong to the E1cB category (+0.3-0.6)³⁶ and comparable to those found for the unactivated 2-pentyl system (+1.35).³⁷

2-Arylethyl Derivatives

Elimination reactions in the 2-arylethyl series have been very thoroughly studied with respect to the criteria mentioned in the introduction, and are conceded by Bordwell² to belong to the E2 category. β-Deuterium isotope effects all point to rate-determining proton transfer. The $k_{\text{H}}/k_{\text{D}}$ values range from about 2.3 up to more than 8.0.⁹ That the α-C-X bond is also partially broken in the rate-determining step is shown by a number of pieces of evidence. Sulfur isotope effects with sulfonium salts and nitrogen isotope effects with ammonium salts are substantial in nearly

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all cases, but not so large as the maximum values (ca. 1.3 and 4.5%, respectively) expected for complete cleavage.⁹ The element effect with different halogens as leaving groups is substantial, spanning a range of more than 25,000 from the fluoride to the iodide.^{6,38,39} For the reaction of 2-arylethyl benzenesulfonates with *tert*-butoxide in *tert*-butyl alcohol, ρ values for substitution in the benzene ring of the sulfonate run +0.94–1.24, depending on the substituent in the β -phenyl group.⁹ The extensive evidence that both the β -C–H and α -C–X bonds are breaking in the rate-determining step for a wide range of leaving groups and bases effectively excludes the possibility that one is observing an E1cB process in which the two steps happen to be of comparable rates (see above).

A final method of demonstrating concertedness utilizes the procedure by which McLennan and Wong^{30,31} showed that eliminations from DDT and related compounds were probably nonconcerted. 2-Phenylethyldimethylsulfonium ion and its 2,2-*d*₂ analog react with hydroxide ion in water–dimethyl sulfoxide to give a k_H/k_D maximum near 40% dimethyl sulfoxide.⁴⁰ McLennan and Wong estimated the pK_a for this substrate to be 36.8.³¹ The difference between this number and the pK_a for water in 40% dimethyl sulfoxide, calculated according to Bell and Cox,⁴¹ is 20–21 rather than the expected value for the irreversible E1cB mechanism of approximately zero.³¹ In other words, the sulfonium salt behaves as if it were some 20 pK units more acidic than it is estimated to be, strikingly demonstrating the driving force from concomitant carbon–sulfur cleavage in the elimination. Similar calculations on 2-phenylethyltrimethylammonium ion in water–dimethyl sulfoxide⁴² and 2-phenylethyl tosylate in methanol–dimethyl sulfoxide⁴³ also give “apparent pK ’s” far below the estimated ones. Uncertainties in the estimated values are probably around ± 2.5 ,³¹ so there is no reasonable chance that the differences arise from faulty estimation.

Cycloalkyl Derivatives

Bordwell suggests that the anti elimination from neomethyltrimethylammonium ion may occur by a variant of the ion-pair mechanism, and the syn elimination from cyclooctyltrimethylammonium ion by an E1cB mechanism.² Decisive evidence on these particular substrates is not available, but it is on some closely related systems.

The 2-phenylcyclohexyl- and 2-phenylcyclopentyltrimethylammonium ions with ethoxide in 95% ethanol at 60° give nitrogen isotope effects of 0.39 and 0.64% and k_H/k_D values of 2.63 and 3.08, for syn elimination (from the *trans* substrate). Corresponding values for the anti elimination (from the *cis* substrate) are nitrogen isotope effects 1.23 and 1.08% and k_H/k_D 5.40 and 4.44.^{9,44,45} The nitrogen isotope

effects, even for the syn eliminations, are too large for the C–N bond not to be partially broken in the transition state, and all the deuterium isotope effects point to rate-determining proton transfer.

Cyclodecyltrimethylammonium ion with *tert*-butoxide in *tert*-butyl alcohol at 55° gives a 1.3% nitrogen isotope effect.⁴⁶ The syn elimination from 1,1,4,4-tetramethyl-7-cyclodecyltrimethylammonium ion with methoxide in methanol occurs with a deuterium isotope effect of 2.3.⁴⁷ While nitrogen and deuterium isotope effects on the same substrate under the same conditions would have been preferable, the results certainly strongly suggest that syn eliminations from medium-ring quaternary ammonium salts are concerted.

The same conclusion is even stronger for the syn and anti eliminations in the 2-phenylcyclohexyl and 2-phenylcyclopentyl systems. There is, consequently, no reason to believe that either syn or anti eliminations from unactivated or β -phenyl-activated cycloalkyltrimethylammonium salts involve anything other than the concerted E2 mechanism.

Simple cycloalkyl halides and tosylates without strongly activating β substituents can certainly be assumed not to undergo elimination by the E1cB mechanism, but one must consider the possibility that they follow an ion-pair mechanism, at least in some instances. Elimination reactions of cyclic, secondary or tertiary alkyl halides or sulfonates with bases normally regarded as weak, such as halide ions in dipolar aprotic solvents or thiolate ions in alcoholic solvents, were suggested by Winstein, Parker, and coworkers to involve simultaneous attack of the base on the α carbon and β hydrogen, a mechanism to which they gave the label E2C.⁴⁸ The alternate suggestion that these reactions involved the ion-pair mechanism, eq 4–5, was made by Bordwell² and critically discussed by Ford.⁴⁹

In order for the ion-pair mechanism to show the same kinetics as the E2 mechanism, the slow step must be the attack of base on the carbon–halide or carbonium–sulfonate ion pair (eq 5). Such a reaction should proceed with a deuterium isotope effect, and the elimination reactions of *trans*-cyclohexyl-2-*d* bromide and tosylate do, in fact, give k_H/k_D values at 75° of 2.2–4.0.⁵⁰ As might be expected, the magnitude of k_H/k_D depends on the nature of the base. One would expect, however, little or no dependence on the nature of the leaving group, since the acidity of the β hydrogen of the carbonium ion in an ion pair should not be markedly affected by the nature of the counterion. Contrary to this expectation, the k_H/k_D values for the bromide run 30–60% higher than those for the tosylate with attacking bases as diverse as phenoxide, acetate, and chloride in acetone and *tert*-butoxide in *tert*-butyl alcohol.

If the acidity of the β hydrogen in an ion pair is relatively independent of the nature of the counterion, it follows that any difference in observed rates of two

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(E2)_{ip} reactions involving different leaving groups would reflect primarily the difference in steady-state concentrations of the two ion pairs but not the nature of the base. In fact, k_{OTs}/k_{Br} for the reactions of cycloalkyl derivatives with different bases in acetone increases 40-fold from tetrabutylammonium *p*-nitrophenoxide (0.63) to tetrabutylammonium bromide (25).⁵¹ Such an increase is expected for a concerted elimination having a transition state with increasing product-like character, and hence increasing C–X cleavage. The change not only in magnitude but in direction is difficult if not impossible to reconcile with the ion-pair mechanism.

The above evidence makes it highly unlikely that E2C reactions of simple cycloalkyl derivatives occur via the ion-pair mechanism, but the facts are quite consistent with a concerted process. By extension, it is even less likely that the reactions of the same substrates with stronger bases (reactions labeled E2H by Winstein and Parker⁴⁸) involve an ion-pair mechanism.

Simple Secondary Derivatives

In the preceding section, cyclohexyl bromide and tosylate, which are secondary, were shown with high probability to eliminate via E2-type mechanisms. We can assume that the same mechanisms apply to acyclic secondary derivatives, unless there is some effect of the ring system which particularly favors a concerted process. In fact the reverse is probably true, for the conformation with an axial leaving group which is preferred for anti elimination in the cyclohexane series should be less favored than the analogous conformation for anti elimination from an acyclic secondary derivative. It is worthwhile, however, to consider briefly some evidence applying specifically to secondary acyclic systems.

While few isotope effects have been reported in such systems, those which have point to rate-determining proton transfer. For example, 3-methyl-2-butyl-3-*d* tosylate gives a k_H/k_D value of 2.3 with tetrabutylammonium chloride in acetone at 75°, and 2.6 with ethoxide in ethanol at 50°.⁵² The reactions of 3-pentyl-2,2-*d*₂-trimethylammonium ion with various base-solvent systems all show substantial isotope effects.⁵³ Similarly, isotope effects in E2 reactions of 2-butyl-3-*d* bromide indicate rate-determining proton transfer.^{53b}

Few leaving-group isotope effects have been reported in the literature for simple secondary derivatives. The nitrogen isotope effect for reaction of 5-nonyltrimethylammonium ion with *tert*-butoxide in *tert*-butyl alcohol is 1.0%, pointing to partial C–N cleavage in the transition state.⁴⁶

Relative rates with different leaving groups (the element effect) also point to C–X cleavage in the rate-determining step. As noted above,³⁷ the ρ value for eliminations from 2-pentyl benzenesulfonates has the substantial value of +1.35. Relative rates with fluorine, chlorine, bromine, and iodine as leaving groups

Table I
The Effect of the Leaving Halogen on Rates of Bimolecular Eliminations

Reaction	Relative rates (Cl = 1.00) for			
	F	Cl	Br	I
1. PhCH ₂ CH ₂ X + EtO [−] in EtOH at 30° ^a	0.015	1.00	60.3	391.
2. 2-Hexyl-X + MeO [−] in MeOH at 100° to give ^b				
a. 1-Hexene	0.0014	1.00	38.1	150.
b. <i>trans</i> -2-Hexene	0.00030	1.00	51.2	317.
c. <i>cis</i> -2-Hexene	0.00038	1.00	46.4	283.
3. 2-Methyl-2-butyl-X + <i>n</i> -BuSK in <i>t</i> -BuOH at 35° to give ^c				
a. 2-Methyl-1-pentene		1.00	200.	1560.
b. 2-Methyl-2-pentene		1.00	270.	2270.

^a References 6, 38, and 39. ^b R. A. Bartsch and J. F. Bunnett, *J. Am. Chem. Soc.*, 90, 408 (1968). ^c Reference 64.

are also available. The figures in Table I compare these rates for primary, secondary, and tertiary halides. The 2-phenylethyl halides with ethoxide in ethanol show a spread of more than 25,000 from fluoride to iodide. The spread for the 2-hexyl halides with methoxide in methanol is still wider overall, and comparable from chloride to iodide. The 2-methyl-2-butyl halides with *n*-butanethiolate in *tert*-butyl alcohol show the widest spread from chloride to iodide.

Clearly, C–X cleavage is well advanced but not complete in the transition states for eliminations from 2-hexyl halides. This and the other available evidence on simple secondary alkyl derivatives thus fit the criteria for a concerted process.

Tertiary and α -Arylalkyl Derivatives

The ion-pair mechanism is most likely to be involved in reactions of systems that can produce fairly stable carbonium ions. Tertiary and α -arylalkyl halides in relatively polar solvents readily undergo SN1–E1 solvolyses. Addition of strong base introduces a second-order component to the rate, but it is frequently difficult to suppress the first-order reaction completely, even at high base concentrations. In view of the demonstrated presence of carbonium ions (probably as carbonium-halide ion pairs) in these reaction media, one must consider the possibility that the second-order component of the reaction involves attack of base on an ion pair rather than attack of base on the un-ionized substrate.

So far, hard evidence is scanty. Sneen and Robbins⁵⁴ have studied reaction of 1-phenylethyl bromide with varying concentrations of sodium ethoxide in ethanol. Both ethyl 1-phenylethyl ether and styrene are formed in both first- and second-order processes, and the elimination/substitution ratio increases with increasing base concentration.

If the first- and second-order reactions were com-

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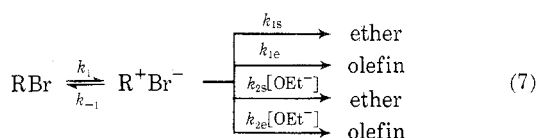
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pletely independent (SN1-E1 vs. SN2-E2), the rate law should be given by eq 6

$$\text{rate} = (k_1 + k_2[\text{NaOEt}])[\text{RBr}] \quad (6)$$

where k_1 represents both substitution and elimination by first-order processes, and k_2 likewise for the second-order processes. In fact, calculated k_2 values decrease 2.6-fold as the base concentration increases from 0.114 to 1.07 M. Sneen and Robbins argue that this decrease is far greater than expected for a salt effect, since k_2 for the reaction of ethyl bromide with sodium ethoxide decreases only 17% over the same concentration range. They then show that the experimental data, both on rates and elimination/substitution ratios, fit the predictions of a mechanism in which a common ion-pair intermediate leads to all products (eq 7).



This analysis of the data has been criticized by McLennan,⁵⁵ who points out that Sneen and Robbins neglected to allow for ion pairing of the sodium ethoxide according to eq 8. He quotes evidence that so-



dium ethoxide is only 50% dissociated even at 0.1 M.⁵⁶ He also argues that salt effects on elimination and substitution need not be the same, so that k_{E2} and k_{SN2} must be treated separately, not lumped together as in eq 6.

Calculated rate constants, k_{E2} , assuming elimination by a normal E2 mechanism, are claimed by McLennan to decrease with increasing base concentration partly because of the lesser reactivity of the ion-paired base (ca. 25% as reactive as free ethoxide) and partly due to what is classified as a normal salt effect. In support of this last point, the decrease is shown to be linearly related to the corresponding decrease in k_{E2} for 2-phenylethyl bromide which we have shown (see above) to follow the E2 mechanism.

McLennan does not, of course, disprove the (E2)_{ip} mechanism; he merely shows that the data of Sneen and Robbins are equally consistent with the concerted E2 mechanism. If the ion-pair mechanism holds, the second step, proton removal, must be mainly or solely rate determining, both from the kinetics and because a k_H/k_D of 3.4 is found for the reaction of 1-phenylethyl-2,2,2-d₃ bromide with sodium ethoxide in ethanol.⁵⁷

Such an isotope effect would be consistent with the Sneen and Robbins mechanism and their values for the various rate-constant ratios at base concentrations around 0.1–0.2 M. At higher base concentrations, however, the second step begins to become fast. An increase in base concentration from 1.0 to 2.0 M, for example, can be calculated to cause only a 17% increase in the pseudo-first-order k_{obsd} , ignoring salt effects and increased base association. Any factor

which markedly retards the ionization step, or markedly speeds the proton-removal step, should thus make the ionization step rate determining, resulting in an overall isotope effect which is only a secondary effect on the ionization rate and which should amount to ca. 1.2.⁵⁸

The change to potassium *tert*-butoxide in *tert*-butyl alcohol should increase the proton-removal rate (stronger base) and decrease the ionization rate (less-polar solvent), yet k_H/k_D is 5.0 under these conditions and is 3.5 even in the still more basic medium potassium *tert*-butoxide in *tert*-butyl alcohol–dimethyl sulfoxide.⁵⁷ The kinetics also remain strictly second order, which they would not if the proton removal were fast compared to the ionization.

The lack of any apparent change in rate-determining step between ethyl and *tert*-butyl alcohols, even when an increase of 10–100-fold in the k_{2e}/k_1 ratio (eq 7) would have sufficed to manifest it, strongly suggests an E2 mechanism in *tert*-butyl alcohol and *tert*-butyl alcohol–dimethyl sulfoxide. While this does not exclude the (E2)_{ip} mechanism for the reactions in ethyl alcohol, the simpler hypothesis is to classify the reactions in all three media as E2.

No other kinetic data on α -aryllalkyl systems are comparable in detail to the study of Sneen and Robbins. Isotope effects and ρ values for reaction of 1-arylethyltrimethylammonium ions with ethoxide in ethanol⁵⁹ and ρ values for the reactions of 1,2-diarylethyl chlorides with ethoxide in ethanol⁶⁰ are more consistent with the E2 than the (E2)_{ip} mechanism. The ρ values for substituents on the α -phenyl are positive, suggesting no development of positive charge at the α carbon in the transition state, contrary to expectations for the (E2)_{ip} mechanism. The effect of α -aryl substitution on the rates of E2C reactions likewise argues against significant development of positive charge.⁶¹

With tertiary halides, the large element effect along the series Cl–Br–I (Table I) clearly shows that the carbon–halogen bond is breaking either in the rate-determining step or in an equilibrium step preceding it. The only reported β -deuterium isotope effects in a tertiary system are the reaction of 1,1-dimethyl-2-phenylethyl chloride with methoxide and thioethoxide ions in methanol at 76°. The values are 2.6 and 2.4, respectively.⁶² The proton-removal step of an (E2)_{ip} mechanism would, if anything, be faster in this case than for a simple *tert*-alkyl halide, so we can probably safely assume that proton removal would be rate determining in most cases of tertiary halides reacting by this mechanism.

The data are also, of course, consistent with the E2 mechanism. More evidence is needed to distinguish the E2 and (E2)_{ip} mechanisms for tertiary halides. One would like to know, for example, whether the bond to the leaving group is incompletely broken in the transition state of the rate-determining step.

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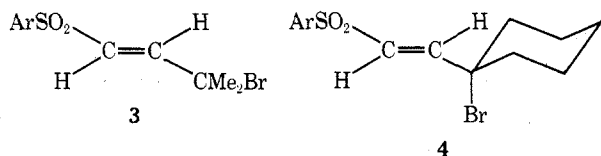
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A suggestive but not conclusive piece of evidence on second-order eliminations from tertiary halides is that product proportions (1-ene/2-ene) generally show a marked dependence on the nature of the leaving group.^{63,64} It does not seem very likely that the nature of the counterion in a carbonium-halide ion pair would have much effect on the relative reactivities toward base of different β protons.⁶⁴ It is, however, quite reasonable that the extent of carbon-halogen cleavage, and hence the degree of double-bond character, might differ in the E2 transition states from different *tert*-alkyl halides.

A final category for which the (E2)_{ip} mechanism has been proposed involves the tertiary allylic bromides **3** and **4** as substrates, with various nucleo-



philes.^{65,66} The main argument for this mechanism is that the evidence suggests an ion-pair mechanism for the accompanying substitution reactions. An interesting modification of the ion-pair mechanism is suggested, an "ion sandwich" process in which the ion pair is formed during rather than prior to base attack on the substrate. This mechanism bears a strong resemblance to the merged mechanism for substitution and elimination which was proposed by Winstein but later abandoned in favor of the E2C mechanism.^{67,68}

Whatever the merits of the ion sandwich vs. the more usual (E2)_{ip} mechanism, none of the evidence so far available on **3** and **4** is decisive for ion-pair mechanisms on the one hand or the E2 mechanism on the other.

Conclusions

One can say with considerable assurance that nearly all second-order elimination reactions of simple primary and secondary derivatives follow the E2 mechanism, up to and including 2,2-diphenylethyl tosylate. The E1cB mechanism requires strong activation of the β hydrogen and/or a poor leaving group. The borderline between E2 and E1cB seems to occur near DDT- and DDD-type substrates.

The range of applicability of the (E2)_{ip} mechanism is much more difficult to define. No unequivocal case of the (E2)_{ip} mechanism has been found, but many elimination reactions of tertiary, allylic, and α -arylalkyl derivatives could occur by either E2 or (E2)_{ip} mechanisms. Where available, the evidence is usually more consistent with the E2 than the (E2)_{ip} mechanism, but it is not compelling.

One should clearly not assume without evidence that all eliminations which can follow a concerted path will. On the other hand, one can define a range of bimolecular, olefin-forming eliminations which are almost certainly concerted. Further investigation of the genuinely uncertain borderline areas is desirable, but the facts do not justify major revisions in present mechanistic assignments.

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I wish to acknowledge support by the National Science Foundation, and the many contributions of my students to both the facts and ideas cited. The major part of this paper was written at Institutionen för organisk kemi, Göteborgs Universitet och Chalmers Tekniska Högskola, Göteborg, Sweden, during the Summer of 1974. I thank Professor Lars Melander for his hospitality and for stimulating discussions.