Base Dependence of Transition-State Structure in Alkene-Forming E2 Reactions

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Among reaction mechanisms, those which involve only a single reaction step might seem to be the easiest to understand. However, for one such mechanism, E2 olefin-forming elimination, it is now recognized that numerous subtle effects influence product composition and/or reaction rates.

In an E2 reaction, a base B attacks and acquires a proton from C_β in concert with the departure of a leaving group X from C_α and the formation of a π bond between C_α and C_β (Scheme I). In this single reaction step, two bonds are formed and two are broken.

Long ago, it was realized, first in principle[1a] and then from experimental evidence,[1b] that in these reactions the breaking and the formation of the various bonds need not be synchronous. This led to the theory of the "variable E2 transition state" which, in its comprehensive formulation,[2] considers a spectrum of transition-state structures ranging (Scheme II)[3] from the E1-like to the E1cb-like. Between these two extremes there is a central structure, exhibiting equal extents of C–H and C–X bond breaking and no development of charge at either C_α or C_β.

Although overwhelming experimental evidence has been accumulated supporting the existence of the central-right portion of the spectrum in Scheme II,[4] formulation of the left of center region has raised considerable controversy. Parker, Winstein, and their coworkers[5] suggested that reactions thought to occur by E1-like transition states actually take place via transition states such as 1 and 2 which involve a loose co-

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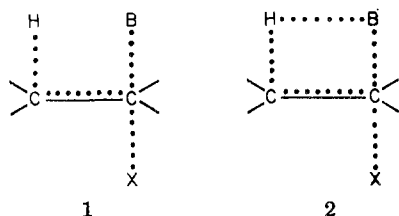
valent interaction between the nucleophile and the α-carbon.[6] These reactions have been named E2C to distinguish them from those occurring by the transition states of Scheme II, which are designated E2H.[8]

The spectrum of Scheme II is usually considered to be valid also for syn eliminations. For syn eliminations promoted by an associated base, a cyclic transition state, 3, has been suggested. In 3, an interaction between the positive counterion and the leaving group is possible.[9]

Determination of the transition-state structure for an E2 reaction and of the effects exerted upon this struc-
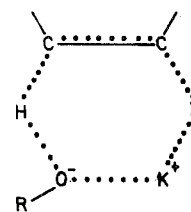
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ture by changes in the nature of the reactants and the reaction conditions has both practical and theoretical interest. There is a close relationship between the transition-state structure of an E2 reaction and the outcome of the reaction itself, with particular regard to stereochemistry and positional and geometrical orientation.[2,10] Since an E2 reaction involves two bond-making and two bond-breaking processes, the knowledge of the response to structural changes of a reaction of such a complexity and flexibility can give information of fundamental importance concerning general theories of structural effects on concerted reactions.

Among the factors which can influence the transition state of an E2 reaction, those derived from changes in the base structure (basicity, steric requirements, and state of association) are certainly of great importance. However, considerable uncertainty on the reality and direction of these effects has existed until recently.[11] Only in the last few years have experimental results which allow unequivocal conclusions been obtained.

(1) (a) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927); (b) D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Am. Chem. Soc.*, 73, 5708 (1951).

(2) J. F. Bunnett, *Angew. Chem. Int. Ed. Engl.*, 1, 225 (1962).

(3) Within any structure, bonds indicated with dashed lines are stronger than those indicated with dotted lines.

(4) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanism of Elimination Reactions", Wiley-Interscience, New York, 1973, Chapter II.

(5) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Am. Chem. Soc.*, 92, 115 (1970); G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, 93, 4735 (1971); P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *ibid.*, 94, 2240 (1972).

(6) A modification of the Parker–Winstein transition states has been recently proposed by McLennan,[7] who has suggested that the interaction between B and C_α is essentially of electrostatic nature.

(7) D. J. McLennan, *Tetrahedron*, 31, 2999 (1975).

(8) In this Account we will not enter into the merit of the E2H–E2C controversy since most of the results which will be considered certainly pertain to E2H reaction.

(9) J. Závada, M. Svoboda, and J. Sicher, *Collect. Czech. Chem. Commun.*, 33, 4027 (1968); M. Svoboda, J. Závada, and J. Sicher, *ibid.*, 33, 1415 (1968).

(10) (a) J. F. Bunnett, *Surv. Prog. Chem.*, 5, 53 (1969). (b) Positional orientation indicates the relative proportion of isomeric alkenes formed differing in the position of the double bond; geometrical orientation indicates the ratio of trans and cis isomeric alkenes formed.

(11) Reference 4, p 92. The ambiguity of the conclusions was mainly due to the fact that reactions carried out in different alcohol–conjugate alkoxide systems were generally compared. Such comparisons can give information of little significance with respect to the base structure effects since the solvent is also changed. For this reason only data referring to the *same* solvent are discussed in this Account.

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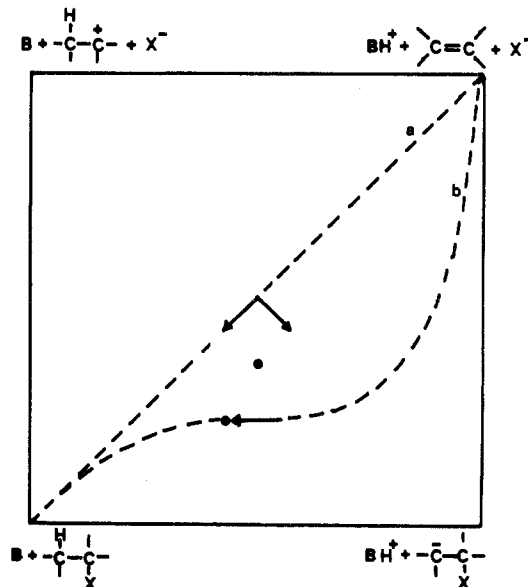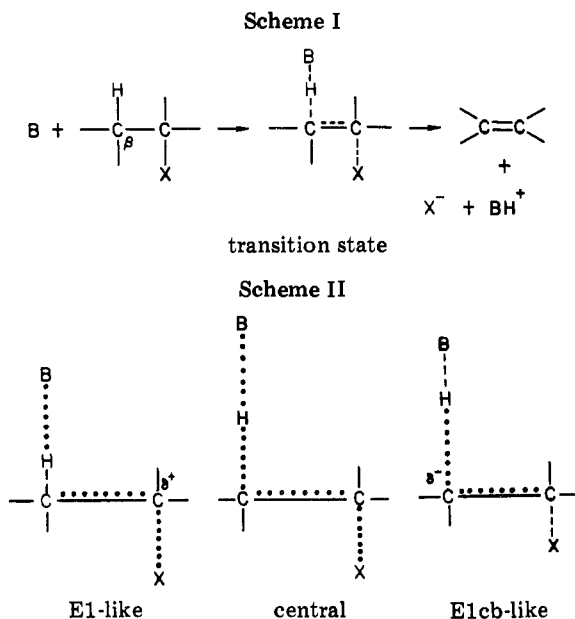
Scheme I

transition state

Scheme II

E1-like   central   E1cb-like

Effects of the Base Strength

Most of the quantitative information concerning base strength effects involves β-aryl-activated substrates and the determination of ρ and k_H/k_D values with different bases in the same solvent. Ad hoc studies have been carried out in our laboratories for eliminations from 2-arylethyl bromides[12,13] (4) and 2-arylethyltrimethyl-ammonium ions[14] (5), promoted by phenoxides in $N,$-N-dimethylformamide (DMF). However pertinent results are also found in investigations of eliminations from 1,1-diaryl-2,2,2-trichloroethanes[15,16] (6), 1,1-di-methyl-2-phenylethyl chloride[17] (7), and 2-aryl-2-bromo-1-indanones[18] (8). The data of interest, together with those for eliminations from 2-arylsulfonylethyl chlorides (9, X = Cl) and tosylates (9, X = OTs),[19] are reported in Table I.[20-22]

The first remarkable observation is that in *all* the systems investigated an increase in the base strength leads to an increase in the ρ value, *thus clearly indicating a shift of the transition-state structure toward the carbanion side.* This behavior appears to be general and independent of the character of the transition state itself. Thus the same trend in the ρ values is observed in reactions characterized by highly carbanionic transition states, such as eliminations from 2-arylethyltri-methylammonium ions[14] and 2-arylsulfonylethyl derivatives[19,23] and in reactions where there is little de-

(12) S. Alunni and E. Baciocchi, *Tetrahedron Lett.*, 4665 (1973).

(13) S. Alunni, E. Baciocchi, and V. Mancini, *J. Chem. Soc., Perkin Trans. 2*, 1866 (1974).

(14) S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, 42, 205 (1977).

(15) D. J. McLennan and R. J. Wong, *J. Chem. Soc., Perkin Trans. 2*, 1818 (1974).

(16) O. R. Jackson, D. J. McLennan, S. A. Short, and R. J. Wong, *J. Chem. Soc., Perkin Trans. 2*, 2308 (1972).

(17) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, 84, 1606 (1962).

(18) D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Am. Chem. Soc.*, 88, 4489 (1966).

(19) Y. Yano and S. Oae, *Tetrahedron*, 26, 27 (1970).

(20) Attributing an E2 mechanism to the eliminations from 4, 5, 7, and 8 is well substantiated.[15-18,21] The evidence for the reactions of 5 refers to alcoholic solvents. For the eliminations from 9 the mechanistic pathway is less certain, but an E2 mechanism appears to be the most likely.[22]

(21) W. H. Saunders, Jr., *Acc. Chem. Res.*, 9, 19 (1976).

(22) V. Fiandanese, G. Marchese, and F. Naso, *J. Chem. Soc., Perkin Trans. 2*, 1538 (1973).

Figure 1. Changes in transition-state geometry caused by an increase in base strength evaluated by schematic potential energy diagram (contour lines omitted) for β-elimination reactions B + H–C–C–X → BH$^+$ + >C=C< + X$^-$. Approximate reaction coordinates for processes occurring via central and E1cb-like transition states are indicated by the dashed lines a and b, respectively. The arrows give the direction of parallel (along the reaction coordinates) and perpendicular effects. The position of the unperturbed transition state is at the origin of the arrow(s). The new position, resulting by the increase in base strength, is indicated by the dot.

velopment of negative charge at the β-carbon, such as those of 2-benzyl-2-bromo-1-indanones.[18,24]

A second important observation is that for the reactions of 2-arylethyl bromides with phenoxides and 2-arylsulfonylethyl tosylates with amines (where structurally related bases are compared), k_H/k_D values are only slightly influenced by the base strength. If, as has been indicated by recent calculations,[25,26] k_H/k_D in E2 eliminations can be interpreted in terms of the degree of transition-state proton transfer, the observed changes in ρ suggest that the effect of enhanced base strength on transition-state structure is mainly that of decreasing the extent of C–X bond breaking while leaving the degree of C–H bond rupture practically unaffected.[27-29]

(23) The ρ value is relatively small in this case because there is a group SO$_2$ interposed between the phenyl group and the β-carbon.

(24) In these reactions a curved Hammett plot was obtained. However the effect on the rate of a p-NO$_2$ group was clearly larger in the reaction with LiCl than in that with LiBr. It has been suggested[16] that these reactions may occur via a central transition state.

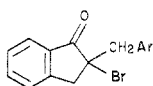(25) W. H. Saunders, Jr., *Chem. Scripta*, 10, 82 (1976); (b) *ibid.*, 8, 27 (1975).

(26) G. W. Burton, L. B. Sims, and D. J. McLennan, *J. Chem. Soc., Perkin Trans. 2*, 1763 (1977).

(27) The primary deuterium kinetic isotope effect has a double valued nature,[28] and similar k_H/k_D values can correspond to more than 50% or less than 50% proton transfer. However, the operation of such a fortuitous coincidence appears unlikely in view of the two structurally different systems which are considered.

(28) F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

(29) It has also been suggested[26] that in the reactions of 2-arylethyl bromides the small change in k_H/k_D (barely outside the experimental error) in going from phenoxide to p-nitrophenoxide could indicate 30% of proton transfer with the former nucleophile and 50% of proton transfer with the second. However, it seems unlikely that the proton transfer has not yet passed the midpoint in a reaction with a ρ value of +2.64. Moreover, this suggestion, if correct, would confirm that the effect of base strength on the extent of C–X bond-breaking plays the major role in determining changes in the transition-state structure.

Table I

Base Strength Effects on the Transition-State Structure of Some Elimination Reactions of 2-Aryl Activated Substrates

substrates	solvent (temp, °C)	base (p$K_a{}^a$)	ρ	$k_H/k_D{}^b$	ref
$ArCH_2CH_2Br$ (4)	DMF^c	C_6H_5ONa (18)	2.64	7.6	12, 13
		$p\text{-}ClC_6H_4ONa$ (16.8)		7.8	
		$p\text{-}NO_2C_6H_4ONa$ (12.3)	1.84	9.0	
$ArCH_2CH_2N^+(CH_3)_3$ (5)	DMF (55.7)	C_6H_5ONa (18)	4.25	2.8	14
		$m\text{-}NO_2C_6H_4ONa$ (15.4)	3.81	2.3	
$(Ar)_2CHCCl_3$ (6)	DMF (65)	$p\text{-}NO_2C_6H_4SNBu_4$ (6.3)	1.25	5.14	15, 16
		LiCl (3.4)	0.99	4.30	
		LiBr (1.8)		5.01	
$PhCH_2C(CH_3)_2Cl$ (7)	CH_3OH (75.8)	CH_3ONa (16.3^d)		2.6	17
		C_2H_5SNa (14.4^d)		2.4	
(structure) (8)	CH_3CN (60)	Et_4NCl (11.9^e)	0.44		18
		Et_4NBr (10.3^e)	0.17		
$ArSO_2CH_2CH_2X^f$ (9)	CH_3CN (50)	Et_3N (19)	1.81	2.1	19
		$Et_2NCH_2CH_2OH$ (17.9)	1.75	2.0	
		$EtN(CH_2CH_2OH)_2$ (16.9)	1.72	2.0	
		$N(CH_2CH_2OH)_3$ (15.3)	1.64	2.0	

^{a} Of the conjugate acid of the base, in the solvent used for the elimination reaction. Unless otherwise stated these pK_a values come from the references cited in the last column of the table. ^{b} Rate ratio between the unsubstituted substrates (Ar = Ph) and the β-deuterated analogue. ^{c} The ρ values have been determined at 0 °C, k_H/k_D at 21 °C. ^{d} J. F. Bunnett and L. Retallick, *J. Am. Chem. Soc.*, 89, 423 (1967). ^{e} From the values of ref 15 and 16 by adding 8.5: I. M. Kolthoff, M. K. Chantooni, and H. Smagowski, *Anal. Chem.*, 42, 1622 (1970). ^{f} ρ values refer to X = Cl k_H/k_D to X = OTs.

It is also possible that this conclusion applies to eliminations from 6 and 7 which exhibit only slight influence of base strength upon the k_H/k_D values. However, in these cases unrelated bases are compared, and the relation between k_H/k_D and the extent of proton transfer at the transition state may be significantly influenced by the nature of the base itself.[30]

Changes in the degree of C–X bond-breaking also appear to play the major role in determining the observed effects of the base strength on the carbanion character of the transition state for eliminations from 2-arylethyltrimethylammonium ions. The small rise in k_H/k_D as the base strength increases suggests less transition-state C–H bond-breaking for reaction with the stronger base. (In these reactions, the proton should certainly be more than 50% transferred to the base in the transition state.) Since reaction with the stronger base displays a higher ρ value, the increased carbanionic character of the transition state should result also in this case from a dominant effect of base strength upon the extent of C–X bond breaking. It would be interesting to test this conclusion by determining the nitrogen isotope effect of the leaving group.

Predictions concerning the effects of base strength on the E2 transition state can be made by using the More O'Ferrall potential-energy diagram[31] (Figure 1) and the suggestion[31,32] that changes in base strength modify the transition-state geometry through the operation of effects on the vibrational modes of the transition state itself which involve the C–H bond motions parallel and perpendicular to the reaction coordinate (parallel and perpendicular effects). According to the theory of Winey and Thornton,[32] as shown in Figure 1, when a reaction occurs via a central transition state parallel and perpendicular effects have the same

weight and a change to a stronger base decreases the degree of C–X bond-breaking but does not significantly influence the extent of C–H bond cleavage. However, when the transition state is highly carbanionic, only parallel effects should be operating (perpendicular vibration does not involve the C–H motion), and with a stronger base a less carbanionic transition state is predicted as a consequence of less C–H bond stretching. These predictions can be considered in good agreement with the results in Table I if it is assumed that in the reactions of 2-arylethyltrimethylammonium ions the extreme situation has not yet been reached where only parallel effects are considered.[33]

The conclusion that the E2 transition state becomes more carbanionic (with a less extent of C–X bond breaking) as the base strength increases seems extendable also to reactions of substrates lacking β-phenyl activation.[34] However, since ρ determinations in these systems are not possible, the information available is less direct.

Information concerning the transition-state structure for eliminations from nonactivated substrates is furnished by positional orientation data since there is now little doubt that this behavior is mainly governed by the character of the transition state itself.[2,10a] In particular, an increase in the proportion of the least substituted olefin (Hofmann product) is indicative of an increase in the carbanion character of the transition state. Thus, the finding by Bartsch and co-workers[35] that, in oxyanion-promoted eliminations from 2-iodobutane in dimethyl sulfoxide (Me_2SO), the relative amount of

(30) (a) D. J. McLennan and R. J. Wong, *J. Chem. Soc., Perkin Trans. 2*, 1373 (1974). (b) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967). (c) It cannot be excluded that the reactions of 7 with CH_3O^- and $C_2H_5S^-$ involve linear and nonlinear proton transfer, respectively.

(31) R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970).

(32) D. A. Winey and E. R. Thornton, *J. Am. Chem. Soc.*, 97, 3102 (1975).

(33) Theory works well when the effects of electron-withdrawing substituents at C_β upon the E1cb-like transition state are considered (P.J. Smith and A. N. Bourns, *Can. J. Chem.*, 52, 749 (1974)). However, in such a case both parallel and perpendicular effects of similar magnitude are operating.[32]

(34) The extension is not obvious since β-phenyl activated systems can in some case behave quite differently than the nonactivated ones. S. Alunni, E. Baciocchi, R. Ruzziconi, and M. Tingoli, *J. Org. Chem.*, 39, 3299 (1974); S. Alunni and E. Baciocchi, *J. Chem. Soc., Perkin Trans. 2*, 877 (1976).

(35) (a) R. A. Bartsch, G. M. Pruss, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, 95, 3405 (1973); (b) R. A. Bartsch, K. E. Wiegers, and D. M. Guritz, *ibid.*, 96, 430 (1974).

base[a]	ΔpK_a[b]	k_H/k_D[c]
$C_6H_5O^-$	16	2.1
$CH_3CO_2^-$	10	3.7
$4-NO_2C_6H_4S^-$	4	6.2
Cl^-	1	6.0
Br^-	0	3.5

[a] The cation is in each case the tetra-*n*-butylammonium ion. [b] ΔpK_a(HB − HBr) in DMF; values estimated by Figure 2 in ref 38. It is assumed[38] that ΔpK_a(HB − HBr)$_{DMF}$ = ΔpK_a(HB − HBr)$_{acetone}$. [c] Reactivity rate ratio between *cis*-2-cyanocyclohexyl bromide and *cis*-2-cyano-2-deuteriocyclohexyl bromide.

1-butene increases as the base becomes stronger is evidence of a corresponding increase in the carbanion character of the transition state. Similar results have also been obtained in the reactions of some pentyl derivatives with F^- and Br^-, the former halogen base affording the larger amount of the Hofmann product.[36]

On the other hand, for reactions of 2-chloro-2-methylbutane with substituted thiophenoxides[37] changes in base strength lead to very small variations in the proportion of the least substituted olefin. This has been attributed to the very weak interaction between the base and the substrate in the transition states for these reactions.

Another indication that a stronger base provides a more carbanionic transition state is given by some reactions of cyclohexyl bromides in acetone[38] where the introduction of a β-*cis*-cyano group in the cyclohexyl bromide moiety increases the reaction rate by factors of 20 with Br^-, 160 with Cl^-, and 250 000 with $CH_3CO_2^-$. Certainly, these results are indicative of a larger accumulation of negative charge on the β-carbon in the transition state of the reaction involving the stronger base. Moreover in the eliminations from 1-halocyclohexanes in ethanol,[39] the bromine–chlorine leaving group effect (k_{Br}/k_{Cl}) decreases from 144 to 57 when the nucleophile is changed from $C_6H_5S^-$ to $C_2H_5O^-$, thus suggesting less C–X bond-breaking in the reaction with the stronger base.

With respect to the effect of base strength on the extent of C–H bond breaking, the eliminations from some cyclohexyl derivatives exhibit behavior quite different from that of 2-aryl activated substrates. For instance, in the reactions of *cis*-2-cyanocyclohexyl bromides large changes in k_H/k_D are observed as the base strength is changed.[38] As the base becomes stronger, k_H/k_D first increases, then decreases, passing through a maximum value of ca. 6 (Table II). Owing to the acidity of the substrate, these reactions should occur for most of the bases via transition states of the E2H type with little, if any, complication by possible E2C → E2H shifts (which could bring about changes in k_H/k_D by passing from nonlinear to linear transition states[25]). Data of Table II have been interpreted as indicating that the transition state goes from a situation

where the proton is less than half-transferred to the base (reaction with Br^-) to a situation where it is more than half-transferred (reaction with $C_6H_5O^-$). Thus it appears that the stronger base produces a more stretched C–H bond in the transition state. This conclusion is not in agreement with that previously reached for 2-aryl activated eliminations. However, structurally unrelated bases are compared in Table II and, as discussed above, the interpretation of k_H/k_D values in terms of changes in the extent of C–H bond-breaking at the transition state is of uncertain validity. Moreover, an increase in the degree of C–H bond-breaking with enhanced base strength is not in agreement with theoretical expectations for E2 reactions when the transition state is in the central E1cb region, as it should probably be for the reactions of *cis*-2-cyanocyclohexyl bromide with phenoxide and acetate ions.

With regard to base strength effects on the elimination rate, reactions of Table I encompass a wide range of situations. With 4 and 9 the E2 rate is very sensitive to base strength. For instance, with 4 (Ar = Ph) sodium phenoxide is ca. 10^5-fold more reactive than sodium *p*-nitrophenoxide and a Brønsted β value of 0.74 has been calculated for the eliminations from 9. In contrast, for reactions of 7, $C_2H_5S^-$ is 10-fold more reactive than the much more basic CH_3O^-. This variation of base strength effects upon elimination is readily rationalized by relative weights of the various factors that determine base reactivity in E2 reactions which in turn are dependent upon the transition-state structure.[10a] For instance basicity will be the main factor in reactions occurring via transition states where a large degree of bond formation between hydrogen and the base has developed (central E1cb-like transition states). Conversely, different factors (desolvation energy, polarizability) can become predominant for transition states where there is little bonding between the base and hydrogen (E1-like E2C transition states). This hypothesis was first advanced by Bunnett and Baciocchi[40] and has been supported by subsequent work.[39,41]

It must be noted, however, that when a series of structurally related bases is used, reaction rate generally parallels basicity and Brønsted β values can be measured.[37,41,42]

Effects of the Steric Requirements of the Base

It has been demonstrated that when the steric requirements of the base become particularly severe, positional and geometrical orientation of E2 reactions can be affected.[35] It is of interest to determine if this is due to modification of the transition-state geometry because, according to a recent hypothesis,[43] the bulkiness of the base may play a significant role.

Quantitative information on this problem is at present available only for the reactions of 2-arylethyl bromides and 1-phenyl-2-arylethyl chlorides (10) with sodium 2,6-di-*tert*-butylphenoxide.[44] The results when compared with those of the corresponding reactions with sodium phenoxide (Table III) show that in both

(36) I. N. Feit, I. K. Breger, A. M. Capobianco, T. W. Cooke, and L. F. Gitlin, *J. Am. Chem. Soc.*, 97, 2477 (1975).
(37) D. S. Bailey and W. H. Saunders, Jr., *J. Org. Chem.*, 38, 3363 (1973).
(38) D. J. Cook, R. E. J. Hutchinson, J. K. MacLeod, and A. J. Parker, *J. Org. Chem.*, 39, 534 (1974).
(39) D. J. McLennan, *J. Chem. Soc. B*, 705 (1966).
(40) J. F. Bunnett and E. Baciocchi, *Proc. Chem. Soc., London*, 238 (1963); *J. Org. Chem.*, 32, 11 (1967).
(41) D. J. McLennan, *J. Chem. Soc. B*, 709 (1966).
(42) Reference 4, p 95.
(43) D. J. McLennan, *J. Chem. Soc., Faraday Trans. 1*, 71, 1515 (1974).
(44) S. Alunni, E. Baciocchi, P. Perucci, and R. Ruzziconi, *J. Org. Chem.*, 43, 2414 (1978).

Table III
Effect of the Steric Requirements of the Base on the
Transition-State Structure of Eliminations from
2-Arylethyl Bromides and 1,2-Diarylethyl Chlorides in
DMF-Me$_2$SO (9:1 v/v)[44]

substrates	base	ρ	$k_H/k_D{}^a$	$k_{Br}/k_{Cl}{}^b$
ArCH$_2$CH$_2$Br	sodium phenoxide	2.64^c	7.6^d	120
	sodium 2,6-di-*tert*-butylphenoxide	2.44^c	9.0^e	146
ArCH$_2$CHClPh (10)	sodium phenoxide	2.40^f		
	sodium 2,6-di-*tert*-butylphenoxide	2.30^f		

^{a} Rate ratio between the unsubstituted compound and the analogous β-deuterated substrates. ^{b} C$_6$H$_5$CH$_2$CH$_2$Br: C$_6$H$_5$CH$_2$CH$_2$Cl rate ratio at 30 °C. ^{c} At 0 °C. ^{d} At 21 °C. ^{e} At 0 °C. ^{f} At 30 °C.

reaction series the geometry of the transition state appears to be practically insensitive to the steric requirements of the base. Similar ρ values are observed, indicating a similar degree of carbanion character in the transition states. At most, a small decrease in the carbanion character of the transition state for the reactions with the more hindered base can be envisaged; this may reflect the fact that 2,6-di-*tert*-butylphenoxide is slightly less basic than sodium phenoxide.[35a,45] The similar k_{Br}/k_{Cl} values indicate comparable stretching of the carbon–halogen bond at the transition states of the two reactions. Values of k_H/k_D are slightly larger in the reaction of 2-phenethyl bromide with sodium 2,6-di-*tert*-butylphenoxide than for sodium phenoxide. However, it is difficult to interpret this finding in terms of significant differences in the degree of C–H bond-breaking at the transition state in view of the above-mentioned similarity in ρ and k_{Br}/k_{Cl} values.[46]

These results suggest that severe steric requirements of a base can significantly influence orientation of an E2 reaction without appreciably modifying the structure of its transition state. It follows that in these cases orientation no longer provides a reliable indication of the E2 transition-state structure.

Effects of Base Association

In solvents of low dielectric constant it has been shown that the outcome of an elimination reaction (with particular regard to orientation and stereochemistry) can be profoundly influenced by the state of association of the base.[47] The role of base association on the E2 transition state can be investigated by studying reactions with potassium *tert*-butoxide (*t*-BuOK) in *tert*-butyl alcohol (*t*-BuOH) in the presence and in the absence of a potassium ion complexing crown ether. In *t*-BuOH, *t*-BuOK is strongly associated and exists nearly exclusively as contact ion pairs or higher aggregates (associated *t*-BuOK). The crown ether converts these species into solvated ions or, more probably, into solvent-separated ion pairs.[48] For the sake of conven-

ience this situation will be identified as dissociated *t*-BuOK.

In Table IV kinetic data are reported for anti eliminations from 2-arylethyl bromides[49,50] and 1-phenyl-2-arylethyl chlorides[51] and syn eliminations from the derivatives of *trans*-2-phenylcyclopentyl tosylate[52] (11) and *trans*-2,3-dichloro-2,3-dihydrobenzofuran (12)[53] in

11   12
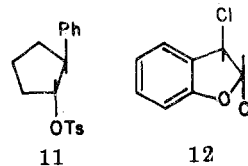
the presence and in the absence of a crown ether (18-crown-6 or dicyclohexyl-18-crown-6). 3-Chlorobenzofuran is the olefin formed from 12.

Considering first the anti eliminations, the remarkably different behavior displayed by 2-arylethyl bromides and 1-phenyl-2-arylethyl chlorides are at once noted. With the former substrate there is no substantial variation in the values of ρ, k_H/k_D, and k_{Br}/k_{Cl} in going from associated to dissociated *t*-BuOK, indicating that the transition-state structure is not significantly influenced by the state of association of the base. In contrast, in the eliminations from 1-phenyl-2-arylethyl chlorides a higher ρ value is observed in the presence of the crown ether, but the value of k_H/k_D remains practically unchanged. The latter result is in agreement with the data of Table I and theoretical predictions since solvent-separated ion pairs or solvated ions are much more basic species than contact ion pairs or higher aggregates. Thus, a more carbanionic transition state with little change in the degree of C–H bond-breaking should be expected in going from *t*-BuOH–*t*-BuOK to *t*-BuOH–*t*-BuOK–crown ether.

The insensitivity of the transition-state structure for elimination from 2-arylethyl bromides to variation in the association state of *t*-BuOK remains very intriguing. It is possible that in changing from associated to dissociated *t*-BuOK the effect of increasing base strength may be offset by some other presently unrecognized factor.

In syn elimination reactions, the main observation is that the change from associated to dissociated *t*-BuOK leads in both cases to a substantial increase in the ρ value, indicating an increase in the carbanion character of the transition state. There is no doubt that this result could again be simply rationalized on the grounds of the greater basicity of dissociated *t*-BuOK. However, it could also be possible that with associated *t*-BuOK the rupture of the carbon–leaving group bond is assisted by the counterion (structure 3) and requires less buildup of negative charge on the β-carbon in the transition state.

A point of contrast for the two syn eliminations is that k_H/k_D remains unchanged in the reactions of *trans*-2-arylcyclopentyl tosylates but increases in those

(45) F. G. Bordwell and co-workers (personal communication) have determined a pK_a of 18.3 for phenol and of 17.27 for 2,6-di-*tert*-butyl-phenol in Me$_2$SO.

(46) According to recent calculations (D. J. McLennan, personal communication) a straight comparison of k_H/k_D values for loose (bases with large steric requirements) and tight transition states could be invalid.

(47) R. A. Bartsch, *Acc. Chem. Res.*, 8, 239 (1975), and references therein.

(48) For an alternative view on the role of the crown ether see M. Schlosser and C. Tarchini, *Helv. Chim. Acta*, 60, 3060 (1977), footnote 2.

(49) S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, 41, 2636 (1976).

(50) A. F. Cockerill, S. Rottshaefer, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 89, 901 (1967).

(51) S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, 42, 2170 (1977).

(52) R. A. Bartsch, E. A. Mintz, and R. A. Parlman, *J. Am. Chem. Soc.*, 96, 4249 (1974).

(53) E. Baciocchi, G. V. Sebastiani, and R. Ruzziconi, *J. Org. Chem.*, 44, 28 (1979).

Table IV
Effects of the Base Association on the Transition-State Structure of Some Elimination Reactions Promoted by *t*-BuOK in *t*-BuOH in the Absence and in the Presence of a Crown Ether

substrates	temp, °C	crown ether	ρ	$k_H/k_D{}^a$	$k_{Br}/k_{Cl}{}^b$	ref
2-arylethyl bromides	30	absent	2.53	8.1	23	49, 50
		present[c]	2.77	8.0	19	
1-phenyl-2-arylethyl chlorides	30	absent	2.20	7.9		51[d]
		present[c]	3.40	8.0		
trans-2-arylcyclopentyl tosylates	50	absent	2.2	5.3		52
		present[e]	3.1	5.1		
trans-2,3-dichloro-2,3-dihydrobenzofurans	30	absent	2.3[f]	2.0		53
		present[c]	3.2[f]	3.0		

[a] k_H/k_D refers to the rate ratio between the unsubstituted substrate and the β-deuterated analogue. [b] $C_6H_5CH_2CH_2Br$: $C_6H_5CH_2CH_2Cl$ rate ratio. [c] The crown ether was 18-crown-6. [d] Unpublished results from this laboratory. [e] The crown ether was dicyclohexyl-18-crown-6. [f] Determined by the reactivity ratio between *trans*-2,3-dibromo-5-chloro-2,3-dihydrobenzofuran and the unsubstituted compound using the σ_m value for the chlorine group.

of *trans*-2,3-dichloro-2,3-dihydrobenzofurans in going from associated to dissociated *t*-BuOK. No convincing rationalization of the different behavior of the two reaction series is available at present.

Changes in the association state of the base also exert significant effects on elimination rate. Rate enhancements of 50–250-fold are generally observed in going from associated to dissociated *t*-BuOK.[49,51,53] Certainly, this enhancement in rate is mainly due to the greater basicity of dissociated *t*-BuOK. The increase is slightly smaller with syn eliminations, where the transition-state stabilization with associated *t*-BuOK due to structure 3 is probably lost in the presence of a crown ether.

In summary, the results discussed above do not allow general conclusions concerning the effects of the changes in the base association on the E2 transition state to be drawn. Probably such changes modify the actual structure of the base to a significant extent, making the interpretation of the data very complex. Unfortunately, little information is presently available concerning the actual structure of the effective base in *t*-BuOK–*t*-BuOH in the presence and in the absence of a crown ether.[54]

Dehalogenation Reactions

These reactions closely resemble E2 reactions even though the base now interacts with a halogen and no longer with the proton.[57] Their inclusion in this Account is therefore appropriate.

Substituent effects on the rate of debromination of *meso*-1,2-dibromo-1,2-diphenylethane (eq 1, X = Y =

$$C_6H_5CHXHYC_6H_5 \xrightarrow[\text{solvent}]{\text{base}} C_6H_5CH{=}CHC_6H_5 + XY$$
$$\text{meso or erythro} \qquad\qquad\qquad \text{trans}$$

(1)

Br) promoted by halide ion[58] and triphenylphosphine[59]

Table V
Effect of the R Substituent on Some Dehalogenation Reactions of *erythro*-1,2-Dibromo-1-phenyl-2-(4-substituted-phenyl)ethanes in DMF[58,59]
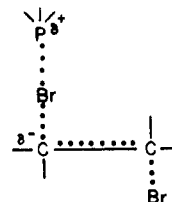
R	temp, °C	nucleophile	$k_R/k_H{}^a$
OCH₃	25	*n*-Bu₄NI	2.7
NO₂			2.2
OCH₃	25	*n*-Bu₄NBr	2.4
NO₂			3.4
OCH₃	59.8	*n*-Bu₄NCl	2.9
NO₂			2.3
OCH₃	50	$(C_6H_5)_3P$	1.5
NO₂			29

[a] Reactivity ratio between the R-substituted compound and *meso*-1,2-dibromo-1,2-diphenylethane.

(Ph₃P) in DMF have been investigated. Some results are reported in Table V.

The first observation is that both electron-withdrawing and electron-releasing substituents increase the reaction rate. With Cl⁻, Br⁻, and I⁻ as bases, the *p*-NO₂ and *p*-OCH₃ groups exert small and comparable effects.[60] The fact that these effects are practically independent of the nature of the halide ions suggests similar transition-state structures (resembling the olefin and with little development of charge at either α- or β-carbon) for the reactions of all three bases.

A different situation, however, arises in the dehalogenations promoted by Ph₃P. In these reactions, the rate enhancement caused by the *p*-NO₂ group is quite substantial, and much larger than that exerted by the *p*-OCH₃ group. Probably the mechanism is no longer synchronous, and a significant amount of negative charge accumulates on the β-carbon in the transition state 13.

13

(54) It is probable that more than one species may act as an eliminating agent in *t*-BuOK–*t*-BuOH. Moreover, the relative reactivity of these species might depend on the nature of the substrate. An indication that this may be the case is the observation that different reactions can exhibit a different rate dependence on the base concentration. Thus, the kinetic order in *t*-BuOK is 1.0 in the eliminations from 2-arylethyl bromides,[49,50] larger than 1.0 in the reactions of 12,[53] and less than 1.0 in 1,4-eliminations from 2,2,7,7-tetramethyl-3,5-octadiyne.[55] An order in base larger than unity is also observed in eliminations promoted by *t*-BuOK in the presence of a crown ether[49,51,53] and in some deprotonations induced by *t*-BuOK.[56]

(55) C. Tarchini, Ph.D. Thesis, Department of Chemistry, University of Lausanne, 1978.
(56) J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, 64, 1271 (1960).
(57) A stepwise mechanism has also been suggested for dehalogenation reactions: C. S. T. Lee, I. M. Mathai, and S. Miller, *J. Am. Chem. Soc.*, 92, 4602 (1970).
(58) E. Baciocchi and A. Schiroli, *J. Chem. Soc. B*, 554 (1969).
(59) S. Alunni, E. Baciocchi, and V. Mancini, *J. Chem. Soc., Perkin Trans. 2*, 140 (1977).
(60) The rate effects observed when two *p*-NO₂ or two *p*-OCH₃ groups or both a *p*-NO₂ and a *p*-OCH₃ group are present[58] make it unlikely that the *p*-NO₂ and *p*-OCH₃ derivatives undergo attack on different bromine atoms.

If this interpretation is correct, the variable transition-state theory seems to be valid also for dehalogenation reactions. With *meso*-1,2-dibromo-1,2-diphenylethane as the substrate, the transition-state structure is central when the nucleophile is a halide ion and shifts toward the E1cb-like side with Ph₃P. It is possible that with the latter base the incipient positive charge on the phosphorus atom in the transition state favors the buildup of negative charge at C_β, thus promoting a transition state with carbanion character.

The factors affecting base reactivity in dehalogenation reactions have been primarily investigated using the reactions of *erythro*-1-chloro-2-iodo-1,2-diphenylethane (eq 1, X = I, Y = Cl).[61] The base attacks the iodine atom in this case, and elimination of ICl takes place. The main conclusion of this study is that polarizability and desolvation energy are by far more important factors than basicity in determinating the reactivity of a base in a dehalogenation process. In particular, the role of polarizability is clearly shown by the reactivity order I⁻ > Br⁻ > Cl⁻ observed in dipolar aprotic solvent in both the reactions of *erythro*-1-chloro-2-iodo-1,2-diphenylethane and *meso*-1,2-dibromo-1,2-diphenylethane.

Concluding Remarks

The above discussion has shown that, despite the fact that quantitative work in this area has started only

recently, some important conclusions regarding the influence of the base on the E2 transition state have been reached. This appears to be particularly true when the effects of basicity are considered. Little doubt now exists that, at least in anti eliminations, the stronger base generally produces a transition state with higher carbanion character. Confirmation of this conclusion in the case of syn eliminations is highly desirable.[62]

Additional work on the effects of base associations appears to be necessary in light of the somewhat contradictory results obtained so far. Moreover, the effects of the steric requirements of the base should be further investigated. Also of great interest would be studies aimed at determining (through α-carbon and leaving group isotope effects) the influence of the base nature on the extent to which the bond between α-carbon and leaving group is weakened in the transition state. Such information would complement that given by ρ and k_H/k_D values, thus allowing a complete picture of the transition-state structure to be obtained.

(61) E. Baciocchi and C. Lillocci, *J. Chem. Soc., Perkin Trans. 2*, 802 (1975).

(62) Unpublished results from this laboratory have however shown that in syn eliminations from 12 promoted by phenoxides in Me₂SO change in base strength does not significantly influence the carbanion character of the transition state.

Stabilization of Oxidized Sulfur Centers in Organic Sulfides. Radical Cations and Odd-Electron Sulfur-Sulfur Bonds
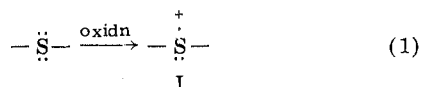
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Organic sulfur compounds, among them sulfides, are known to undergo chemical oxidation reactions fairly readily. This can be related to the relatively low ionization potentials of these molecules which in the gas phase are often found to be considerably below 10 eV. Similar and even lower ionization energies can be expected in the liquid phase. The likely site of oxidative attack is the sulfur atom, from which an electron can be removed with relative ease by suitable oxidants.

What is likely to be the primary result of one-electron oxidation of a sulfide function? Formally the molecular radical cation is expected to be formed (eq 1). Since

$$-\overset{..}{\underset{..}{S}}- \xrightarrow{\text{oxidn}} -\overset{\cdot}{\underset{..}{\overset{+}{S}}}- \qquad (1)$$

$$\text{I}$$

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sulfur bonds usually exhibit a high degree of p character, the two nonbonded electron pairs will not be equivalent; i.e., one of them will have more s, the other more p character. The electron removed in the ionization process (oxidation) is likely on energetic grounds to be one of the nonbonded p electrons. Accordingly the unpaired electron in the radical cation will remain largely in a p orbital.

Radical cations such as I have been shown kinetically and spectroscopically to be intermediates in many oxidation processes of sulfides, and in several cases of heteroaromatic species a positive identification has been possible.[1] Particularly in aprotic solvents, some of

(1) See, for example: (a) K. Kim, S. R. Mani, and H. J. Shine, *J. Org. Chem.*, 40, 3857 (1975); (b) A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 13, 155-278 (1976); (c) H. J. Shine, B. K. Bandlish, S. R. Mani, and A. G. Padilla, *J. Org. Chem.*, 44, 915 (1979); (d) S. Hünig, G. Kieslich, H. Quast, and D. Schentzow, *Justus Liebigs Ann. Chem.*, 310 (1973); (e) K. Deuchert and S. Hünig; *Angew. Chem., Int. Ed. Engl.*, 17, 875 (1978); (f) G. Vincow in "Radical Ions", E. T. Kaiser and L. Kevan, Eds., Interscience, New York, 1968, Chapter 4, pp 190-193.