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TETRAHEDRON REPORT

A REVISED TRANSITION STATE SPECTRUM FOR CONCERTED BIMOLECULAR β-ELIMINATIONS

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Since it was first reported that such weakly basic species as thiolate ions[1] and halide ions in acetone[2] are surprisingly efficacious in promoting second-order elimination reactions (Eqn 1), of secondary and tertiary halides

$$B^- + H—C_\beta—C_\alpha—X \longrightarrow BH + \rangle C{=}C\langle + X^- \qquad (1)$$

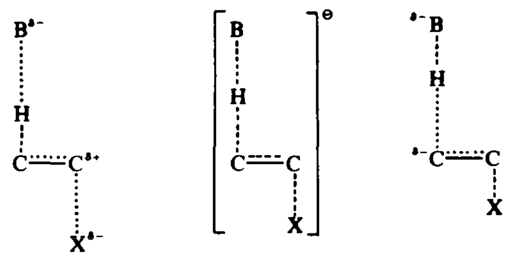
and arenesulfonates, much effort has been expended in ascertaining the general features of such reactions. They are unusual in that, for instance, PhS^- is some ten times more reactive towards t-BuCl in the elimination mode than is OEt^- in EtOH[1] despite the latter's being the stronger base by a factor of about 10^{10}. An even more spectacular example is provided by the observation that $n\text{-}Bu_4NCl$ induces elimination from cyclohexyl tosylate in t-BuOH slightly faster than does t-BuOK, despite the factor of at least 10^{15} in thermodynamic proton basicity favouring the alkoxide.[3] It is clear that the transition states in the eliminations promoted by weak bases (which are also invariably strong C-nucleophiles in S_N2 reactions) are significantly different from those in eliminations involving conventionally strong bases, e.g. OR^-–ROH.

This is perhaps the only general point that various groups of workers active in the field agree on. It is therefore the purpose of this article to examine the proposals that have been made to date and to introduce a new model that seems to accommodate *all* the known experimental patterns. The review of the strengths and weaknesses of current theories will be brief in that Ford has recently presented a more detailed examination covering selected areas.[4]

CURRENT THEORIES

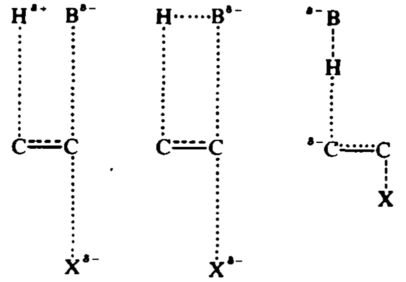
The two most reasonable theoretical models are concerned with transition state spectra, which are shown in Scheme 1.† The Bunnett spectrum[5] is characterized by attack of B^- only on the β-bound proton and will accordingly be labelled *E*2H. The transition state utilized in a particular reaction system is governed by a number of energetic factors, and changes in molecular variable have a predictable effect. For instance, introduction of acidifying electron-withdrawing groups at C_β should shift transition state character to the right, and electron donors at C_α should give a leftwards shift. It is contended that an increase in base strength (in the thermodynamic sense) will result in a rightward shift.[5b] There is little doubt that the transition state will have a greater degree of negative charge on C_β,[6,7] but whether the proton is more completely removed and the base more fully protonated is another matter, depending on whether the steric requirements of the base are also changed.[8]

(*A*) *Bunnett Variable E2H Transition State Spectrum*



(1) paenecarbonium (*E*1-like) | (2) paeneolefinic (central) | (3) paenecarbanion (*E*1cB-like)

(*B*) *Winstein-Parker E2C-E2H Spectrum*



(4) *E*2C | (5) *E*2C-like | (6) *E*2H-like

Scheme 1.

Parker *et al.* favour a spectrum having regions where partial B . . . C_α loose covalent interaction is important (*E*2C and *E*2C-like) and contend that these merge into the Bunnett spectrum near the paenecarbanion region as the base becomes stronger, the substrate acidity increases, or as the leaving group becomes poorer.[3,9-13] Variation in substrate acidity, leaving group ability, etc. are thus predicted to give shifts in the same direction as in the Bunnett spectrum. There is the exception that a change from a strong base to a weak base *which is also a strong C-nucleophile* is held to shift transition state character to the left. The similarity of the *E*2C transition states to S_N2 transition states with respect to the binding of the base to C_α is clear, but the *E*2C–S_N2 analogy should not be pressed much further than this.[13]

There is thus substantial agreement between the

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†In these and following transition state structures, dashed lines represent reasonably strong partial bonds whilst dotted lines depict weak partial bonds.

Bunnett and Parker-Winstein views as far as strong bases reacting with reasonably acidic substrates are concerned, but wide divergence is apparent when the reactions of weak bases with unactivated substrates having a good leaving group bonded to secondary or tertiary C_α† are considered.[4,15,16] Attention will thus necessarily focus on the contentious left hand sides of the $E2$ spectra.

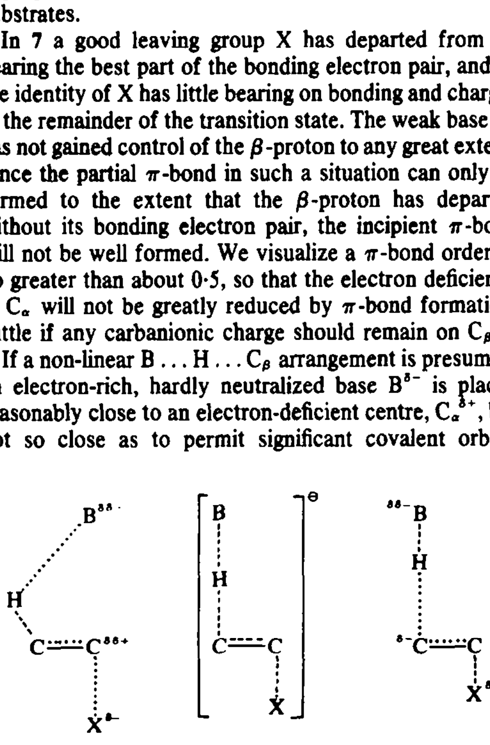
While each of the divergent theories is separately able to accommodate most of the experimental facts accumulated to date, each also exhibits one or more serious deficiencies in explaining isolated results, as Ford has shown.[4] We now attempt to reconcile *all* the factual patterns with a partly new transition state pattern.

THE REVISED SPECTRUM

The spectrum of transition states that we offer for consideration is shown in Scheme 2. The changes in molecular variables already mentioned will occasion shifts in one direction or the other. The $E2$H transition states (2 and 3) have already been discussed so we shall describe in detail the novel species (7) which is deemed appropriate for the reactions of weak bases with loose substrates.

In 7 a good leaving group X has departed from C_α bearing the best part of the bonding electron pair, and so the identity of X has little bearing on bonding and charges in the remainder of the transition state. The weak base B^- has not gained control of the β-proton to any great extent. Since the partial π-bond in such a situation can only be formed to the extent that the β-proton has departed without its bonding electron pair, the incipient π-bond will not be well formed. We visualize a π-bond order of no greater than about 0·5, so that the electron deficiency at C_α will not be greatly reduced by π-bond formation. Little if any carbanionic charge should remain on C_β.

If a non-linear $B \ldots H \ldots C_\beta$ arrangement is presumed, an electron-rich, hardly neutralized base $B^{\delta-}$ is placed reasonably close to an electron-deficient centre, $C_\alpha^{\delta+}$, but not so close as to permit significant covalent orbital overlap. The interaction between the two centres will thus be primarily electrostatic.‡ It will be effective at greater internuclear separations than will an essentially covalent interaction. Most importantly, it will have the effect of further reducing the magnitude of the partial positive charge at C_α *as felt by a substituent bonded to* C_α for the reason that the substituent must interact with a $B^{\delta-} \ldots C_\alpha^{\delta+}$ dipole rather than with the $C_\alpha^{\delta+}$ pole which would exist in the absence of the base. Thus we use double deltas to indicate the charges on B and C_α even though the electrostatic interaction does not reduce the magnitude of the charges in the absolute sense. Note that the base must be anionic for such stabilization to occur. We will return to this point. The energy loss concomitant upon the formation of an unstable non-linear proton transfer arrangement may conceivably be compensated by the stabilizing electrostatic interaction.



(7) (2) (3)

Electron withdrawal at C_β[6] ⟶
Electron donation at C_α ⟵
Changing to poorer leaving group ⟶
Changing to more electronegative leaving group ⟶
Changing C_α from 1° to 2° or 3° ⟵
Increase in base strength[6,8] ⟶

Scheme 2.

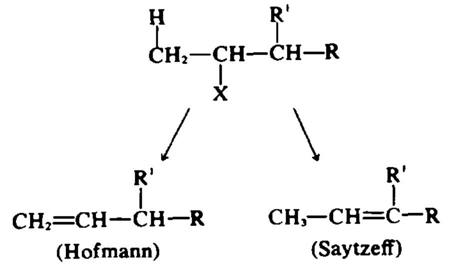
We suggest that the symbol $E2$C be retained to refer to 7. While the $B \ldots C_\alpha$ interaction is quite different from that in the Parker-Winstein $E2$C transition states (and the $H \ldots C_\beta$ and π-bond orders are also different) it is a necessary and important structural feature. To avoid confusion however, it will simply be called 7 in the present paper. We view it as a compromise between the paenecarbonium extreme in the Bunnett spectrum§ and the $E2$C extreme of the Parker-Winstein spectrum, retaining the best features of both. It is re-emphasized that 7 is not the only model that can satisfactorily explain patterns of results in any one of the following factual areas that we explore. Its superiority over previously suggested species lies in its ability to accommodate all the facts.

EXPERIMENTAL OBSERVATIONS AND JUSTIFICATION

Positional orientation.[19] Orientation of the double bond in olefins resulting from the reactions of weak bases with loose substrates is predominantly Saytzeff (formation of more stable olefin, see Scheme 3) and is more so than in the corresponding strong base eliminations.[9–14,20–22] Winstein has stated that the former "are some of the cleanest eliminations that are known to man".[13b]

For instance, $MeCH_2CH(OTs)CHMe_2$ yields 92·5% $MeCH_2CH = CMe_2$ on reaction with $n\text{-}Bu_4NCl$ in acetone, but only 51·1% of this olefin on reaction with t-BuOK–t-BuOH.[21] This can be partly understood in terms of the greater stability of the above olefin over that of the Hofmann product $MeCH = CHCHMe_2$. While transition state 7 is not distinctly olefin-like, the π-bond must be sufficiently well formed to be non-negligible. The t-BuOK–t-BuOH reaction should proceed through a transition state somewhere between 2 and 3 in Scheme 2.

The sceptic may very well protest that the less than half-formed π-bond in 7 is not sufficient to cause such a



Scheme 3.

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† Such substrates will henceforth be termed "loose" although it is to be understood that the transition states arising from them are the loose species in that the base and the leaving group are but loosely bonded to the remainder of the transition state.

‡ An example of this type of transition state interaction has recently been given in another context.[17]

§ It has recently been claimed that sound experimental evidence for (1) is lacking.[18]

predominance of Saytzeff product. The highly olefin-like $E2C$ transition states (4 and 5) run into some credibility problems here too, in that Saytzeff:Hofmann product ratios are sometimes much *greater* than the thermodynamically-controlled equilibrium ratios.[10,21] Thus a factor, of importance only in the transition state, other than the attenuated effect of olefin stability, must be stabilizing the Saytzeff transition state relative to the Hofmann transition state.

We suggest that the size and degree of branching of the R and R^1 groups (Scheme 3) is that factor. It may control orientation in two ways. Firstly, the more bulky or more highly branched is R, the more will initial state Me–R repulsive interactions be relieved in the Saytzeff transition state (for *cis*-destined groups) as hybridization changes from sp^3 to sp^2 (primarily at C_α) in the transition state.[10] Secondly, if the base is in the vicinity of C_α in the Hofmann transition state, as it is in 4, 5 or 7, its presence will hinder free rotation of R and so raise the energy of that transition state. This type of effect has been demonstrated in another context.[23] A combination of all the above factors is clearly important in controlling orientation. Unfortunately, dissected rate and product data with which to check the hypothesis that increased bulk or ramification of R increases the rate of Saytzeff elimination *and* decreases that of Hofmann elimination in weak base reactions are not available. The desired trend in product ratios is, however, illustrated in Table 1. It would also be interesting to compare weak base trends with those for reactions carried out under $E2H$ conditions (strong bases) but unfortunately the latter are bedevilled by competing *anti*- and *syn*-pathways, and α-bound groups are thought to partly control the stereochemical preference.[24] However, 2-butyl bromide eliminates exclusively *anti* (in the Saytzeff mode) under $E2H$ conditions[25] and if it is assumed that the Hofmann pathway is the same, and that 2-pentyl bromide behaves similarly, it would be expected that the change of R from Me to Et in $CH_3CH(Br)CH_2R$ would have little effect on the rate of formation of Hofmann olefin with strong base, since the base will be far from C_α and R. Such is the case.[26]

A corollary of Saytzeff orientation is that β-bound alkyl groups accelerate elimination rates over β-bound hydrogens because of their hyperconjugative ability and for the relief of steric compression reason given above.[10] However, the less than half-formed π-bond in 7 may not be sufficiently strong for the invocation of hyperconjugative stabilization. An alternative explanation is at hand, however. It is well known that α-alkyl groups stabilize carbonium ions, but it is less well appreciated that β-alkyls exhibit the same, although attenuated, characteristic. For instance, the gas phase heat of formation of $Me_2CHCH_2^+$ is 35 kcal mol^{-1} less than that of $CH_3CH_2^+$,[27] and $MeCH_2\overset{+}{C}Me_2$ is 8 kcal mol^{-1} more stable than Me_3C^+.[28] Transition state 7 has a degree of electron deficiency at C_α and it is reasonable to suppose that this assists in allowing the Saytzeff rate pattern.

Geometric orientation.[19] When geometric (*trans-cis*) isomers of an olefinic product are possible (Scheme 4) the general pattern is that the *trans*:*cis* ratio is higher for weak base induced eliminations than for reactions promoted by the strong $E2H$ base t-BuOK–t-BuOH.[10–14,20–22] If high values of this are taken as indices of a high degree of π-bond formation in the transition state then 7 fails the test.

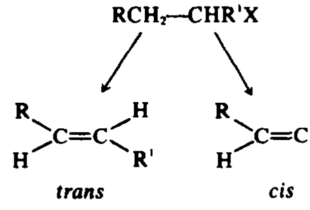
However, it now appears that *trans*:*cis* ratios in reactions promoted by t-BuOK–t-BuOH are *anomalously low* as a result of association of the base with its counter-ion in the low polarity solvent.[29] It is thus safe to state that as long as base association is taken into account, the isomer ratio from a given substrate is largely insensitive to base strength,[23a,30] and we note for instance, that the reactions of 2-butyl halides with both NaOMe in MeOH and LiCl in DMF (largely dissociated bases) yield *trans*- and *cis*-2-butenes in almost the same proportions.[22]

Stereochemistry. The stereochemical course of weak base induced eliminations is almost exclusively *anti*,[3,9,25,31] even to the point of overcoming the strong Saytzeff preference as is shown by the system in Scheme 5.[3,31] The *anti* preference in $E2$ reactions of strong bases with acidic substrates is not as strong as was previously

Table 1. Effects of non-reacting groups on Saytzeff:Hofmann ratios from secondary substrates

Substrate	R[a]	Base/Solvent	Saytzeff[b] / Hofmann
2-propyl bromide	H	$n\text{-}Bu_4NBr/Me_2CO$	0[c,d]
2-butyl bromide	Me	$n\text{-}Bu_4NBr/Me_2CO$	20[c]
1-phenyl-2-propyl bromide	Ph	$n\text{-}Bu_4NBr/Me_2CO$	185[c]
2-butyl bromide	Me	$n\text{-}Bu_4NBr/Me_2CO$	20[c]
2,3-dibromobutane	Br	$n\text{-}Bu_4NCl/Me_2CO$	Very large[c,e]
2-butyl bromide	Me	$n\text{-}Bu_4NBr/Me_2CO$	20[c]
2-pentyl bromide	Et	$n\text{-}Bu_4NBr/Me_2CO$	40[f]
2-bromo-4-methyl pentane	i-Pr	$n\text{-}Bu_4NBr/Me_2CO$	45[f]
2-butyl bromide	Me	Et_4NF/Me_2CO	6·9[f]
2-pentyl bromide	Et	Et_4NF/Me_2CO	6·9[f]
2-bromo-4-methyl pentane	i-Pr	Et_4NF/Me_2CO	7·6[f]
2-butyl bromide	Me	t-BuOK/t-BuOH	0·79[f,g]
2-pentyl bromide	Et	t-BuOK/t-BuOH	0·27[f,g]
2-bromo-4-methyl pentane	i-Pr	t-BuOK/t-BuOH	0·042[f,g]

[a] See Scheme 3; $R^1 = H$ in all cases. No tertiary substrates are considered because of the possibility that larger than usual steric strains between R, R^1 and the alkyl groups on C_α are being relieved as C_α changes from sp^3 to near sp^2. [b] Formation of *trans*-olefin in the Saytzeff mode is considered. The restricted rotation effect diminishes production of *cis*-olefin (Ref. 23b). [c] Ref. 10. [d] No Saytzeff olefin possible. [e] No Hofmann olefin detected. [f] Ref. 95. [g] Quoted to illustrate the opposite trend observed in strong base eliminations. A similar situation obtains for EtOK in EtOH (Ref. 95).



Scheme 4.

thought[32] but it does appear to be a strict requirement for weak base eliminations. The Parker-Winstein explanation in terms of transition states 4 and 5 is that the preference is a consequence of the S_N2 rule demanding inversion of configuration at C_α in these S_N2-like transition states.[3,10,13] Transition state 7 also accounts nicely for the preference in that a *syn*-form would place $B^{\delta\delta-}$ and $X^{\delta-}$ in uncomfortable juxtaposition. But the Parker-Winstein rationale is at odds with the formation of 9% of a non-solvolytic[31] product via a *syn*-pathway in a chloride-induced reaction (Scheme 5). However, 7 allows an explanation in that the lack of consequential covalent bonding between B and C_α permits a relaxation of the requirement for S_N2-like inversion. A *syn*-pathway involving 7 is conceivable if, as in strong base $E2H$ reactions,[33] the anionic base is significantly associated with its counter ion as an ion-pair. We have found, however, that the *anti*:*syn* ratio for reaction of *trans*-2-phenylcyclopentyl brosylate with LiCl in Me_2CO is the same as when the less associated n-Bu_4NCl is used, but kinetic analysis reveals that the lithium chloride ion-pair is completely unreactive and the stereochemistry is thus unaffected.[34]

Leaving group effects. Element effects, e.g. k_{Br}/k_{Cl}, are large in the reactions of interest, implying that the $C_\alpha \ldots X$ bond is well-severed at the transition state.[3,9,10,16,35,36] Note that the extremely high k_{Br}/k_{Cl} ratios (*ca.* 10^3) often encountered with reactions in dipolar aprotic solvents† are most likely a consequence of a solvent effect, in that such solvents differentiate leaving group mobilities.[37] Protic solvents capable of H-bond donation will have a levelling tendency but a clear distinction between the strong and the weak base situations can be seen in Table 2. As α-hydrogen in the cyclohexanes is replaced by an acidifying (and non-reacting) α-halogen, the k_{Br}/k_{Cl} ratios for both bases fall as transition state character shifts, probably from 7 towards 2 when PhS^- is the base and from 2 to 3 for OEt^-.

Table 2. Bromide:chloride leaving group rate ratios in the dehydrohalogenation of cyclohexyl halides in ethanol at 55°

Substrate	Base	k_{Br}/k_{Cl}[a]
Halocyclohexane	OEt^-	66
Halocyclohexane	PhS^-	140
1,1-Dihalocyclohexane	OEt^-	17
1,1-Dihalocyclohexane	PhS^-	50

[a] Results from Ref. 35.

Reactivity ratios of tosylates and bromides have been interpreted in terms of $E2C$ transition states 4 and 5.[3,38,39] However, an ambiguity in the use of k_{OTs}/k_{Br} as an index of transition state character in β-eliminations has been noted by Cockerill,[40,41] and it now seems clear that a high value of this ratio is indicative of either a well-cleaved or a nearly intact $C_\alpha \ldots X$ bond. Results confirming this view, and which may be equally well interpreted in terms of the spectrum in Scheme 2, have been presented by Lloyd and Parker.[3,39]

Disposition of charges. The magnitude of rate changes induced by changing the medium from a protic to a dipolar aprotic solvent requires that most of the charge originally on B^- in the initial state be localized on B and X in the transition states of loose substrate-weak base eliminations.[20,42–44] It is likewise considered that such transition states are looser than those for the corresponding S_N2 and $E2H$ reactions.[14] Transition state 7 fits into this pattern.

Note that the general rule of acceleration of anion-molecule reactions on transfer from protic to dipolar aprotic solvents is not followed by the reaction of cyclohexyl tosylate with p-nitrothiophenoxide in DMF and MeOH.[3] This attests to the fact that, because of transition state charge localization on B and X, the $E2C$ transition state is a good H-bond acceptor. The rates of concurrent S_N2 reactions of loose substrates respond to solvent change in much the same way as do the elimination rates.[3,4,41–43] This is understandable if the S_N2 transition states are also loose: ${}^{\delta-}B \ldots {}^{\delta\delta+}R \ldots X^{\delta-}$.

Hydrogen isotope effects.[45,46] Primary β-effects are generally low in weak base-loose substrate eliminations,[11,36,47–50] and are significantly smaller than the theoretical maximum (k_H/k_D *ca* 7 at 25°) for proton transfers through a linear symmetrical $B \ldots H \ldots C_\alpha$ arrangement.[51] Both the less than half-transferred proton[51] and the non-linear structure of 7[52] are predicted to lower isotope effects. As the strength of bases reacting with a given loose substrate is increased, k_H/k_D should increase as transition state structure approaches 2, and should again decrease as further increases in basicity engender an approach to 3. A similar variation in k_H/k_D is expected if the acidity of a substrate reacting with a given base is increased by electron withdrawal from C_β or by introducing a poorer and more electronegative leaving group.

Such expectations have been beautifully realised by

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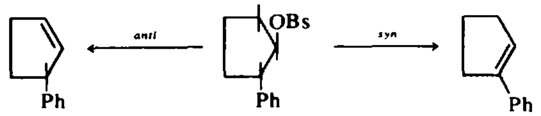
†For a reassessment of k_{Br}/k_{Cl} as an index of transition state character, see R. Bird and C. J. M. Stirling, *J. Chem. Soc.* Perkin II, 1221 (1973).



t-BuOK—t-BuOH	15·1%	84·9%
PhOK—t-BuOH	34·4%	65·6%
n-Bu_4NOAc—t-BuOH	84·7%	15·3%
n-Bu_4NOAc—Me_2CO	99·2%	0·8%
n-Bu_4NCl—Me_2CO	91%	9%

Scheme 5.

Parker *et al.* (Table 3).[50] If any doubts remain as to the very existence of *E*2 transition state spectra, they should be dispelled by these results. In Table 4 are shown other isotope effects for halide-induced eliminations, and the same pattern may be discerned. The Ar_2CHCCl_3 system is of interest in that the assignment, via the large isotope effect, of an *E*2H-like transition state,[53] is supported by the substantial Hammett ρ value (0·99).[54]

The aforementioned low isotope effects may be taken as evidence against the involvement of paeneolefinic *E*2H transition states (2) in the reactions in question, since near-maximal isotope effects would be expected. There is a proviso that k_H/k_D is predicted to decrease if, in a system having a half-transferred proton, the proton transfer is coupled to an increasing extent with other atomic motions such as π-bond formation.[55] Were a late variety of 2 to be postulated, the base must retain a goodly proportion of its original negative charge (previous section) and the proton must exist under comparatively little total bonding. As it is therefore unlikely that its motions will be strongly coupled to other events, the proviso should not apply.

Parker's group has also measured secondary hydrogen isotope effects for reactions of cyclohexyl tosylate and bromide.[56] Secondary α-effects are of the order of 15% in the elimination mode, pointing to substantial rehybridization of C_α in the transition state. However, the α-isotope effect for the competing S_N2 reaction of OAc^- in Me_2CO is only 2%. The point that an *E*2C transition state is looser than the corresponding S_N2 transition state is again illustrated. Transition state 7 has a looser $B \ldots C_\alpha$ interaction than is postulated for 4 or 5, where the interaction must be S_N2-like to some extent, and so appears to be the better model for rationalizing these results. Other secondary rehybridization and hyperconjugative isotope effects connected with hydrogens bonded to the reactive and non-reactive β-carbons are large, but lead to no distinction.[56] Of interest in this regard is the fact that the reaction induced by t-BuOK in t-BuOH also exhibits large secondary β-effects. The transition state might thus still be far from the paenecarbanion extreme 3.

β-Substituent effects. The effects of β-alkyl groups have been discussed in the section on positional orientation. Rates of loose substrate-weak base eliminations are far less sensitive to the electronic demands of β-bound substituents than they are in the corresponding strong base reactions.[10,36,39,54,57–59] Hammett ρ values for

Table 3. Primary hydrogen-deuterium isotope effects[a] on rates of elimination from cyclohexyl derivatives at 75° in acetone[b]

Base	Substrate: $1,2\text{-}C_6H_{10}CN(Br)$[d,e]	$1,2\text{-}C_6H_{10}Br_2$[d]	$C_6H_{11}Br$	$C_6H_{11}OT_s$
OPh^-	2·1	6·0	4·0	2·7
OAc^-	3·7	5·8	3·9	2·4
ArS^-[c]	6·2	5·1	3·5	2·4
Cl^-	6·0	4·9	3·2	2·3
Br^-	3·5	3·8	—	2·2

[a] For *anti*-elimination of HX or DX. [b] In terms of base strength and substrate acidity, the top left corner of the Table represents the *E*2H extreme and the lower right corner represents the *E*2C extreme. [c] Ar = $p\text{-}NO_2C_6H_4$. [d] *cis*-isomers. [e] Dehydrobromination.

Table 4. Primary hydrogen isotope effects in halide-induced eliminations

Substrate	Base-Solvent	Temp.(°C)	k_H/k_D	Ref.
$Me_2CHCH(OTs)CH_3$	$n\text{-}Bu_4NCl\text{-}Me_2CO$	75·0	2·3[a]	11
trans-2-methylcyclohexyl tosylate	$n\text{-}Bu_4NCl\text{-}Me_2CO$	75·0	2·7[b]	11
cis-2-methylcyclohexyl tosylate	$n\text{-}Bu_4NCl\text{-}Me_2CO$	50·0	3·0[c]	11
trans-4-t-butylcyclohexyl tosylate	$n\text{-}Bu_4NCl\text{-}Me_2CO$	75·0	3·2	11
2-benzyl-2-bromo-indan-1-one	$Et_4NBr\text{-}MeCN$	59·8	3·4[d]	36
2-benzyl-2-bromo-indan-1-one	$Et_4NBr\text{-}MeCN$	74·8	3·3[d]	36
2-benzyl-2-bromo-indan-1-one	$Et_4NBr\text{-}MeCN$	89·8	2·8[d]	36
2-benzyl-2-bromo-indan-1-one	$Et_4NBr\text{-}MeCN$	100·8	3·0[d]	36
2-benzyl-2-bromo-3,3-dimethylindan-1-one	$Et_4NBr\text{-}MeCN$	74·0	2·5	47
2-benzyl-2-bromo-3,3-dimethylindan-1-one	$Et_4NBr\text{-}MeCN$	89·9	2·3	47
2-benzyl-2-bromo-3,3-dimethylindan-1-one	$Et_4NBr\text{-}MeCN$	98·3	2·0	47
t-BuCl	$Et_4NCl\text{-}MeCN$	45·0	3·81	48
$PhCH_2CH_2Br$	$Et_4NF\text{-}MeCN$	5·0	5·03	61(a)
$PhCH_2CH_2Cl$	$Et_4NF\text{-}MeCN$	25·0	4·38	61(a)
$PhCH_2CH_2Cl$	$Et_4NF\text{-}MeCN$	35·0	3·99	61(a)
$(p\text{-}MeOC_6H_4)_2CHCCl_3$	LiCl-DMF	65·0	5·2	53
Ph_2CHCCl_3	LiCl-DMF	65·0	4·3	53
$(p\text{-}ClC_6H_4)_2CHCCl_3$	LiCl-DMF	65·0	5·6	53
$(p\text{-}NO_2C_6H_4)_2CHCCl_3$	LiCl-DMF	65·0	5·3	53
Ph_2CHCCl_3	LiBr-DMF	65·0	5·0	53
$(p\text{-}ClC_6H_4)_2CHCCl_3$	LiBr-DMF	65·0	5·2	53

[a] Formation of 2-methylbut-2-ene. [b] Formation of 3-methylcyclohexene. [c] Formation of 1-methylcyclohexene. [d] Formation of exocyclic olefin.

β-bound aryl groups are around 0·5.† Transition state **7** satisfactorily allows rationalization of these observations, as do **4** and **5**. A moderate increase in substrate acidity should not affect the rate of a weak base induced reaction to any great extent, since a **7**→**2** shift is predicted, and C_β in **2** is not particularly carbanionic either. When n-Bu_4NCl in acetone is the base, $MeO_2CCH(Br)CH(Br)CH_3$ is only 2·6 times more reactive than $Me_2CHCH(Br)CH_3$. But when the stronger base n-Bu_4NOAc is employed, the former is $1{\cdot}5\times10^8$ times more reactive, indicating that a stronger base induces a shift towards **3**, where the β-bound carbomethoxy and bromine are at an advantage.[10,58] A comparatively large β-effect for the dehydrochlorination of Ar_2CHCCl_3 compounds by LiCl in DMF and n-Bu_4NCl in acetone is observed.[54] These are highly acidic substrates[60] and have leaving groups in poor environments for departure, so **3** is again the transition state of choice. Two other similar examples are available.[61]

A puzzling result in terms of the highly olefinic transition states (**4** and **5**) is the lack of β-phenyl over β-methyl acceleration in eliminations induced by weak bases.[3,10,21] Transition state **7** accounts nicely for this, however, in that it lacks a strong π-bond. β-Phenyl vs β-methyl accelerations are large when tighter substrates (primary C_α) and/or stronger bases are used[10,62] for here transition states tending towards **3** can be utilized, with delocalization of the partial carbanionic charge. Even accelerations by β-phenyl vs β-hydrogen are comparatively small in some of the reactions of interest,[16,49] which on both steric and electronic grounds is incompatible with near sp^2 hybridization of C_β as is postulated for **4** and **5**. However, in several systems, large β-bound groups markedly accelerate halide-induced eliminations irrespective of the electronic requirements of these substituents. Changing R from H to Me in RR'CHCH(OTs)Me (R' = H) accelerates the rate of production of Saytzeff olefin 200-fold when the base is Bu_4NBr in acetone but only 1·2-fold under *E*2H conditions ($OEt^- - EtOH$).[10] The compound having R,R' = Me is only four times less reactive than that with R = Br, R' = CO_2Me (which in turn is $2{\cdot}5\times10^4$ times more reactive than the R,R' = H substrate) under the above *E*2C conditions, but the latter activated substrate is more reactive by a factor of $1{\cdot}7\times10^7$ when the stronger base OAc^- in acetone is employed.[10] It is suggested that the relief of steric interactions between the R and R' groups (van der Waals and dipole-dipole repulsions) attendent on a change in the hybridization of the largely uncharged C_β from initial state sp^3 to near sp^2 in the transition state in the *E*2C-like processes is the controlling factor.[10] In the eliminations induced by strong bases, this steric effect may oppose an electronic effect associated with the more carbanionic C_β as in the substituent change H→Me, or reinforce it, as with Me, Me→Br, CO_2Me. The large secondary β-hydrogen isotope effects in *E*2C reactions of cyclohexyl tosylate (see earlier) also point to substantial rehybridization of C_β.[56] If this is so, the β-carbon of (**7**) must be significantly rehybridized, and this is not necessarily incompatible with a poorly-formed π-bond and a not well-transferred proton, since the proton may be partly bound to C_β by an orbital having some *p*-character. The rehybridization may be a factor in the system's attaining the transition state energy level. On the other hand, simple "molecular mechanics" calculations that we have performed[59] indicate that for the transformation-$CYCl(sp^3)\rightarrow$-$CYCl(sp^2)$, the steric consequences of changing Y from H to Cl are negligible, in that relief of repulsive interactions associated with the larger atom are almost balanced by a decrease in the magnitude of attractive dispersion forces. Chlorine is admittedly probably smaller than methyl and so the theoretical result may not be directly relevant. We note that Winstein, Parker, and their coworkers have remarked on the possible consequences of substituents' attractive dispersion interactions in a slightly different context.[3]

Preliminary results show that the Hammett ρ for formation of $ArCH{=}CMe_2$ from $ArCH_2CMe_2Cl$ compounds using EtS^- in MeOH is low and negative (*ca.* −0·4) for electron-releasing groups,[63] which points to electron-deficient C_α. When electron-withdrawing groups are present on the ring, ρ is positive,[63] and this suggests that a substituent-induced transition state shift is being observed. These results allow **1**→**2** or **7**→**2** changes in transition state character to be considered, but **4** or **5** do not seem to be able to account for these results in that their α-carbons bear little or no charge. The OMe^-–MeOH induced eliminations from the same substrates yield a constant ρ value of 1·0, which in turn suggests that transition state character has been shifted towards **3** by the agency of the stronger base.[64]

α-Substituent effects. Transition state **7** has a degree of electron deficiency at C_α, but from the point of view of substituents bonded to C_α, the partial positive charge is not as great as would be expected in a transition state leading to a carbonium ion, as in S_N1 solvolysis, or for that matter in the *E*2 paenecarbonium transition state **1**. Thus small but significant α-effects of electronic origin should be exhibited by reactions proceeding via **7**, whereas they are not expected if **4** or **5** are involved.

Comparison of the dehydrobromination rate constants of *p*-$MeC_6H_4CH(Br)CH_2CH_3$ and $PhCH(Br)CH_2CH_3$ (*n*-Bu_4NCl in acetone)[65] leads to the not insubstantial Hammett ρ constants of −2·7 (σ scale) or −1·5 (σ^+ scale), which are diagnostic of a reasonably positive C_α. On the other hand, when $PhCH(Br)CH_2CH_3$ and *p*-$NO_2C_6H_4CH(Br)CH_2CH_3$ are compared under the same conditions[65] the insignificant ρ value of −0·28 may be derived. Again these results are most logically interpreted in terms of a substituent-induced transition state shift, from **7** towards **2** (where insignificant electronic α-effects are expected), occurring as the electron demanding power of the substituent is increased. A similar situation may prevail for the reactions of $ArCH(Br)CH_3$ compounds with OEt^-–EtOH, where curved Hammett plots are again observed.[66]

A cautionary note is appropriate here. Strong bases in protic solvents *may* give rise to *E*2C-like transition states if substrate structure and solvent polarity are such that a well-broken $C_\alpha \ldots X$ bond at the transition state may be supported, along with poor support for $C_\beta \ldots H$ rupture. Conversely, the use of weakly basic halide or mercaptide reagents does not guarantee the involvement of an *E*2C-like transition state if the substrate is highly acidic and has a poor leaving group in an unfavourable

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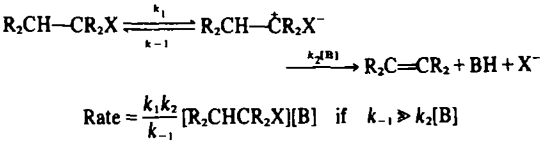
†The effect of *para*-substituents in the Ar ring on the reactivities of $ArCH(Me)CH_2OSO_2Ar'$ compounds (CN^- in DMF) are vastly different in the S_N2 (U-shaped Hammett plot) and *E*2 (linear Hammett plot, $\rho = 0{\cdot}82$) modes. Thus the base is not similarly attached in the respective transition states. However, Ar' substituent effects in S_N2 and *E*2 are similar, suggesting that the leaving group has departed to about the same extent in both transition states. A. Loupy, D.Sc. Thesis, Université de Paris-Sud (1975).

environment for departure. Naturally, this base-substrate combination is kinetically unsuitable,[54,59,61] and unless structural features which disfavour competition by S_N2 reactions are present, the elimination reaction may not proceed at all.

Hammett ρ values for S_N2 reactions of benzylic halides with anionic nucleophiles in solvents of low polarity are positive for groups in the σ range from H to p-NO$_2$.[67] Thus the S_N2 $B\ldots C_\alpha$ interaction must be much different from that in loose elimination transition states.

In halide-induced eliminations from loose substrates, phenyl groups have a larger accelerating effect relative to methyl when both are bonded to C_α rather than to C_β. Values of k_{Ph}/k_{Me} are in the range 17–26 for α-bound substituents, but are only 1·2–3·2 for substituents on C_β.[10] This is difficult to understand in terms of any of **2**, **4** or **5**, all of which have C_α and C_β almost equivalent as far as charge (or rather the lack of it) is concerned. However, **7** explains the results nicely since the two carbons are not equivalent.

The smallness of α-effects in $E2C$ situations relative to those in solvolysis can be used as evidence against the intermediacy of discrete ion-pairs, which are attacked by base in a rate-limiting step (Scheme 6).[68] If such an ion-pair is a high energy intermediate relative to reactants and products we would expect a typically large α-substituent effect on k_1/k_{-1} as in S_N1 solyolysis. But since the transition state for the second rate-limiting step should resemble the ion-pair (Hammond postulate), the substituent effect on k_2 should be small. Thus the overall substituent effect on the observed second-order rate constant should be only a little less than that observed in solvolysis, but this is not so.



$$R_2CH{-}CR_2X \underset{k-1}{\overset{k_1}{\rightleftharpoons}} R_2CH{-}\overset{+}{C}R_2X^- \xrightarrow{k_2[B]} R_2C{=}CR_2 + BH + X^-$$

$$\text{Rate} = \frac{k_1k_2}{k_{-1}}[R_2CHCR_2X][B] \quad \text{if} \quad k_{-1} \gg k_2[B]$$

Scheme 6.

An argument to the effect that the electron deficiency at C_α in these postulated ion-pairs is diminished by a degree of covalent overlap with orbitals of X^- has been advanced.[69] In the limit of *reductio ad absurdum*, such arguments could be used to label as an ion-pair any species with a polarized bond,[70] whether it rested in a potential well or existed momentarily at the top of a potential barrier. It is our view that the very practice of ascribing non-ionic character to purported ion-pairs actually provides a strong case for viewing them as highly polarized *transition states*. Nonetheless an ion-pair mechanism has recently been assigned to a relatively rapid thiolate-induced dehydrobromination on little more grounds than that the reactivity of the base was inappropriate for a concerted mechanism.[71] This point will be rebutted in the following section. There can certainly be no objection to the designation of species such as **7** as "ion-pair like" (or more accurately, ion-triplet like) but definitive evidence must be available before the *intermediacy* of ion-pairs can be supported.

If in Scheme 6, $k_{-1} \approx k_2[B]$, a characteristic borderline region between second-order ($k_{-1} \gg k_2[B]$) and first-order ($k_{-1} \ll k_2[B]$) can be envisaged, and if sustained, can provide positive kinetic evidence for the intervention of intermediates.[69] Such a claim has been made with respect to the dehydrobromination of PhCH(Br)CH$_3$ by NaOEt–EtOH.[72] However, an alternative method of data treatment which takes into account the dissociation of sodium ethoxide ion-pairs enables the data to be interpreted in terms of second-order

$$Na^+OEt^- \rightleftharpoons Na^+ + OEt^-$$

kinetics.[73] Furthermore, the addition of an excess of NaClO$_4$, which has the effect of rendering the degree of dissociation of Na$^+$OEt$^-$ independent of stoichiometric NaOEt concentration, makes the kinetics unambiguously second-order. Thus the mechanism is either the $k_{-1} \gg k_2[B]$ variant of Scheme 6 or is a concerted process. The borderline formulation remains to be unambiguously demonstrated. Other cogent objections to ion-pair mechanisms have been given.[5b,74]

Reactivity of strong C-*nucleophiles in elimination*. The most important question that a mechanistic model must answer concerns the high reactivity of the reagents, which are weakly basic but also strongly nucleophilic towards saturated carbon in S_N2 reactions. Thiolate and halide ions are two distinct species within this category. Firstly we dispel two possible delusions.

Differential anion solvation is not primarily responsible for the RS$^-$ > RO$^-$ reactivity order, since it persists in dipolar aprotic solvents[3,10] where in fact the polarizable thiolate ions may be more strongly solvated. Secondly, halide ions in dipolar aprotic solvents (and indeed in t-BuOH[75]) are measurably basic[76] and not completely non-basic as they are in water, with the exception of F$^-$.

The first suggested solution to the problem was the merged mechanism of Winstein *et al.*[2] It was proposed that a normal S_N2 transition state (or even a pentacovalent intermediate!) is partitioned to give substitution and elimination products, with the leaving group abstracting a β-bound proton in the elimination mode, which must then necessarily be *syn*. Stereochemical studies and an ingenious experiment involving the chloride ion induced dehydrochlorinations of menthyl and neomenthyl chlorides quickly led Winstein to reject this model.[9,13b] In any case, the idea of a single transition state being common to two distinct products runs counter to symmetry considerations.[77]

The $E2C$ model of Winstein and Parker provided a considerable advance. Elimination and substitution transition states are now distinctly different species, but **4** and **5** retain the S_N2 characteristic of a partly covalent S_N2-like linkage between the base and C_α so as to account for the formers' high reactivity. But arguments presented here and elsewhere[4] suggest that modification is required.

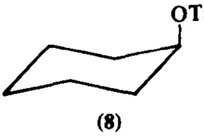
At one time we believed that paenecarbonium transition states (**1**) were implicated and that the RS$^-$ > RO$^-$ order was a consequence of the formers' greater polarizability, with the basicity factor being of minor importance because of the hardly-severed $C_\beta\ldots H$ bond.[55,57] This view was demolished by the α-effect evidence mentioned earlier. In retrospect it is also clear that such an explanation is fallacious on the grounds that the polarizable nucleophile is held to attack the substrate at a point several atoms removed from the seat of polarization, namely the easily broken $C_\alpha\ldots X$ bond. Explanations in terms of paeneolefinic $E2H$ transition states are attractive in some respects, but they fail to answer the crucial question of this section in that it must be supposed that, in some way, a weak base has an energetic advantage over a strong base in effecting a substantial degree of deprotonation at the transition state.

Transition state 7 forms the basis of an eminently reasonable explanation. Bases of high charge density, e.g. Cl^- in dipolar aprotic solvents, will interact with C_α by the electrostatic mechanism more strongly than will stronger bases of lesser charge density such as OAc^- and ArO^- (and even $t\text{-}BuO^-$ in t-BuOH, since the negative charge here can be "delocalized" by rapid proton transfers) and hence will stabilize 7 on these grounds to a greater extent. The reactivity order of $Cl^- > Br^- > I^-$ supports this contention[2,3] and while this is also the basicity[76] and B–H bond energy order, the latter two factors do not explain the anomalous reactivity of $t\text{-}BuO^-$. The effect of the greater basicity of species such as this and OAc^-, etc. (primarily a B–H bond energy factor) will be largely nullified since the B . . . H bond in 7 is but poorly formed.

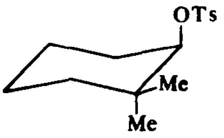
The explanation for the $RS^- > RO^-$ reactivity order in terms of 7 is similar, except that the greater polarizability of sulphur anions[78] must be invoked. This may now be properly done as the base is closer to the seat of polarity, the $C_\alpha \ldots X$ bond, than it is in 1. The long-range stabilizing interaction between $RS^{\delta-}$ and $C_\alpha^{\delta+}$ will thus be stronger than that between $RO^{\delta-}$ and $C_\alpha^{\delta+}$. The high reactivity of thiolates towards cationic carbon in stable carbonium ions[79] is testimony to this.

On the basis of the spectrum in Scheme 2, it may be predicted that as substrate acidity increases the effect of B–H bond energies will begin to predominate as transition state character shifts rightwards. Thus the reactivity order will eventually be reversed and so will mimic the thermodynamic basicity order: $RO^- > RS^-$. Examples of this type of behaviour are shown in Table 5, wherein substrates of each structural type are arranged in order of increasing acidity. Note that OTs bonded to secondary C_α is classed as a weakly acidifying leaving group for the reason that it will have largely departed the remainder of the transition state and so will have little effect as far as activation of the $C_\beta \ldots H$ bond is concerned.[40]

Effect of steric crowding at C_α. Bunnett and Eck have compared the reactivities of cyclohexyl tosylate (8) and 2,2-dimethylcyclohexyl tosylate (9) towards $n\text{-}Bu_4NCl$ in Me_2CO[81a] and of isopropyl bromide (10) and 2-bromo-3,3-dimethylbutane (11) towards EtS^- in MeOH.[81b] As expected, the S_N2 reactivities of the hindered analogues (9 and 11) were considerably lower than those of 8 and 10 respectively, which is a normal neopentyl-type effect for reactions of secondary substrates.[14] However, the rates of the competing second-order eliminations were hardly affected by steric congestion. Their interpretation was that no relatively short, partially covalent $B \ldots C_\alpha$ bond with S_N2-like characteristics was present in the elimination transition states. This observation effectively disqualifies the *E*2C transition states (4 and 5) unless the extreme and improbable view is taken that they are of such looseness that the base is barely present. Transition state 7 is a more reasonable basis for understanding, for although a $B \ldots C_\alpha$ interaction is an important structural component, it is a long-range electrostatic interaction and thus the base may be positioned sufficiently far from C_α so as to suffer only minimal steric hindrance. The arguments of Bunnett and Eck have been extended to the context of carbonyl group reactions.[82]



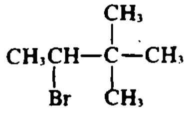
(8)



(9)

$$\underset{\displaystyle Br}{CH_3CH}CH_3$$

10



$$\underset{\displaystyle Br}{CH_3CH}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

11

Reactivity correlations of bases. A linear plot (Fig. 1) of log k_E for olefin formation *vs* log k_S for competing S_N2 substitution is found for the reactions of cyclohexyl tosylate with a variety of weak anionic bases in acetone.[3] The slope is close to unity, and these observations have been used to uphold the suggestion that there is a degree of similarity between the S_N2 transition states arising from this loose substrate and the respective elimination transition states, which leads to the implication of 4 or 5 as the transition states in elimination.[3] There is, however, no correlation between the cyclohexyl tosylate log k_E values and the n-BuBr log k_S values, which pertain to the reactions of a tighter S_N2 substrate.[7]

This important L.F.E.R. has been tested in two ways. Firstly, it is shown in the Appendix that, given a reasonable array of assumptions, such an L.F.E.R. is expected to obtain even if the elimination is purely *E*2H, with the base partially bound *only* to hydrogen. An

Table 5. Elimination rate ratios for sulphur *vs* oxygen bases

Substrate	S-base	O-base	Solvent	k_S/k_O	Ref.
Cyclohexyl tosylate	PhS^-	OEt^-	EtOH	7·0	35
Cyclohexyl bromide	PhS^-	OEt^-	EtOH	1·6	35
Cyclohexyl chloride	PhS^-	OEt^-	EtOH	0·73	35
1,1-Dibromocyclohexane	PhS^-	OEt^-	EtOH	0·63	35
1,1-Dichlorocyclohexane	PhS^-	OEt^-	EtOH	0·21	35
t-BuCl	PhS^-	OEt^-	EtOH	8·3	80
$t\text{-}BuSMe_2^+$	PhS^-	OEt^-	EtOH	0·31	80
$t\text{-}BuSO_2Me$	PhS^-	OEt^-	EtOH	small	80
$PhCH_2CMe_2Cl$	EtS^-	OMe^-	MeOH	6·5[a]	15
$PhCH_2CMe_2SMe_2^+$	EtS^-	OMe^-	MeOH	0·8[a]	15
$PhCH_2CMe_2SO_2Me$	EtS^-	OMe^-	MeOH	0·05[a]	15
Cyclohexyl tosylate	ArS^-[b]	ArO^-[b]	Me_2CO	3·0	3
Cyclohexyl bromide	ArS^-[b]	ArO^-[b]	Me_2CO	0·63	3
Cis-1,2-dibromocyclohexane	ArS^-[b]	ArO^-[b]	Me_2CO	0·04	3
Cyclohexyl tosylate	PhS^-	PhO^-	Me_2CO	8·1	3
Cis-1,2-dibromocyclohexane	PhS^-	PhO^-	Me_2CO	1·2	3

[a] For formation of conjugated olefin. [b] $Ar = p\text{-}NO_2C_6H_4$.

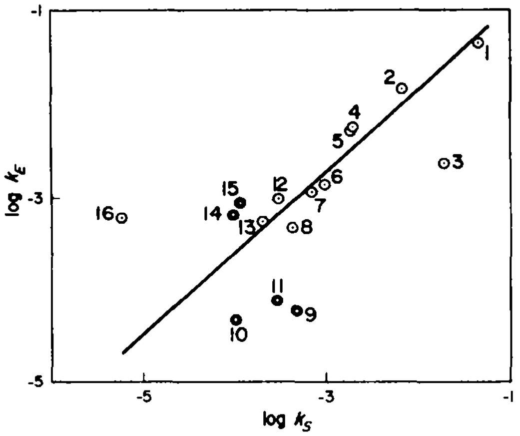


Fig. 1. Plot of log k_E vs log k_S for reactions of cyclohexyl tosylate with anionic bases (open circles) and neutral bases (closed circles) in acetone and t-BuOH. Numbers refer to the following bases: 1, PhS^-; 2, OAc^-; 3, N_3^-; 4, Cl^-; 5, PhO^-; 6, ArS^-; 7, Br^-; 8, ArO^-; 9, thiourea; 10, Ph_3P (all in acetone); 11, Ph_3P; 12, Cl^-; 13, Br^-; 14, Et_3N; 15, DBN; 16, t-BuO^- (all in t-BuOH). The least-squares line for anionic bases (excluding t-BuO^-) is shown. The point for t-BuO^- is based on the assumption of 1% substitution.[3]

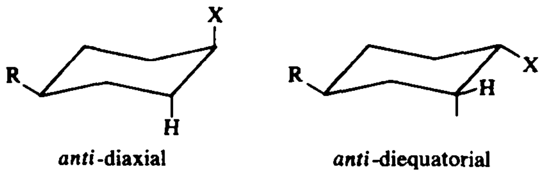
important proviso is that the respective E2H and S_N2 transition states must be loose. Thus the experimental demonstration of such an L.F.E.R. is not a sufficient condition for the postulation of S_N2-like elimination transition states. Since 7 can be regarded as a hybrid of loose E2H and E2C transition states, it remains in contention. It is notable in this regard that the log k_E/log k_S diagram for the reactions of cyclohexyl bromide (a tighter substrate by virtue of its poorer and more electronegative leaving group) with the same series of anions is a scatter plot.[3]

Secondly, we have examined the reactions of cyclohexyl tosylate with thiourea and triphenylphosphine in acetone, and, as shown in Fig. 1, have found that the L.F.E.R. applies only to anionic bases.[83] These neutral reagents are weak but polarizable bases and are strong carbon nucleophiles in protic solvents.[84] They should thus be effective E2C bases if either of 4 or 5 is the transition state. They are not. If 7 is a better representation of the E2C transition state, weak neutral bases should be at a disadvantage since electrostatic stabilization will be unavailable. Their use implies either that the energy of 7 will be raised or that a transition state shift in the direction of 2 will occur with a decrease in rate consequent upon the necessity of forming a stronger B...H bond with a weak base. In any case the electrostatic nature of the B...C_α interaction in the E2C transition state stands clearly revealed. The behaviour of the stronger neutral base Et_3N in t-BuOH is as expected. The elimination rate is accelerated relative to that for the weak anionic and neutral bases, suggesting a base-induced transition state shift towards 2. It is noteworthy that azide ion also deviates markedly from the L.F.E.R.[3] This can now be understood in terms of repulsive forces between $C_\alpha^{\delta+}$ and the formally positive central nitrogen in $\bar{N}{=}\overset{+}{N}{=}\bar{N}$. An explanation in terms of a possible enhancement of the S_N2 rate by an "α-effect" is unlikely in view of the looseness of the transition state.[85]

Conclusions on the structure of elimination transition states based on the goodness or otherwise of Brönsted plots generated by the use of structurally unrelated bases[3] must also be regarded with caution. The dehydrochlorination of $(p\text{-}ClC_6H_4)_2CHCCl_3$ (DDT) by ArS^-, ArO^- and OR^- bases in EtOH proceeds by an E2H mechanism *par excellence* in that the activation process involves proton transfer alone, i.e. the mechanism is E1cB[32(a)] with rate-determining carbanion formation.[60,86] Yet the Brönsted plot is non-linear.[60] Nor is a regular plot obtained for an E2H case involving the reactions of DDT with weak bases in DMF.[53] A similar observation has been made concerning the E2H reactivities of alkoxides and hydroxide towards $PhCH_2CH_2Br$ in dioxan.[87] Thus the absence of a linear log k_E vs pK_a relationship can scarcely be held to imply the lack of base-proton bonding in E2C-like transition states if authentic E2H reactions behave in a like manner.

Leaving group correlations. It is shown in the Appendix that, for substrates predisposed to react through loose transition states, log k_E should correlate linearly with log k_S when a base reacts competitively in the elimination and substitution modes with a substrate series where the leaving group is the molecular variable. This will obviously apply if the elimination transition state has S_N2 characteristics, e.g. **4** or **5**, but the semi-empirical treatment shows that the relationship will also hold if a loose E2H species, having no B...C_α interaction, is involved. Transition state 7 again remains in contention. Reaction systems that follow this prediction are cyclohexyl–X with n-Bu_4NCl in Me_2CO (X = Cl, SMe_2^+, Br, OTs, I)[3,39] and 2-hexyl halides with NaOMe[19] (the point for OTs deviates). However, a scatter plot is found for the CH_3CH_2X–NaOEt–EtOH system[39] where tighter E2H transition states will be involved. Thus the poorer leaving groups in the latter series, e.g. NMe_3^+ will not be particularly well severed from C_α and so can influence the electron distribution in the remainder of the transition state by interacting with the partial carbanionic charge on C_β generated by the strong base. Nitrogen isotope effect studies indicate that the C_α–N bond in the $CH_3CH_2NMe_3^+$–NaOEt–EtOH system is less than 50% broken at the transition state.[88]

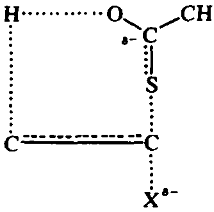
Miscellaneous. In cyclohexane systems, *anti*-diaxial elimination is not favoured to any great extent over *anti*-diequatorial elimination (Scheme 7) when weak bases are employed, unlike the situation met with in strong base eliminations.[3,9,13] For instance, menthyl tosylate reacts with n-Bu_4NCl in Me_2CO to form menth-2-ene (*anti*-diequatorial) only 13 times more slowly than neomenthyl tosylate forms the same olefin by an *anti*-diaxial process.[9] This is understandable in terms of 7 for two reasons. Firstly, the well-severed C_α...X bond means that conformational distinction between the two systems will be partially lost. Secondly, the position of the base with respect to the leaving group is not governed to any extent by stereoelectronic considerations involving alignment of reacting orbitals.



Scheme 7.

It might be expected that patterns of geometric and positional orientation for reactions proceeding via 7 would be similar to those observed in $E1$ reactions involving carbonium ions or ion-pairs as intermediates. Several results are in fact suggestive of this.[20,21,89] For instance, $Me_2CHCH(OTs)CH_2CH_3$ yields $Me_2C{=}CHCH_2CH_3$ and $Me_2CHCH{=}CHMe$ in the ratio of 12:1 in the $E2C$ reaction with n-Bu_4NBr in Me_2CO, and these products of solvolysis in t-BuOH are produced in the ratio of 11:1. Furthermore the latter olefin is almost exclusively the *trans*-isomer under both $E2C$ and $E1$ conditions.[20] However, there are some spectacular exceptions that render this expectation untenable. Menthyl tosylate yields 70% menth-3-ene on solvolysis in acetone, but the product of the second-order reaction with n-Bu_4NCl in the same solvent is almost 100% menth-2-ene.[9] 2-Bromo-2-methylbutane yields 2-methylbut-1-ene and 2-methylbut-2-ene in a 1:1 ratio on solvolysis in acetone, but the ratio changes to 1:10 when n-Bu_4NCl is present.[10] Solvolysis of *cis*-2-phenylcyclopentyl brosylate in acetone yields 9·5% of the Hofmann product 3-phenylcyclopentene, but only 0·3% of this product is formed in the $E2C$ reactions with n-Bu_4NCl and n-Bu_4NOAc.[3] The difference between solvolysis and $E2C$ product patterns is obviously a consequence of the charges on the proton acceptors, which are neutral in $E1$ cases and anionic in $E2C$ reactions.

Thioacetate ion behaves as a normal $E2C$-type base. The necessarily bidentate character of the base required in transition states (**4** and **5**) would lead one to expect that thioacetate would be spectacularly effective in forming a cyclic transition state (**12**), in which the basic oxygen attacks the proton whilst the C-nucleophilic sulphur co-ordinates to C_α. Yet this is apparently not the case.[50]



12

In solvents of low basicity (Me_2CO, etc.), halide-induced eliminations are generally reversible and one normally adds a kinetically ineffective base such as 2,6-lutidine to scavenge the halogen acid and prevent its readdition to the olefin.[13] Fahey, Pasto *et al.* have studied the hydrochlorination of several olefins[91] and have found that in some cases third-order rate terms of the form: rate = k_3[olefin][HCl][Cl^-] are required in the overall rate equation. Such additions proceed by a *trans*-pathway. This is exactly as required for the microscopic reverse of eliminations proceeding through any of **4**, **5** or **7**. Studies by Berliner indicate that the transition states for third-order halogen additions to multiple bonds (first-order each in substrate, X_2 and X^-) are not symmetrical as far as charge at C_α and C_β is concerned.[92] An $E2Hal$[10] transition state analogous to **7** rather than to **4** or **5** is suggested.

Dehydrochlorination of Ar_2CHCCl_3 compounds by weak bases in acetone and DMF proceeds via $E2H$-like transition states.[53,54] The deuterium isotope effect is insensitive to base identity as the base strength is increased along the series Br^-, Cl^-, 2,4-dinitrophenoxide and *p*-nitrothiophenoxide in DMF,[53] and remains close to 5·2. This could be taken to mean that transition state character is also insensitive to base strength over this range, but such an interpretation is at odds with the increase of the Hammett ρ value from 0·99(Cl^-) to 1·24(ArS^-). In all possibility the position of the proton in the $B \ldots H \ldots C_\beta$ moiety is largely unaltered by the change in base, but the $C_\alpha \ldots Cl$ bond becomes less severed as base strength increases. The negative charge on C_β, and hence ρ, thus increases. This phenomenon has been noted in another $E2H$ reaction series[93] and is in accordance with More O'Ferrall's rules on $E2H$ transition state character.[6]

Two recent studies have appeared too late to be considered in the appropriate sections. Ford and Pietsek[94] have extended the examination of α-substituent effects in the reactions of 1-aryl-1-bromopropanes with n-Bu_4NBr in Me_2CO. Their findings confirm those of Lloyd and Parker.[65] They reject the possibility of intermediacy of ion-pairs and of charge deficiency on C_α, without considering the consequences of the $C_\alpha{}^{\delta+} \ldots B^{\delta-}$ electrostatic dipole. However, they find that α-k_H/k_D (secondary) is large, so that C_α must be near sp^2 hybridized, as is required for a transition state such as **7**. Feit *et al.*[95] have examined product proportions from a variety of secondary alkyl bromides reacting with a variety of weak and strong bases, in both protic and dipolar aprotic solvents. Their results agree with others discussed in the sections on positional and geometrical orientation, and are thus in accordance with **7** as transition state. A proposal that $E2C$-like transition states do not have a well-formed π-bond[95] is also in line with this view.

CONCLUSION

Parker has independently anticipated our interest in **7** and in two recent papers has stated that he knows of no experimental distinction between **7** on one hand and **4** or **5** on the other.[50,56] Our recent work[83] provides that distinction. And, as we have attempted to show in this article, many other areas of elimination chemistry become more comprehensible if **7** is accepted as a component of the transition state spectrum.

The larger question of whether concerted β-eliminations exist at all[96] has not been considered in detail. We have discussed some aspects of the proposed carbonium ion-pair mechanism, but have ignored the possibility of carbanionic intermediates in weak base-loose substrate reactions for obvious reasons. The reader is referred to the recent paper of Saunders for a more complete argument in favour of concerted ionic β-eliminations in solution.[74]

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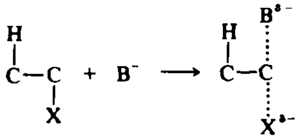
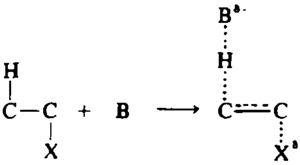
APPENDIX

The following treatment is based on Hudson's analysis of nucleophilic reactivity.[97] Consider a substrate entering into an S_N2 reaction with a base B^- (Eqn 1). If $\Delta G^{\neq}_S$ is the free energy of activation it may be dissected into various energy terms (see the glossary of terms which follows) according to Eqn 2. In the latter, α, β *etc* are fractions representing the fact that the chemical and solvational bonds are only fractionally made or broken on progressing from initial to transition state. The constant term C_1 gathers together those factors not explicitly considered in Eqn (2). We require its magnitude to be independent of the identity of B and X and for this to be so, $B^{\delta-}$ and $X^{\delta-}$ must be as far as possible from the remainder of the transition state so as to have as little secondary influence as possible. Thus a loose S_N2 transition state is required.


(1)

$$\Delta G^{\neq}_S = \alpha E_B - \beta D_{CB} + \gamma D_{CX} - \delta E_X + C_1 \qquad (2)$$

Now consider the same substrate and base entering into an $E2H$ reaction as in Eqn (3). The free energy of activation, $\Delta G^{\neq}_E$ is given by Eqn (4). It has assumed that the fractional terms are the same as in the S_N2 reaction and while this cannot be rigorously justified, neither is it outrageous. The same assumption would be necessary were we to replace the $E2H$ process by an $E2C$ mechanism in justifying linear log k_E vs log k_S plots within this framework. The constant energy term C_2 incorporates among other things the π-bond energy and the C–H bond dissociation energy. It must again be independent of B and X and so a loose elimination transition state is required.


(3)

$$\Delta G^{\neq}_E = \alpha E_B - \beta D_{BH} + \gamma D_{CX} - \delta E_X + C_2 \qquad (4)$$

Equation (5) results from Eqns (2) and (4). It may be further simplified on

$$\Delta G^{\neq}_E - \Delta G^{\neq}_S = \beta(D_{CB} - D_{BH}) + (C_2 - C_1) \qquad (5)$$

recalling that, for many of the bases of interest, D_{CB} varies almost linearly (slope *ca* 1) with D_{BH}[97] as expressed in Eqn (6). On combining Eqns (5) and (6),

$$D_{CB} = D_{BH} + C_3 \qquad (6)$$

and converting the $\Delta G^{\neq}$ terms to rate constants for elimination (k_E) and substitution (k_S) we obtain Eqn (7).

$$\ln k_E = \ln k_S - \frac{\beta C_3 + C_2 - C_1}{RT} \qquad (7)$$

In view of the assumptions concerning C_1 and C_2, Eqn (7) expresses the fact that log k_E should correlate linearly with log k_S (slope = 1·0) if (a) a series of bases, sufficiently similar in nature for shifts in transition state character to be negligible, react competitively in the elimination and substitution modes with a given substrate or (b) if substrates differing only in the identity of the leaving group react with a given base.

A similar relationship may of course be derived if the elimination proceeds through a transition state such as **4** or **5** in which the B … C_α interaction is the same or similar to that in Eqn (1). The object of the present treatment is to show, however, that this is not the *only* formulation that admits linear log k_E vs log k_S plots.

E_B = energy required to remove electron from B^- in solution

D_{CB} = C – B homolytic bond dissociation energy

D_{CX} = C – X homolytic bond dissociation energy

D_{BH} = B – H homolytic bond dissociation energy

E_X = energy required to place an electron on X· in solution.