CHIMIA

Volumen 18 Fasc. 2 1964 Pag. 37–72

New Mechanistic Interpretation of E2 Reactions

By JOSEPH CSAPILLA*

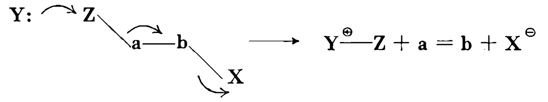
Abstract

The driving-force for the rate enhancement of α-substituents with a –M-effect in Sn 2 and E 2 reactions (U-shaped Hammett ϱ-curves) has been re-examined. Instead of orbital overlap between the nucleophile and the –M-group (energetic acceleration), as most of the existing explanations state, the enhanced probability of the collision of the reaction partners (acceleration by entropy) is suggested to account for this phenomenon. A new transition state is proposed for the base-induced *trans*-eliminations which emphasizes the nucleophilic role of the base. The following problems involving elimination reactions will be discussed with the help of the new transition state: difference between thermodynamic and kinetic basicity; why *trans*-eliminations are generally favored over *cis*-eliminations; substituent isotope effects; orientation; competition between Sn 2 and E 2 reactions; and solvent effects in the debrominative decarboxylation reactions.

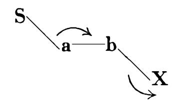
Although E 2 reactions have been extensively and well reviewed,[1] some features of them cannot convincingly be explained. The new general transition state proposed in this article is believed to account somewhat better for what happens in E 2 reactions than does the presently accepted or "classical" one. In the discussions which follow, the discrepancies in current explanations will be pointed out, and a comprehensive and consistent picture for the situation existing in a molecule experiencing these reactions will be presented.

The heterolytic β-elimination reactions are of two major types:

a) eliminations induced by base



b) and fragmentation reactions[2]



$$S^{\oplus} + a = b + X^{\ominus}$$

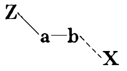
The atoms a and b are capable of bearing double or triple bonds, e. g. C, N, O.

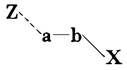
X is a nucleofuge[3] such as halogen, $-OSO_2R$, H_2O^+-, HO– etc., while Z is an electrofuge[3] such as H, halogen, etc.

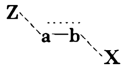
Y is a group of atoms with a lone pair of electrons such as RO^-, RS^-, $>N:$, $Hal\cdot^-$, $>N:^-$, etc.

S is a group of atoms which is capable of giving up its binding electron pair to a, e. g., $-\overset{|}{\underset{|}{C}}-\ddot{N}<$, $-CO_2^-$ etc.[2]

According to the present state of the theory,[1] there are three different possibilities for the timing of bond-breaking in the transition state:


I


II


III

I	E 1	mechanism	multi step processes
II	E1cB	mechanism	
III	E 2		concerted or synchronous process

---

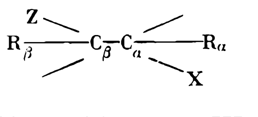
* Present address: American Cyanamid Company, Stamford (Connecticut).

[1] a) C. K. INGOLD, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca (N.Y.) 1953, p. 420–72.
b) D. J. CRAM, Olefin-Forming Elimination Reactions, in NEWMAN'S *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York 1956, p. 305–48.
c) E. S. GOULD, *Mechanism and Structure in Organic Chemistry*, Henry Holt & Co., Inc., New York 1959, p. 472–504.
d) J. HINE, *Physical Organic Chemistry*, Second Edition, McGraw-Hill Book Co., Inc., New York 1962, p. 186–212.
e) J. F. BUNNETT, *Angew. Chem.* (International Edition) *1* (1962) 225.
f) D. V. BANTHORPE, Elimination Reactions, in *Reaction Mechanisms in Organic Chemistry*, Vol. 2, Elsevier, Amsterdam / London / New York 1963.

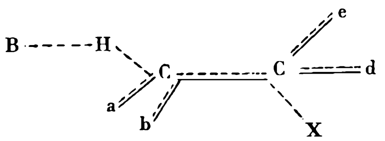
[2] C. A. GROB and F. OSTERMAYER, *Helv. Chim. Acta 45* (1962) 1119, and preceding papers.

[3] There is no systematic nomenclature in the literature concerning the groups X, S and Z. These groups are the so-called departing or leaving groups, especially X, but a proper attributive, which indicates which group respectively gives up or retains its binding electron pair with the corresponding carbon atom in the ground state in order to proceed to the final state, is still lacking. In the ground state of the substrate, X necessarily has to be termed as an electrophilic leaving group (S and Z are then consequently nucleophilic groups) but unfortunately the appearance of the nucleophile X^- in the product (final state consideration) confuses the picture. MATHIEU, ALLAIS and VALLS [*Angew. Chem.* 72 (1960) 71] introduced the terms «nucleofuge» and «electrofuge» Austritt (leaving, departure) to characterize the heterolysis of the C–X and respectively C–S and C–Z bonds. Perhaps the confusion will not be substantially decreased but the nomenclature becomes more meaningful, and therefore in this article X will be termed nucleofuge and S and Z will be termed electrofuge.

In most cases a and b are carbon atoms, so the molecule may be substituted on these two atoms:

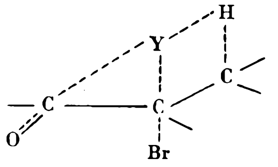


The "classical" E2 transition state (III), originally proposed by Ingold[4] does not explain the discrepancy between kinetic and thermodynamic basicity and does not allow a clear understanding of the influence of the groups R_α and R_β, especially if they are aryl groups, on the rate and activation parameters of a given reaction. Cram's[1b] transition state tries to express Ingold's basic idea as a possible conjugation or hyperconjugation with the incipient double bond and groups a, b, e and d; but this picture is not specific enough in nature:



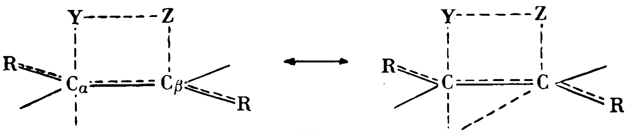
III b

The transition state of the merged substitution and elimination reaction[5] (IV), suggested by Cromwell[5c], tries to explain the great reactivity of α-halo ketones, but the picture does not correspond to the activation parameters of these reactions and other related eliminations:



IV

In order to discuss the influences of structure and medium, it seems necessary to propose a new picture for the transition state, since no variant of the E2 transition state (III), affords a consistent understanding of the presently available data concerning elimination reactions:



V

The dotted lines indicate a possible orbital overlap between the corresponding two atoms or groups

This representation of a general transition state for *trans*-elimination reactions is related to the transition state of the merged substitution and elimination reactions (IV), proposed by Cromwell[5c], but *Y does not overlap with R_α in the transition state.* In the following an attempt will be made to apply this transition state to various problems encountered in elimination reactions, and thereby to obtain more satisfactory explanations for these problems than is possible by the "classical" E2 transition state (III).

A. The Role of the Base Y

The observation that there is occasionally a difference between thermodynamic and kinetic basicity has been discussed.[6]

It is noteworthy that HX can be eliminated from tertiary halides, which are resistant to Sn2 reactions, by means of strong nucleophiles[7,8] (Br^-, Cl^-, RS^-); but very strong bases such as alkoxide ion tend to retard the elimination reaction.[8]

Not only does the substrate reveal this remarkable discrimination toward the base, but also the base attacks in several cases in an unusual manner, as it is demonstrated by the following examples:

a) Pfeiffer observed that from cinammic acid dibromide and stilbene dibromide and its substituted derivatives, not only hydrogen bromide is eliminated by pyridine and potassium hydroxide but also bromine.[9]

b) *trans*-1,2-Dibromoindane-2-carboxylic acid loses only bromine upon treatment with sodium hydroxide in methanol.[10]

c) N,N-diethylcinnamamide dibromide leads exclusively to the *trans*-cinnamamide derivative with various bases.[11]

If the classical E2 transition state (III) governs the elimination, it is not readily apparent why there should be a difference between thermodynamic and kinetic basicity and, on the other hand, why the base does not attack the hydrogen instead of the electrofugal bromine, especially since the hydroxide ion is much more reactive toward the hydrogen than toward the bromine atom because the HO–H bond is more stable than the HO–Br bond.

It is not readily apparent either why the β-phenyl group, in some cases,[5,8], has no directive influence on product formation; i. e., the new bond between the base and proton in the transition state of the rate determining step appears unimportant. This fact is unusual because, among others, 2-phenylethyl bromide eliminates hydro-

---

[4] W. Hanhart and C. K. Ingold, *J. Chem. Soc. 1927*, 977, and ref. 1a.

[5] a) S. Winstein, D. Darwish and N. J. Holness, *J. Amer. Chem. Soc. 78* (1956) 2915.
b) E. L. Eliel and R. S. Ro, *Tetrahedron 2* (1958) 353.
c) D. N. Kevill and N. H. Cromwell, *J. Amer. Chem. Soc. 83* (1961) 3815, and D. N. Kevill, P. H. Hess, P. W. Foster and N. H. Cromwell, *J. Amer. Chem. Soc. 84* (1962) 983, and preceding papers.

[6] J. F. Bunnett, C. F. Hauser and K. V. Nahabedian, *Proc. Chem. Soc. 1961*, 305.

[7] a) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc. 1956*, 41.
b) S. Winstein, S. Smith and D. Darwish, *Tetrahedron Letters 16* (1959) 24.

[8] J. F. Bunnett, G. T. Davis and H. Tanida, *J. Amer. Chem. Soc. 84* (1962) 1606.

[9] P. Pfeiffer, *Ber. dtsch. chem. Ges. 45* (1912) 1810, and *48* (1915) 1048.

[10] J. Csapilla, unpublished results.

[11] A. J. Speziale and C. C. Tung, *J. Org. Chem. 28* (1963) 1353.

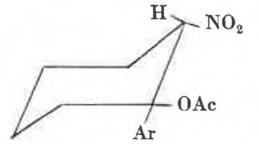
gen bromide > 300 times as fast as ethyl bromide.[12] With the bifunctional role of the base (base *and* nucleophile) in the mechanism proposed it is easy to explain these anomalies. The stronger the nucleophilic participation of the base the weaker must be the base-H bond. A strong nucleophilic participation is necessary a) in the α-bromoketones[5c] because of the deactivated C–Br bond,[13] and b) in the tertiary halides because of the steric hindrance to nucleophilic participation. Such hindrance to this participation requires readily polarizable bases such as mercaptide in order to form an effective Y----C bond from a relatively long distance; but the strongly deformed electron shell of the base probably does not allow additional strong orbital overlap with the proton.

The above-mentioned bromine eliminations from various activated systems (this term will be defined later), which reveal either a *cis*-effect[14] or *cis* arrangement of the leaving groups in the competitive hydrogen bromide elimination, also suggest that the bond-breaking between the electrofuge (H^+ or Br^+) and C_β is negligible in the transition state. This is further supported by the following example:[10] acetone is not well known to be a nucleophile,[15] but the spontaneous debromination of *erythro-p*-methoxycinnamic acid dibromide in pure acetone at the boiling point can best be explained by the nucleophilic participation of acetone in the process. The character of this nucleophilic participation may be not only electrostatic in nature (field effect or solvation effect),[16] but in addition, to a certain degree, of a covalent bond-forming nature.

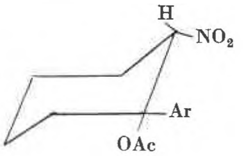
B. The Role of R

It is reasonable to assume that *the elimination proceeds faster when the independent ionization of the bonds C–X and C–H occurs readily.* As a matter of fact, R_β exhibits a positive Hammett ϱ-curve[17] just as expected. The influence of R_α is less simple. Under solvolytic conditions, R_α with a negative σ value accelerates, and with a positive σ value slows down the reaction, e. g., Sn1 reactions correlate well with the σ^+ values,[18] but the elimination does not. Similarly, elimination as for the Sn2 reactions,[19] the plot of the Hammett $\sigma\varrho$-function is U-shaped. This is to be seen in reaction (2) (cf. the corresponding table) and in the following observation:[10] The rates of bromine elimination from cinnamic acid dibromide and its *p*-substituted derivatives and from the corresponding methyl esters by means of iodide ion in acetone increase in the order: $CH_3O > NO_2 > H$. The velocity of the hydrogen bromide elimination by hydroxide ion from the methyl esters also increase in the same order.

Bordwell and co-workers have recently found that introduction of an electron-withdrawing substituent into the benzene ring in VI and VII increased the rate of elimination.[20]



VI

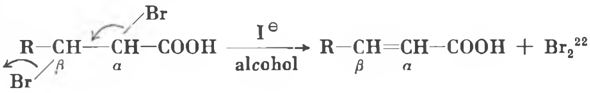


VII

The fact that –M-groups[21] accelerate the elimination is also supported by the easy elimination of HX from α-halo ketones, even with bromide ion as base[5c].

As in the Sn2 reaction[19d,e], there are two competitive possibilities to explain the rate enhancement by –M-substituents. One is given by **Cromwell** (acceleration by extended orbital overlap),[5c] but his transition state (IV), does not reflect the activation parameters of reactions (1), (2) and (3). It seems more probable that *the acceleration is due to the higher probability of a successful collision of the reaction partners.* This is illustrated by the activation parameters for the reactions (1), (2) and (3).

(1)



$$R{-}\underset{\substack{\diagup \\ Br}}{\overset{\beta}{CH}}{-}\overset{\substack{Br \\ \diagup}}{\underset{\alpha}{CH}}{-}COOH \xrightarrow[\text{alcohol}]{I^{\ominus}} R{-}\underset{\beta}{CH}{=}\underset{\alpha}{CH}{-}COOH + Br_2{}^{22}$$

Table 1. Kinetic Effects for Reaction (1)

R	k_{rel}	E	P (A = PZ)
H	1.00	19.2	0.007
CH_3	0.28	17.9	0.000 13
COOH	2.5	19.6	0.022

---

[12] M. L. Dhar, E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc. 1948*, 2055.

[13] S. Oae, *J. Amer. Chem. Soc. 78* (1956) 4030.

[14] D. Y. Curtin, *Thirteenth National Organic Chemical Symposium*, Ann Arbor, Michigan, June, 1953, abstract of papers, p. 40–9.

[15] H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc. 85* (1963) 2181.

[16] Cf. the phenomenon of backside solvation by C. A. Grob and F. A. Jenny, *Tetrahedron Letters 23* (1960) 25.

[17] a) C. R. Hauser, J. W. LeMaistre and A. E. Rainsford, *J. Amer. Chem. Soc. 57* (1935) 1056.
b) W. H. Saunders, Jr., C. B. Gibbons and R. A. Williams, *J. Amer. Chem. Soc. 80* (1958) 4099, W. H. Saunders and D. H. Edison, *J. Amer. Chem. Soc. 82* (1960) 138, and preceding papers.
c) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc. 82* (1960) 2532.
d) S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc. 76* (1954) 3005.
e) C. H. DePuy, R. D. Thurn and G. F. Morris, *J. Amer. Chem. Soc. 84* (1962) 1314.

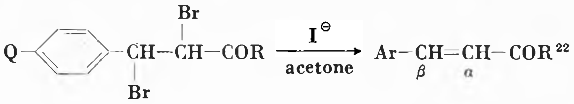
[18] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc. 79* (1957) 1913.

[19] a) J. W. Baker and W. S. Nathan, *J. Chem. Soc. 1935*, 1840.
b) C. G. Swain and W. P. Langsdorf, Jr., *J. Amer. Chem. Soc. 73* (1951) 2813.
c) G. Baddeley and G. M. Bennett, *J. Chem. Soc. 1935*, 1819.
d) S. Sugdgen and J. B. Willis, *J. Chem. Soc. 1951*, 1360.
e) R. F. Hudson and G. Klopman, *J. Chem. Soc. 1962*, 1062.
f) R. Fuchs and A. Nisbet, *J. Amer. Chem. Soc. 81* (1959) 2371.

[20] F. G. Bordwell, R. L. Arnold and F. B. Birnanowski, *J. Org. Chem. 28* (1963) 2496, and Abstracts, Meeting of the American Chemical Society at Los Angeles, California, 1963, p. 9M.

[21] M will be used in the following as a symbol of resonance or conjugative effects in the ground as well as in the transition state, instead of R, proposed by Gould[1c], because R is generally used as symbol of a substituent in organic chemistry.

[22] T. L. Davis and R. Heggie, *J. Org. Chem. 2* (1938) 470.

(2) 

$$Q\text{-}C_6H_4\text{-}\underset{\text{Br}}{CH}-\overset{\text{Br}}{CH}-COR \xrightarrow[\text{acetone}]{I^{\ominus}} Ar-\underset{\beta}{CH}=\underset{\alpha}{CH}-COR^{22}$$

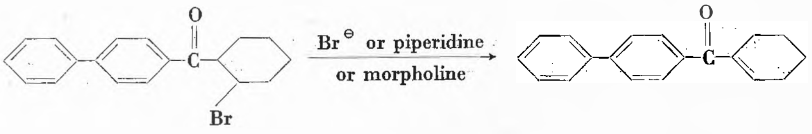
The reactivity increases in the order:

$$Q = p\text{-}CH_3O > p\text{-}NO_2 > m\text{-}Cl > H.$$

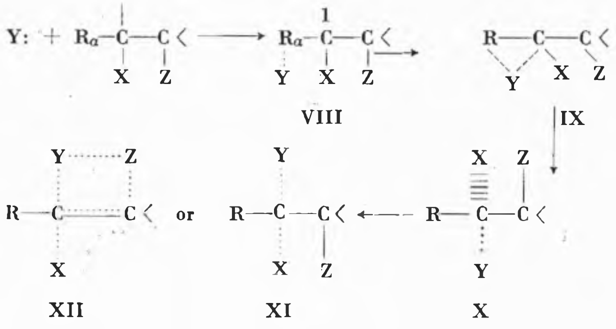
Table 2. Kinetic Effects for Reaction (2)

Q	R	k_{rel}	E	P
H	C_6H_5	1.0	17.7	1.2
p-NO_2	C_6H_5	1.5	19.1	31.0

Crotonic acid dibromide allows less nucleophilic participation at C_β than does acrylic acid dibromide because of the bulk of the methyl group; but the heterolytic cleavage of the C_β–Br bond is activated by the β-methyl-substituent. Consequently, it is expected that crotonic acid dibromide will have a lower energy of activation and a lower probability factor, P, than the related acrylic acid dibromide (cf. Table 1). An analogous situation exists in p-NO_2-benzalacetophenone and benzalacetophenone dibromides (cf. Table 2), and it is especially informative because the same steric requirements exist in the two molecules. The acceleration is clearly due to the greater reaction probabilities, as the energies of activation are once again in the reverse order to the reaction velocities. The ratio of the rate constants does not reflect the relative base strengths of piperidine and morpholine in reaction (3).[5c] With morpholine the reaction is faster than would be expected if it were a function of the base strength. The activation parameters show that in benzene and acetonitrile the frequency factor favors a higher rate for the reactions of morpholine relative to piperidine. This is understandable because morpholine has more lone-pairs of electrons which are responsible for the secondary attractive forces between the "trapping" ketone and the nucleophile Y. This is strongly supported by what happens in the elimination catalyzed by bromide ion. The rate is almost the same as with piperidine but the logarithm of the frequency factor is nearly twice as great. It seems, as expected, that the "trapping effect" is considerably higher for negative ions than for neutral molecules.

(3) 

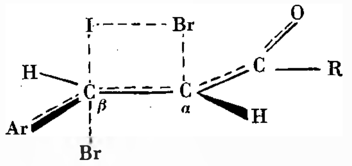
The activation parameters of the above E2 reactions and Sn2 reaction[19d] show that an overlap picture[5c, 19e] of their transition state is very probably not correct. An extended overlap between the entering nucleophile and α-substituent should be revealed in decreasing energy of activation, but the introduction of a –M-substituent into the molecule increases the activation energy. Apparently, the –M-substituent only intercepts the nucleophile (acceleration by entropy) and then forms some sort of a complex[23] (VIII), which probably leads to the actual transition states for Sn2 and/or E2 reactions, (XI) and (XII), via an overlap structure (IX), and an Sn2 type pre-transition state (X):



...... Lines mean weak bonding
|||||| Lines mean strong bonding
Lines mean no specific bond strength

The structures IX and X do not, however, necessarily represent a relative minimum along the reaction coordinate.

The transition state of the rate determining step for the debromination in reactions (1) and (2) may also be represented in the same manner:

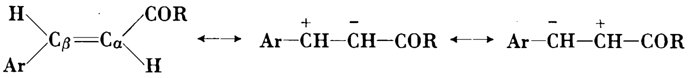


Since Br_β leaves the molecule as a nucleofuge, C_β is especially electron poor in the transition state. Three electron sources may fill the deficit: the nucleophile I^- (σ-orbital overlap), the aryl group which reveals its +M-effect (π-orbital overlap) and the new π-orbital overlap, which already has been formed to a certain de-

---

[23] Swain and Taylor recently have stated (*J. Amer. Chem. Soc. 84* [1962] 2456) that the "second-order reaction of phenoxide ion with benzyldimethylsulfonium ion in water at 80° appears to be accelerated by ancillary molecular bonding of the π-complex or charge transfer type at the transition state".

gree in the transition state between C_α and C_β. As Br_α is the electrofuge, a partial negative charge in the transition state remains on C_α from the partially broken C_α–Br bond. This charge can be neutralized by the π-orbital overlap between C_α and C_β and C_α and the $>$CO function. In other words *the product is represented in the transition state by the more stable of the two possible polar resonance forms (XIII):*

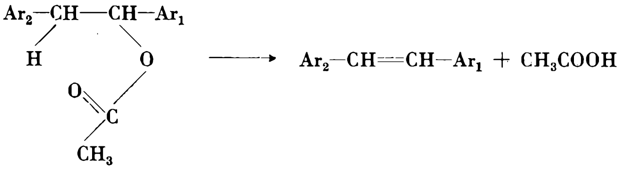


$$\underset{Ar}{\overset{H}{>}}C_\beta=C_\alpha\underset{H}{\overset{COR}{<}} \longleftrightarrow Ar-\overset{+}{C}H-\overset{-}{C}H-COR \longleftrightarrow Ar-\overset{-}{C}H-\overset{+}{C}H-COR$$

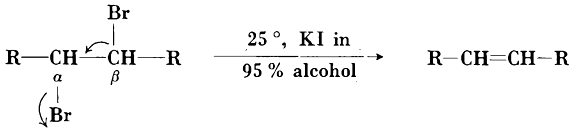
XIII

This assumption allows an understanding of the following two examples:

Bagley and Smith observed that the acetate pyrolysis of 1,2-diaryl ethanes is accelerated by positive σ-substituents on Ar_2 and by negative σ-substituents on Ar_1:[24]



Van Duin found that the debromination of dibromoethane derivatives in particular occurs readily when phenyl and acetyl groups are attached to the molecule (cf. Table 3).[25]

(4) 

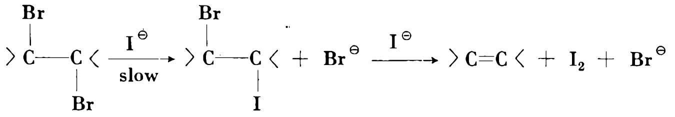
$$R-\underset{\substack{\alpha\\ Br}}{CH}-\overset{Br}{\underset{\beta}{CH}}-R \xrightarrow[95\,\%\text{ alcohol}]{25\,°,\text{ KI in}} R-CH=CH-R$$

Table 3. k_{rel} Values for Reaction (4)

R	H	H	H	C_6H_5 [c]	C_6H_5	C_6H_5	COOH [a]	COOH [b]	C_6H_5	Br
R	H	COOH	$COCH_3$	H	COOH	$COCH_3$	COOH	COOH	Br	Br
k_{rel}	1	2.1	16	3.5	80	180	3.7	0.22	0.5	3.10^{-3}

a) meso form
b) racemic form
c) The position of the phenyl group vs. hydrogen can be decided by Schwartzman's and Corson's experiment (*J. Amer. Chem. Soc. 78* [1956] 322), who found that *para* and *meta* methyl substituents accelerate the debromination of styrene dibromide; therefore, the phenyl group must be attached to C_α.

Another possible mechanism (5), which assumes a rate-determining Sn2 reaction followed by a fast elimination of iodobromide, has been discussed by Hine[26] and applied to monosubstituted dibromoethanes and also considered for disubstituted dibromoethanes to explain Van Duin's data (cf. Table 3). This mechanism can be excluded as follows:

(5) 

$$>\overset{Br}{C}-\underset{Br}{C}< \xrightarrow[\text{slow}]{I^{\ominus}} >\overset{Br}{C}-\underset{I}{C}< + Br^{\ominus} \xrightarrow{I^{\ominus}} >C=C< + I_2 + Br^{\ominus}$$

a) This reaction sequence requires an over-all *cis*-elimination, but it is not observed in most cases.[25, 27, 28]

b) The relative rate k_H / k_R varies only between 2 and 16, whereas the Sn2 reaction is accelerated by the same substituents up to $> 10^4$ times.[29]

c) The alleged rate-determining Sn2 step is indeed accelerated by one substituent, i. e., either by a carbonyl group or phenyl group, but the presence of both in the molecule in vicinal position should slow down the rate because of steric hindrance.[30] The acetyl group causes a 16-fold acceleration and the phenyl only a 3.6-fold acceleration. This means that the phenyl group should have no accelerating effect on the rate if the acetyl group is also attached to the molecule. Nevertheless, the rate ennhacement is 180.

d) The *trans*-olefins expected by a *trans* one-step elimination in which the reaction path is generally favored over *cis*-elimination (discussed below) form faster than the corresponding *cis* isomers.[25, 27, 28] The slower rate for *cis*-olefin formation is attributed to the *cis*-effect[14] in the transition state of *trans*-elimination (discussed below).

e) In the tosylate and brosylate of 2-bromocyclohexanol[31] and 1,2-dibromocyclohexane,[32] the *trans* isomers exhibit a greater rate than the *cis* isomers. An alleged rate-determining Sn2 step should be faster in the *cis* series because the electrofuge exhibits a smaller shielding effect toward iodide ion than in the corresponding *trans* compound.

f) Symmetrical tetrabromoethane is debrominated by iodide ions in methanol in a simple elimination process

---

[24] G. G. Smith, F. D. Bagley and R. Taylor, *J. Amer. Chem. Soc. 83* (1961) 3647.

[25] C. F. Van Duin, *Rec. Trav. Chim. Pay-Bas 45* (1926) 345.

[26] J. Hine and W. H. Brader, Jr., *J. Amer. Chem. Soc. 77* (1955) 361.

[27] S. Winstein, D. Pressman and W. G. Young, *J. Amer. Chem. Soc. 61* (1939) 1645.

[28] E. R. Trumbull and K. M. Ibne-Rasa, *J. Org. Chem. 28* (1963) 1907.

[29] J. B. Conant, W. R. Kirner and R. E. Hussey, *J. Amer. Chem. Soc. 47* (1925) 488.

[30] J. Hine and W. H. Brader, Jr., *J. Amer. Chem. Soc. 75* (1953) 3964.

[31] S. J. Cristol, J. Q. Weber and M. C. Brindell, *J. Amer. Chem. Soc. 78* (1956) 598.

[32] H. L. Goering and H. H. Espy, *J. Amer. Chem. Soc. 77* (1955) 5023.

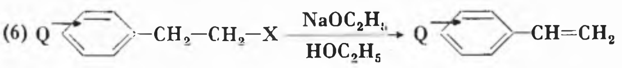
without passing preliminarily through an Sn2 step.[33] The strikingly low rate of this reaction (cf. Table 3) also excludes the possibility of a classical transition state, as the molecule can easily avoid the *cis*-effect here as well as in the ground state. Instead, the reason for the low rate is the hindered nucleophilic participation of iodide ion.

Nevertheless, it has been proved that the elimination of bromine by means of iodide ion from 1,2-dibromo-1,2-dideuteroethane is a *cis*-elimination[34] and this should give a strong support to the mechanism (5). In this case the Sn2 reaction is certainly preferred compared with 1,2-dibromopropane or with higher substituted dibromo ethanes because the bulk of the substituents hinder any nucleophilic attack. The electron repelling ability of alkyl substituents also favors elimination over substitution (discussed below), thus the mechanism (5) may be correct here.

C. The Role of the Nucleofuge X

The discrepancy between the "leaving strength" of the tosyloxy group in elimination *and* substitution reactions has been discussed recently.[17c] In Sn2 and Sn1 reactions the following order is observed: OTs > I > Br but in HX eliminations OTs is the poorest leaving group among them (I > Br > OTs). However, *trans*-2-bromocyclohexyl tosylate and brosylate react faster with iodide ion than *trans*-1,2-dibromocyclohexane.[31] This fact is probably due to the greater Sn/E character (the bond-breaking ratio between C–X and C–Z bonds) in the transition state for debromination with iodide ion than is present in base-promoted HX eliminations.

It is noteworthy that the Hammett ϱ_β-values[17c] for the different nucleofuges in HX elimination reactions are about in the reverse order to their "leaving strength", but the kinetic H/D isotope effect on C_β is in parallel order:[17b]

(6)


The intensity of the overlap between the corresponding orbitals of the five centers mentioned above determines the character of the transition state which determines the trend of kinetic effects. A less effective nucleofuge needs a relatively strong nucleophilic participation; thus, the breaking of the C–H bond in the transition state is less advanced than it would be with a more effective nucleofuge. Since the kinetic isotope effect can be considered as reflecting the importance of the corresponding bond-breaking in the transition state (for a more detailed discussion see ref. 1e), it is apparent that with the increase of the "leaving strength" the breaking of the C–H bond becomes more and more important; and therefore the isotope effect increases too.

Table 4. Dependence of Kinetic Effects on the Nucleofuge in Reaction (6)[17b, c]

X = F	Cl	Br	I	OTs	S^+	N^+
$\varrho+$ = 3.12	2.61	2.14	2.07	2.27	2.75	3.77[a]
k_H/k_D = –	–	7.11	–	5.66	5.07	3

a) W. S. Saunders, Jr., and D. G. Bushman, unpublished work (cf. ref. 1e).

The Hammett ϱ-value evidently cannot be considered in the same manner as the isotope effect. Rho measures only the relative ease of bond-breaking in substitution, but does not show the actual importance of this bond-breaking in the transition state. A less effective nucleofuge needs more nucleophilic participation than a more effective one, but upon a strong activation of the C–H bond, a leveling effect appears; e.g., the same activation (introduction of a group with – M character) causes a greater rate enhancement (larger ϱ) in the same molecule but with a poorer nucleofuge. Evidence for the leveling effect of strongly electron withdrawing groups is the small ratio (k_{Br} $k_{Cl} \sim 6$) for the dehydrohalogenation of sodium 2-haloethane sulfonates[35], whereas in unactivated systems the ratio is about 30–70.[36, 37]

D. *Cis*- vs. *trans*-elimination

The concept of nucleophilic participation also allows one to affer a reasonable explanation for an important and yet unsolved problem: Why is *trans*-elimination generally preferable to *cis*-elimination? This preference is usually attributed to the repulsive interaction between the negative base and the nucleofuge in the transition state and between the two leaving groups X and Z; but these repulsions cannot be the major reason, because *trans*-elimination is favored even with amines[38] in spite of the opposite partial charges of the base and nucleofuge in the transition state, favoring only the *cis*-elimination. The transition state V, proposed in this article, allows a clear explanation of this situation: the nucleophilic participation and the attack of Y: on Z are possible only in the *trans* configuration.[39]

---

[33] W. G. Lee and S. I. Miller, *J. Physic. Chem. 66* (1962) 655.

[34] a) W. M. Schubert, H. Steadly and B. S. Rabinovitch, *J. Amer. Chem. Soc. 77* (1955) 5755.
b) F. Declerck, J. Mulders and J. Nasielski, *Bull. Soc. Chim. Belges 71* (1962) 518.

[35] E. F. Landau, W. F. Whitmore and P. Doty, *J. Amer. Chem. Soc. 68* (1946) 816.

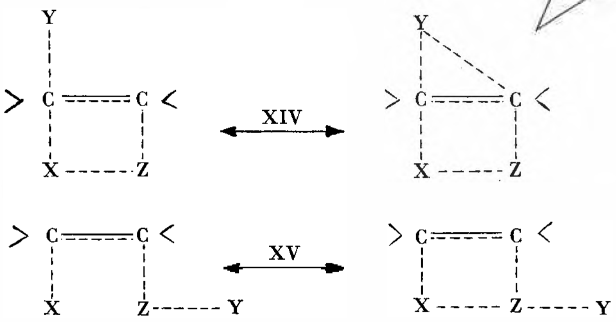
[36] a) E. D. Hughes and U. G. Shapiro, *J. Chem. Soc. 1937*, 1177.
b) H. C. Brown and I. Moritani, *J. Amer Chem. Soc. 76* (1954) 455.

[37] J. Csapilla, Dissertation, Basel (Switzerland) 1961.

[38] J. Weinstock, R. G. Pearson and F. G. Bordwell, *J. Amer. Chem. Soc. 78* (1956) 3473.

[39] It is obvious that the nucleophilic participation can only be effective when the electron pair of the base is free (no covalent bond

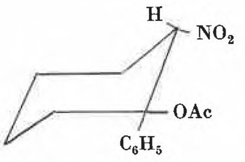
Since the dual role of Y is not conceivable in *cis*-elimination one can expect two different transition states for concerted processes depending upon the nature of Y:



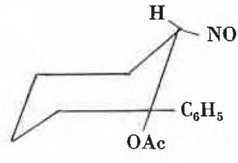
Transition State XIV

This transition state, where Y acts only as a nucleophile, may be realized if, a) X is a fragment such as an acetate pyrolysis) or, b) the nucleofuge is of about the same basic strength as the base. The following two examples could demonstrate the possible existence of both cases:

a) BORDWELL and co-workers[20] observed that *cis*-elimination initiated by piperidine proceeds about four times faster with XVI than *trans*-elimination with the epimeric XVII:



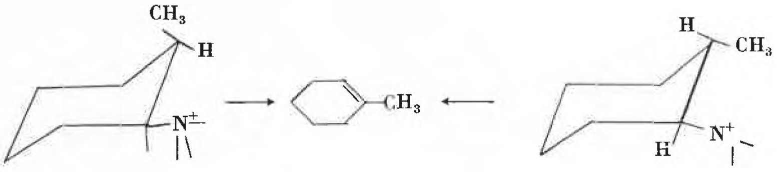
XVI



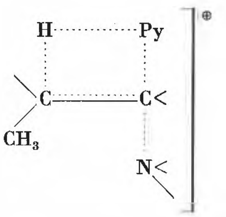
XVII

The similarity of kinetic effects for both epimers is not unexpected because the acetate group is a weak nucleofuge; thus a strong nucleophilic participation is required by piperidine, a participation which makes the transition state similar to that an Sn2 reaction to the first approximation. The strong acidifying effect of the nitro group, however, strongly promotes the breaking of the C–H bond, hence the substantial hydrogen isotope effect (4.9). The conclusion is that the transition states must be alike in both cases and must resemble the polar resonance form of the product (cf. structure XIII).

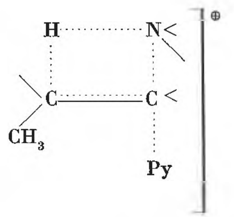
b) The transition state XIV may also be realized if the nucleofuge is of about the same basic strength as the base, which is the case in the following system.[40]



With pyridine both isomers produce 95% 1-methylcyclohexene but with alkoxide in the corresponding alcohol as solvent the *trans* isomer yields only 1% 1-methylcyclohexene. With pyridine an Sn2 type pretransition state can collapse to either cyclic elimination transition state with about the same energy requirement:



XVIII



XIX

But with a very strong base such as alkoxide the base-H bond in the transition state is stronger than the possible X–H bond. Consequently, this mechanism with a transition state like XIX is not favored with alkoxide.

Transition State XV

Although nucleophilic participation is apparently an important factor in elimination reactions which favor the *trans*-elimination, there are two other important factors which occasionally may counter-act the nucleophilic participation and so *favor the* cis-*elimination over* trans-*elimination.* These are the acidity of the hydrogen and the coplanarity of the five reaction centers C_α, C_β, X, Y and Z in the transition state (discussed below). The following elimination reactions from *rigid systems* will reveal that, in general, *cis*-eliminations pass trough the transition state XV:

a) The smaller Hammett ϱ-value for elimination in *trans*-2-arylcyclopentyl tosylates than in the corresponding open chain system under the same conditions.[17 e]

b) The general base-catalyzed *cis*-elimination of *trans*-2-*p*-toluene-sulfonylcyclohexyl-*p*-toluenesulfonate, which precludes a rapid proton exchange between anion and solvent; thus the possibility that the rate determining step is the elimination step.[38]

---

formation with any cation). LETSINGER and BOBKO (*J. Amer. Chem. Soc. 75* [1953] 2649) and CRISTOL and BLY (*J. Amer. Chem. Soc. 83* [1961] 4027) observed that *cis*-elimination proceeds faster than the corresponding *trans*-elimination with butyllithium and phenyllithium, which do not dissociate and therefore cannot provide the necessary electron pair for the nucleophilic participation.

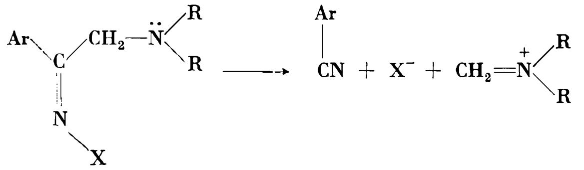
[40] T. H. BROWNLEE and W. H. SAUNDERS, Jr., *Proc. Chem. Soc. 1961*, 314.

c) The estimated (10^3 times faster) rate of *cis*-elimination over deuterium exchange in the same reaction as in b.[41,42]

d) The rate dependence on the nucleofuge in the HX elimination from *trans*-2-X-cyclohexyl-*p*-toluenesulfonate, which is inconsistent with the proposed rate-determining proton abstraction followed by a fast elimination step and which is the same order as that for concerted *trans*-eliminations in activated systems.[43]

e) The 8–80 times more favored *cis* over *trans* hydrogen chloride elimination from vicinal dichlorobicyclo (2.2.2) octane derivatives and 2,3-dichloronorbornane,[44] and the 30–67 times faster hydrogen halide elimination from *trans*-2,3-dihalonorbornane than from the *endo* or *exo cis* analogs[45] can be attributed to the importance of the π-orbital overlap in the transition state between C_α and C_β. In order to achieve maximum orbital overlaps between the participating five centers (C_α, C_β, X, Y, Z) in the transition state it is necessary for these centers to be in the same plane. This desired coplanarity in the *trans*-transition state can only be reached by strong distortion of the bicyclic molecule, especially in the norbornane system, but for the *cis*-elimination the coplanarity is already present in the ground state. Carbanion formation is expected to be more facile in the *cis*-dihalo compounds because of less shielding of the proton than in the *trans*-isomers. Also, the larger steric strain in the *cis*-isomer should favor *trans*-elimination. It seems likely that the better overlap of the above mentioned π-orbital in the *cis*-transition state more than compensates for any other advantage of the *trans*-elimination and so is most important.

f) Fischer, Grob and Renk observed a sychronous *cis*-fragmentation, proved by the rate-dependence on the nature of the nucleofuge and electrofuge.[46]



All this evidence leads to the obvious conclusion that a concerted cis-*elimination can be regarded as real.*

Not only compounds with a fixed *cis* arrangement of the leaving groups (cyclic and olefinic compounds) yield products via *cis*-elimination, but also some *open chain systems* from which *trans*-eliminations are also theoretically possible. These nonsterospecific *(cis* and *trans* olefins as products) and occasionally stereoconvergent (only one olefin from both diastereomeres) eliminations are usually characteristic for systems with large groups R_α and R_β, mostly with conjugative properties (+M and − M groups), which groups would interfere with each other in the transition state for *trans*-eliminations. This so-called *cis*-effect[14] is the reason why the groups R_α and R_β are not able to be in the same plane in the transition state, but the planarity is necessary for the maximum possible π-orbital overlap between these two groups and C_α and C_β. In order to avoid the *cis*-effect, the elimination could proceed either via a carbanion intermediate (E1cB mechanism) or via *cis*-elimination. If the concerted *cis*-elimination is real in the cyclic systems, why should it not be conceivable in the open chain molecules with strongly activating groups, R_α and/or R_β, which tend to offset the rate difference between *cis*- and *trans*-eliminations.[17d, 38, 42b, 44b, c, 47] Since in the activated rigid systems k_{trans}/k_{cis} is between 1 and few hundreds,[38, 42b, 44b, c, 47] the nonstereospecificity or stereoconvergency can be explained on the grounds of competitive, concerted *cis*- and *trans*-eliminations. In these molecules, such as the dihalides of cinnamic acid,[48] chalcone,[49] stilbene[50] and their derivatives, the *cis*-effect in addition slows down the *trans*-elimination, thus relatively favoring the *cis*-elimination.

Similarly to the elimination reactions from open chain systems with acidic hydrogens, one can account for the debrominative decarboxylation of *erythro-α,β-*

---

[41] J. Weinstock, J. L. Bernardi and R. G. Pearson, *J. Amer. Chem. Soc. 80* (1958) 4961.

[42] a) Recently, Hine and Ramsey *(J. Amer. Chem. Soc. 84* [1962] 973) came to the conclusion that "it seems quite possible that the activated *cis*-eliminations of cyclic sulfonyl derivatives proceed via the intermediate formation of carbanions, although the uncertainties associated with the linear free-energy relationship used are certainly too great for the carbanion mechanism to be regarded as established unequivocally." In addition to these "great uncertainties" is the following: the configuration of the key compound in the study (*cis*-2-methoxycyclohexyl-*p*-tolyl sulfone) should be *trans* in order to approximate more closely the shielding effect of the *trans*-tosyloxy group, which still might shield the β-proton much more than does the methoxy group in the same configuration.

b) Goering, Relyea and Howe *(J. Amer. Chem. Soc. 79* [1957] 2502) suggest that the reprotonation of the carbanion formed is prevented in a 0.004 to 0.03 N basic solution, thus a formation of a stable carbanion without specific base catalysis is still possible. This argument, however, is highly questionable because the base concentration relative to the solvent concentration is negligible, therefore, the anion will find enough solvent for reprotonation.

[43] T. F. Sullivan, *Diss. Abstr. 19* (1958) 1211.

[44] a) S. J. Cristol and H. L. Hause, *J. Amer. Chem. Soc. 74* (1952) 2193.

b) S. J. Cristol and E. Hoegger, *J. Amer. Chem. Soc. 79* (1957) 3438.

c) S. J. Cristol and R. P. Arganbright, *J. Amer. Chem. Soc. 79* (1957) 3441.

[45] N. A. Lebell, P. D. Beirne, E. R. Karger, J. C. Powers and P. M. Subramanian, *J. Amer. Chem. Soc. 85* (1963) 3199.

[46] H. Fischer, C. A. Grob and E. Renk, *Helv. Chim. Acta 45* (1962) 2539.

[47] S. J. Cristol and F. R. Stermitz, *J. Amer. Chem. Soc. 82* (1960) 4692.

[48] J. J. Sudborough and K. J. Thompson, *J. Chem. Soc. 1903*, 666. J. C. James, *J. Chem. Soc. 89* (1906) 105.

[49] a) R. E. Lutz, D. Hinkley and R. H. Jordan, *J. Amer. Chem. Soc. 73* (1951) 4647.

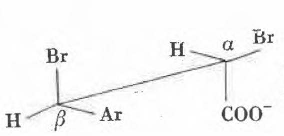
b) T. I. Crowell, A. A. Wall, R. T. Kemp and R. E. Lutz, *J. Amer. Chem. Soc. 85* (1963) 2521.

[50] S. J. Cristol and P. Pappas, *J. Org. Chem. 28* (1963) 2066.

dibromo-β-arylpropionates in terms of competitive synchronous *cis-* and *trans*-elimination rather than by invoking a combination of E1 and E2 reactions.[51] In support of this idea the following considerations should be conclusive:

a) The ratio of *cis*-β-bromostyrene (by *trans*-fragmentation) to *trans*-β-bromostyrene (by "*cis*"-fragmentation) is strongly dependent *on the nature of the substituent* on the benzene ring (cf. Table 5). If a carbonium ion is responsible for the non-stereospecific course of the elimination, as it has been proposed,[51] then ratio of the products is expected to be independent of p-substituents in a good ionizing solvent, such as water and alcohol, because of the identical steric requirement in the resultant *cis*-β-bromostyrenes. Consequently, a thermodynamically controlled product-determining step does not seem very probable.

(7)



→ *cis* and / or *trans* Ar—CH=CH—Br

b) The exclusive formation of *trans*-p-methoxy-β-bromostyrene in the poorly ionizing solvent acetone does not support the idea of a twostep process either. Presumably the electron supplying effect of the aryl group is more important for the *cis*-elimination because there is no back-side nucleophilic participation.

Table 5[a]. Olefin Compositions by Fragmentations of Cinnamate Dibromides According to Eq. (7)

p-substituted	Water		Alcohol		Acetone or EtCOCH$_3$	
	% *cis*	% *trans*	% *cis*	% *trans*	% *cis*	% *trans*
H	22	78	80	20	100	–
NO$_2$	67	33	100	–	–	–
CH$_3$O	–	100	–	–	–	100

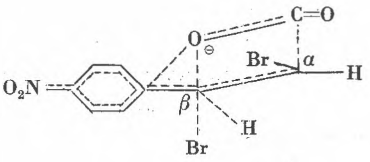
a) For recent compilation of data see ref. 51c.

b) Cinnamate dibromide liberates bromide ions about 180 times faster in alcohol than does styrene dibromide.[51c, 52] A field or inductive effect of the carboxylate anion would account for about a 5-fold acceleration;[53] therefore, the ratio E1/E2 (ionization vs. fragmentation) should be about 1/30 instead of 1/3 as proposed.[51c]

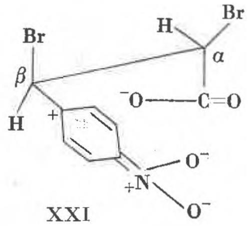
c) The lack of a positive kinetic salt effect in the decomposition of cinnamate dibromide[51c] is rather indicative of assisted bromide release by the carboxylate group, since styrene dibromide reveals a pronounced salt effect.[52]

The *solvent effect on product distribution* also can be explained in this way. The more polar the solvent, the more importance the solvent effect has for the C$_\beta$–Br bond-breaking and the less will be the nucleophilic participation of the carboxylate anion, which is more stabilized in more polar solvents. Consequently, poorly ionizing solvents favor the *trans*-course of the fragmentation.

A remarkable *solvent effect influences the rate* of these reactions also. In polar solvents, such as water and alcohol, where the field effect of the acylate ion is less pronounced, the presence of the nitro group slows down the reaction, but in acetone the plot of the Hammett $\sigma\varrho$-function is U-shaped again.[10, 51c] Since there is no trapping effect possible for the nucleophile, in the sense previously mentioned, the reason for the acceleration by the nitro group in the *para* position can be either an orbital overlap between the oxygen and phenyl ring (XX) (energetic acceleration), or ground state control of the required (and because of the *cis*-effect), unfavored configuration for the *trans*-fragmentation (XXI) (statistical acceleration). The question, which factor accounts for the rate enhancement in non-polar solvents cannot be answered with certainty because of the lack of the necessary experimental data.



XX



XXI

In these systems the solvent affects the rate-determining step in two ways. A polar solvent facilitates the breaking of the C$_\beta$–Br bond (stabilization of the transition state), but decreases the aid of the acylate ion (ground state stabilization). Therefore, *a minimum is expected in the rate as a function of solvent polarity.* Indeed the cinnamate dibromide and its p-nitro derivative react faster in water and acetone or methylethyl ketone than in alcohol or in 80% acetone-20% methanol mixture.[10, 51c] Nevertheless the p-methoxy derivative reacts faster in water and alcohol than in methylethyl ketone. Since in this compound the fragmentation does not occur in the *trans* sense the role of acylate ion is of less importance. *trans*-2-Bromocyclohexane carboxylate also decomposes more readily in 80% alcohol than in water.[53]

---

[51] a) E. GROVENSTEIN and D. E. LEE, *J. Amer. Chem. Soc. 75* (1953) 2639.
b) S. J. CRISTOL and W. P. NORRIS, *J. Amer Chem. Soc. 75* (1953) 2645.
c) E. R. TRUMBULL, R. T. FINN, K. M. IBNE-RASA and C. K. SAUERS, *J. Org. Chem. 27* (1962) 2339.

[52] S. WINSTEIN and E. GRUNWALD, *J. Amer. Chem. Soc. 70* (1948) 828.

[53] W. R. VAUGHAN, P. SCHEINER and J. CSAPILLA, unpublished results.

E. Orientation

If the elimination normally leads to more than one olefin, we are faced with the problem of orientation. The Hofmann and Saytzeff rules provide useful generalizations concerning the products expected, depending upon the nature of the nucleofuge, X. With uncharged nucleofuges, such as the halogens and sulfonates, the Saytzeff product (the most substituted olefin) is dominant in the olefinic mixture, but an onium nucleofuge, such as ammonium and sulfonium groups, tends to lead to more Hofmann product (the least branched olefin). In spite of a great amount of research, the theoretical basis for the Saytzeff and Hofmann rules remains controversial. HUGHES, INGOLD and their coworkers[1a] attribute Hofmann behavior to inductive influence by the positive charge of the onium ion, resulting in the abstraction of the most acidic hydrogen, usually attached to a terminal β-carbon atom, whereas the Saytzeff behavior is a result of hyperconjugative stabilization in the transition state.

SCHRAMM[54] and BROWN and his coworkers[55] propose instead that only the steric requirement of the nucleofuge, under given conditions, determines the product distribution. The larger the nucleofuge, the more Hofmann product is expected.

Neither the inductive nor the steric effect alone is convincingly able to account for the observed orientations, because with increased bulkiness, the inductive effect on the nucleofuge also increases in the model compounds used by both schools (halogen $<$ OTs $<$ S^+). More informative are the following two examples:

a) SAUNDERS[56] found that the distribution of olefins formed from 2-pentyl halides do not obey the steric hypothesis. The chloride forms 37% 1-pentene, the bromide 25% and the iodide 20%. Also 2-halo-2-methylbutane provides more Hofmann product with a smaller halogen as nucleofuge.

b) COLTER and JOHNSON[57] have more recently examined the role of the nucleofuge in a system with a constant steric requirement. The proportion of 2-pentenes from the elimination of 2-pentylarenesulfonates showed a very slight, but regular increase as the substituent on the aryl ring was varied from NH_2 through NO_2. According to Hughes' and Ingold's theory one would expect more 1-pentene with the more electronegative substituent NO_2.

As a result of these two experiments, the reason for the controversy between the two theories mentioned above becomes clearer: neither the steric nor the inductive effect alone appears to be product determining, as expected by BROWN and INGOLD, respectively. Therefore, an explanation has been suggested[56, 57] which can be summarized as follows: The more the transition state resembles the product, the more of the stabler olefin (Saytzeff) will be formed. The extent of the unsaturation formed in the transition state depends upon the ratio of the stretching of the bonds of the two departing groups H and X. Assuming that the C–H bond stretching proceeds to a greater extent than that of the C–X bond, a more effective nucleofuge increases the double bond character in the transition state, and thus the amount of the Saytzeff product.

This picture is presumably essentially correct, but the assumption concerning the identity of which bond is stretched to the greater extent is inconsistent with the corresponding considerations used in this article (cf. the necessity of introducing the term, nucleophilic participation). Therefore, it is suggested that the C–X bond-breaking is generally more advanced in the transition state than the C–H bond-breaking. Since nucleophilic participation is less necessary with a more effective nucleofuge (i.e., the base-H bond becomes stronger), the obviously increased extent of breaking of the C–X bond may be counteracted by that of the C–H bond, thus the double bond character of the transition state increases (more Saytzeff product).

F. Competition Between Sn and E Reactions

From the nature of the transition state for elimination reactions proposed in this article, it is possible to predict the influence of R and nucleofuge, X, with respect to the competition between Sn and E reactions.

Nucleofuges of the same type, such as the three common halogens, should reveal the highest elimination/substitution ratio with the best nucleofuge. The better it is, the easier is the breaking of the C–X bond and the weaker is the Y–C bond; i.e., the covalent portion of the nucleophilic participation, in the transition state. An *electron donating group,* R_α, increases the ratio also because the additional stabilization of the (incipient) carbonium ion lowers the attractive force between nucleophile and the electrophilic center C_α. *According to the classical picture of E2 and Sn2 reactions, however, one would expect the reverse trend,* since in the Sn2 reaction *only* the C–X bond is broken; hence, the more readily it breaks the more substitution product is to be expected. In the following tables (6 and 7) some examples are collected in support of this statement.

The *effect of solvent* on the product distribution is relatively clear in dehalogenative decarboxylation reactions. In a poor ionizing solvent the field effect of the carboxylate group is larger than in a good ionizing solvent; the greater field effect allows less efficient

---

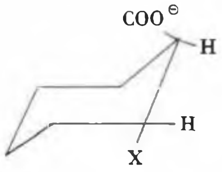
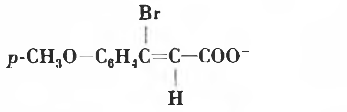
[54] C. H. SCHRAMM, *Science 112* (1950) 367.

[55] H. C. BROWN and O. H. WHEELER, *J. Amer. Chem. Soc. 78* (1956) 2199; H. C. BROWN and I. MORITANI, *J. Amer. Chem. Soc. 78* (1956) 2203, and H. C. BROWN, *J. Chem. Soc. 1956,* 1248.

[56] W. H. SAUNDERS, JR., R. S. FAHRENHOLTZ and J. P. LOWE, *Tetrahedron Letters 1960,* No. 18, 1.

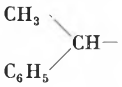
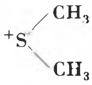
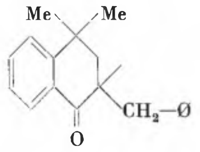
[57] A. K. COLTER and R. D. JOHNSON, *J. Amer. Chem. Soc. 84* (1962) 3289.

Table 6. Extent of Debrominative Decarboxylations as a Function of Structure

Acylate	X	Total Yield of Fragmentation Product if Time = ∞, in %	T °C	Ref.
$X-CH_2-C(C_6H_5)_2-COO^-$	Cl	0	25	a
	Br	27	25	a
	I	68	25	a
β-halo-α-methylbutyrate	Br	67	25	b
(HX + tiglic acid)	J	84	10–45	c
	Cl	42	25	d
	Br	50	25	d
α,β-dibromo-propionate	Br	0	100	e
-butyrate	Br	16	100	f
-i-valerate	Br	88	100	e
p-$CH_3O-C_6H_4-CHBr-CHBr-COO^-$		86	25	g
H– ,,		60	40	g
p-NO_2– ,,		40–50	84	g
 p-$CH_3O-C_6H_4C(Br)=C(H)-COO^-$		100	90	h
H– ,,		80	130	h

a) H. E. ZAUGG, *J. Amer. Chem. Soc. 72* (1950) 2998.
b) H. JOHANNSON and S. M. HAGMAN, *Ber. dtsch. chem. Ges. 55* (1922) 647.
c) W. G. YOUNG, R. T. DILLON and H. J. LUCAS, *J. Amer. Chem. Soc. 51* (1929) 2528.
d) W. R. VAUGHAN and R. L. CRAVEN, *J. Amer. Chem. Soc. 77* (1955) 4629.
e) J. K. FARRELL and G. B. BACHMAN, *J. Amer. Chem. Soc. 57* (1935) 1281.
f) E. A. BRAUDE and J. A. COLES, *J. Chem. Soc. 1951*, 2078.
g) For recent compilation of data see ref. 51 c.
h) Ref. 37.

Table 7. Structure Dependent Yields of Olefins in E 2 Reactions

R	X	% Olefin	Solvent	Base	T °C	Ref.
Et–	Br–	1	dry EtOH	$EtO^{\ominus}$	55	a
 $(CH_3)(C_6H_5)CH-$	Br–	34	,,	,,	55	b
iPr–	Br–	79	,,	,,	55	a
tBu–	Br–	100	,,	,,	55	a
Et	 $^{+}S(CH_3)_2$	12	,,	,,	45	a
iPr	,,	61	,,	,,	45	a
,,	Br	53	60% EtOH	$HO^{\ominus}$	45	a
,,	I	70	,,	,,	50	a
,,	Cl	59[c]	80% EtOH	,,	80	a
,,	Br	61	,,	,,	80	a
	Cl	1/59[d]	CH_3CN	$^{*}Cl^{\ominus}$	90.6	e
,,	Br	1/200[d]	,,	,,	24.5	e

a) HUGHES, INGOLD and co-workers, *J. Chem. Soc. 1948*, 2038–119.
b) E. D. HUGHES, C. K. INGOLD, S. MASTERMAN and B. J. MCNULTY, *J. Chem. Soc. 1940*, 899.
c) Interpolated from values 57.1% at 70° and 60.6% at 90°.
d) This number represents the ratio of substitution / elimination.
e) D. N. KEVILL, G. A. COPPENS and N. H. CROMWELL, *J. Org. Chem. 28* (1963) 567.

covalent participation of the carboxylate group and thus inhibits possible strong coordinative bond-formation (lactonization). The following table shows the supporting data:

Table 8. Extent of Debrominative Decarboxylations as a Function of Solvent

Compound	X	% Olefin in: H_2O	EtOH	Acetone
trans-2 X-cyclohexyl carboxylate[a]	Cl	42	–	96
	Br	50	–	96
p-NO_2-cinnamate dibromide[b]	–	40	73	94

a) Table 6, footnote d.
b) Table 6, footnote g.

It must be mentioned that in addition to the foregoing phenomena the product ratio is obviously also dependent on the strength of the C–H bond. Electron-withdrawing substituents favor elimination,[17c] and in addition, the D/H isotope effect reveals its contribution in the product ratio.[17b]

The *temperature effect* on the elimination/substitution ratio has been discussed thorougly by Ingold,[1a] consequently, no attempt has been made to cover this aspect of the subject. Elevation of the temperature usually raises this ratio.

Summary

i) The rate enhancement in Sn2 and E2 reactions by α-substituents with –M-effect (phenomenon leading to a U-shaped Hammett ϱ-curve) is due to an entropy effect and probably not to an extended orbital overlap effect. This suggestion is based on activation parameter considerations of available data.

ii) In E2 reactions the base operates in two ways: as base and nucleophile. The character of this nucleophilic participation may not only be of electrostatic nature (field effect or solvation effect) but also of covalent bond-forming to a certain degree.

iii) The more easily the C–X bond breaks the more favored is elimination over substitution. However, one would expect the reverse, because in the Sn2 reaction only the C–X bond is broken; and therefore, its breaking must be more important in this reaction. The reason for this surprising effect is the lesser importance of nucleophilic participation if the C–X bond breaks easily.

iv) The Hammett ϱ value is in reverse order to the corresponding kinetic isotope effect with respect to the breaking of the C–H bond. The better the nucleofuge, X, is, the smaller is ϱ and the larger is the isotope effect because the Sn/E character in the transition state is relatively small. The isotope effect measures the actual importance of a given bond-breaking process, while ϱ is only a bond-breaking coefficient; and this is larger if the bond-breaking is less advanced in the transition state.

v) Nucleophilic participation also explains why *trans*-eliminations are generally favored over *cis*-eliminations.

vi) It is valid to consider concerted *cis*-eliminations.

vii) An understanding of orientation may be based on the facility of heterolysis of the C–X bond. An effective nucleofuge, X, and/or an α-substituent with +M-effect, as well as an acidic hydrogen, make possible a transition state with relatively great double bond character (Sn/E character is relatively small); therefore, the stability of the olefin formed is of importance (Saytzeff behavior). A less effective nucleofuge, X (ónium leaving group), and/or an α-substituent with —M-effect, instead requires a greater nucleophilic participation of the base; and thus the base does not distinguish between hydrogen with different electromeric properties. In the latter case the orientation is probably due to the different steric requirements of the different N-substituents, but a reasonably complete spectrum of the Saytzeff and Hofmann olefins does not appear as a linear function of the steric requirements of the nucleofuge. In general, the steric and inductive effects of the nucleofuge do not seem important enough to account for the orientation.

Acknowledgment

I am indebted to the Professors Dr. W. R. Vaughan and Dr. C. A. Grob for their assistance with this manuscript. I also wish to thank Dr. Urs Burckhardt for his discussions and many suggestions as well as my other colleagues for reading and correcting the text.