Mechanisms of Elimination Reactions. Part III.[1] Rate Coefficients for Elimination from Substituted 2-Phenylethyl Arenesulphonates with Potassium in t-Butyl Alcohol

By **J. Banger,** School of Chemical Sciences, University of East Anglia, Norwich
Anthony F. Cockerill * and (in part) **G. L. O. Davies,** Lilly Research Centre, Erl Wood Manor, Windlesham, Surrey

The rate coefficients for elimination from 24 substrates in the series 2-Z-phenylethyl *p*-Y-arenesulphonate with potassium t-butoxide in t-butyl alcohol at 40 °C have been correlated with the Hammett equation. The reaction constants ρ_Z decrease linearly with the electronic properties of the group Y only for the most electron-withdrawing substituents, indicative of a shift to transition states with less carbanion character. The reaction constants ρ_Y become less positive as Z become more electron-withdrawing, suggesting that increased C_β–H bond breaking is accompanied by decreased C_α–X bond breaking, and a shift to a transition state with greater carbanion character. This result supports earlier secondary deuterium isotope studies in establishing a new interpretation of the reactivity ratio k_{OTs}/k_{Br} as a measure of C–X bond breaking.

WITHIN the bounds of a concerted reaction, it is now widely accepted that there exists a spectrum of transition states for base-induced *E*2 reactions.[2] When C_β–H bond breaking runs ahead of C_α–X bond breaking, carbanion character develops at the β-carbon. Carbonium ion character arises at the α-carbon when the relative extent of bond breaking is reversed. In between these extremes lie the so-called central transition states where C_β–H and C_α–X bond breaking are more closely balanced (Figure 1). A number of kinetic approaches have been used to support the concept of a continuous spectrum of transition states. These include kinetic isotope effects,[3,4] eclipsing effects,[5] and the application of linear free energy relationships such as the Hammett [6] and Brønsted equations.[7] The position of the transition state is

---

[1] (*a*) Part I, A. F. Cockerill, *J. Chem. Soc.* (*B*), 1967, 964; (*b*) Part II, A. F. Cockerill, *Tetrahedron Letters*, 1969, 4913.

[2] For reviews, see (*a*) D. V. Banthorpe, 'Elimination Reactions,' Elsevier, Amsterdam, 1963, vol. 2; (*b*) W. H. Saunders, jun., 'Elimination Reactions in Solution,' in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience Publishers, J. Wiley and Sons, London, 1964, chap. 2; (*c*) J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225; (*d*) A. F. Cockerill, 'Elimination Reactions,' in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. H. F. Tipper, Elsevier, Amsterdam, in the press.

[3] W. H. Saunders, jun., and D. H. Edison, *J. Amer. Chem. Soc.*, 1960, **82**, 138.

[4] W. H. Saunders, jun., A. F. Cockerill, S. Ašperger, L. Klasinć, and D. Stefanović, *J. Amer. Chem. Soc.*, 1966, **88**, 848.

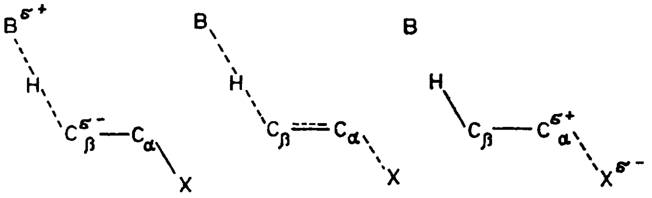
[5] D. J. Cram, C. H. DePuy, and F. D. Greene, *J. Amer. Chem. Soc.*, 1956, **78**, 790.

[6] (*a*) C. H. DePuy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, 1957, **79**, 3710; (*b*) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2532, 2535; (*c*) W. H. Saunders, jun., and R. A. Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 3712.

[7] R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1964, 5.

greatly dependent on the structure of the reactants and possibly the leaving group exerts the greatest influence.

The Hammett equation has been applied successfully to correlate the rate of elimination of substituted 2-phenylethyl compounds.[6] For eliminations in ethanol containing sodium ethoxide, as the leaving group is changed along the series I, Br, Cl, F, the Hammett reaction constant, ρ, increases in the order 2·07, 2·14, 2·61, 3·12.[6] The continual increase in ρ reflects an increase in the degree of negative charge which accumulates on the β-carbon atom in the transition state, and consequently carbanion character increases with the electron-withdrawing power of the leaving group. However, the ionising tendency of the C–X bond decreases along the same series, and this property could be responsible for the observed trend. In an attempt to decide whether electron withdrawal in the leaving group influences mainly C_β–H or C_α–X bond breaking, it was decided to investigate the rate of elimination from a series of substituted 2-phenylethyl arenesulphonates (I). The electron-withdrawing power of the sulphonate ester can be modified by the choice of different substituents Y, without causing gross changes in the steric size of the leaving group or in the strength of the C–O bond. The Hammett equation (for various Z) can be used as a measure of changes in carbanion character brought about by variations in Y. The initial studies were performed in t-butyl alcohol containing potassium t-butoxide. In this system, the sulphonate esters are known to undergo almost quantitative conversion into the corresponding styrenes with negligible contributions arising from unimolecular decompositions.[6]

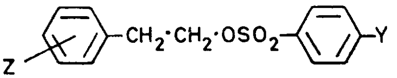


Carbanion-like transition state

Central transition state

Carbonium ion-like transition state

FIGURE 1



(I)

EXPERIMENTAL

Preparation and Purification of Reagents.—Solvent and base. All solvents and solutions for kinetics were stored and handled in a dry-box which was maintained at 30 ± 1 °C. The purification of t-butyl alcohol and the preparation and standardisation of potassium t-butoxide solutions in t-butyl alcohol have been described.[8]

Substituted 2-phenylethyl arenesulphonates.—The substituted 2-phenylethyl arenesulphonates were prepared from the corresponding 2-phenylethanol and the appropriate *para*-substituted benzenesulphonyl chloride in pyridine at −10 °C, according to the procedure of Tipson.[9] The physical parameters are in Table 1.

The substituted 2-phenylethanols were prepared by one of two routes. In some cases (*p*-Me, *p*-Cl, *m*-Cl), the Grignard reagent of the corresponding bromobenzene was treated with ethylene oxide.[10] Alternatively (*m*-OMe, *p*-OMe) the substituted phenylacetic acid was esterified with methanol saturated with hydrogen chloride, and the ester was subsequently reduced with lithium aluminium hydride.

TABLE 1

Physical properties of substituted 2-phenylethyl arenesulphonates (I)

Substituents				
Z	*p*-Y	M.p.	Lit. m.p.	Ref.
H	H	15—16	16 †	*a*
H	Me	39—39·5	38—39	6*a*
H	Br	58—59·5	59—60	*b*
p-OMe	Me	59—59·5	58—58·5	*c*
m-OMe	Me	35·5—36	37·5—38·5	*d*
m-OMe	Br	44·5—45	40·5—41·5	*b*
p-Me	Me	68—69	69—70	*e*
p-Cl	Me	80—80·5	80—80·5	6*a*

			Analysis (%)			
Substituents			Found		Required	
Z	*p*-Y	M.p.	C	H	C	H
H	NO_2	101·5—102	54·52	4·08	54·73	4·24
p-OMe	H	72—73	61·85	5·43	61·65	5·48
p-OMe	Br	45—45·5	48·65	4·04	48·52	4·04
p-OMe	NO_2	98—98·5	53·23	4·41	53·42	4·45
m-OMe	H	26·5—27	61·60	5·54	61·65	5·48
m-OMe	NO_2	92·5—93	53·40	4·40	53·42	4·45
p-Me	H	61·5—62·5	65·20	5·92	65·22	5·80
p-Me	Br	79·5—80·5	50·52	4·18	50·70	4·23
p-Me	NO_2	84—85	56·08	4·74	56·08	4·67
p-Cl	H	41—42	56·86	4·49	56·66	4·38
p-Cl	Br	82—82·5	45·00	3·39	44·94	3·20
p-Cl	NO_2	121—122	49·40	3·72	49·20	3·51
m-Cl	H	Oil	56·41	4·30	56·66	4·38
m-Cl	Me	47·5—48·5	58·20	4·92	58·00	4·83
m-Cl	Br	55·5—56·5	44·89	3·02	44·94	3·20
m-Cl	NO_2	90·5—91·5	49·41	3·70	49·20	3·51

† n_D^{22} 1·5570 (lit.,[a] n_D^{20} 1·5584).

[a] D. Klamann, *Monatsh.*, 1953, **84**, 54. [b] S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, 1956, **78**, 4801. [c] W. H. Saunders, jun., and R. Glaser, *J. Amer. Chem. Soc.*, 1960, **82**, 3586. [d] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Amer. Chem. Soc.*, 1967, **89**, 370. [e] N. A. Nelson and J. C. Wollensak, *J. Amer. Chem. Soc.*, 1958, **80**, 6626.

Potassium benzenesulphonates. The substituted benzenesulphonyl chlorides were hydrolysed to the corresponding sulphonic acids. These were neutralised with potassium carbonate and the solutions evaporated to dryness. The potassium salts were recrystallised from aqueous or absolute alcohol.

Substituted styrenes. These were prepared in almost quantitative yield (±1%) by treating the corresponding 2-arylethyl arenesulphonate with potassium t-butoxide in t-butyl alcohol at 40 °C. The absorption maxima and the

---

[8] A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 901.

[9] R. S. Tipson, *J. Org. Chem.*, 1944, **9**, 235.

[10] R. C. Huston and A. H. Agett, *J. Org. Chem.*, 1941, **6**, 123.

molar extinction coefficients at the maxima were in close agreement with the values reported.[6c,11]

Kinetic Studies.—The rate of elimination from the sulphonate esters was measured by monitoring the appearance of the substituted styrene spectrophotometrically. To simplify the kinetics, a large excess of the base ($KOBu^t$) over the substrate was always employed and pseudo-first-order rate constants were determined from the slope of a plot of log ($D_\infty - D_t$) against time, where D_t is the absorbance at time t and D_∞ the absorbance after at least ten half-lives. In the absence of base, none of the substrates underwent unimolecular elimination to the styrene during the corresponding D_∞ times. Absorbance of the styrenes was monitored at 258—260 nm rather than at the alkene maxima, because absorption due to the base at lower wavelengths reduced the precision of measurement.

For the benzene-, *p*-tolyl-, and *p*-bromobenzene-sulphonates, kinetic solutions were prepared in a two-limbed reaction vessel, which was connected by a ground-glass joint to a 1 cm silica cell (*cf.* apparatus described in Figure 1 of ref. 12). The base solution (3·00 ml) was placed in one limb and the substrate solution (0·100 ml of *ca.* 3 × 10^{-3}M) in the other. The stoppered reaction vessel was then thermostatted for 45 min, the reactants were mixed thoroughly, and the apparatus was inverted (allowing the solution to drain into the cell) and rapidly placed in the cell compartment of a Unicam SP500 spectrophotometer. The cell compartment was maintained at 40 ± 0·1 °C by circulation of water from a constant-temperature bath. All reactions were followed for at least three half-lives and first-order rate coefficients were based on the best straight line through 20—28 points. The second-order rate coefficients, obtained by dividing the first-order values by the base concentration, are in Table 2. They were independent of the base concentration over the five-fold variation employed in the studies.

Table 2

Second-order rate coefficients * for elimination from substituted 2-phenylethyl arenesulphonates in t-butyl alcohol with potassium t-butoxide at 40 °C

Z	[Base]/M	
p-Nitrobenzenesulphonates		
		10^2k_2/l mol^{-1} s^{-1}
p-OMe	0·0414	1·29 ± 0·02
p-Me	0·0414	2·01 ± 0·07
H	0·0414	4·17 ± 0·00
m-OMe	0·0207	6·83 ± 0·13
p-Cl	0·0161	12·5 ± 0·1
m-Cl	0·0161	26·9 ± 0·5
	0·0803	
Toluene-*p*-sulphonates		
		10^4k_2/l mol^{-1} s^{-1}
p-OMe	0·0877	9·35 ± 0·32
p-Me	0·0726	15·1 ± 0·1
H	0·1045	40·1 ± 0·6
m-OMe	0·0774	68·5 ± 0·4
p-Cl	0·0774	144 ± 5
m-Cl	0·0774	372 ± 3
p-Bromobenzenesulphonates		
		10^3k_2/l mol^{-1} s^{-1}
p-OMe	0·0877	2·48 ± 0·01
p-Me	0·0726	4·59 ± 0·00
		10^2k_2/l mol^{-1} s^{-1}
H	0·0822	1·20 ± 0·01
m-OMe	0·0822	1·96 ± 0·00
p-Cl	0·0774	4·13 ± 0·02
m-Cl	0·0822	8·24 ± 0·01
Benzenesulphonates		
		10^3k_2/l mol^{-1} s^{-1}
p-OMe	0·0877	1·17 ± 0·02
p-Me	0·0822	1·99 ± 0·02
H	0·0974	6·17 ± 0·04
m-OMe	0·0974	9·77 ± 0·02
p-Cl	0·0726	20·7 ± 0·1
m-Cl	0·0813	47·2 ± 0·2

* Average of two kinetic runs with deviation from the mean.

Potassium *p*-nitrobenzenesulphonate and all the *p*-nitrobenzenesulphonates absorb appreciably in the region of maximum absorption of the styrenes. Fortunately, the salt and all the *p*-nitro-substrates have similar absorption spectra, which can be used to cancel each other, enabling absorption measurements between 0 and 0·9 to be made during the kinetic run. Into two silica 1 cm cells, solutions (2·60 ml) of equal concentration of the sulphonate ester and the potassium *p*-nitrobenzenesulphonate were placed, respectively. The cells were stoppered and placed in the thermostatically controlled cell compartment of an automatically recording SP700 spectrophotometer. After equilibration for 30 min, the wavelength was adjusted to give the minimum optical density difference between the two solutions (usually absorbance = *ca.* 0·04 at 270 nm). An aliquot portion of base (0·100 ml) was rapidly injected into each solution and, with the cells tightly stoppered, the solutions were efficiently mixed and the cells were replaced in the spectrophotometer. Essentially, the recorded absorbance change ($D_\infty \simeq 1{\cdot}0$) was almost entirely due to the produced styrene. The spectral properties of the *p*-nitro-compounds and the wavelengths selected for the kinetic studies are in Table 3.

Table 3

Spectral characteristics of *p*-nitro-substituted compounds in t-butyl alcohol at 40 °C

R in $R{\cdot}OSO_2{\cdot}C_6H_4{\cdot}NO_2$	$\lambda_{max.}$/nm	$10^{-4}\varepsilon_{max.}$
2-Phenylethyl	250	1·17
2-(*p*-Anisyl)ethyl	250	1·21
2-(*m*-Anisyl)ethyl	250	1·08
2-(*p*-Tolyl)ethyl	250	1·18
2-*m*-Chlorophenylethyl	250	1·08
2-*p*-Chlorophenylethyl	250	1·21
K *	251	1·08

* Solvent 1% dimethyl sulphoxide.

DISCUSSION

The substituents in the substrates were varied in two positions. Consequently, it was possible to apply the Hammett equation in two ways and the Discussion section has therefore been divided into sections governed by the reaction constants ρ_Z and ρ_Y.

(1) *The Reaction Constant* ρ_Z.—The rate coefficients for elimination from each series of sulphonate esters (Y constant, Z varying for each correlation) correlate in an excellent linear fashion with the Hammett equation (see Table 4 and Figure 2). There is a marked difference between the reaction constant obtained by us for elimination from the substituted toluene-*p*-sulphonates at 40 °C and the value ($\rho = 3{\cdot}39 \pm 0{\cdot}029$, $r = 0{\cdot}995$) re-

---

[11] J. R. Joy and M. Orchin, *J. Amer. Chem. Soc.*, 1959, **81**, 305.

[12] K. Bowden and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1970, 173.

ported by DePuy and Bishop at 30 °C.[6b] Although the magnitude of the Hammett reaction constant usually varies inversely with the reaction temperature,[13] the discrepancy between the results is too large to be explained by this artefact. The earlier work was based on only four substituents and the value of the reaction constant is thus more highly influenced by one erroneous point. Moreover, the rate coefficients were measured by a titrimetric procedure which is less accurate than a spectrophotometric approach. We feel that the present value is more precise.

The Hammett constant reflects predominantly changes in the electron density at the β-carbon atom in passing from the substrate into its transition state for elimination. The greater the carbanion character, the more positive the reaction constant. A decrease in the extent of C_β–H bond breaking, or greater delocalisation of the developing negative charge into the forming C_β–C_α double bond brought about by increased C_α–O bond breaking, cause a reduction in the reaction constant, the transition state shifting from the carbanion-like towards the central and carbonium ion-like regions. As the leaving group is changed from toluene-*p*-sulphonate to benzenesulphonate the reaction constant ρ_Z remains essentially constant. Therefore, any increase in C_β–H bond breaking is counterbalanced by greater C_α–O heterolysis or little change in the extent of bond breaking occurs. Studies of secondary isotope effects on the rates of elimination of 2-arylethyl 1,1-dideuterioarenesulphonates would shed light on which explanation is correct. Further increases in the electron-withdrawing power of the leaving group (as measured by σ_Y) cause a linear decrease in ρ_Z. This trend represents a shift away from the carbanion region towards the central transition states. As t-butyl alcohol is a poorly ionising solvent,[14] it is not surprising that only the more strongly electron-withdrawing substituents, by imparting greater stability on the developing anion, promote greater C_α–O bond breaking.

Willi has reported primary kinetic isotope effects of 5·27, 5·42, and 6·70 for elimination from 2-deuterio-2,2-diphenylethyl *p*-Y-benzenesulphonates with sodium methoxide in methyl cellosolve, Y being OMe, H, and NO_2, respectively.[15] Along this series, as the maximum isotope effect occurs when the proton is half-transferred in the transition state,[16] the change could represent either an increase or decrease in proton transfer, the *p*-nitro result reflecting half-transference approximately. Under these more ionising conditions, it is highly probable that small substituent changes in the leaving group exert a more pronounced effect than in t-butyl alcohol, and C_α–O bond breaking may increase with the electron-withdrawing power of the substituent over the entire range. Thus, by analogy with our results in t-butyl alcohol, a decrease in carbanion character along the above series is expected, and proton transfer should be most extensive for the *p*-methoxy-compound.

TABLE 4

Hammett reaction constants, ρ_Z, at 40 °C for compounds (I)

p-Y	ρ_Z	*r* *
Me	2·49 ± 0·03 †	0·998
H	2·50 ± 0·02	0·998
Br	2·36 ± 0·02	0·999
NO_2	2·03 ± 0·04	0·998

Z = *p*-OMe, *p*-Me, H, *m*-OMe, *p*-Cl, *m*-Cl; σ_Z = −0·268, −0·170, 0·000, 0·115, 0·226, 0·373, respectively.

* *r* = correlation coefficient. † Standard deviation (see ref. 13).

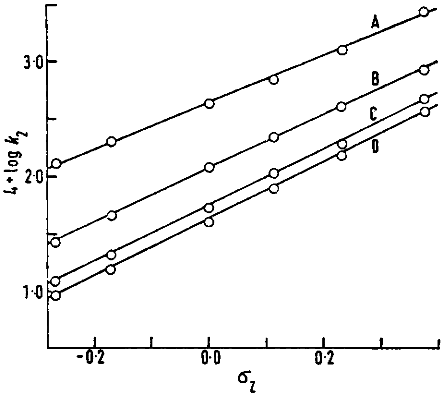


FIGURE 2 Graph of log k_2 against σ_Z for compounds (I): A, Y = NO_2; B, Y = Br; C, Y = H; D, Y = Me. Values of the slope ρ_Z = log $(k/k_0)/\sigma_z$ are in Table 4

(2) *The Reaction Constant* ρ_Y.—The Hammett equation can also be applied successfully to correlate the reaction constants ρ_Y (Z constant, Y varying for each correlation; see Table 5 and Figure 3). The magnitude of ρ_Y reflects the extent of negative charge accumulating in the sulphonate group in the transition state and is thus a measure of the extent of C_α–O bond breaking. As the substituent Z becomes more electron-withdrawing, a linear decrease in ρ_Y with σ_Z (see Figure 4) is observed. Thus, as the C_β–H bond becomes more acidic, C_α–O bond breaking becomes less advanced in the transition state. The Brønsted components β, for elimination from 2-*p*-nitrophenylethyl and 2-phenylethyl bromides with substituted phenoxides in ethanol, are 0·67 and 0·54 respectively.[7] As might be expected, these values suggest

TABLE 5

Hammett reaction constants, ρ_Y, at 40 °C for compounds (I)

Z	ρ_Y	*r* *
p-OMe	1·24 ± 0·02 †	0·999
p-Me	1·24 ± 0·05	0·997
H	1·08 ± 0·03	0·999
m-OMe	1·06 ± 0·03	0·999
p-Cl	1·01 ± 0·04	0·996
m-Cl	0·94 ± 0·02	0·997

Y = *p*-Me, H, *p*-Br, *p*-NO_2; σ_Y = −0·170, 0·000, 0·232, 0·778, respectively.

* *r* = correlation coefficient. † Standard deviation (see ref. 13).

---

[13] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[14] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[15] A. V. Willi, *Helv. Chim. Acta*, 1966, **49**, 1725.

[16] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

that proton transfer to the base increases with the electron-withdrawing power of the substituent Z. Consequently, our results show that increased C_{β}–H bond breaking causes decreased C_{α}–O bond breaking in the transition state.

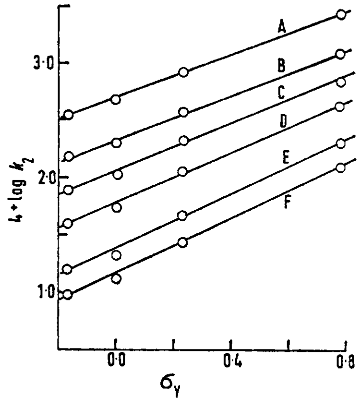


FIGURE 3 Graph of log k_2 against σ_Y for compounds (I): A, Z = *m*-Cl; B, Z = *p*-Cl; C, Z = *m*-OMe; D, Z = H; E, Z = *p*-Me; F, Z = *p*-OMe. Values of the slope ρ_Y = log $(k/k_0)/\sigma_Y$ are in Table 5

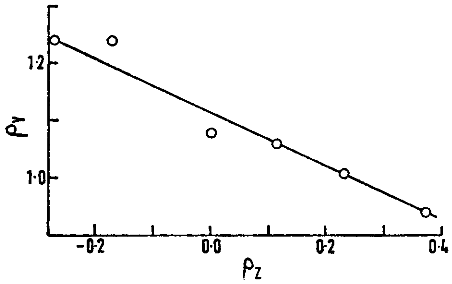


FIGURE 4 Graph of ρ_Y against σ_Z; slope = −0·496; correlation coefficient = 0·979

The rate ratio k_{OTs}/k_{Br} (rate of reaction of a toluene-*p*-sulphonate ester compared with the rate of reaction of the corresponding bromide) has been suggested as a criterion of reaction mechanism.[17] For S_N1 reactions, in which C–X bond breaking is extensive in the transition state, the ratio is large, the developing negative charge being more effectively delocalised by the sulphonate group. In S_N2 reactions in dipolar aprotic solvents or elimination reactions, in which C–X bond breaking is less developed in the transition state, k_{OTs}/k_{Br} is small and often less than unity. The greater polarisability of the C–Br than the C–O bond offsets the delocalisation factor. For elimination from substituted 2-Z-phenylethyl derivatives in t-butyl alcohol containing $KOBu^t$ at 30 °C, k_{OTs}/k_{Br} increases from 0·2 to 1·6 as Z is changed from *p*-OMe along the series H, *p*-Cl, and *m*-Br to *p*-NO_2. Interpreting k_{OTs}/k_{Br} as a linear function of the extent of C–X bond breaking, Hoffmann suggested that increased C_{β}–H bond breaking induced greater C_{α}–X bond breaking, making the *E*1*CB* mechanism paradoxical. This conclusion is the exact opposite of our deductions from the ρ_Y values above.

Recently, one of us[17b] proposed a reinterpretation of k_{OTs}/k_{Br}. For cases when no C–X bond breaking occurs, the toluene-*p*-sulphonate should be slightly more reactive than the bromide as the relative reactivity is dependent on the electrophilic nature of the α-carbon atom. The four electronegative atoms of the sulphonate group are expected to be more electron-withdrawing than the single halogen atom [a prediction supported by σ^* values of 1·31 (OTs) and 1·00 (Br)[18]]. A gradual increase in bond breaking causes a decrease in the ratio until it is dominated by polarisability considerations. Further increases in C–X bond breaking produce a rise in k_{OTs}/k_{Br} as the delocalisation factor gains in importance. Thus trends in the values of the ratio which are in the small or less than unity region can be interpreted as indicating increasing or decreasing C–X bond breaking. As support for the new interpretation, secondary deuterium isotope effects were cited for elimination from 2-Z-phenylethyl 1,1-dideuterio-toluene-*p*-sulphonates in t-butyl alcohol at 40 °C. As Z is changed from *p*-OMe to H to *p*-Cl, k_H/k_D decreases from 1·047 to 1·043 to 1·017. In this instance, the secondary isotope effects arise predominantly from a hybridisation change at the α-carbon atom in attaining the transition state.[19] The hybridisation at the α-carbon progresses more towards the sp^2 extreme and the value of the secondary isotope effect rises as C_{α}–O bond breaking increases. Thus, C_{α}–O bond breaking is more advanced in the case of the *p*-methoxy-compound than the *p*-chloro-substrate, a conclusion now supported by the trend in the above ρ_Y values.

We thank the S.R.C. for a research studentship (to J. B.).

[0/1166 *Received, July 8th,* 1970]

---

[17] (*a*) H. M. R. Hoffmann, *J. Chem. Soc.*, 1965, **6753**, 6762; (*b*) G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc.* (*B*), 1967, 265; (*c*) H. M. R. Hoffman, *Tetrahedron Letters*, 1967, 4393.

[18] J. Hine and O. B. Ramsay, *J. Amer. Chem. Soc.*, 1962, **84**, 973.

[19] A. Streitwieser, jun., R. H. Fahey, R. C. Jagow, and S. Suzuki, *J. Amer. Chem. Soc.*, 1958, **80**, 2326.