of Br⁻ and Cl⁻ progressively decrease from that of I⁻. Using this model as a basis for extrapolation, one would predict that the ^{27}Al shift for AlF_4^- will be found in the region of -140 ppm.

Acknowledgments. This work was supported by the Dow Chemical Co. and the National Research Council of Canada, both of whom we wish to thank.

R. G. Kidd, D. R. Truax[11]

Department of Chemistry University of Western Ontario London, Canada
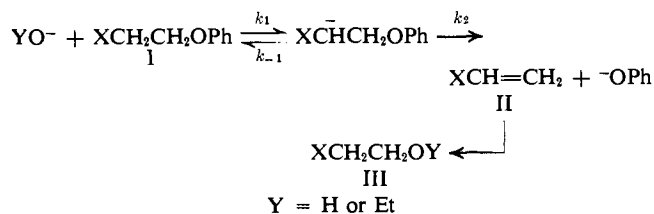
Effects on Reactivity in E1cB Reactions

Sir:

The E1cB mechanism for 1,2-elimination reactions has been much discussed[1-3] but rather seldom observed. Previously claimed instances have usually involved a substrate possessing a poor leaving group and exceptionally good carbanion stabilization at the β-carbon atom.

In connection with a study of activation in β elimination, we have measured the rates of elimination of phenoxide from the phenyl ethers Ic and In in aqueous sodium hydroxide. The former system has also been studied qualitatively by Rydon.[4]

$$YO^- + XCH_2CH_2OPh \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X\bar{C}HCH_2OPh \overset{k_2}{\longrightarrow}$$
$$\text{I}$$

$$XCH=CH_2 + {}^-OPh$$
$$\text{II}$$

$$XCH_2CH_2OY \longleftarrow\rfloor$$
$$\text{III}$$
$$Y = H \text{ or } Et$$

Reactions (at 25°) were followed by ultraviolet spectrophotometric determination of liberated phenoxide and were first order with respect to base and substrate. Rates of reactions of the β-deuterio compounds $I^-Me_2S^+CD_2CH_2OPh$ (Ic') and $MeSOCD_2$-CH_2OPh (In') with NaOD in D_2O were also determined under otherwise identical conditions.

The sulfonium salt Ic' was obtained from Ic by treatment with sodium phenoxide in D_2O; the nmr spectrum showed complete exchange at the β-methylene group and about 30% exchange at the S-methyl groups. Pyrolysis (at 100°) of the deuterated salt gave methyl iodide and the sulfide $MeSCD_2CH_2OPh$ which, on oxidation with peracetic acid, gave the sulfoxide In' containing not less than 98% β-d_2.

The isotope effects k_H/k_D for the sulfonium salt and the sulfoxide are 0.66 and 0.78, respectively. For reactions with substrates in the same base–solvent system, the value of the primary isotope effect to be expected[5] for a fully concerted elimination is $\sim$5. We interpret the inverse isotope effects found in the above systems as follows: deuterioxide ion is about 1.6 times (at 80°) as strong a base as hydroxide ion, and this factor would lead[6] to a value of $k_H/k_D \simeq 0.7$. If the

(1) D. J. McLennan, *Quart. Rev.* (London), **21**, 490 (1967).
(2) Z. Rappoport, *Tetrahedron Letters*, 3601 (1968).
(3) H. M. R. Hoffmann, *ibid.*, 4393 (1967).
(4) C. W. Crane and H. N. Rydon, *J. Chem. Soc.*, 766 (1947).
(5) A. J. Cockerill, *ibid.*, *B*, 964 (1967).
(6) L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 6149 (1967).

secondary and solvent deuterium isotope effects are ignored for the moment, the primary isotope effect must be close to unity. We consider, therefore, that both of these reactions occur by an E1cB mechanism.

In an E1cB process, transfer of the reaction from H_2O to D_2O should favor the equilibrium formation of the intermediate carbanion.[7] Further, since the transition state of the second stage of the reaction involves dispersal of charge, release of phenoxide ion from the carbanion should be slightly more rapid in the heavy solvent. Both factors reduce the value of k_H/k_D. Acting in opposition to them is the secondary deuterium isotope effect; Streitwieser[8] has shown that α-deuterium substitution depresses the dissociation constants of carbon acids by a factor of $\sim$1.15. All of these secondary effects are, however, small ones and do not modify our conclusions.

There is little quantitative information on the ability of substituents to promote β elimination,[9] and in this connection we have measured in a similar way the rates of elimination of phenoxide from the series of substrates in Table I. The medium used was ethanolic sodium ethoxide and, in most cases studied, the β-ethoxy compound III (Y = Et) was isolated together with phenol. Proof that the reaction is elimination and not substitution has been obtained in several cases by interception of the electrophilic olefin II with piperidine.[10]

Table I. Rates of Elimination in β-Substituted Phenyl Ethyl Ethers[a]

X	I[b]	k_{obsd}, M^{-1} sec^{-1} EtOH⁻–EtOH	k_{obsd}, M^{-1} sec^{-1} OH⁻–H_2O	$k_{t\text{-BuS}}-/k_{EtO}-$
NO_2	a	(1500)	300	
$Br^-Ph_3P^+$	b	(6000)	1.98	
$I^-Me_2S^+$	c	195	4.8×10^{-2}	
	c'		7.3×10^{-2}	
Ac	d	32	3.12	0.23
CHO	e	26.3		
$EtOSO_2$	f	7.28×10^{-1}	4.46×10^{-1}	
$PhSO_2$	g	3.49×10^{-1}		0.26
$MeSO_2$	h	1.45×10^{-1}		
CN	i	9.44×10^{-2}		
CO_2Et	j	6.05×10^{-2}	1.49×10^{-2}	0.24
$(PhCH_2)_2NSO_2$	k	1.60×10^{-2}		
PhSO	l	1.19×10^{-3}		
$CONH_2$	m	1.13×10^{-3}	1.38×10^{-3}	
MeSO	n	4.3×10^{-4}	9.2×10^{-5}	
	n'		1.18×10^{-4}	
$CONEt_2$	o	2.56×10^{-4}		
$Br^-Me_3N^+$	p	3×10^{-7}		
CO_2^-	q	7×10^{-8}		

[a] Estimated values in parentheses. [b] See text.

There is strong implication, from the results of the aqueous reactions, that these are E1cB reactions. Rate constants for Ic and In are almost at opposite ends of the range of values, and two further lines of evidence suggest a common E1cB mechanism. (i) Ratios of the constants obtained with ethoxide and with *t*-butyl thiolate as bases in ethanol ($k_{t\text{-BuS}}-/k_{EtO}-$) do not vary appreciably over a wide range of substrate reactivity. This suggests that there is no change in the degree of

(7) R. Bird and C. J. M. Stirling, *J. Chem. Soc.*, *B*, 111 (1968).
(8) A. Streitwieser and D. E. Van Sickle, *J. Amer. Chem. Soc.*, **84**, 254 (1962).
(9) W. H. Saunders in "The Chemistry of the Alkanes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964.
(10) A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 3686 (1962).

C–H bond cleavage in the transition state.[11] This is not consistent with an E2 mechanism. (ii) Addition of t-butylthiol depresses reaction rates. This observation is consistent with an ElcB mechanism or at least with an E2 process that lies well to the carbanion side.[11]

Rate constants for ethoxide reactions cover a 10^{11}-fold range of reactivity. Reactions with compounds Ia and Ib were too fast to measure in ethanol; estimates from rate constants obtained in water are included. The enormous difference between the constants for the first (Ip) and second (Ib and Ic) row onium salts[12] strongly suggests participation of d orbitals in stabilization of the intermediate carbanion. As expected, the sulfonamide Ik and the carboxamides Im and Io are less reactive than the corresponding esters If and Ij. Further, the phenyl sulfone Ig is more reactive than the methyl sulfone Ih, and these sulfones are much more reactive than the corresponding sulfoxides Il and In.

A rectilinear relationship is found between log $k_{\text{elimination}}$ and the limited available values of σR^-,[13] confirming that direct resonance interaction between the substituent and the intermediate carbanion is important. This correlation makes it likely that in the expression for the rate constant, k_{obsd}, of this second-order ElcB process, $k_{\text{obsd}} = Kk_2$, the magnitude of k_{obsd} is primarily controlled by the dissociation constant, K.[14] The observed rate constants thus provide a measure of the effects of these substituents on the dissociation of the adjacent C–H bond. Support for the conclusion that the magnitude of k_2 is insensitive to the nature of the activating substituent comes from the effect of substituents in the eliminated aryloxy group upon the rate of elimination. In the substrates Ic, Ig, and Il, whose rate constants cover a range of 10^5, approximate Hammett ρ values so far obtained differ only very slightly.

Acknowledgment. We wish to thank the Science Research Council of Great Britain for a maintenance grant (to J. C.).

(11) J. F. Bunnett and E. Bacciochi, *J. Org. Chem.*, **32**, 11 (1967).

(12) With the onium salts as with some other substrates, such as Ii, elimination of the activating group is formally possible as a competitive reaction. In all cases quantitative yields of phenol are obtained, together with high yields of products derived from olefin II.

(13) R. W. Taft Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.* **9**, 292 (1958).

(14) If so, a direct relationship between elimination rate and the thermodynamic acidity of the substrate should exist. Acidity data in this range of pK_a is too sparse, scattered, and inconsistent to be of very much value in this respect.

J. Crosby, C. J. M. Stirling

Department of Chemistry, King's College,
Strand, London, W.C. 2, England

Complete Determination of the Alignment of CH_2Cl_2–CD_2Cl_2 Molecules in Poly-γ-benzyl-L-glutamate Solution by the Nuclear Magnetic Resonance of ^{35}Cl, ^2D, and ^1H. Comparison of Electric and Magnetic Ordering[1]

Sir:

Concentrated solutions of poly-γ-benzyl-L-glutamate dissolved in CH_2Cl_2 (and CD_2Cl_2) are liquid crystalline[2] and acquire order when placed in magnetic[3,4] and

electric[5,6] fields. Solute ordering constrains the motion of the *solvent* molecules so that their intramolecular traceless tensor interactions are not averaged to zero.

We have determined additional *nmr characteristics of the solvent* in the liquid crystalline state of this system.[3,4] Comparison of the integrated signal intensity of the high-resolution (hr) proton magnetic resonance (pmr) with that of a measured quantity of added TMS indicates that to within experimental error *all* the solvent molecules contribute to the hr pmr spectra.

We have extended the nmr measurements to the ^{35}Cl and ^2D nuclei to extract, insofar as possible, information about the ordering of the solvent. The anisotropic motion is reflected by the residual dipolar splitting of the pmr,[7,8] by the quadrupolar splitting of the deuterium magnetic resonance (dmr),[8] and by the occurrence of quadrupolar-induced satellites in the ^{35}Cl nmr spectrum, reported here for the first time.

For calculating the "distortion theory" orientation parameters, S_{ii},[7] we defined a molecule-fixed frame in which the $1 = x$ axis is parallel to the Cl–Cl direction, the $2 = y$ axis is parallel to the H–H direction, and $3 = z$ is the C_{2v} axis, and assumed that the axis of constraint[7] of the solvent was directed along the magnetic field H_0 ($\Omega = 0$). Neglecting asymmetry parameters, the frequency separation, in hertz, between the two lines in the dmr in CD_2Cl_2 is[7,8]

$$\Delta_D{}^Q = \pm \frac{e^2 Qq(D)}{2h}[-S_{11} + S_{22}(3 \sin^2 \alpha - 1) + S_{33}(3 \cos^2 \alpha - 1)] \quad (1)$$

where $eq(D)$ is the gradient along the CD bond, assumed to be the largest component of the electric field gradient, and $2\alpha = 112.0°$ is the DCD bond angle.

The frequency separation between the outer two lines of the triplet ^{35}Cl nmr is

$$\Delta_{Cl}{}^Q = \pm \frac{e^2 Qq(^{35}Cl)}{3h}[S_{11}(3 \sin^2 \beta - 1) - S_{22} + S_{33}(3 \cos^2 \beta - 1)] \quad (2)$$

where $2\beta = 111.8°$ is the Cl–C–Cl bond angle.

The separation, in hertz, between the two dipolar components of the solvent pmr is

$$\Delta_{HH} = \pm 3h(\gamma/2\pi)^2 R_{HH}{}^{-3} S_{22} \quad (3)$$

where $\gamma/2\pi = 4.257 \times 10^3$, and $R_{HH} = 1.771$ Å.

For ^{35}Cl, $e^2Qq/2h$ is 36.2 MHz.[9] We deduced $e^2 Qq(D)/h = 150$ kHz for deuterium from a dmr T_1 measurement.[10] The values of $\Delta_{Cl}{}^Q$, $\Delta_D{}^Q$, and Δ_{HH} measured at 24° in solutions which contained ten solvent molecules for each monomer residue are given in Table I.

(2) (a) C. Robinson, *Tetrahedron* **13**, 219 (1961); (b) A. Saupe and G. Englert, *Phys. Rev. Letters*, **11**, 462 (1963).

(3) S. Sobajima, *J. Phys. Soc. Japan*, **23**, 1070 (1967).

(4) M. Panar and W. D. Phillips, *J. Am. Chem. Soc.*, **90**, 3880 (1968).

(5) A. Wada, "Poly-α-Amino Acids," G. D. Fasman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 369.

(6) J. C. Powers and W. L. Peticolas, Advances in Chemistry Series, No. 63, American Chemical Society, Washington, D.C., 1967, p 217.

(7) A. D. Buckingham and K. A. McLauchlan in "Progress in High Resolution NMR Spectroscopy," Vol. 2, J. W. Emsley, J. Feeney, and L. H. Sutcliff, Ed., Pergamon Press, Oxford, 1967.

(8) J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).

(9) R. L. Livingston, *ibid.*, **19**, 1434 (1951).

(10) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 196.