methyl groups were randomly labeled with deuterium to the extent of about 50% and (2) the ion **3** which was specifically labeled to the extent of about 93% with two deuterium atoms in each methyl group. In the former case the product isotope ratio was 5.1 and in the latter case it was 4.1. When the latter value is corrected for the degree of deuteration, the calculated isotope effect is 7.6.[6] It is thus clear that the lack of isotopic discrimination in the compound bearing one deuterated and one undeuterated methyl group is due to a hydrogen transfer which is very rapid compared to rotation about the carbonyl C–N bond. In view of the product isotope ratio of 4.1 in the case of **3**, it is also clear that the rate of this transfer is much less than that of rotation about the methyl C–N bond; if the relative rates were reversed, the maximum product isotope ratio would be 2.0.[7]

Unfortunately, the rate of hydrogen transfer is not well defined by these limits alone since the two rates of bond rotation in this case might differ by a factor of 10^{12} or greater. However, this work suggests a novel technique for studying such rapid reactions, and we are in the process of applying this general principle to other systems. In a subsequent paper we will show by the use of somewhat similar experiments that the transfer is probably also more rapid than rotation about the C–C bond between the ring and the carbonyl group.

The assertion[2] that the thermal decomposition involves an entirely different type of hydrogen transfer (a hydride transfer is strongly indicated[2,8]) from the catalyzed decomposition is strongly supported by the finding that the product isotope ratio in the thermal reaction under the same conditions is 1.4 for both the randomly labeled sample and the dideuteriomethyl compound **3**. The cause of these isotope ratios in the cationic process is now under investigation.

(6) The value of 5.1 obtained for the randomly labeled sample must be corrected for the fact that finite percentages of the methyl groups will be completely deuterated and completely undeuterated. The calculated isotope effect is thus extremely sensitive to the exact extent of deuteration and of randomness of the label. Since the degree of deuteration was determined by nmr integration, it is not sufficiently accurate to yield a meaningful isotope effect.

(7) This value could be attained if, in the decomposition product of **3**, the aryl carbon atom bearing the odd electron were equidistant from two of the three methyl hydrogen atoms just prior to transfer. One-third of the time only deuterium atoms would flank this carbon atom and a deuterium atom would always be transferred. Two-thirds of the time there would be a choice of hydrogen or deuterium transfer and, assuming an infinite isotope effect, only hydrogen would be transferred.

(8) T. Cohen, R. M. Moran, and G. Sowinski, *J. Org. Chem.*, **26**, 1 (1961); T. Cohen, A. H. Dinwoodie, and L. D. McKeever, *Ibid.*, **27**, 3385 (1962); T. Cohen and J. Lipowitz, *J. Am. Chem. Soc.*, **86**, 2514 (1964); T. Cohen and J. Lipowitz, *Tetrahedron Letters*, 3721 (1964).

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The Occurrence of Mixed Tetrahaloaluminate Ions Shown by Aluminum-27 Nuclear Magnetic Resonance Spectroscopy

Sir:

The existence of the tetrahaloaluminate ions $AlCl_4^-$ and $AlBr_4^-$ has been known for many years, and the tetrahedral structure of $AlCl_4^-$ in the solid state has been verified by X-ray crystallography.[1] The occurrence of these ions as intermediates essential to the functioning of Al_2Cl_6 and Al_2Br_6 in certain Friedel–Crafts catalyst systems has generated considerable activity in this area of aluminum chemistry.[2] While the existence of AlI_4^- has been reported by several workers,[3,4] it has never been characterized. In spite of the current interest in redistribution and exchange reactions generally,[5] no mixed tetrahaloaluminate ion of the type $AlX_nY_{4-n}^-$, where X and Y are different halogens, has yet been reported. By dissolving Al_2I_6 and $(n\text{-}C_3H_4)_4N^+I$ in anhydrous CH_2Cl_2 functioning both as solvent and as chloride ion source, we have prepared a solution[6] containing all five theoretically possible $AlCl_nI_{4-n}^-$ ions $(0 \leq n \leq 4)$. These have been identified by the characteristic ^{27}Al nmr line generated by each ion. The spectrum for this solution, taken at 15.1 MHz and 27°, is shown in Figure 1a and spectral parameters are listed in Table I.

Table I. ^{27}Al Chemical Shifts[a] and Line Widths for Tetrahaloaluminate Ions

Anion	Shift, ppm	Line width, Hz
AlI_4^-	$+27.0 \pm 0.2$	23.9 ± 2.2
AlI_3Cl^-	-21.7 ± 0.4	46.0 ± 0.8
$AlI_2Cl_2^-$	-59.4 ± 0.3	57.6 ± 4.6
$AlICl_3^-$	-86.2 ± 0.3	42.0
$AlCl_4^-$	-102.4 ± 0.5	15.1 ± 0.5
AlI_2ClBr^-	-47.7	
$AlBr_2ICl^-$	-69.3	
$AlCl_2BrI^-$	$Ca.\ -79$	

[a] Chemical shifts relative to external aqueous acidic $Al(H_2O)_6^{3+}$; positive shifts indicate signals on the high-field side of the reference.

The lines at -102 and $+27$ ppm have been assigned to $AlCl_4^-$ from AlI_4^-, respectively, on the basis of ^{27}Al spectra obtained from separate solutions containing only the single AlX_4^- ion. The other three signals have been assigned by interpolation on the assumption that successive substitution of I^- for Cl^- in AlI_4^- causes a monotonic upfield shift in the resonance line of the resulting $AlCl_nI_{4-n}^-$ ion. These assignments are supported by the line widths given in Table I. The AlI_4^- and $AlCl_4^-$ ions with T_d symmetry give rise to the narrowest lines. The AlI_3Cl^- and $AlICl_3^-$ ions with

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(2) M. Baaz and V. Gutmann, "Friedel-Crafts and Related Reactions," Vol. 1, G. Olah, Ed., Interscience Publishers, New York, N. Y., 1963, pp 367–397.
(3) I. Zlotowski, A. Polaczek, and H. Wincel, *Nukleonika*, **6**, 415 (1961); *Chem. Abstr.*, **61**, 2689g (1964).
(4) I. Zlotowski and A. Polaczek, *Nucleonika*, **6**, 229 (1961); *Chem. Abstr.*, **59**, 6022h (1963).
(5) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).
(6) In this solution, as well as in those discussed below, the aluminum concentration was in the range 0.5–1.0 M. The molar ratio of tetraalkylammonium halide to aluminum trihalide ([MX]/[AlX₃]) lay in the range 1.1–1.9. Values for this ratio of less than unity give rise to solutions whose ^{27}Al nmr spectra consist of a single, time-averaged line, the position and line width of which indicate rapid exchange of halide ions at the aluminum atom.
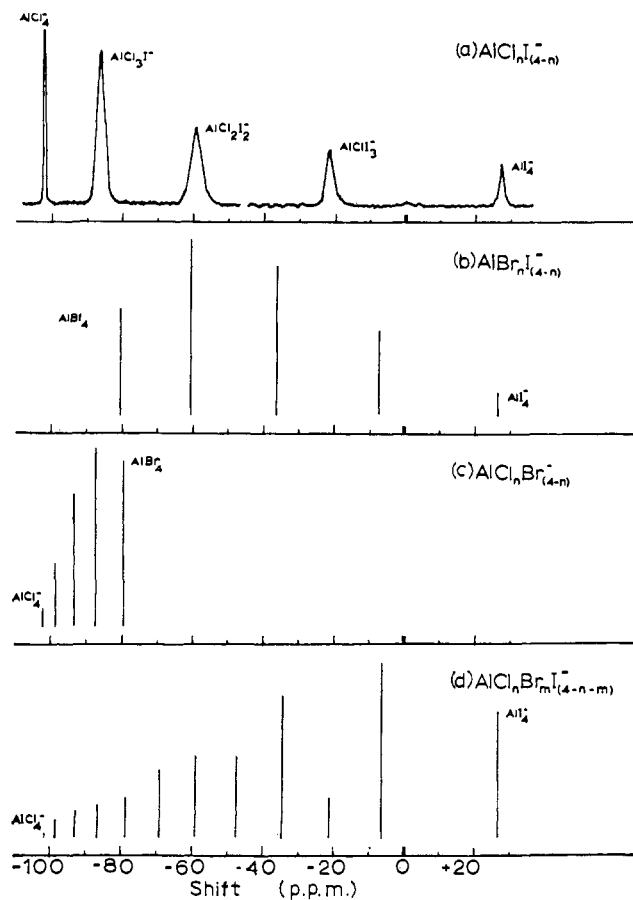
Figure 1. The ^{27}Al nmr spectra of four different solutions, containing (a) the five $AlCl_nI_{4-n}^-$ ions; (b) the five $AlBr_nI_{4-n}^-$ ions; (c) the five $AlCl_nBr_{4-n}^-$ ions; and (d) the $AlCl_nBr_mI_{4-n-m}^-$ ions.

C_{3v} symmetry have lines at least twice as wide, while the $AlI_2Cl_2^-$ ion with C_{2v} symmetry gives the widest signal of the five.

The ^{27}Al nucleus has spin $I = 5/2$ and therefore possesses a nuclear electric quadrupole moment, the interaction of which with the local electric field gradient at the nucleus will make the dominant contribution to the nuclear relaxation process and thus to the line width.[7] Symmetry arguments reveal that, provided the Al–Cl and Al–I bond lengths do not vary excessively among AlI_3Cl^-, $AlI_2Cl_2^-$, and $AlICl_3^-$, the electric field gradient for the C_{2v} ion will be about 15% greater than those for the C_{3v} ions. The higher electric field gradient for $AlI_2Cl_2^-$ will give rise to a broader ^{27}Al resonance line, thereby supporting our spectral assignment. The contributions of both the magnetic dipolar and the electric quadrupolar mechanisms to nuclear relaxation in liquids depend upon the rotational correlation time of the molecular entity containing the nucleus under observation. Since this correlation time is directly proportional to the cube of the molecular radius, the fact that AlI_4^- and AlI_3Cl^- generate wider resonances, respectively, than $AlCl_4^-$ and $AlICl_3^-$ is consistent with the currently accepted model for nuclear relaxation[8] and thereby provides further support for the spectral assignment.

(7) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge University Press, London, 1955, pp 203–205.
(8) E. R. Andrew, ref 7, Chapter 5.

By dissolving Al_2I_6 and $(n\text{-}C_3H_7)_4N^+I^-$ in CH_2Br_2, all five $AlI_nBr_{4-n}^-$ ions were obtained in a solution whose spectrum is shown in Figure 1b. The spectrum of a solution containing all five $AlBr_nCl_{4-n}^-$ ions, prepared by dissolving Al_2Br_6 and $(n\text{-}C_3H_7)_4N^+Br^-$ in CH_2Cl_2, is shown in Figure 1c. The spectral assignments follow an application of the principles outlined above, and all the line widths and chemical shifts are consistent with these principles. Finally by dissolving Al_2I_3 and $(n\text{-}C_3H_7)_4N^+Br^-$ in CH_2Cl_2, a ^{27}Al spectrum (Figure 1d) consisting of 12, of the theoretically possible 15, lines is observed. Two of the missing lines can be accounted for by the fact that the $AlBr_3I^-$ (-60.6 ppm) and $AlCl_2I_2^-$ (-59.4 ppm) lines will overlap and be unresolved, as will also those for $AlCl_3I^-$ (-86.2 ppm) and $AlClBr_3^-$ (-87.2 ppm). The other missing peak is that for $AlCl_2BrI^-$. Strong evidence based upon the width of the $AlBr_4^-$ line at -79.6 ppm in this spectrum indicates that $AlCl_2BrI^-$ is indeed present in the solution and that it lies at $ca.$ -79 ppm. There is no alternative explanation for the fact that the line at -78.6 ppm assignable to $AlBr_4^-$ is wider than that for the two C_{3v} species immediately adjacent to it at -86.8 ppm in the spectrum.

Although substitution of I^- for Cl^- in $AlCl_4^-$ causes a monotonic increase in the shielding of the ^{27}Al nucleus, this increase is *not* a linear function of the number of iodine atoms attached to aluminum. This indicates that each halogen does not contribute a fixed increment to the aluminum shielding, but rather the contribution of each halogen is dependent upon the other substituents bonded to aluminum.

The AlI_4^- ion contains the most highly shielded aluminum nucleus yet observed, while among the aluminum halides studied, the $AlCl_4^-$ ion exhibits the largest ^{27}Al paramagnetic shift. The shielding of the aluminum atom which increases in the order $AlCl_4^-$ < $AlBr_4^-$ < AlI_4^- can be rationalized on the basis of the relative *nephelauxetic* or "cloud-expanding" effects of the halide ions concerned.[9] For atoms other than hydrogen, it has been established[10] that the second-order paramagnetic term in Ramsay's general equation for nuclear screening is predominant and therefore determines the chemical shift. This paramagnetic term for the aluminum atom in a tetrahaloaluminate ion can be expressed in the form[10]

$$\sigma_p = -\frac{2}{3}(e^2\hbar^2/m^2c^2)\frac{1}{\Delta E}\left\langle\frac{1}{r^3}\right\rangle_p P_u$$

where ΔE is the average electronic excitation energy for the ion, P_u is the "unbalance" of the valence electrons in the p orbitals centered on aluminum, and $\langle 1/r^3\rangle_p$ is the average value of the inverse cube radius of the aluminum p electrons. Of these three variable parameters, it is the $\langle 1/r^3\rangle_p$ parameter which will show the greatest variation between $AlCl_4^-$ and AlI_4^-. Among the halide ions, the iodide ion exerts the highest *nephelauxetic* effect,[9] giving the lowest value of $\langle 1/r^3\rangle_p$ and the smallest σ_p term for the AlI_4^- ion. The paramagnetic terms and hence the downfield shifts for $AlBr_4^-$ and $AlCl_4^-$ will be progressively larger as the *nephelauxetic* effects

(9) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 138.
(10) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 40, 1714 (1964).

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.

(11) Holder of a Dow Chemical Co. Fellowship.

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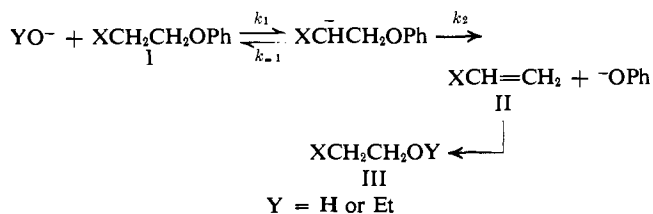*Department of Chemistry University of Western Ontario
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Effects on Reactivity in E1cB Reactions

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 ∼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

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 ∼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	OH⁻–H₂O	$k_{t\text{-BuS}}$-/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

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