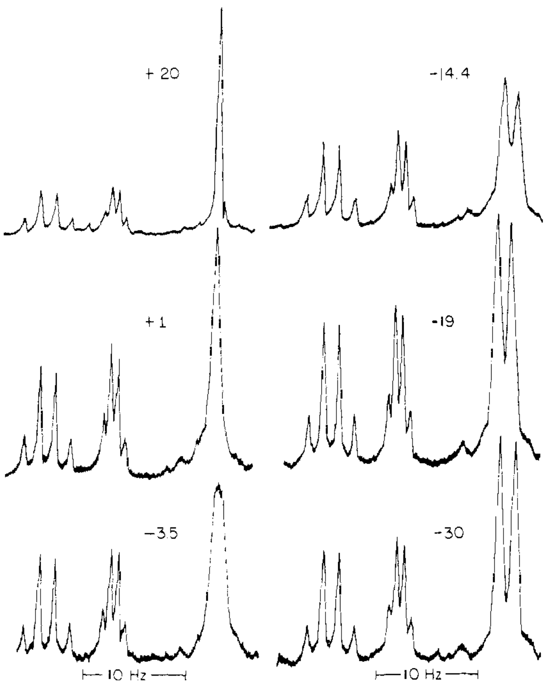
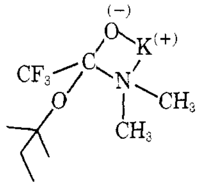


**Figure 1.** Nmr 60-MHz spectra for *N*-methyl hydrogens in a mixture of *N,N*-dimethyltrifluoroacetamide 1 *M* and potassium *tert*-amyloxide 1.3 *M* (starting concentrations) at different temperatures.

version at nitrogen is determined by the rate at which potassium ion exchanges in and out of the intimate ion pair. Thus, a mean lifetime between inversions is the minimum lifetime of the intimate ion pair in the hydrocarbon medium. An Arrhenius plot of the data obtained here gives an apparent activation energy of 12 ± 0.7 kcal/mol.



**2**

The mechanism(s) whereby potassium nitrogen coordination exchange takes place is still a mystery pending the completion of kinetic studies and determinations of the association of adduct **1** in hydrocarbons. Such exchanges could take place either within the aggregates **1** or between one aggregate and another. Also, further work on other adducts is still in progress.

In summary, we have found a potassium alkoxide adduct of *N,N*-dimethyltrifluoroacetamide to be stable in hydrocarbon solution, **1**, to consist of at least one bidentate chelate and have employed nmr line-shape analysis to measure the mean lifetime of the intimate ion pair.

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(11) An alternative interpretation of these results, that the electronegative substituents are responsible for the large barrier to inversion (see S. J. Brois, *J. Amer. Chem. Soc.*, **90**, 506 (1968).) is discounted since dicyclohexyl-18-crown-6 appears to increase the inversion rate of adduct I. Furthermore where inversion is slow the electronegative atom is directly bonded to nitrogen.

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## Chlorine Kinetic Isotope Effects in the Cyclization of Chloroalcohols

*Sir:*

The cyclization of 4-chlorobutanol to tetrahydrofuran is an intriguing reaction, for it is apparently the only example of a displacement on saturated carbon that occurs with general base catalysis.[1,2] From solvent ($H_2O$-$D_2O$) isotope effects for hydroxide catalyzed cyclizations, it was concluded that the transition state for cyclization of 2-chloroethanol, a specific base catalyzed reaction,[3] has a *more* broken carbon-chlorine bond than the transition state for the general base catalyzed cyclization of 4-chlorobutanol.[1] This conclusion appears to contradict both the Hammond postulate[4] as it is generally used[5] and the reacting bond rule,[6] both of which predict an earlier transition state (less broken carbon-chlorine bond) for the cyclization of 2-chloroethanol, which occurs from the strongly basic 2-chloroethoxide, than for the cyclization of 4-chlorobutanol, which occurs through a partially protonated and hence less basic oxygen atom.

We now wish to report that the chlorine kinetic isotope effects for the base-catalyzed cyclizations of 2-chloroethanol and 4-chlorobutanol to ethylene oxide and tetrahydrofuran, respectively, in water at 25° confirm the conclusion drawn from the solvent isotope effects for these reactions.[1] Comparison of the first and second entries of Table I shows that the chlorine kinetic isotope effect for the hydroxide-catalyzed cyclization of 2-chloroethanol is significantly greater than that for the corresponding cyclization of 4-chlorobutanol.[7] According to the theory of heavy atom isotope effects,[8] larger isotope effects are associated with greater loss of the initial carbon-chlorine bonding of the reactant. Thus the transition state for the cyclization of 2-chloroethanol does have more extensive carbon-chlorine bond rupture at the transition state than does 4-chlorobutanol, in agreement with the earlier interpretation of the solvent isotope effects for these reactions. The resolution of the apparent contradiction between these experimental observations and the predictions of the Hammond postulate and the reacting bond rule lies in consideration of the large strain energy of ethylene oxide.[1] In the back-reactions with chloride ion, the oxygen atom of ethylene oxide is a much better leaving group, because of release of the strain energy

**Table I.** Chlorine Kinetic Isotopic Effects for the Cyclization of Chloroalcohols in Water at 25°[a]

| Chloroalcohol | Base | $k_2$, $M^{-1}$ sec$^{-1}$ | Isotope effect ($k_{35}/k_{37}$) |
|---|---|---|---|
| 2-Chloroethanol | $(CH_3)_4N^+HO^-$ | $1.13 \times 10^{-2}$ | $1.00815 \pm 0.00011$[b] |
| 4-Chlorobutanol | $(CH_3)_4N^+HO^-$ | $1.70 \times 10^{-3}$ | $1.00757 \pm 0.00015$[b] |
| 4-Chlorobutanol | $H_2O$ | $2.86 \times 10^{-8}$ | $1.00796 \pm 0.00013$[b] |

[a] 4-Chloroethanol and hydroxide each initially 0.03–0.08 *M*. [b] Standard deviation of five–seven independent determinations.

**Table II.** Kinetic Data for the Cyclization of 4-Chlorobutanol in Water at 25°[a]

| Base | p$K_A$[b] | $k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| $(CH_3)_4N^+HO^-$ | 14.00 | $1.70 \times 10^{-3}$ |
| $Na^+F_3CCH_2O^-$ | 12.37[c] | $1.80 \times 10^{-4}$ |
| $Na^+C_6H_5O^-$ | 9.97 | $3.88 \times 10^{-5}$ |
| $Na^+$4-$O_2NC_6H_4O^-$ | 7.17 | $1.83 \times 10^{-6}$ |
| $Na^+$2,4,6-$Cl_3C_6H_2O^-$ | 6.41 | $1.97 \times 10^{-6}$ |
| $Na^+$2,4-$(O_2N)_2C_6H_3O^-$ | 4.09 | $4.48 \times 10^{-7}$ |
| $H_2O$ | −1.74 | $2.86 \times 10^{-8}$ [d] |

[a] 4-Chlorobutanol initially 0.004–0.08 *M;* basic solutes 0.1–0.4 *M;* $NaClO_4$ to make ionic strength 0.45 *M*. [b] R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc., Ser. A*, **197**, 141 (1949). [c] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **81**, 1050 (1959). [d] Calcd for 55.5 *M* water.

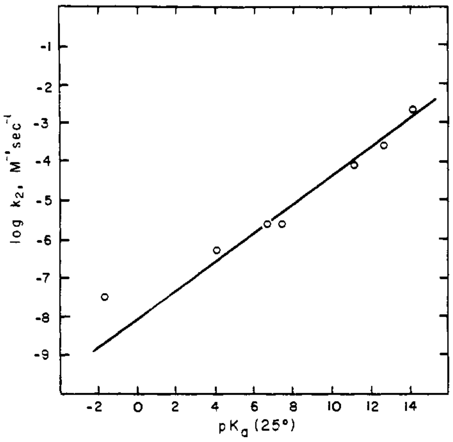

**Figure 1.** Brønsted plot for the cyclization of 4-chlorobutanol in water at 25°. Data points (left to right) correspond to water, 2,4-dinitrophenoxide, 2,4,6-trichlorophenoxide, 4-nitrophenoxide, phenoxide, 2,2,2-trifluoroethoxide, and hydroxide. The Brønsted $\beta$ of 0.36 was determined by least-squares analysis excluding the datum for water.

of ethylene oxide, than even the fully protonated oxygen atom of tetrahydrofuran. Therefore, the oxygen atom of 2-chloroethoxide must be a poorer nucleophile (albeit a stronger base) than the partially deprotonated oxygen atom in the transition state for the cyclization of 4-chlorobutanol. The entropic difference between the two ring closures allows the cyclization with the weaker nucleophile (2-chloroethoxide) to occur more readily than that of the stronger nucleophile (the partially deprotonated 4-chlorobutanol).

The original claim of general base catalysis for the cyclization of 4-chlorobutanol rested on a Brønsted plot including only one base other than water and hydroxide. Although general base catalysis for this reaction has been confirmed,[9] we redetermined the Brønsted slope for this cyclization with a series of oxygen bases. The results of this study are presented in Figure 1 and Table II. The reaction in water is ten times faster than predicted from the basicity of water and the best line determined by the other bases, a deviation well outside experimental error. Although water and hydroxide ion often deviate in Brønsted plots (though not in all[10]), the fact that only water was observed to do so in this system led us to determine the chlorine kinetic isotope effect for the neutral cyclization of 4-chlorobutanol. Comparison of the second and third entries of Table I shows that the isotope effects for the hydroxide ion and water reactions are different with a confidence limit above 99% by Student's *t* test. The difference in chlorine isotope effects requires that the carbon–chlorine, and therefore the carbon–oxygen, bonding be different in the transition states for the two reactions. Moreover, the relative magnitudes for the isotope effects demonstrate that the transition state for the hydroxide ion catalyzed reaction has less weakening of the carbon–chlorine bond, *i.e.*, occurs earlier along the reaction coordinate. Two explanations equally well account for the isotope effect data and the apparent curvature of the Brønsted plot. The cyclization in water may represent the rather abrupt onset of a cyclization in which water does not act as a general base.[10] In this case the cyclization is an uncatalyzed ring closure to a fully protonated tetrahydrofuran from which the proton is lost in a subsequent fast step. A more likely alternative is that the transition state for the cyclization is gradually changing in response to the difference in p*K* between the base and the alcohol.[11] Both explanations predict an earlier transition state for the hydroxide-catalyzed cyclization and distinction between them must await further experimentation.

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## Electron Paramagnetic Resonance Spectra and Structure of Some Vinyl Radicals in Solution[1]

*Sir:*

Almost all types of carbon-centered radicals have been studied extensively in solution by epr spectroscopy. How-