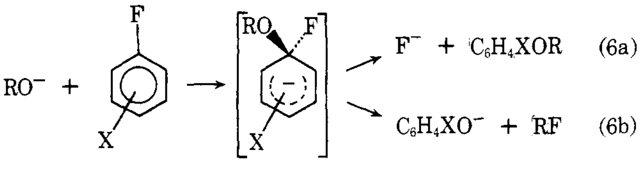
rationalized by a Meisenheimer-type intermediate. Appreciable stabilization of the postulated intermediate may be



achieved through an inductive effect for $X = F$, Cl, or by charge delocalization for $X = NO_2$. A longer lived species[14] might then undergo bond reorganization along the energetically preferred channel.[15,16]

The mechanistic aspects of these reactions are presently under further study to establish the general reactivity of aryl halides.

Acknowledgment. We thank Dr. Simon Campbell for bringing the hexafluorobenzene problem to our attention. This research was made possible by the support of the Conselho Nacional de Pesquisas of Brazil and a FAPESP scholarship (S.M.J.B.).

References and Notes

(1) For earlier work concerning substituent effects in ion–molecule reactions, see (a) R. C. Dunbar, J. Shen, and G. A. Olah, *J. Amer. Chem. Soc.*, **94,** 6862 (1972); (b) F. Cacace and E. Possagno, *ibid.*, **95,** 3397 (1973); (c) R. C. Dunbar, J. Shen, E. Melby, and G. A. Olah, *ibid.*, **95,** 7200 (1973).

(2) J. F. Bunnett, *Quart. Rev., Chem. Soc.*, **12,** 1 (1958).

(3) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, Chapter 4, pp 61–132.

(4) J. Miller and H. W. Yeung, *Aust. J. Chem.*, **20,** 379 (1967).

(5) For an explanation, see (a) J. Burdon, *Tetrahedron*, **21,** 3373 (1965); (b) R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc., Chem. Commun.*, 239 (1974).

(6) The experimental details were similar to those described by L. K. Blair, P. C. Isolani, and J. M. Riveros, *J. Amer. Chem. Soc.*, **95,** 1057 (1973). Alkoxide ions were generated in the kinetic experiments by low energy electrons (1.5 eV). Rate constants were determined according to S. E. Buttrill, Jr., *J. Chem. Phys.*, **50,** 4125 (1969), with simultaneous ejection of trapped thermal electrons. Residence times are probably poorly defined in these cases, and rate constants are not believed to be better than 25% accurate. Pressure measurements were carried out as in W. T. Huntress, Jr., and R. F. Pinizzotto, Jr., *J. Chem. Phys.*, **59,** 4742 (1973). The icr spectra of the fluorobenzenes, both positive and negative, show no detectable impurities, or conflicting mass peaks.

(7) F. Kaplan, *J. Amer. Chem. Soc.*, **90,** 4483 (1968).

(8) In reaction 3, 4, and 5, $R = CH_3$, C_2H_5, and $i\text{-}C_3H_7$.

(9) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90,** 5636 (1968); **90,** 6561 (1968); **92,** 5986 (1970); **93,** 3911 (1971).

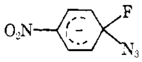
(10) The word comparable is used because alkoxide ions generated from nitrites can undergo slightly endothermic reactions. However, ΔH must be ≤ 2 kcal/mol: P. C. Isolani, Ph.D. Thesis, University of Sao Paulo, 1974, p 65.

(11) Reactions with 1-chloro-2-fluorobenzene and *p*-nitrofluorobenzene also yield chlorophenoxide and nitrophenoxide ions.

(12) P. W. Tiedemann and J. M. Riveros, *J. Amer. Chem. Soc.*, **96,** 185 (1974).

(13) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92,** 7484 (1970).

(14) Observation of



has been claimed in solution by R. Bolton, J. Miller, and A. J. Parker, *Chem. Ind. (London)*, 1026 (1960).

(15) For $X = H$ and $R = CH_3$, $\Delta H_{6a} = -12$ and $\Delta H_{6b} = -48$ kcal/mol. Electron affinities, EA (CH_3O), R. T. McIver and J. S. Miller, *J. Amer. Chem. Soc.*, **96,** 4323 (1974); EA(C_6H_5O), I. Dzidic, D. I. Carroll, R. N. Stilwell, and E. C. Horning, *ibid.*, **96,** 5258 (1974); EA(F.), R. S. Berry, *Chem. Rev.*, **69,** 533 (1969). Neutral heats of formation from: J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26** (1969).

(16) Similar bond reorganization processes occur in ion–molecule reactions of esters (J. M. Riveros, S. M. J. Briscese, and P. C. Isolani, to be submitted for publication).

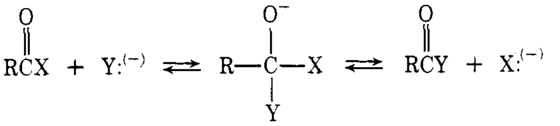
Sonia Maria J. Briscese, José M. Riveros*
Instituto de Química, University of São Paulo
São Paulo, Brasil

Received July 29, 1974

Alkoxide Adduct of an Amide. Mean Lifetime of an Intimate Ion Pair

Sir:

The general mechanism by which nucleophiles interconvert carboxylic acids and their derivatives is now believed to involve a tetrahedral intermediate.[1-3] With the exception of



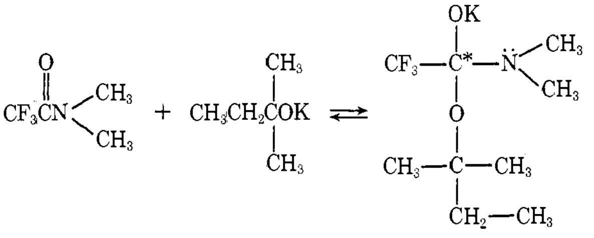
$$\overset{O}{\overset{\|}{R C X}} + Y{:}^{(-)} \rightleftharpoons R{-}\underset{Y}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}{-}X \rightleftharpoons \overset{O}{\overset{\|}{R C Y}} + X{:}^{(-)}$$

perfluoro derivatives[4] and special cyclic systems[5-7] where intermediates have been isolated, in most of this research the concentrations involved are so low that evidence about tetrahedral intermediates can only be inferred from kinetic and isotope exchange data.[1-3]

Herein, we report the first direct nmr spectroscopic observation of a potassium alkoxide adduct of *N,N*-dimethyltrifluoroacetamide which provides detailed information of structure and at the same time some estimate of the mean lifetime of an intimate ion pair in a hydrocarbon medium.

Employing as precedent Bender's observation in 1953 that esters and amides of perfluoroacids form isolable tetrahedral adducts with alkoxides,[4] we anticipated that a tertiary amide of a perfluoroacid would form similar adducts.

When *N,N*-dimethyltrifluoracetamide is added to a solution of potassium *tert*-amyloxide (made up to be *ca.* 1 *M* in each constituent) in methyl cyclohexane or isooctane, the resulting solution gives the *N*-methyl nmr absorption shown in Figure 1. Alkoxide resonance in this solution is obscured by the solvent. The *N*-methyl proton resonance consists of two closely spaced quartets for the free amide (indicating slow internal rotation) and a sharp single line ascribed to the adduct **1.** This line disappears when water is added to the solution. Only the amide and *tert*-amyl alcohol are obtained on hydrolysis, and there is no evidence for dimethylamine. Also these results show equilibrium 1 to be slow on the nmr time scale.



(1)

1

As the temperature of the sample containing the reaction mixture (1) is lowered, the *N*-methyl resonance of **1,** Figure 1, progressively broadens and finally splits into an equal doublet of separation 2 Hz by −50°. Careful inspection of the shift with respect to internal standards and of the line-shape itself reveals that these effects come from an exchange process. Tentatively, we propose the magnetic nonequivalence of the *N*-methyls of **1** to come from the asymmetry at the central carbon (starred) and its averaging due to inversion at nitrogen, that is the inversion rate at nitrogen is on the nmr time scale −50 to +10°. Comparison of experimental and theoretical line shapes[8,9] shows the first-order rate constant for inversion to be 2.3 sec^{-1} at −17°. Considering that most acyclic amines invert at rates many orders of magnitude faster than this[10] around 0°, some special effect must be inhibiting inversion in **1.** That effect is most likely the bidentate chelation of nitrogen and oxygen with potassium ion (**2**). Then it would appear that the rate of in-

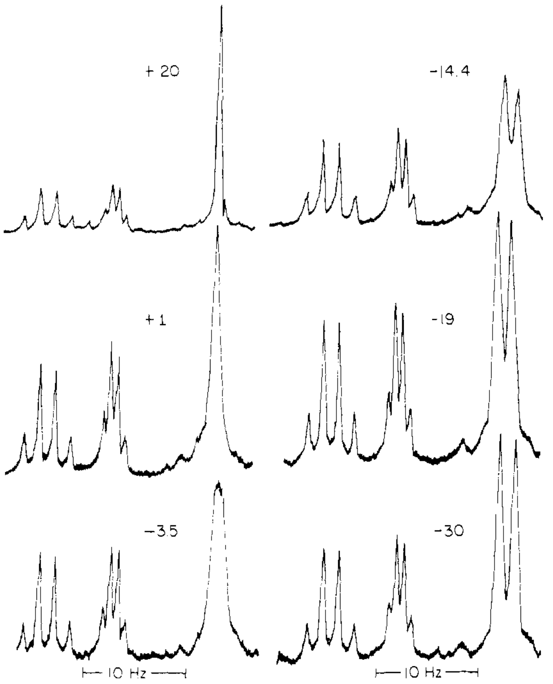
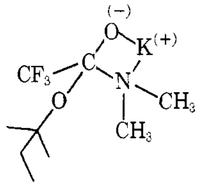


Figure 1. Nmr 60-MHz spectra for *N*-methyl hydrogens in a mixture of *N,N*-dimethyltrifluoroacetamide 1 *M* and potassium *tert*-amyloxide 1.3 *M* (starting concentrations) at different temperatures.

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.

Acknowledgment. This research was supported by a grant from the National Science Foundation Grant No. GP 16402 and GP 36633 X and in part by the National Institutes of Health Grant No. R 01 CA 11820.

References and Notes

(1) W. P. Jenks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N.Y., 1968, p 463; T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, New York, N.Y., 1966, p 1.

(2) W. P. Jenks and K. Salveson, *J. Amer. Chem. Soc.*, **93**, 1419 (1971); T. Okuyama, D. J. Saku, and G. L. Schmir, *ibid.*, **95**, 2345 (1973); T. Maugh and T. C. Bruice, *Chem. Commun.*, 1056 (1969); E. G. Sander, *J. Amer. Chem. Soc.*, **91**, 3629 (1969); G. M. Blackburn, *Chem. Commun.*, 249 (1970).

(3) J. P. Guthrie, *J. Amer. Chem. Soc.*, **96**, 588 (1974). Recent references are listed here.

(4) M. L. Bender, *J. Amer. Chem. Soc.*, **75**, 5986 (1953).

(5) D. R. Robinson, *Tetrahedron Lett.*, 5007 (1968); *J. Amer. Chem. Soc.*, **92**, 3138 (1970).

(6) G. Fodor, F. Letourneau, and N. Mandova, *Can. J. Chem.*, **48**, 174 (1970).

(7) R. B. Woodward, *Pure Appl. Chem.*, **9**, 49 (1964).

(8) H. S. Gutowsky, D. M. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1288 (1956); C. S. Johnson, *Advan. Magn. Resonance*, 1, 33 (1965).

(9) J. I. Kaplan, *J. Chem. Phys.*, **28**, 278, 462 (1958); L. M. Reeves and K. M. Shaw, *Can. J. Chem.*, **48**, 3641 (1970); G. Fraenkel and J. I. Kaplan, *J. Amer. Chem. Soc.*, **94**, 2907 (1972).

(10) C. H. Bushweller and J. N. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970); M. J. S. Dewar and W. B. Jennings, *ibid.*, **93**, 401 (1971); C. H. Bushweller, J. N. O'Neil, and H. S. Bilofsky, *Tetrahedron*, **28**, 2697 (1972).

(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.

Gideon Fraenkel,* Debra Watson
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received May 28, 1974

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