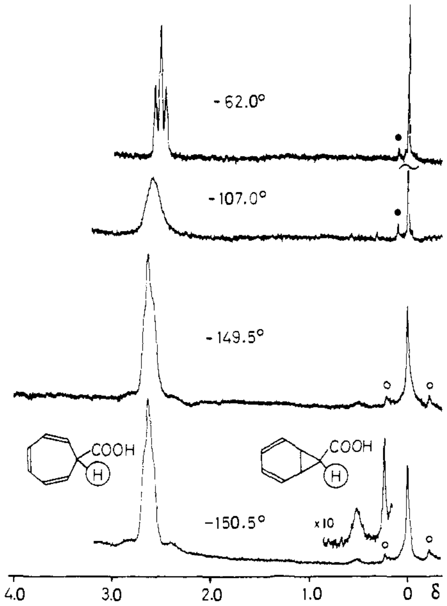


Figure 2. Temperature dependence of the 100-MHz ^1H NMR spectrum of **2** in the region of aliphatic ^1H resonances: internal reference TMS, solvent vinyl chloride, concentration 0.42 *M;* (●) unidentified impurity, (○) spinning side bands.

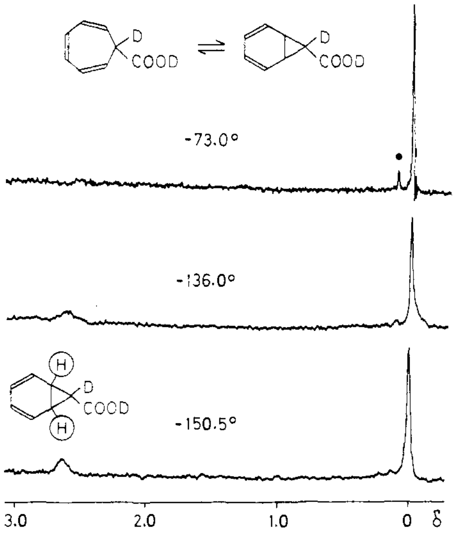


Figure 3. Temperature dependence of the 100-MHz ^1H NMR spectrum of 7-deuterio-**2**; experimental conditions as above; (●) unidentified impurity.

From peak area measurements the concentration of **3** was determined as ca. 3%, leading to $\Delta G°(-150°) = 900$ cal/mol in favor of **2**. According to the high field absorption of H(7) we conclude that **3** exists as the exo isomer *exo*-**3**. Using model compounds[13] δ 0.97 or 0.87 ppm is predicted, in good agreement with our findings. Additional support comes from the half-width of ca. 10 Hz measured for the signal of H(7) in **3** at −150° that is only consistent with a trans coupling constant.[19]

Our results and findings recently reported by Klärner[20] for 7-methyl-**1** and 7-methyl-**2** show that an exo-carboxyl group in 7-position is more effective in stabilizing the norcaradiene than an exo- or endo-cyano group. This conforms to the MO model of norcaradiene stabilization,[21,22] since according to MO energies[23] the COOH group should interact more strongly with the Walsh orbital than the cyano group. For endo substitution the situation is complicated by steric[4,20] and additional electronic[24] effects.

Acknowledgments. We are indebted to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support.

References and Notes

(1) C. H. Bushweller, M. Sharpe, and S. J. Weininger, *Tetrahedron Lett.*, 453 (1970).
(2) W. Braren and E. Buchner, *Ber. Dtsch. Chem. Ges.*, **34**, 982 (1901), and earlier references cited therein; for a review see G. Maier, *Angew. Chem.*, **79**, 446 (1967).
(3) W. v. E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956).
(4) H. Günther, W. Peters, and R. Wehner, *Chem. Ber.*, **106**, 3683 (1973).
(5) Synthesis see W. Betz and J. Daub, *Chem. Ber.*, **105**, 1778 (1972).
(6) H. Klose and H. Günther, *Chem. Ber.*, **102**, 2230 (1969).
(7) H. Günther, J. B. Pawliczek, B. D. Tunggal, H. Prinzbach, and R. H. Levin, *Chem. Ber.*, **106**, 984 (1973).
(8) Prepared from **2** by treatment with 2.6 *M* NaOD–D_2O for 20 hr at room temperature.
(9) M. Görlitz and H. Günther, *Tetrahedron*, **25**, 4467 (1969).
(10) H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968).
(11) F. R. Jensen and L. A. Smith, *J. Am. Chem. Soc.*, **86**, 956 (1964).
(12) The unsymmetry shown by the broadened H(7) resonance of **2** (Figure 2, −107°) also indicates that coalescence occurs with a high field signal. However, in order to use this effect unambiguously, deuterated solvents are necessary since the line shape depends critically on phase adjustments for the large solvent peak.
(13) Cyclopropane δ 0.22;[14] cyclopropyl carboxylic acid δ (CH) 1.59;[15] 2,3-benzonorcaradiene $\delta(H_{endo})$ −0.35;[16] 2,3-benzonorcaradiene-*exo*-7-carboxylic acid $\delta(H_{endo})$ 0.92;[17] tricyclo[$4.3.1.0^{1,6}$]decadiene-2,4 $\delta(H_{endo})$ −0.40, (H_{exo}) 1.42.[18]
(14) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).
(15) K. M. Crecely, V. S. Watts, and J. H. Goldstein, *J. Mol. Spectrosc.* **30**, 184 (1969).
(16) E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).
(17) H. Günther, H. Klose, and D. Cremer, *Chem. Ber.*, **104**, 3884 (1971).
(18) E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Günther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).
(19) J_{trans} = 4.57 and J_{cis} = 8.04 Hz has been reported for cyclopropyl carboxylic acid.[15]
(20) F.-G. Klärner, *Tetrahedron Lett.*, 19 (1974).
(21) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).
(22) H. Günther, *Tetrahedron Lett.*, 5173 (1970).
(23) W. J. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York, N.Y., 1973.
(24) W.-D. Stohrer and J. Daub, *Angew. Chem.*, **86**, 54 (1974).

Rainer Wehner, Harald Günther*
Institut für Organische Chemie, Universität Köln
5-Köln, Germany
Received November 22, 1974

Reactions of Alkali Ions with Organic Molecules in the Gas Phase. Low Energy Pathways for Carbonium Ion Formation and Novel Methods for Generating Alkali Ion Complexes with π- and n-Donor Bases

Sir:

While the reactivity of alkali atoms with halogenated hydrocarbons has been recognized for several decades, the interesting possibility that alkali ions may also undergo rapid reactions with these species has not been explored. We have recently demonstrated that halide ion transfer reactions between carbonium ions are rapid and can be employed to determine R^+-X^- heterolytic bond energies, $D(R^+\text{-}X^-)$.[1-3] A comparison of M^+-X^- heterolytic bond energies of alkali halides to $D(R^+\text{-}X^-)$ for various carbonium ions R^+, Table I, reveals several examples of reaction 1 which are exothermic.

$$M^+ + RX \longrightarrow MX + R^+ \qquad (1)$$

To investigate such reactions a thermionic source[4] was mounted inside the source region of an ICR cell.[5,6] While the spectrometer was operated in the drift mode for the studies reported herein, we have also performed trapped ion experiments using the thermionic source.

Typical results are shown in Figure 1. Double resonance

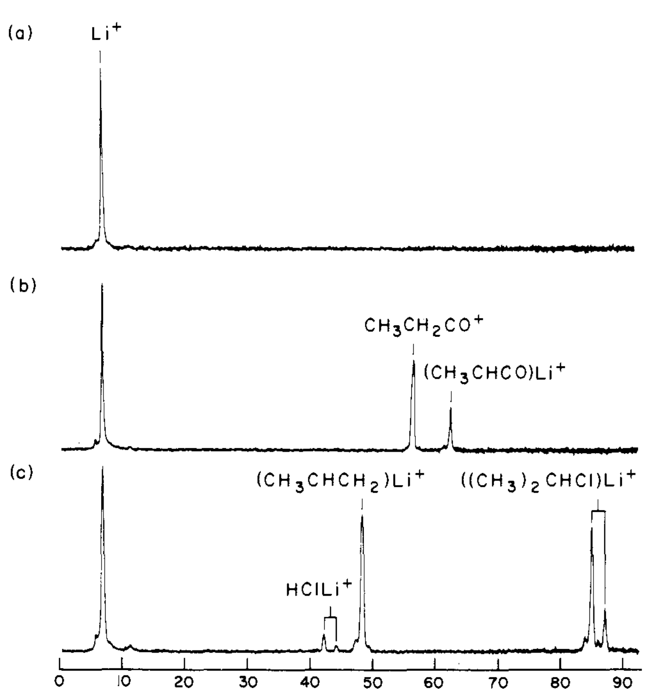


Figure 1. Mass spectra observed with (a) Li^+ source only, (b) propionyl bromide added at 4×10^{-6} Torr and, (c) isopropyl chloride added at 3×10^{-5} Torr. Note that species containing Li or Cl show additional peaks due to the minor isotopic species ^6Li (7%) and ^{37}Cl (24%).

experiments clearly identify Li^+ as the precursor to the reaction products observed when propionyl bromide is added, Figure 1b. The halide transfer process 2 accounts for the product ion at *m/e* 57. Quite unexpected, however, is the product at *m/e* 63 (reaction 3).

$$\mathrm{Li^+ + CH_3CH_2COBr} \begin{cases} \rightarrow \mathrm{CH_3CH_2CO^+ \;\; LiBr} & (2) \\ \rightarrow \mathrm{[CH_3CHCO]Li^+ + HBr} & (3) \end{cases}$$

Observed halide transfer processes involving Li^+ are consistent with the thermochemical data in Table I.[7] With $(CH_3)_2CHCl$, only the elimination processes 4 and 5 are

$$\mathrm{Li^+ + (CH_3)_2CHCl} \begin{cases} \rightarrow \mathrm{[C_3H_6]Li^+ + HCl} & (4) \\ \rightarrow \mathrm{LiClH^+ + CH_3CH{=}CH_2} & (5) \end{cases}$$

observed (Figure 1c). With $(CD_3)_2CHCl$, a 1,2-elimination process is exclusively indicated in both cases. The products of reactions 4 and 5 react further, transferring Li^+ to $(CH_3)_2CHCl$.

Observed Li^+ transfer reactions indicate the possibility of determining relative binding energies of Li^+ to various bases. For example, the complex of isobutylene with Li^+ formed by reaction of the latter with *tert*-butyl chloride transfers Li^+ to benzene, acetonitrile, acetaldehyde, dimethyl ether, and HCN. These results indicate reversals of base strengths when the acid Li^+ is compared to H^+.

Scheme I

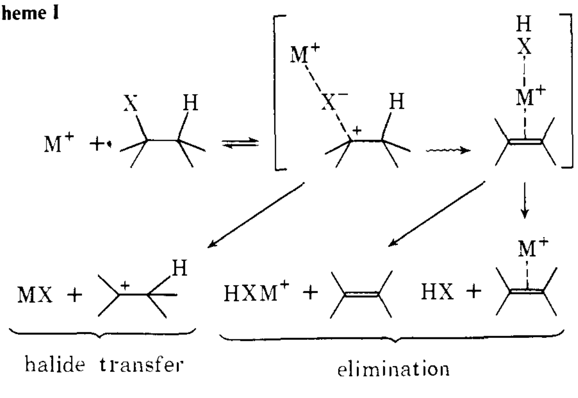
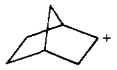
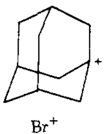
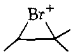
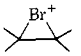


Table I. Heterolytic Bond Dissociation Energies for Various Organic and Alkali Chlorides and Bromides

R^+	$D(R^+–Cl^-)^{a,b}$	$D(R^+–Br^-)^{a,b}$
$i\text{-}Pr^+$	169.4 ± 1	162.9 ± 1
CH_3CO^+	162.5 ± 1	153.3 ± 1
$t\text{-}Bu^+$	156.9 ± 1	148.7 ± 1
$C_6H_5CH_2^+$	152.6 ± 2	143.8 ± 2
$C_2H_5CO^+$	150.5 ± 2	141.3 ± 2
	144.3 ± 2	138.5 ± 2
	<146.3	<137.5
	<143.4	<134.6
	<143.4	<134.6
Li^+	155.1 ± 3.0	148.7 ± 3.0
Na^+	133.2 ± 0.5	127.9 ± 0.5
K^+	118.4 ± 0.1	113.7 ± 0.5

[a] All data in kcal/mol. [b] Calculated using $D(R^+–X^-) = \Delta H^\circ_f(R^+) + \Delta H^\circ_f(X^-) - \Delta H^\circ_f(RX)$, see ref 5. $\Delta H^\circ_f(Cl^-)$ and all values for the alkali halides are from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C., 1971. $\Delta H^\circ_f(RCl)$ from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970, or calculated using group heats; see S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968.

To summarize, association of an alkali ion and organic halide (Scheme I) leads to the formation of a chemically activated species which may dissociate to an alkali halide and carbonium ion. The intermediate may also eliminate HX to give an alkene, with the alkali ion remaining bound to either species in the products. Thermal generation of reagent ions combined with halide transfer reactions provide low energy pathways to the formation of carbonium ions. Alkali ions may prove to be useful as specific reagents for analytical chemical ionization studies;[8] reactions with other functional groups will likely be discovered. Of greatest significance is the opportunity to determine binding energies of alkali ions to π- and n-donor bases. These data have implications for general theories of acid-base interactions and may lead to a better understanding of chemical transformations effected by Lewis acid catalysts.

Acknowledgment. This research was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-03)767-8.

References and Notes

(1) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **94**, 8934 (1972).
(2) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1269 (1974).
(3) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974).
(4) J. P. Blewett and E. J. Jones, *Phys. Rev.*, **50**, 464 (1936); D. P. Ridge, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1973.
(5) For a general review of ICR see, J. L. Beauchamp. *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(6) T. B. McMahon and J. L. Beauchmp. *Rev. Sci. Instrum.*, **43**, 509 (1972).
(7) No reactions of K^+ were observed with the organic halides listed in Table I. Formation of the tetramethylethylene bromonium ion from the parent bromide was the only observed reaction of Na^+.

(8) F. H. Field in "Ion-Molecule Reactions," J. L. Franklin, Ed., Plenum Press, New York, N.Y., 1972, Chapter 6.
(9) National Science Foundation Undergraduate Research Program participant, Summer, 1974.
(10) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.

Robert D. Wieting,[9] Ralph H. Staley, J. L. Beauchamp*[10]
Contribution No. 4976, Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

Received September 28, 1974

Thermolysis of the Cyclic Peroxide 4-Ethylidene-3,3,5,5-tetramethyl-1,2-dioxolane. Generation and Trapping of a 1,5-Diradical[1]

Sir:

Due to the short lifetime ($\tau \leq 10^{-7}$ sec) of diradicals, it has been difficult to trap such reaction intermediates by external chemical means.[2] Factors that increase diradical lifetimes, e.g., electronic, conformational, and steric constraints, should enhance the chances of diradical trapping. Presently we report on such evidence in the thermolysis of the cyclic peroxide **1**. For example, static gas phase pyrolysis of **1** at 315° and 10 μ resulted in complete destruction of **1** within 5 hr, affording no less than 30 volatile products, of which **3a, b, 4, 6, 8, 9, 11, 12, 15, 17a, b,** and **18** (Scheme I) were isolated and characterized. Also ca. 19% involatile residue was formed in this thermolysis. However, heating of a benzene solution 1.3 *M* in **1** and 2.6 *M* in benzhydrol at 200° for 48 hr gave 1,3-diol **16** and benzophenone in stoichiometric amounts with no traces of rearrangement or cleavage products. In the absence of benzhydrol and under the same liquid phase thermolysis conditions, **1** did not decompose even after weeks of heating. Furthermore, in an effort of testing for surface catalysis and free radical chain processes, the gas phase pyrolysis was performed in an aged Pyrex vessel and in the presence of acetone, methanol, helium, nitrogen, and oxygen gases as diluents. The rate of decomposition and relative product composition of **1** were not affected, indicating that we were dealing with a clean unimolecular decompositon.

In Scheme I we offer a mechanistic rationalization for the formation of the gas phase thermolysis products of **1** in terms of the 1,5-diradical **2** as precursor, in analogy to our previous work on the thermolysis and photolysis of cyclic peroxides such as the 1,2-dixolanes,[3] β-peroxylactones,[4] γ-peroxylactones,[5] and 1,2-dioxanes,[6] which are efficient sources for diradicals. On thermal activation the oxygen-oxygen bond is cleaved in **1**, affording initially the 1,5-diradical **2**, which subsequently recyclizes into the isomeric epoxyoxetanes **3a** and **b**, fragments into acetone (**4**) and the 1,3-diradical **5**, or double hydrogen-abstracts to give the 1,3-diol **16** as major pathways. The latter dehydrates into the trienes **17a** and **b** under the thermolysis conditions, as confirmed by a control experiment for the authentic **16**. The 1,3-diradical **5** undergoes a 1,2-methyl shift to give the enone **6** or cyclizes to the allene oxide **7a**. The latter readily valence tautomerizes into the cyclopropanone **7b** and subse-

Scheme I