J. Am. Chem. Soc. 1986, 108, 6915–6921

Energy Requirements for Remote Charge Site Ion Decompositions and Structural Information from Collisional Activation of Alkali Metal Cationized Fatty Alcohols

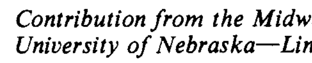
Jeanette Adams and Michael L. Gross*

Contribution from the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0362.

Received April 22, 1986

Abstract: Collisional activation of long-chain fatty alcohols cationized with certain alkali metal cations results in decompositions originating remote from the site of charge. These charge-remote fragmentations, like the previously discovered reactions of fatty acid carboxylates, are structurally informative and fill a need in structural chemistry which is not met by spectroscopic methods such as NMR, IR, and UV–vis. The decompositions produce closed-shell organic ions containing the alkali cations and are analogous to those observed previously for fatty acid anions. There are two alkali metal ion containing radical cations which may be produced by remote fragmentation to give distonic ions. The decompositions clearly indicate double bond position for both monounsaturated and polyunsaturated fatty alcohols. However, fragmentation of homoconjugated polyunsaturated fatty alcohols is complicated by the presence of daughter ions representing cationization of the double bonds in addition to cationization of the terminal hydroxyl. The types of decompositions of the $[M + Li]^+$, $[M + Na]^+$, $[M + K]^+$, and $[M + Rb]^+$ ions of oleyl alcohol change smoothly, and the variations can be understood in terms of the gas-phase enthalpies of solvation for the alkali metal ions. On the basis of changes in fragmentation to favor release of the alkali metal cation, an estimate of 1.3–1.9 eV for the internal energy required for remote charge site decompositions is made.

High energy collisional activation (CA) of gas-phase carboxylate anions results in decompositions which originate remote from the site of charge.[1] The probable mechanism for this unusual class of gas-phase decompositions involves 1,4-hydrogen eliminations to produce neutral alkenes and terminally-unsaturated carboxylate anions (eq 1).[1]



(1)

These recently identified decompositions represent a new class of fragmentation reactions with immediate implications for structure determination of molecules that are not amenable to other physical-chemical methods such as NMR, IR, and UV–vis. The characteristic losses of the elements of C_nH_{2n+2} originate from the alkyl terminus of carboxylate, alkyl sulfate, and alkyl sulfonate anions,[2] and ammonium and phosphonium cations.[3] The decompositions give rise to mass spectra, or collisional activation decomposition (CAD) spectra, which clearly show length of the hydrocarbon chain and location of important structural features such as double bonds, branch points, and other functional groups.[2a,b,4] Recently other types of remote decompositions have been shown to be important for determining structures of bile salts.[5]

Knowledge of the mechanism(s), energy requirements, and basic structural properties required for remote fragmentations would facilitate their application to a greater variety of structural problems. On-going research in our laboratory is directed toward investigating further the mechanism. We known from varying the laboratory collisional energy that only ions of high translational energy (keV) undergo remote charge site decompositions.[3b] However, these measurements provide only a crude estimate of the upper limit of internal energy required for the decompositions.

To address these fundamental questions, we present results here from a study of collisionally activated decompositions of fatty alcohols cationized with alkali metal ions. These CA decompositions show that a strongly localized charge is required for the initiation of remote fragmentations. The internal energy required for the decompositions is estimated from the gas-phase enthalpies of solvation of alkali metal ions[6] and from the CA decompositions of oleyl alcohol cationized with lithium and sodium.[7]

In addition to addressing these fundamental questions, this study also shows that CA decompositions of alcohol $[M + Li]^+$ ions are an effective source of structural information for determining features of long-chain fatty alcohols. Present analytical techniques have involved stringent analyses of ion abundances from electron ionization (EI),[8] derivatization followed by EI,[9] in situ derivization by chemical ionization,[10] or derivatization followed by tandem MS to generate parent ion spectra.[11] Problems associated with some of these methods include double bond migration,[12] inconsistent fragmentation patterns,[10b] and the need for prior sample derivatization.[9,11] Here, fast atom bombardment (FAB) and collisional activation tandem mass spectrometry are shown to provide an entirely instrumental technique for determining double bond location in long-chain fatty alcohols.

---

* Author to whom correspondence should be addressed.

(1) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1863–1868.

(2) (a) Tomer, K. B.; Crow, F. W.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5487–5488. (b) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 2018–2021. (c) Lyon, P. A.; Stebbings, W. L.; Crow, F. W.; Tomer, K. B.; Lippstreu, D. L.; Gross, M. L. *Anal. Chem.* **1984**, *56*, 8–13. (d) Lyon, P. A.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 2984–2989.

(3) (a) Lyon, P. A.; Crow, F. W.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1984**, *56*, 2278–2284. (b) McCrery, D. A.; Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 1181–1186.

(4) Jensen, N. J.; Gross, M. L. *Lipids* **1986**, *21*, 362–365.

(5) Tomer, K. B.; Jensen, N. J.; Gross, M. L.; Whitney, J. *Biomed. Mass Spectrom.* **1986**, *13*, 265–272.

(6) (a) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466–1474. (b) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501–508.

(7) Related techniques for evaluating internal energy recently have been reported for CA decompositions of triethyl phosphate ions [Kenttamaa, H. L.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *64*, 79–83] and of methane ions [Rabrenovic, M.; Beynon, J. H.; Lee, S. H.; Kim, M. S. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *65*, 197–210].

(8) (a) Horiike, M.; Hirano, C. *Biomed. Mass Spectrom.* **1984**, *11*, 145–148. (b) Leonhard, B. A.; DeVilbiss, E. D.; Klun, J. A. *Org. Mass Spectrom.* **1983**, *18*, 9–11. (c) Ando, T.; Katagiri, Y.; Uchiyama, M. *Agr. Biol. Chem.* **1985**, *49*, 413–421.

(9) (a) Vetter, W.; Meister, W. *Org. Mass Spectrom.* **1981**, *16*, 118–122. (b) Vetter, W.; Meister, W.; Oesterhelt, G. *Helv. Chim. Acta* **1978**, *61*, 1287–1295. (c) Eihorn, J.; Virelizier, H.; Guerrero, A. *Les Mediateurs Chimiques (Versailles)* **1981**, *(16–20)*, 95–105. (d) Einhorn, J.; Virelizier, H.; Guerrero, A.; Tabel, J. C. *Biomed. Mass Spectrom.* **1985**, *12*, 200–207. (e) Leonhard, B. A.; DeVilbiss, E. D. *J. Chromatogr.* **1985**, *322*, 484–490.

(10) (a) Brauner, A.; Budzikiewicz, H.; Boland, W. *Org. Mass Spectrom.* **1982**, *17*, 161–164. (b) Bauner, A.; Budzikiewicz, H. *Org. Mass Spectrom.* **1983**, *18*, 324–326. (c) Budzikiewicz, H. *Fres. Z. Anal. Chem.* **1985**, *321*, 150–158. (d) Einhorn, J.; Virelizier, H.; Gemal, A. L.; Tabet, J. C. *Tetrahedron Lett.* **1985**, *26*, 1445–1448.

(11) Horman, I. *Biomed. Mass Spectrom.* **1983**, *10*, 343–346.

(12) Ryhage, R.; Stenhagen, E. *J. Lipid Res.* **1960**, *1*, 361–390.

0002-7863/86/1508-6915$01.50/0

Experimental Section

Reagents and Procedures. Unsaturated and saturated alcohols were from Applied Science and Analabs, respectively. Hexadecanoic-*7,7,8,8*-d_4 acid was from MSD Isotopes; oleic acid was from Analabs. Triethanolamine, LiI, NaI, and CsI, $LiAlH_4$, and $LiAlD_4$ were from Aldrich; RbI was from Alfa. The matrix for fast atom bombardment (FAB), abbreviated here as DT and also known as "Magic Bullet",[13] was prepared by heating at 40 °C and mixing 25 g of dithiothreitol with 5 g of dithioerythreitol (Aldrich).

Hexadecanol-*7,7,8,8*-d_4 was prepared by reducing 10 mg of hexadecanoic-*7,7,8,8*-d_4 acid with a 20-fold equivalent excess of $LiAlH_4$ in diethyl ether. After being stirred at room temperature for 12 h, the reaction was quenched by adding small aliquots of water. The precipitate was removed by filtration, and the alcohol was isolated by evaporating the solvent from the filtrate. Oleyl-*1,1*-d_2 alcohol was similarly prepared from oleic acid by reduction with $LiAlD_4$.

Cationization was effected by using the DT matrix saturated with each alkali iodide. Each salt was added to a small aliquot of DT, and to maximize dissolution, the DT/alkali iodide mixtures were heated to 50 °C and repeatedly vortexed. The iodides were used because they are more soluble in DT than the other halides. Less concentrated mixtures of the alkali iodides in DT might have been acceptable, but effects of concentration were not investigated.

For the FAB-collisional activation decomposition (CAD) experiments, small amounts (μg–mg) of the alcohols were mixed on the copper probe tip with either triethanolamine for negative ion MS or DT or DT/alkali iodide for positive ion MS. For the trace determination of oleyl alcohol, approximately 0.5 μL of DT/LiI was applied to the probe tip followed by 1–2 μL of a solution containing 15 $\mu g\ \mu L^{-1}$ of oleyl alcohol in methanol. The methanol was gently evaporated as the sample, and DT/LiI were thoroughly mixed.

Instrumentation. The EB/E configuration tandem mass spectrometer used in this study is a Kratos MS-50 Triple Analyzer.[14] MS-I is a standard Kratos double-focusing MS-50 (ESA·I and magnet). MS-II is an electrostatic analyzer (ESA-II). There are three field-free regions: first is between source and ESA-I; second is between ESA-I and magnet; third is between magnet and ESA-II.

The Triple Analyzer is equipped with a commercial Kratos FAB source, an Ion Tech saddle-field gun (Ion Tech, Middlesex, England), and a Data General Nova 4X computer. For the FAB-CAD experiments, ions were produced by bombarding the sample with 7–8 keV of Ar atoms (atom gun output current of 2 mA) and then accelerated through a potential of 8 kV. Ions of interest were selected at a mass resolution of approximately 2000 (width at 10% height) by using MS-I. The 8 keV mass-selected ions were then activated by collision with He (approximately 50% main beam suppression) in a collision chamber located in the third field-free region between MS-I and MS-II. Mass selected ion kinetic energy-analyzed daughter ion spectra were obtained by scanning MS-II and by averaging the results of 20–40 scans by using software written in our laboratory.

Results and Discussion

Decompositions of $[M - H]^-$ Anions. Neither FAB-desorbed nor metastable fatty acid $[M - H]^-$ anions decompose unimolecularly to give structurally informative fragment ions. However, high energy collisional activation (CA) of fatty acid $[M - H]^-$ anions causes decompositions which clearly show the length of the hydrocarbon chain.[1] Monounsaturated acids decompose to give closed-shell, even-electron daughter ions which also indicate double bond location.[2a] The dominant fragments arise from losses of the elements of C_nH_{2n+2}. The ion decompositions originate at the alkyl terminus, remote from the charge site (see eq 1).[1]

In contrast to decompositions of fatty acid anions, fragmentations of fatty alcohol anions are almost identical whether they occur unimolecularly in the ion source or in the third field-free region of the mass spectrometer (as metastable ion decompositions), or whether they occur by collisional activation. FAB-desorbed anions are primarily the $[M - H - H_2]^-$ enolates followed in abundance by the $[M - H]^-$ alkoxides. There is also a small abundance of $[M - H - CH_2O]^-$ carbanions.

Decompositions of metastable, mass-selected alcohol $[M - H]^-$ anions are similar to those which occur in the source except that saturated alkoxides only lose H_2 to give the $[M - H - H_2]^-$ enolates. Metastable unsaturated alkoxides decompose to produce predominantly the $[M - H - CH_2O]^-$ carbanions, followed in abundance by the $[M - H - H_2]^-$ enolates. Collisional activation causes a small increase in the relative abundance of the enolates; the relative abundance of the unsaturated $[M - H - CH_2O]^-$ carbanions is virtually unaffected. The chemistry of these decompositions is a subject of further investigation and will be discussed elsewhere.

Decompositions of $[M + H]^+$ Ions. FAB-desorbed monounsaturated, protonated fatty alcohols decompose in the source to give abundant fragment ions. Except for the abundant $[M + H]^+$ ions, the ions are mainly distributed toward the lower masses, with the predominant series being the closed-shell $[C_nH_{2n-3}]^+$ carbocations. Another major series is the $[C_nH_{2n-1}]^+$ carbocations. The decompositions give no indication of double bond location. They are similar to those which occur upon chemical ionization (CI),[15] except the FAB spectra reveal no $[M + H - H_2O]^+$ ions. In contrast to CI, a small abundance of open-shell, odd-electron $[M - H_2O]^{\cdot +}$ ions is observed.

Metastable and collisional activation decompositions of alcohol $[M + H]^+$ ions also give an abundance of fragment ions (Figure 1). The three major series, $[C_nH_{2n+1}]^+$, $[C_nH_{2n-1}]^+$, and $[C_nH_{2n+1}O]^+$, have been assigned on the basis of analogies with the chemistry of protonated fatty acids[16] and with results from electron ionization (EI),[17] CI,[15] and field ionization.[18]

Mass-selected $[M + H]^+$ ions of oleyl alcohol decompose, giving significantly abundant $[M + H - H_2O]^+$ carbocations (Figure 1). This daughter $[M + H - H_2O]^+$ carbocation then presumably decomposes by losing neutral C_nH_{2n} to give the major series $[C_nH_{2n-1}]^+$. Olefin eliminations from such aliphatic carbocations are classical gas-phase reactions,[19] and the pattern of daughter ions shown in Figure 1 is entirely analogous to the pattern of closed-shell carbocations seen in the EI mass spectra of aliphatic alcohols[17a] and the CI mass spectra of alcohols[15] and other highly aliphatic substances.[15,19b] Losses of C_nH_{2n} from $[M + H - H_2O]^+$ and $[M + H - 2H_2O]^+$ daughter ions are directly seen in the metastable and collisionally activated decompositions of protonated fatty acids by mass-selecting the FAB-desorbed $[M + H - H_2O]^+$ and the $[M + H - 2H_2O]^+$ ions.[16] However, because protonated long-chain fatty alcohols do not lose H_2O upon desorption by FAB, the intermediacy of a $[M + H - H_2O]^+$ carbocation cannot be directly proven. As shown in Figure 1, the collisionally activated $[M + H]^+$ ions decompose more extensively to shift the daughter ion distribution to lower masses.

An unfortunate practical consequence of the source, metastable, and collisionally activated decompositions of the $[M + H]^+$ ions of oleyl alcohol is that no fragments are formed which indicate double bond location. Double bond migration or hydrogen scrambling in the daughter carbocations, as with EI[12] and CI,[19b] prevents unequivocal assignment of double bond location. Decompositions of the $[M + H]^+$ ions are predominantly charge-mediated, as with EI and CI, and no apparent decompositions originate remote from the site of charge.

Decompositions of $[M + Li]^+$ Ions of Monounsaturated Alcohols. Early field ionization and field desorption studies showed that alkali cations can be used to produce more stable $[M + Cat]^+$ species when no abundant $[M + H]^+$ ions are formed.[20] Ca-

---

[13] Witten, J. L.; Schaffer, M. H.; O'Shea, M.; Cook, J. C.; Hemling, M. E.; Rinehart, K. L., Jr. *Biochem. Biophys. Res. Commun.* **1984**, *124*, 350–358.

[14] Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243–254.

[15] (a) Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1966**, *88*, 2621–2630. (b) Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC: Boca Raton, FL, 1983; pp 87–127.

[16] Adams, J.; Gross, M. L. *Anal Chem.*, submitted for publication.

[17] (a) Dolejs, L.; Beran, P.; Hradec, J. *Org. Mass Spectrom.* **1968**, *1*, 563–566. (b) Brown, R. A.; Young, W. S.; Nicolaides, N. *Anal. Chem.* **1954**, *26*, 1653–1654. (c) McLafferty, F. W. *Interpretation of Mass Spectra*, 2nd ed.; W. A. Benjamin: Reading, MA, 1973; p 115.

[18] Beckey, H. D.; Schulze, P. *Z. Naturforsch.* **1966**, *21a*, 214–225.

[19] (a) Bowen, R. D.; William, D. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1479–1485. (b) Hunt, D. F.; McEwen, C. N. *Org. Mass Spectrom.* **1976**, 1479–1485. (c) Hunt, D. F.; McEwen, C. N. *Org. Mass Spectrom.* **1973**, *7*, 441–448.

[20] (a) Schulten, H. R.; Games, D. E. *Biomed. Mass Spectrom.* **1974**, *1*, 120–123. (b) Rollgen, F. W.; Schulten, H.-R. *Org. Mass Spectrom.* **1975**, *10*, 660–668.

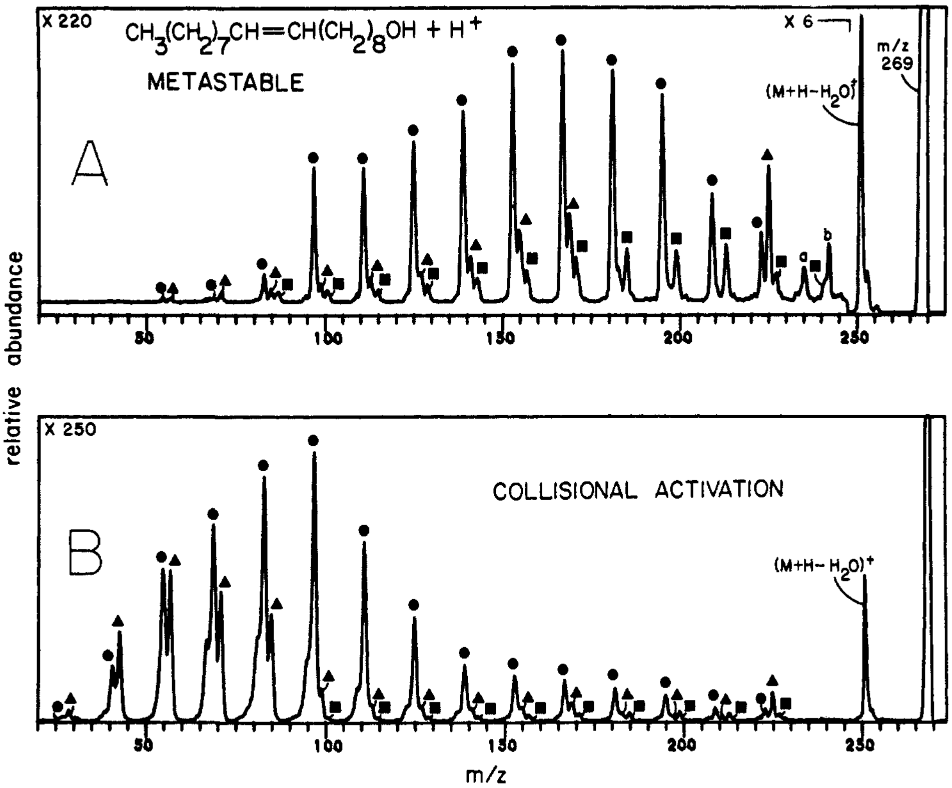


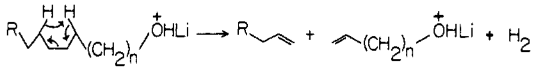
Figure 1. Spectra of the metastable (A) and collisionally activated (B) decompositions of the $[M + H]^+$ ions of 9-octadecenol (oleyl alcohol). Ion series are $[C_nH_{2n+1}]^+$ (▲); $[C_nH_{2n-1}]^+$ (●); and $[C_nH_{2n+1}O]^+$ (■). Fragments **a** and **b** are $[M - H_2O - CH_4]^+$ and $[M - C_2H_3]^{\cdot +}$, respectively. Spectra were magnified by the factors shown in the upper left corners (A, B) and in the upper right corner (A).

tionization for molecular weight determination has been used since with fission fragment ionization,[21] laser desorption,[22] CI,[23] EI,[24] and FAB.[25] Tandem mass spectrometric determination of cationized substances was demonstrated to be useful for structure elucidation of bile salts;[26] alkyl sulfate surfactants;[27] propyl and butyl alcohols, carbonyl compounds, and saccharides;[28] and peptides.[29] Although the $[M + H]^+$ ions of bile salts were reported to decompose analogously to the $[M + Na]^+$ species,[26] the collisionally activated decompositions of other cationized compounds are frequently distinctly different than those of the $[M + H]^+$ ions.[28a–c,29]

Fast atom bombardment of long-chain unsaturated fatty alcohols in the matrix DT saturated with LiI leads to desorption of abundant $[M + Li]^+$ ions. However, neither the lithiated alcohols desorbed by FAB nor the metastable mass-selected $[M + Li]^+$ ions undergo facile unimolecular fragmentations as compared to the $[M + H]^+$ species. Collisional activation of the $[M + Li]^+$ ions does, however, open up a set of decomposition reactions that are significantly different from the CA decompositions of the $[M + H]^+$ ions (Figure 2A).

It is apparent from the spectra in Figure 2 that collisionally activated $[M + Li]^+$ ions of oleyl alcohol (Figure 2A) decompose in an analogous manner to the $[M - H]^-$ ions of oleic acid (Figure 2B). Similarly, $[M + Li]^+$ ions of saturated octadecanol decompose analogously to the $[M - H]^-$ ions of octadecanoic acid to give a homologous series of closed-shell ions spaced 14 mass units apart. These ions are produced from losses of the elements of C_nH_{2n+2}.

The mechanism for the collisionally activated decompositions of $[M + Li]^+$ ions of fatty alcohols is the same as that for the $[M - H]^-$ ions of fatty acids. Collisionally activating the $[M + Li]^+$ ions of hexadecanol-7,7,8,8-d_4 shows that the decompositions originate remote from the charge site and probably involve 1,4-hydrogen eliminations to give neutral alkenes and terminally unsaturated lithiated alcohols (eq 2).



(2)

As with the fatty acid anions,[2a] the presence of the double bond disrupts the smooth pattern of ion abundances to give two intense peaks representing cleavage allylic to the double bond. Between these two intense peaks are three very minor peaks (Figure 2). Thus, the CAD spectrum of the $[M + Li]^+$ ions of oleyl alcohol (Figure 2A) clearly shows the location of the double bond and length of the hydrocarbon chain.

Decompositions of oleyl alcohol $[M + Li]^+$ ions (Figure 2A) clearly contrast with those of $[M + H]^+$ ions (Figure 1). Loss of LiOH from $[M + Li]^+$ ions must be more energetically unfavorable than loss of H_2O from $[M + H]^+$ ions. Thus, there are no $[M + Li - LiOH]^+$ daughter carbocations, analogous to $[M + H - H_2O]^+$ carbocations, which would undergo hydrogen scrambling and double bond migration. Instead, the site of charge is strongly localized on the hydroxyl, and decompositions occur remote from the charge site without migraion of either the charge or the double bond.

The collisionally activated decompositions of the $[M + Li]^+$ ions of oleyl alcohol are typical of all the monounsaturated alcohols

---

(21) (a) Chait, B. T.; Shpungin, J.; Field, F. H. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 121–137. (b) Sundqvist, B.; MacFarlane, R. D. *Mass Spectrom. Rev.* **1985**, *4*, 421–460.

(22) Rollgen, F. W.; Stoll, R. *Org. Mass Spectrom.* **1979**, *14*, 642–645.

(23) (a) Hodges, R. V.; Beauchamp, J. L. *Anal. Chem.* **1976**, *48*, 825–829. (b) Bombick, D.; Pinkston, J. D.; Allison, J. *Anal. Chem.* **1984**, *56*, 396–402. (c) Schmelzeisen-Redeker, G.; Giessmann, U.; Rollgen, F. W. *Org. Mass Spectrom.* **1985**, *20*, 305–309.

(24) Constantin, E. *Org. Mass Spectrom.* **1982**, *17*, 346–347.

(25) (a) Puzo, G.; Prome, J. C. *Org. Mass Spectrom.* **1985**, *20*, 288–291. (b) Keough, T. *Anal. Chem.* **1985**, *57*, 2027–2034. (c) Puzo, G.; Fournie, J.-J.; Prome, J.-C. *Anal. Chem.* **1985**, *57*, 892–894.

(26) Liehr, J. G.; Kingston, E. E.; Beynon, J. H. *Biomed. Mass Spectrom.* **1985**, *12*, 95–99.

(27) Wèber, R.; Levsen, K.; Boerboom, A. J. H.; Haverkamp, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 305–308.

(28) (a) Rollgen, F. W.; Borchers, F.; Giessmann, U.; Levsen, K. *Org. Mass Spectrom.* **1977**, *12*, 541–543. (b) Rollgen, F. W.; Giessmann, U.; Borchers, J.; Levsen, K. *Org. Mass Spectrom.* **1978**, *13*, 459–461. (c) Puzo, G.; Prome, J.-C.; Maxime, B. *Adv. Mass Spectrom.* **1980**, *8*, 1003–1011. (d) Wright, L. G.; Cooks, R. G.; Wood, K. V. *Biomed. Mass Spectrom.* **1985**, *12*, 159–162.

(29) Mallis, L. M.; Russell, D. H. *Anal. Chem.* **1986**, *58*, 1076–1080.

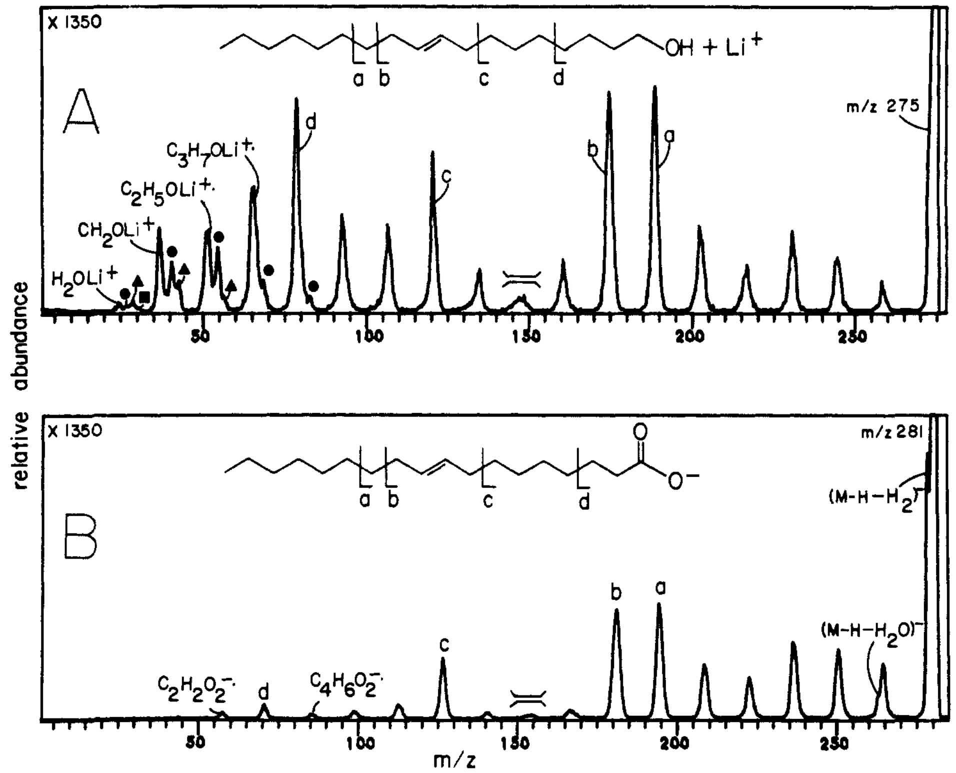


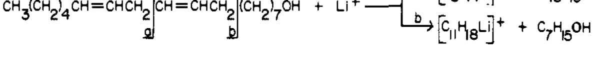
Figure 2. CAD spectra of $[M + Li]^+$ ions of oleyl alcohol (A) and $[M - H]^-$ ions of oleic acid (B). Symbols representing different ion series are described in Figure 1. Symbols for double bonds are added at appropriate sites to indicate their locations. Spectra were magnified by the factors shown in the upper left corners. The CAD spectrum of the oleate anion is described in more detail elsewhere.[1,2a]

studied (C_{16}–C_{24}). As exemplified in Figure 2A, there are two series of closed-shell, even-electron ions resulting from cleavages on either side of the double bond. (We have assigned all members of these two series to be closed-shell ions. It is possible, however, that fragmentations allylic to the double bond may be in part simple cleavages, without accompanying H-rearrangement, giving distonic radical cations. A tandem mass spectrometer affording unit resolution daughter ion spectra is required to settle this question.) The lower mass series of $[C_nH_{2n}OLi]^+$ ions begins with $[CH_2OLi]^+$ of *m/z* 37 and is interrupted by the two radical cations of *m/z* 52 and of *m/z* 66 described below. The series then continues from $[C_4H_8OLi]^+$ of *m/z* 79 (ion **d** in Figure 2A) through $[C_8H_{16}OLi]^+$ of *m/z* 135. At this point the double bond disrupts the continuity, and a new series of higher mass ions, $[C_nH_{2n-2}OLi]^+$, begins. This series begins with $[C_{10}H_{18}OLi]^+$ of *m/z* 161 and continues through $[C_{17}H_{32}OLi]^+$ of *m/z* 259. This highest mass daughter ion arises from loss of the elements of CH_4 from the $[M + Li]^+$ parent ion. The most abundant ions, as shown in the spectrum in Figure 2A, are those formed from cleavage β and γ to the double bond (fragments **a**–**c**) and ion **d** $[C_4H_8OLi]^+$. Another characteristic closed-shell ion containing lithium is $[H_2OLi]^+$ of *m/z* 25.

Collisional activation of lithiated alcohols also produces closed-shell ions, which do not contain lithium, and two lithium-containing radical cations. The low-mass end of the spectrum shown in Figure 2A reveals a small abundance of even-electron alkyl and alkenyl ions and $[CH_2OH]^+$ of *m/z* 31. Two distinct radical cations containing lithium are formed: $[C_2H_5OLi]^{\bullet+}$ of *m/z* 52 and $[C_3H_7OLi]^{\bullet+}$ of *m/z* 66. This was determined by deconvoluting the peaks from narrow energy scans of the mass regions of the $[C_2H_5OLi]^{\bullet+}$ (*m/z* 52) ions of lithiated oleyl alcohol and the $[C_2H_3D_2OLi]^{\bullet+}$ (*m/z* 54) and $[C_3H_5D_2OLi]^{\bullet+}$ (*m/z* 68) ions of lithiated oleyl-*1,1*-d_2 alcohol. These experiments also show that there are no peaks representing analogous closed-shell lithium-containing ions, for instance of *m/z* 52 $[C_2H_3DOLi]^+$ or of *m/z* 67 $[C_3H_4D_2OLi]^+$, adjacent to the radical cations. The two prominent radical cations, $[C_2H_5OLi]^{\bullet+}$ of *m/z* 52 and $[C_3H_7OLi]^{\bullet+}$ of *m/z* 66, also appear to be unique in spectra of saturated alcohols: narrow energy scans of the $[C_7H_{12}D_2OLi]^+$ (*m/z* 123), $[C_8H_{13}D_3OLi]^+$ (*m/z* 138), and $[C_9H_{15}D_3OLi]^+$ (*m/z* 152) ions of lithiated hexadecanol-*7,7,8,8*-d_4 indicate that there are no radical cations adjacent to these closed-shell ions.

The decompositions of the $[M + Li]^+$ ions of oleyl-*1,1*-d_2 alcohol to give cleanly $[C_2H_3D_2OLi]^{\bullet+}$ (*m/z* 54) and $[C_3H_5D_2OLi]^{\bullet+}$ (*m/z* 68) suggest that these two radical cations are also formed by remote fragmentations. Here, remote charge site homolytic cleavage would give initially distonic, where the charge site is separated from the radical site, daughter ions such as $\dot{C}H_2CD_2{}^+OHLi$. Distonic ions are a subject of active investigation, and they are unexpectedly stable.[30] A precedent for remote decompositions leading to distonic ions may be the alkyl losses from fluoroalkane sulfonates.[2d] Similar lithium-containing radical cations are also produced by collisionally activating lithiated fatty acids.[16]

CAD of $[M + Li]^+$ Ions of Polyunsaturated Alcohols. The $[M + Li]^+$ ions of homoconjugated polyunsaturated alcohols also decompose, giving daughter ions indicative of double bond location (Figure 3). However, the gas-phase chemistry of these activated ions is complicated by decompositions involving association of lithium with the double bonds. The $[M + Li]^+$ ions decompose to give lithiated hydrocarbon ions, as exemplified by fragments **1**–**4** in Figure 3. As suggested in eq 3, the ion of *m/z* 157 from



$$CH_3(CH_2)_4CH{=}CHCH_2\underset{a}{|}CH{=}CHCH_2\underset{b}{|}(CH_2)_7OH + Li^+ \longrightarrow \begin{cases} \xrightarrow{a} [C_8H_{14}Li]^+ + C_{10}H_{19}OH \\ \xrightarrow{b} [C_{11}H_{18}Li]^+ + C_7H_{15}OH \end{cases} \quad (3)$$

doubly unsaturated linoleyl alcohol (**2** in Figure 3A) probably represents cleavage β to the 9,10-double bond to give $[C_{11}H_{18}Li]^+$; the less abundant $[C_8H_{14}Li]^+$ of *m/z* 117 (**3** in Figure 3A) arises from cleavage β to the 12,13-double bond.

Collisional activation of triply unsaturated linolenyl alcohol produces even more abundant ions representing lithium bound to hydrocarbons. There are two main ions resulting from cleavage

---

[30] (a) Sack, T. M.; Cerny, R. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 4562–4564 and references therein. (b) Wesdemiotis, C.; Danis, P. O.; Feng, R.; Tso, J.; McLafferty, F. W. *J. Am. Chem. Soc.* **1985**, *107*, 8059–8066.

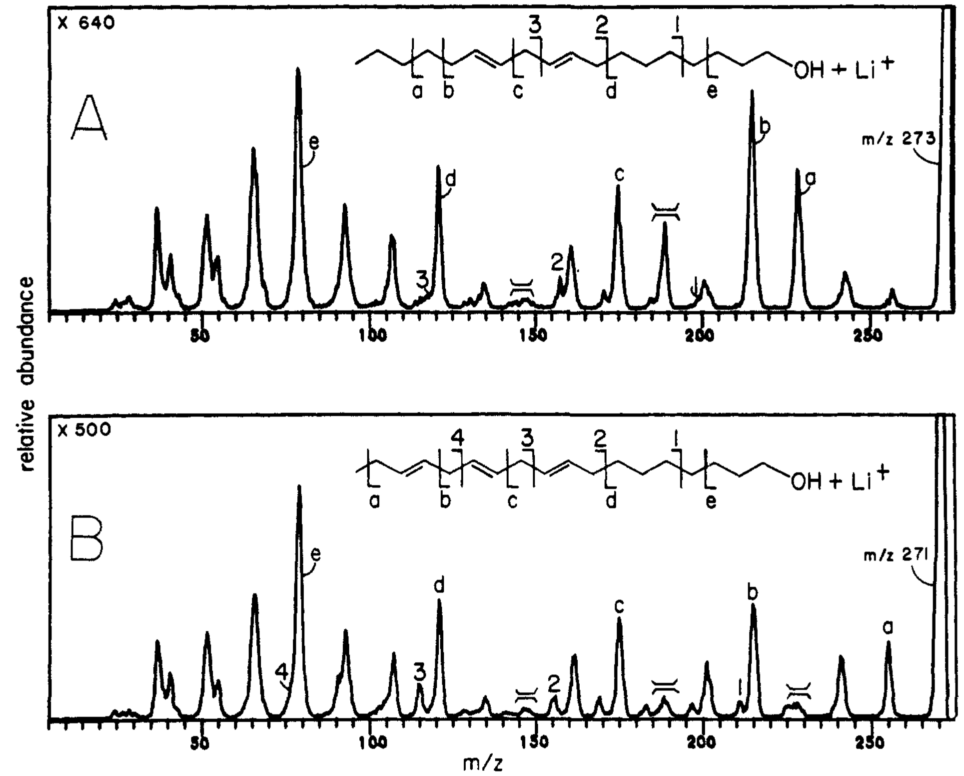


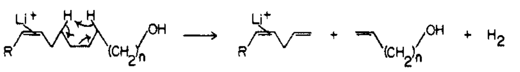
Figure 3. CAD spectra of the $[M + Li]^+$ ions of polyunsaturated linoleyl (A) and linolenyl (B) alcohols. Ions **a–e** result from lithiation of the terminal hydroxyl; **1–4** result from lithiation of a double bond. Symbols for double bonds are added at appropriate sites to indicate their locations. Spectra were magnified by the factors shown in the upper left corners.

β to the double bonds: $[C_{11}H_{16}Li]^+$ of m/z 155, fragment **2** in Figure 3B, and $[C_8H_{12}Li]^+$ of m/z 115, fragment **3**. The very low abundance ion of m/z 75 $[C_5H_8Li]^+$, fragment **4**, represents cleavage β to the lithiated 15,16-double bond.

Lithium should interact more strongly with a terminal hydroxyl than with a double bond of a monounsaturated alcohol. This should pertain if lithiation is occurring in solution, on the probe tip, or in the gas-phase. Aqueous-phase basicity of a methanolic hydroxyl is approximately 0.05 eV greater than an ethenic double bond;[31] the gas-phase basicity of methanol is 0.8 eV greater than ethene.[32] For lithium ion transfer, the gas-phase Lewis basicity of methanol is approximately 0.02 eV greater than that of benzene.[6b] However, as the number of double bonds increases, the probability of localizing lithium at the site of the double bonds should also increase. This increase should be reflected by an increase in the abundance of ion fragments representing lithiated double bonds, as is observed.

There is a possibility that the stereochemistry of the double bonds is such that two or three double bonds can concertedly interact with the Li^+ ion. However, there are no significant differences in the CA decompositions which occur for linoleyl alcohol (*cis*-9,*cis*-11-octadecadien-1-ol) and linolelaidyl alcohol (*trans*-9,-*trans*-11-octadecadien-1-ol).

The mechanism responsible for the formation of lithium-containing hydrocarbon ions also involves decompositions occurring remote from the site of lithiation, which is now the double bonds. The production of ions with lithium bound to the hydrocarbon chain could proceed via a remote loss of H_2O followed by remote losses of C_nH_{2n}. Another mechanism, analogous to the remote losses of the elements of C_nH_{2n+2}, could involve expulsion of the elements of $C_nH_{2n+1}OH$, as suggested in eq 4. This mechanism has not been proven.



(4)

The positions of double bonds in homoconjugated polyunsaturated fatty alcohols, in contrast to monounsaturated fatty alcohols, are less easily determined from simple inspection of the CAD spectra of the $[M + Li]^+$ ions. This is also true for the collisionally activated decompositions of polyunsaturated fatty acids.[2b] The spectra are complicated by competition between different decompositions occurring β and γ to the double bonds. However, on the basis of results from lithiated fatty acids,[16] the remote decompositions of lithiated fatty alcohols are expected to predominate even with increasing unsaturation. This contrasts with the decompositions of fatty acid anions: if four or more double bonds are present, only loss of 44 or 45 amu occurs, and remote charge site fragmentation virtually ceases.[2b]

Fragmentation Energetics. Previous research on the collisionally activated decompositions of alkyltriphenylphosphonium ions shows that remote charge site fragmentations cease at laboratory collisional energies of approximately 175 eV.[3b] This value, with He as the target gas, can be substituted into eq 5 where E_t is ion kinetic energy, and m_t and m_p are target and projectile masses, respectively.[33]

$$E_i = E_t\left(\frac{m_t}{m_t + m_p}\right) \qquad (5)$$

The maximum internal energy, E_i, which can be acquired from translational energy during collisional activation is calculated to be 1.2–7.0 eV. This is the maximum internal energy range required for remote fragmentation of ions of mass 600 (perfluorodecanesulfonate[2d]) through 100 (pentanoic acid[1]), respectively.

More reliable estimates of internal energy available for particular ion decompositions are usually made by evaluating relative abundances of daughter ions vs. their ionizing energies (known as measurements of appearance energies.)[7] These measurements are not possible here, and the internal energy required for the remote decompositions must be bracketed instead on the basis of the competitive loss of the alkali cation vs. the remote fragmen-

---

(31) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 3rd ed.; McGraw-Hill: New York, 1970; pp 306–307.

(32) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808.

(33) Dolder, K. T.; Peart, B. In *Rep. Prog. Phys.*; Ziman, J. M., Ed.; The Institute of Physics: London, 1976; Vol. 39, pp 693–749.

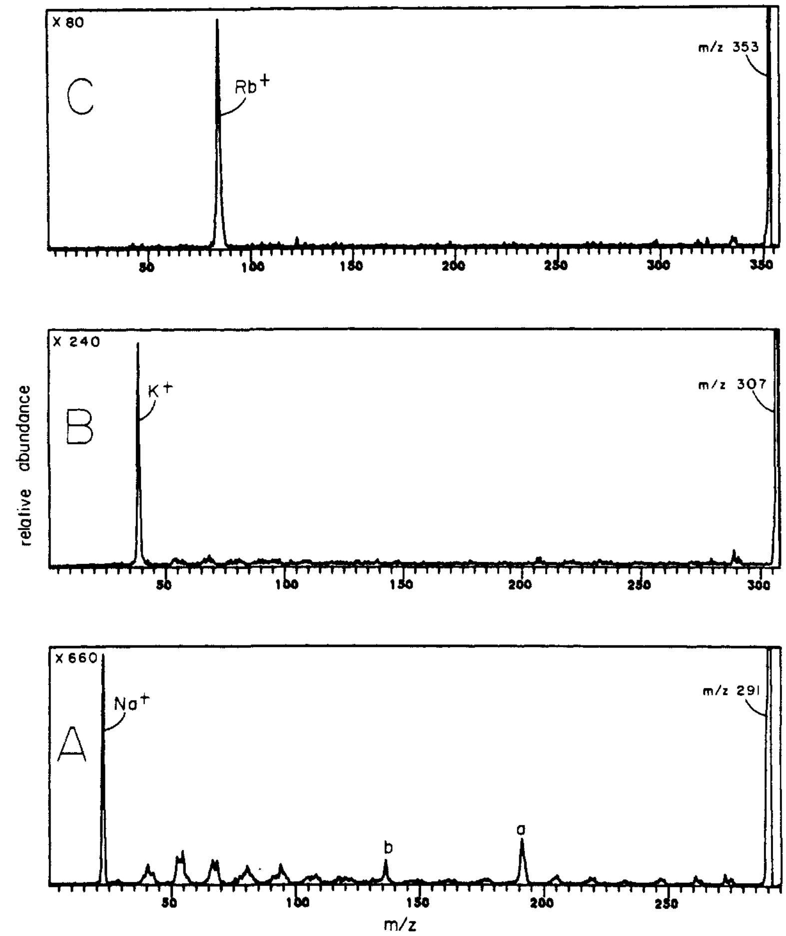


Figure 4. CAD spectra of the [M + Cat]$^+$ ions of oleyl alcohol cationized with Na$^+$ (A), K$^+$ (B), and Rb$^+$ (C). Spectra were magnified by the factors shown in the upper left corners.

tations produced by collisionally activating the [M + Cat]$^+$ ions of oleyl alcohol.

The CA decompositions of alkali-metal-cationized oleyl alcohol progressively become dominated by release of free alkali cation as lithium is replaced by other alkali metal ions (sodium to rubidium) (Figure 4). Approximately 3% Na$^+$ loss from [M + Na]$^+$ occurs unimolecularly, whereas unimolecular loss of K$^+$ and Rb$^+$ from [M + K]$^+$ and [M + Rb]$^+$ approaches 8% of that observed by CA. The competition between direct loss of the metal ion and remote decompositions leading to cationized organic ions is apparent in the CAD spectrum of [M + Na]$^+$. For [M + Rb]$^+$, the competition so strongly favors loss of Rb$^+$ that there are no clearly discernable organic fragments which contain Rb$^+$.

A first estimate of the internal energy required for the remote decompositions can be made on the basis of the CA decompositions of the [M + Na]$^+$ and [M + Li]$^+$ ions of oleyl alcohol and the enthalpies for the gas-phase dehydration of the alkali cations.[6a] Collisionally activated sodiated oleyl alcohol decomposes to form both Na$^+$ and remote charge site ion fragments. Therefore, the energy required to produce these competitive decompositions is comparable, although clearly not identical.[34] In contrast, oleyl alcohol [M + Li]$^+$ ions decompose by CA to form lithiated remote charge site ion fragments without any detectable release of Li$^+$. Thus, the internal energy of the ions decomposing by remote fragmentation is clearly less than the energy required to release Li$^+$.

The enthalpy for the gas-phase release of Na$^+$ from [H$_2$ONa]$^+$ is +1.04 eV.[6a] It follows as a first approximation that at least 1.0 eV of internal energy is required to produce the remote decompositions which lead to sodiated organic ions. The enthalpy for the release of Li$^+$ from [H$_2$OLi]$^+$ is 1.47 eV.[6a] Thus, as a first approximation, it also follows that the remote decompositions are occurring from ions having less than 1.5 eV but more than 1.0 eV of internal energy.

The enthalpies of dehydration leading to this first approximation of 1.0–1.5 eV are underestimates of the required energy. For example, the gas-phase enthalpy for the release of Li$^+$ from [CH$_3$OHLi]$^+$ is approximately 0.2 eV higher than that from [H$_2$OLi]$^+$ because polarization of the methyl group adds stability to the oxygen–alkali ion bond.[6b] Moreover, because the gas-phase proton affinities increase for methanol through *n*-butyl alcohol and level at 3–4 carbons,[33] the presence of the extra 2–3 carbons of the fatty alcohol alkyl chain also should increase the strength of the oxygen–alkali ion bond by approximately 0.1–0.2 eV. Thus, a more appropriate estimate of the internal energy required for the remote decompositions is 1.3–1.9 eV.

Conclusions

Fundamental gas-phase chemistry involved in the novel remote charge site decompositions has been elucidated by studying the CA decompositions of fatty alcohols cationized with alkali metal ions. For such remote decompositions to occur, the charged parent ion and the site of charge must be quite stable. Decompositions occurring remote from the charge dominate for most resonance-stabilized carboxylate anions and the lithiated fatty alcohols where the oxygen–cation bond may be partially covalent.[6a] Weakening the alkali metal–oxygen bond by changing the metal to sodium, potassium, or rubidium leads to increasingly dominant losses of the alkali metal ion. Thus, from the CA decompositions and enthalpies of solvation for Li$^+$ and Na$^+$, internal energies leading to the remote decompositions are estimated to be between 1.3 and 1.9 eV.

Remote decompositions of long-chain fatty alcohols are entirely dependent on the presence of a bound alkali metal ion. Therefore, cationization in conjunction with fast atom bombardment and

---

(34) In this and the following arguments, differences in reverse activation energies for metal ion release vs. remote site fragmentations are not considered.

collisional activation can provide an entirely instrumental method for determining double bond location in long-chain fatty alcohols. The limitation of the approach is sensitivity: 30 μg of lithiated oleyl alcohol can be identified from its CAD spectrum with the most abundant fragment ion at a S/N of 4. (This contrasts with a 10-ng detection limit for analogous cationized oleic acid.[16]) Cis and trans isomers cannot be distinguished, and this is also true for the CAD of fatty acid carboxylates.[2a] Although the location of double bonds in polyunsaturated homoconjugated fatty alcohols is complicated by competitive fragmentation and cationization of the double bond(s), the structurally informative remote decompositions are expected to predominate even with increasing unsaturation.

The combination of FAB to produce lithiated alcohols and MS–MS to give CAD is also expected to be useful for determining other structural features of long-chain fatty alcohols such as branch points and other functional groups. This is under investigation.

Acknowledgment. We are grateful to Kenneth B. Tomer for helpful suggestions. This work was supported by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8211164), and by the National Science Foundation (Grant No. CHE-8320388).

Registry No. Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8; Li^+, 17341-24-1; $H_3C(CH_2)_7(CD_2)_2(CH_2)_6OH$, 104373-47-9; $H_3C(CH_2)_7(CD_2)_2(CH_2)_5CO_2H$, 75736-49-1; (*Z*)-$H_3C(CH_2)_7CH{=}CH(CH_2)_7CD_2OH$, 104373-46-8; (*Z*)-$H_3C(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, 112-80-1; (*E*,*E*)-$H_3C(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_8OH$, 20063-91-6; (*Z*)-$H_3C(CH_2)_7CH{=}CH(CH_2)_8OH$, 143-28-2; (*Z*,*Z*)-$H_3C(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_8OH$, 506-43-4; (*Z*,*Z*,*Z*)-$H_3C(CH_2CH{=}CH)_3(CH_2)_8OH$, 506-44-5.

Isolation and Structural Characterization of the Solvated Lithium Salts of the Main Group 5 Anions $[EPh_2]^-$ (E = N, P, As, or Sb) and $[Sb_3Ph_4]^-$

Ruth A. Bartlett, H. V. Rasika Dias, Håkon Hope, Brendan D. Murray,[1] Marilyn M. Olmstead, and Philip P. Power*[2]

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received May 27, 1986*

Abstract: The X-ray crystal structures of five novel complexes of the general formula $Li(solvate)_nEPh_2$ (E = N, As, or Sb and solvate = Et_2O, THF, 1,4-dioxane, or 12-crown-4) are described and discussed in conjunction with their previously published phosphorus analogues. The five new complexes are $[Li(12\text{-crown-}4)NPh_2]$ (**1**), $[Li(1,4\text{-dioxane})_3AsPh_2]$ (**2**), $[\{Li(Et_2O)_2AsPh_2\}_2]$ (**3**), the ion pairs $[Li(12\text{-crown-}4)_2][SbPh_2]\cdot{}^1/_3THF$ (**4**), and $[Li(12\text{-crown-}4)_2][Sb_3Ph_4]\cdot THF$ (**5**). The structures are indicative of, inter alia, the anomalous characteristics of As relative to P or Sb and the unique planar nature of the nitrogen derivative relative to the heavier pyramidal analogues. The complexes **2–5** are also the first reports of structurally characterized lithium diorganoarsenides and -stibinides. The complexes **4** and **5** are the first examples of a structurally characterized two-coordinate antimony species. Crystal data at 130 K with Mo Kα (λ = 0.71069 Å) for **1**, **3**, **4**, and **5** and Cu Kα (λ = 1.54178 Å) for **2** radiation are as follows: **1**, $C_{20}H_{26}LiNO_4$, M = 351.38, monoclinic, $C2/c$, a = 23.271 (9) Å, b = 13.641 (3) Å, c = 21.375 (7) Å, β = 124.77 (2)°, R = 0.043, 353 parameters, 3264 unique observed data; **2**, $C_{24}H_{34}AsLiO_6$, M = 500.4, monoclinic, $P2_1/c$, a = 15.570 (1) Å, b = 9.354 (1) Å, c = 17.334 (1) Å, β = 102.14 (1)°, R = 0.063, 280 parameters, 3336 unique observed data; **3**, $C_{40}H_{60}As_2Li_2O_4$, M = 768.6, monoclinic, $C2/c$, a = 13.804 (4) Å, b = 15.777 (5) Å, c = 19.967 (4) Å, β = 95.62 (2)°, R = 0.056, 218 parameters, 2202 unique observed data; **4**, $C_{28}H_{42}LiO_8Sb$, M = 659.37, triclinic, $P\bar{1}$, a = 12.660 (6) Å, b = 17.349 (11) Å, c = 23.761 (19) Å, α = 75.79 (6)°, β = 89.27 (5)°, γ = 68.37 (4)°, R = 0.092, 558 parameters, 8419 unique observed data; **5**, $C_{44}H_{60}O_9LiSb_3$, M = 1105.1, monoclinic, $C2/c$, a = 16.240 (4) Å; b = 19.162 (4) Å, c = 16.863 (4) Å, β = 118.38 (2)°, R = 0.056, 158 parameters, 2448 unique observed data.

Lithium diorganoamides[3] and phosphides[4] have been widely used as reagents in organic chemistry and as ligand-transfer agents in inorganic and organometallic chemistry. The corresponding arsenic and antimony complexes have received much less attention probably because of a more restricted interest, decreased stability, and less ready availability of starting materials.[5] Also it has often been thought that the physical and chemical properties of heavier main group elements vary in a consistent manner going down a group. However, there is now a fairly large body of data which shows that there are significant periodic anomalies in the heavier main group elements. The unexpected behavior has been partly rationalized[6] on the basis of an increased effective nuclear charge as a consequence of the filling of the first d (i.e., 3d) sublevel. Thus, elements such as Ge, As, Se, and Br display interesting differences from their other group members which are not expected on the basis of interpolation. The simplest example of this lies

---

[1] Present address: Shell Development, West Hollow Research Center, Houston, TX 77001.

[2] A. P. Sloan Foundation Fellow, 1985–1987.

[3] Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis-Horwood: Chichester, 1980.

[4] Issleib, K.; Wenschuh, E. *Chem. Ber.* **1964**, *97*, 175. Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163. Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. Breen, M. J.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1437. Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670. Hayter, R. G. *Inorg. Chem.* **1962**, *2*, 1031. Madach, T.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1979**, *34*, 1195. Arif, A. M.; Jones, R. A.; Schwab, S. T.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1986**, *108*, 1703. Jones, R. A.; Whittlesey, B. R. *Inorg. Chem.* **1986**, *25*, 852.

[5] Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley: New York, 1970. Aylett, B. J. *Organometallic Compounds*, 4th ed.; Chapman and Hall: London, 1979; vol. 1, Part 2.

[6] For a discussion and references, see: Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 230–232, 847.

0002-7863/86/1508-6921$01.50/0