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Characterization of the Vapor Species of Methyllithium by Flash Vaporization Mass Spectroscopy

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The electron-impact mass spectrum of halide-free methyllithium has been obtained by using flash vaporization mass spectroscopy. Positive ions corresponding to the lithiated species $(CH_3)_{n-1}Li_n^+$, $CH_mLi_3^+$, and $CH_mLi_2^+$ (n = 2–4, m = 0–2) were observed.

Introduction

Methyllithium $[(CH_3Li)_4]$ is the simplest metal–alkyl compound known and has been the subject of numerous theoretical[1,2] and experimental[3,4] investigations concerning the nature of its structure and bonding. However, apart from determination of its X-ray powder structure,[3] nearly all of the aforementioned experimental work has been limited to NMR studies of its aggregation behavior in various solvents.[4] These X-ray and NMR studies have shown that methyllithium forms a tetrametric structure in both the solid[3] and solution[4] phases. Gas-phase studies of methyllithium have not been reported other than data from the mass spectrum of $LiB(CH_3)_4$ which is peripherally related.[5,6] These studies are important in light of the amount of theoretical work on small clusters of methyllithium.[1,2]

Electron-impact (EI) mass spectra have been reported for ethyllithium[7] and *tert*-butyllithium[8] by Brown and co-workers, and both studies show that RLi_2^+ and $R_3Li_4^+$ (R = alkyl) are the most abundant ions (see Table II). An attempt was also made to observe the mass spectrum of a methyllithium-containing vapor from a 1:1 mixture of methyllithium and ethyllithium.[7b] However, only ions from the more volatile ethyllithium could be confirmed. Furthermore, it has been postulated that the high-temperature mass spectrum of $LiB(CH_3)_4$ corresponds to that of methyllithium,[6] and yet, the only ion later reported from that work was $CH_3Li_2^+$ (which was found to be the base peak).[2b]

Recently, we have demonstrated that polylithiated organic compounds undergo rapid disproportionation reactions above 225 °C to tetralithiopropyne $[(C_3Li_4)_n]$ and lithium carbide $[(C_2Li_2)_n]$.[9] Methyllithium also disproportionates above this temperature to dilithiomethane $[(CH_2Li_2)_n]$ and methane. The method of choice for the synthesis of dilithiomethane is this disproportionation (eq 1).[10,11] We also have found that methyllithium and polylithiated compounds yield no polylithium vapor species at temperatures below about 650 °C in a mass spectrometer, which is well above the stability temperature of these materials and may be the reason Brown and co-workers chose to study other organolithium compounds. Fortunately, we discovered that gram amounts of polylithiated compounds could be transported over a 10-cm distance with less than 10% decomposition using a flash-heated, Knudsen cell reactor.[9] With use of a similar flash heating process outlined below, we were able to rapidly vaporize methyllithium in a mass spectrometer and observe its positive ion spectrum.

$$2(CH_3Li)_n(s) \xrightarrow[8\ h]{225\ °C} (CH_2Li_2)_n(s) + CH_4(g) \qquad (1)$$

Experimental Section

Halide-free methyllithium was prepared by transmetalation of dimethylmercury with lithium metal in dry, degassed ether,[12] after which the solution was filtered to remove the mercury and unreacted lithium. Vacuum drying at 120 °C removed nearly all of the ether, producing a fine white powder. The dry powder was dusted onto a conically wound tungsten wire sample probe (which could be heated resistively from room temperature to incandescence [1500–2000 °C] in less than 2 s) and transported from the preparation drybox to the mass spectrometer source chamber using an isolation valve.

Low-resolution spectra were recorded by using a Finnigan Model 4023 automated gas chromatograph/mass spectrometer with a quadrupole analyzer and an INCOS data system. The ionizing energy (for EI mode) was maintained at 70 eV, and the spectrometer was set to scan the full mass range of interest (usually 19–200 amu) in 1 s. High-resolution spectra were recorded on Ilford "Q" photographic plates using a CEC Model 21-110C double-focusing mass spectrometer (resolution 12 000+). The EI ionizing energy also was maintained at 70 eV, with the accelerating voltage held at 8 kV. The plates were analyzed by using a Grant series 800 comparator–microphotometer having a 1-μm resolution. Both photoplate and separate peak-matching[13] experiments were

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Table I. Positive Ions in the Flash-Heated High-Resolution Mass Spectrum of Halide-Free Methyllithium

ion[a]	calcd mass[b]	measd mass	rel error, ppm	rel intensity[c]
$Me_3Li_4^+$	73.134 42	73.134 79	5.1	8
$Me_2Li_3^+$	51.094 95	51.095 12	3.3	4
$CH_2Li_3^+$	35.063 65	35.063 80	4.3	1.5
$CHLi_3^{+\cdot}$	34.055 83	34.055 96	3.8	1
CLi_3^+	33.048 00	33.048 15	4.5	<1
$CH_3Li_2^+$	29.055 48	29.055 59	3.8	100
$CH_2Li_2^{+\cdot}$	28.047 65	28.047 74	3.2	2
$CHLi_2^+$	27.039 83	27.039 96	4.8	3
$CLi_2^{+\cdot}$	26.032 00	26.032 06	2.3	1

[a] Me = methyl. [b] Based on C = 12.000..., H = 1.007 824 6, and Li = 7.016 001 amu. [c] Intensities varied ±2-3% from spectrum to spectrum and were determined by comparison of sample line densities to standard $Ar^{2+}/Ar^{+\cdot}$ spectra whose line densities were known relative to integrated ion current.

used to confirm the existence of the lithiated carbocations in the methyllithium mass spectrum.

Initially, methyllithium samples large enough to produce momentary ion source pressure surges into the 1–2 torr range were flash heated to enable the easy detection of the carbocations on the photoplate. Later, during the peak-matching studies, samples barely visible to the eye were used to eliminate as much as possible the effects of ion–molecule reactions in producing the ions observed. Ion source pressures in these latter experiments rarely exceeded 10^{-4} torr.

Results and Discussion

The low-resolution spectrum for methyllithium suggested the presence not only of the monomer through tetramer ions ($Me_nLi_n^{+\cdot}$, n = 1–4, Me = methyl) but also of ions formed by the loss of combinations of methyl radicals and lithium atoms ($Me_{n-1}Li_n^+$ species, n = 2–4). Most of the ions in the spectrum had low relative intensities (<5%), but a few were strong enough to produce adjacent peaks having approximately the correct ^6Li:^7Li isotope abundance ratio. Because the flash heating process produced a significant background spectrum with both large and small sample sizes, confirmation of the observed ionic species was sought by high-resolution techniques.

The high-resolution spectra did not show the presence of the $Me_nLi_n^{+\cdot}$ ions that appeared to be in the low-resolution spectra. The data suggest that high-temperature reactions between methyllithium and trapped ether, as well as the decomposition of these species themselves, produced fragment ions mistaken for the $Me_nLi_n^{+\cdot}$ cations. In fact, it was determined that nominal masses 43 and 44 amu were due primarily to $C_2H_3O^+$ and $CO_2^{+\cdot}$ and not to the methyllithium dimer $(CH_3Li)_2^{+\cdot}$, as reported earlier.[14] It was fortuitous that those peaks had nearly the correct ^6Li:^7Li isotope ratio in the low-resolution spectra.

However, the high-resolution spectra did reveal a number of lithiated carbocations, several of which are of substantial theoretical interest, and these are listed in Table I. As in the other alkyllithium spectra, all of the $R_{n-1}Li_n^+$ (n = 2–4) species were present, and the RLi_2^+ ion was found to be the base peak (see Table II). Furthermore, the presence of the $Me_3Li_4^+$ ion leads to the important conclusion that methyllithium is tetrameric in the gas phase, as it is in the solid and solution phases.[3,4]

Table II. Comparison of the Positive Ion Mass Spectrum of Methyllithium with Those of Ethyllithium and *tert*-Butyllithium[a]

R		
CH_3[b]	CH_2CH_3[c]	$C(CH_3)_3$[d]
not found	$R_5Li_6^+$ (24)	
not found	$R_4Li_5^+$ (1.3)	
$R_3Li_4^+$ (8)	$R_3Li_4^+$ (47.5)	$R_3Li_4^+$ (43)
$R_2Li_3^+$ (4)	$R_2Li_3^+$ (15)	$R_2Li_3^+$ (4.5)
RLi_2^+ (100)	RLi_2^+ (100)	RLi_2^+ (100)

[a] Relative intensities in parentheses. 70-eV electrons used, except where noted. [b] This work. [c] Reference 7. Intensities are for saturated ethyllithium vapor. 75-eV electrons used. [d] Reference 8. Intensities are for a mixture of 88% *tert*-Butyllithium and 12% *tert*-butoxylithium.

Scheme I. Possible Fragmentation Modes Leading to the Mass Spectrum of Methyllithium (Me = methyl)[18]

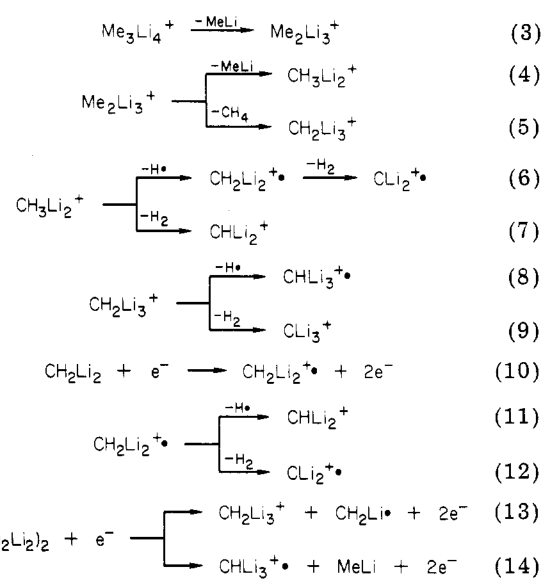
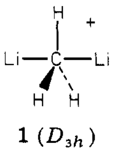
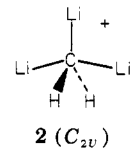


Table I indicates the presence of two important pentacoordinate cations in the mass spectrum: $CH_3Li_2^+$ (1) and $CH_2Li_3^+$ (2). 1 has been postulated to have D_{3h} symmetry



1 (D_{3h})



2 (C_{2v})

and a linear three-center, two-electron Li–C–Li bond,[2b] whereas 2 is expected to have a C_{2v} structure.[15] Since the CLi_5^+ ion had been observed previously in the mass spectrum of tetralithiomethane $[(CLi_4)_n]$,[14] we hoped to be able to complete the series $CH_{5-n}Li_n^+$ (n = 1–5) by finding both the CH_4Li^+ and $CHLi_4^+$ ions. However, separate peak-matching experiments failed to produce any evidence for those species. Since theoretical studies in-

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[13] In the peak-matching studies, the reference ion was positioned in the center of one oscilloscope channel, and the correct $\Delta m/m$ value was selected to position the desired sample ion in the center of the second channel. While sweeping rapidly (<0.5 s/cycle) across the sample ion channel, the appearance of a rising and falling peak in the oscilloscope center with concomitant heating of the sample was considered to be confirmatory evidence for the existence of the cation. This procedure was followed at least twice for each lithiated ion examined.

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dicated that CH_4Li^+ should dissociate readily to CH_4 and Li^+ (and therefore, might only be observed at low temperatures),[15] it may not have been possible to detect it in these high-temperature experiments.[16] On the other hand, there is a good possibility that the $CHLi_4^+$ ion will be present in the high-resolution spectrum of dilithiomethane or trilithiomethane $[(CHLi_3)_n]$, and experiments are in progress to determine if that is the case.

Molecular orbital calculations also have indicated that planar structures of dilithiomethane[1c,17] and trilithiomethane[1c] are just a few kilocalories per mole higher in energy than the tetrahedral-like structures. Removal of a single electron from such molecules may make the planar forms of the $CH_2Li_2^{+\cdot}$ and $CHLi_3^{+\cdot}$ ions (both confirmed here) even more favorable than the tetrahedral-like ones.

In Scheme I, suggested pathways for forming the ions in Table I are listed. As shown, it is feasible to generate all of the ions by fragmentation of the methyllithium tetramer (eq 2–9), even though some of the pathways (notably eq 6 and 8) are less favorable than others. However, one cannot discount the possibility that some of the monocarbon species could have come from ionization of dilithiomethane (eq 10–14), formed by disproportionation of methyllithium (see eq 1) either prior to or during vaporization. Indeed, peaks corresponding to several of these ions have been observed in the flash-heated low-resolution mass spectrum of dilithiomethane.[11] The fact that $CH_4^{+\cdot}$ is an intense peak in the methyllithium spectrum may support this possibility. Also, since we have observed the $(CH_2Li_2)_2^{+\cdot}$ species in the mass spectrum of dilithiomethane, it is possible that some of the carbocations were derived from ionization of gas phase $(CH_2Li_2)_2$ species (eq 13 and 14).

Though the lithiated carbenium ions $CHLi_2^+$ and CLi_3^+ have been previously observed,[11,14,19] their presence here correlates well with the predictions that they would be stable and that they would be formed preferentially according to the dissociation pathways in eq 7 and 9.[2b,15] CH_2Li^+ also is expected to be a stable species,[15] but it is not found in this mass spectrum, possibly because the parent ion from which it might be derived, (CH_4Li^+), is absent.

It is worth noting that there are several cluster ions present in other alkyllithium spectra which are absent in this study. The photoionization spectrum of *tert*-butyllithium was reported to contain the $R_nLi_4^+$ (n = 1–3) and RLi_2^+ ions (R = *tert*-butyl) as the principal lithiated species.[20] Both $R_3Li_4^+$ and RLi_2^+ had been observed earlier by Brown and co-workers; $R_2Li_4^{+\cdot}$ and RLi_4^+ had not.[8] Futhermore, the $R_2Li_3^+$ cluster (which was present in Brown's EI study) notably was missing from the photoionization results. On the basis of this latter work, McClean and co-workers predicted that the $Me_2Li_4^{+\cdot}$ and $MeLi_4^+$ ions also should be present in the mass spectrum of methyllithium.[2c] In fact, they incorrectly claimed that analogous cluster ions had been found by Brown in the mass spectrum of ethyllithium (see ref 7). However, repeated high-resolution attempts to observe these species for methyllithium were unsuccessful in this study. We conclude, therefore, that either (a) the ions in question are *not* present in alkyllithium mass spectra (implying that McClean et al. misassigned their low resolution data) or (b) the presence of $R_2Li_4^{+\cdot}$ and RLi_4^+ and absence of $R_2Li_3^+$ ions is peculiar to spectra obtained by the photoionization process (and possibly by other soft ionization techniques).

Finally, it has been demonstrated that ethyllithium forms both tetrameric and hexameric aggregates in the solution[4,21] and gas (see Table II)[7] phases. Consequently, it was supposed that methyllithium also might form the $Me_4Li_5^+$ and $Me_5Li_6^+$ ions under flash heating because of the small size of the methyl group. Unfortunately, $Me_3Li_4^+$ was the largest lithiated ion observed, and we conclude that no larger cluster will be seen in an EI spectrum of methyllithium.

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Registry No. CH_3Li, 917-54-4.

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[16] It is worth noting that CH_4Li^+ has been detected in time of flight ion–molecule reactions of CH_4 with Li^+. See: (a) Eastes, W.; Ross, U.; Thoennies, J. P. *J. Chem. Phys.* **1979**, *70*, 1652. (b) Ellenbrock, T.; Gierz, U.; Noll, M.; Thoennies, J. P. *J. Phys. Chem.* **1982**, *86*, 1153.

[17] Laidig, W. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1978**, *100*, 5972.

[18] Secondary processes such as ion–molecule reactions [e.g., $CH_2Li_2 + CH_2Li_2^{+\cdot} \rightarrow CHLi_3^{+\cdot} + CH_3Li$] are not depicted in the fragmentation patterns since the carbocations found were produced even when very small samples were flash heated.

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