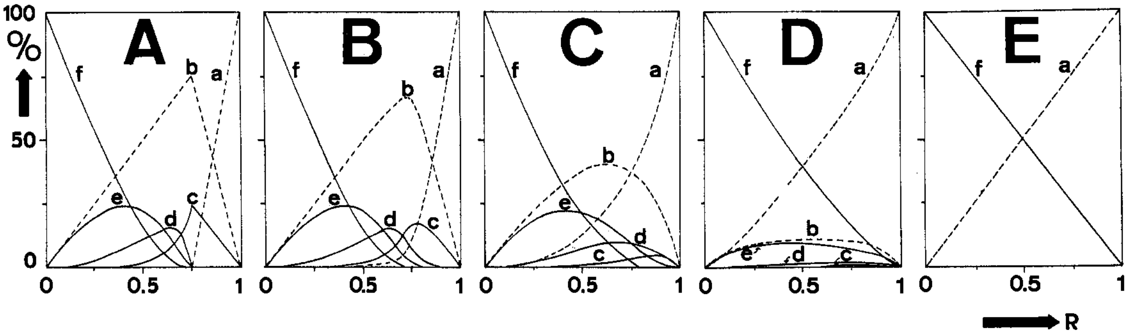

Figure 1.—Theoretical equilibrium curves in systems QT$_3$ *vs.* MZ for $K_1 = K_2 = 0.333$ (ideal randomness) and varying K_I. A: $K_I = 10^{-20}$; B: $K_I = 10^{-5}$; C: $K_I = 1.00$ (ideal randomness); D: $K_I = 10^{+5}$; E: $K_I = 10^{+20}$. a = MZ, b = MT, c = QZ$_3$, d = QZ$_2$T, e = QZT$_2$, f = QT$_3$, with R = Z/(Q + M), and R' = M/(Q + M).

monofunctional substituents for various methylsilicon moieties. Considering the pair chlorine–bromine, it is found that, at equilibrium in each of the three types of systems, the chlorine atoms tend to associate with the silicon moiety containing the lesser amount of methyl groups. On the other hand, in relation to all other substituents used in these studies, chlorine as well as bromine atoms prefer to be with the silicon moiety containing the larger number of methyl groups. A similar trend also has been observed[9] for the equilibria involving exchange of chlorine with hydrogen, thus placing the hydrogen on the silicon atom bearing the least number of organic substituents.

Estimations of the enthalpy of the reaction of eq 1 based on the bond energy approach[2] show that the values of ΔH assuming only σ-bond contributions differ considerably from ΔH values that were calculated from the intersystem constant K_I according to the approximation[10] given by

$$\Delta H \approx \delta\Delta F = -RT \ln [K_I/(K_I)_{\text{rand}}] \qquad (7)$$

These differences are attributable to π-bonding effects which, therefore, appear to be the major driving force for the nonrandom equilibrations of eq 1. Quantum mechanical calculations[11] support the concept of the major influence of π contributions in these reactions.

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The Mass Spectra of Lithiomethyltrimethylsilane and Lithium *t*-Butoxide[1]

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The mass spectra of lithiomethyltrimethylsilane, I, and lithium *t*-butoxide, II, have been observed in the vapor phase, using a time-of-flight mass spectrometer and a direct inlet sample system. The data show that I is essentially entirely in the form of tetramers; II, on the other hand, consists entirely of hexamers. Molecular weight data on II obtained from freezing point lowering measurements on benzene solutions also indicate hexameric association.

It was shown in a study of the mass spectrum of ethyllithium[3] that the association observed in solution[4] is reflected in the vapor composition. Ions produced by electron impact provided evidence for the existence of tetrameric and hexameric species. Since that time a determination of the crystal structure[5] of ethyllithium has also revealed the existence of association in the solid state.

It is our intent to extend the range of mass spectral

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[2] (a) National Science Foundation Summer Fellow, 1965; (b) Alfred P. Sloan Research Fellow.

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data to correlate solution and vapor phase association of volatile organolithium compounds and from fragmentation patterns and appearance potentials to gain an insight into the bonding involved. We report here the mass spectrum of lithiomethyltrimethylsilane (I) and lithium *t*-butoxide (II).

It has been shown that I is tetrameric in hydrocarbon solvents[6,7] and thus must be considered a "normal" alkyllithium compound. The alkoxides have only recently attracted attention as their relationship with the lithium alkyls has been realized.[8-10] There is evidence for substitution of alkoxide for alkyl groups in alkyllithium compounds.[11,12] Talalaeva, *et al.*,[13] report the infrared spectrum of II at 180° in the vapor is similar to the solid-state spectrum and conclude that there is association in the vapor, with Li···O bonds similar to Li···C bonds of the lithium alkyls. In further solution work[14] associations of 6.4 ± 0.7 in cyclohexane (0.01 to 0.07 *N*) and 9.4 ± 0.9 in benzene (0.001 to 0.08 *N*) were reported; it was thus concluded that the structure of II is built of "storied trimers." Bains[15] found sixfold association in cyclohexane, but he reports an association of only four in benzene. There is clearly a need for reexamination of the association of II in benzene.

Experimental Section

All vapor phase measurements were carried out in a Bendix 14-206 time-of-flight mass spectrometer, which was adapted to the retarding potential difference (RPD) technique for measuring appearance potentials.[16] The standard five-grid electron gun system was altered, while in the mass analysis mode, in the following manner.

(1) Grid one (the first after the filament) was about −10.0 v relative to the electron energy. Every 0.10 msec a 15-v pulse was superimposed upon this d.c. level, admitting the electron beam into the ionization region.

(2) Grid two was set at about −0.80 v relative to the electron energy and then varied to −0.90 v for each RPD measurement. The potential on this RPD grid was supplied by mercury batteries and varied with a 10-turn helipot accurate to ±1 mv.

(3) Grids three, four, and five were grounded.

(4) The trap current was left unregulated; negligible changes were noticed for each determination, when monitored.

(5) The electron energy was measured to ±0.005 ev by a differential voltmeter and was steady at all electron energies.

In determining the appearance potential of an ion, changes in ion current (Δ*I*) resulting from the 0.1-v changes in the retarding potential were measured by the output channel using a strip chart recorder, at 0.2-v intervals in electron energy for a 1- to 1.5-v range above the threshold. A least-squares line was drawn and the intercept corrected using the appearance potential of Xe (12.13 v), which was admitted with the compound studied.

The sample system utilized the Bendix sample inlet system, Model 919, for the xenon gas and a separate heated inlet for the sample. The compounds, after purification by sublimation, were loaded, in a glove box with an argon atmosphere, into sample tubes which were evacuated and then sealed. The tubes were attached to the mass spectrometer using a Kovar seal with Hoke valves with Teflon gaskets. The system was evacuated up to the break-seal and heated before opening the sample to the ionization chamber. After breaking the seal, the system was reheated until the pressure in the mass spectrometer attained an equilibrium value of 10^{-7} to 10^{-6} torr, while pumping on the system, and with a steady leak of xenon calibrating gas.

Lithiomethyltrimethylsilane was prepared in the usual manner[17] and sublimed under vacuum at about 100° before use. Purity was checked by nmr.

Lithium *t*-butoxide was obtained from The Lithium Corp. of America, Inc., and sublimed under vacuum at about 140° before use. Purity was checked by nmr.

Xenon was obtained from Matheson Co. and used as received.

The molecular weight determinations, from freezing point lowering data, were carried out as described elsewhere.[4]

Results and Discussion

The RPD method for appearance potentials was tested using a mixture of argon (ionization potential 15.76 ev) and xenon (ionization potential 12.13 ev). Repeated experiments gave an average difference in the appearance potentials of 3.62 ± 0.03, compared to the ionization potential difference of 3.63. The major source of error in the experimental setup used arises in the time lapse between collecting of data for a sample peak and the calibrating gas, during which slight changes in temperature may occur in the sample system. Therefore, the appearance potential of xenon was checked frequently while obtaining data for each sample. Duplicate determinations of three mass peaks of the II sample on different days gave the following results.

Ion	Appearance potential (cor)
$Li_6R_5^+$	9.66, 9.57
$Li_3R_2^+$	17.25, 17.35, 17.44
$Li_6R_6{-}CH_3^+$	8.82, 8.71

An example of the uncorrected data is shown in Figure 1, which also illustrates the poorest set of data used, that for $Li_3R_2^+$ of sample I. Although there is considerably more difficulty in obtaining good data for such low-intensity peaks, we believe that the results presented in Table I are accurate to within ±0.20 ev in all cases.

The main feature of the fragmentation pattern of both compounds is a series of mass peaks corresponding to $Li_nR_{n-1}^+$ species. The formulas of these ions were easily determined from the intensity distribution in adjacent mass peaks, resulting from the Li^6, Si^{30}, and C^{13} abundances.

As in the spectrum of ethyllithium,[3] parent ion species $Li_nR_n^+$ were not present in sufficient concentration for unambiguous identification. A very low-intensity (less than 1% of Li_2R^+ at 75-ev energy) mass peak at 462 was observed in the spectrum of compound

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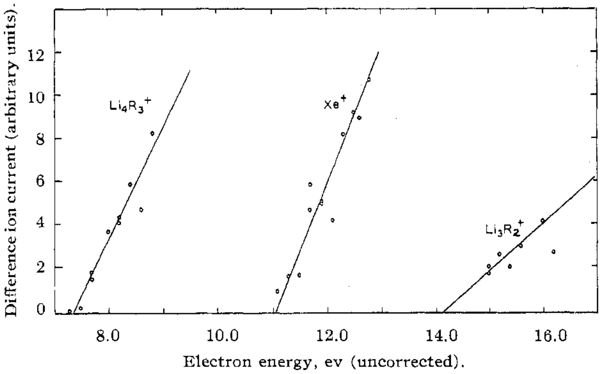


Figure 1.—Sample appearance potential RPD data for $LiCH_2Si(CH_3)_3$.

I. This mass number does not correspond to a recognizable fragment of an associated species of I and remains unexplained. Also initially observed in the spectrum of I was a series of peaks corresponding to $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$,[18] which either formed during the preparation of I and carried through in sublimation or resulted as a decomposition product during sample storage. This impurity distilled off within 1 hr or so after sample opening. In all other respects the data on I indicate a nearly 100% tetrameric composition at 100° in the vapor phase. As noted previously in the case of ethyllithium,[3] the largest mass peak at 75-v electron energy is Li_2R^+; a comparison of the appearance potentials and relative abundances of $Li_3R_2^+$ and Li_2R^+ corroborates the impression obtained from the ethyllithium data that the process

$$Li_nR_n + e^- \longrightarrow L_{n-x}R_{n-x-1}^+ + R + Li_xR_x + 2e^-$$

has a larger cross section, and is energetically more favored, when x is an even integer. Thus, it might be said that the alkyllithium polyhedra of high stability are hexamer and tetramer and that the dimer—considerably higher in energy—is the next most stable species.

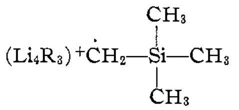
Compound II behaves in a manner similar to I, as can be seen from the data in Table I. From the appearance potential data, however, it is clear that the only parent species present to any significant extent in the vapor is hexamer. The very high appearance potentials observed for all other ions resulting from fragmentation processes are further evidence of a very high stability of the hexameric unit. The general similarity of the mass spectrum of II to those of alkyllithium compounds suggests that the structural hexameric unit is similar to that proposed for the hexameric alkyllithium polyhedron. The structure proposed is analogous to that shown in Figure 2 of ref 4. The lithium atoms are arranged in a distorted octahedral configuration, with alkoxide groups placed upon six of the octahedral faces. The framework consisting of six lithium atoms and six oxygens would possess D_{3d} symmetry. In view of the obvious structural similarities, polyhedral units with mixed alkyl and alkoxide groups on the faces are to be expected and have been observed.[11,12]

TABLE I

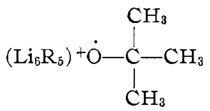
Ion	$LiCH_2Si(CH_3)_3$ at 98°		$LiOC(CH_3)_3$ at 130°	
	I^a	AP, ev^b	I^a	AP, ev^b
$Li_6R_5^+$	...	...	87	9.6
$Li_5R_4^+$	...	...	5	25.7
$Li_4R_3^+$	24	8.4	40	17.4
$Li_3R_2^+$	2	15.2	11	25.8
Li_2R^+	100	11.8	100	25.5
Li^+	38	24.9	0.5	52
$Li_6R_6–CH_3^+$	...	...	4	8.8
$Li_4R_4–CH_3^+$	2	9.7	...	...
$Li_2R_2–CH_3^+$	5	11.9	7	(>20) estd

^{a} Intensities (at 75-ev energy) related to Li_2R^+ = 100. ^{b} AP using RPD method with Xe = 12.13 ev as a reference.

The mass spectra of both I and II show the presence of an ion corresponding to loss of one methyl group from the parent species, rather than the loss of an entire alkyl or alkoxide group. It is of interest that, whereas the appearance potential of this type of ion is higher than that of the $Li_nR_{n-1}^+$ species by 1.3 ev in the case of I, it is *lower* by 0.8 ev in the case of II. Further, at an electron energy in the range of 15 ev, the intensity of this ion is the largest of any in the spectrum of II, with the exception of $Li_6R_5^+$. These results can be interpreted by recognizing that the Li···C or Li···O bonds are quite polar; as a rough approximation we can imagine the polyhedral structures to consist of a core of Li^+ ions surrounded by R^- anions. Electron impact then results in the formation of a "local" radical, in each case of the form

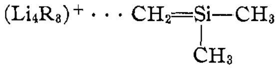

$(\mathrm{Li_4R_3})^+\dot{\mathrm{C}}\mathrm{H_2}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$

I

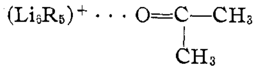

$(\mathrm{Li_6R_5})^+\dot{\mathrm{O}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3}$

II

Dissociation of a methyl group from each of these species leads to the formation of species in which some double bond character is possible


$(\mathrm{Li_4R_3})^+\cdots\mathrm{CH_2}{=}\underset{\mathrm{CH_3}}{\mathrm{Si}}-\mathrm{CH_3}$

I


$(\mathrm{Li_6R_5})^+\cdots\mathrm{O}{=}\underset{\mathrm{CH_3}}{\mathrm{C}}-\mathrm{CH_3}$

II

In view of the obviously greater tendency for carbon–oxygen double-bond formation, it is clear that the methyl group dissociation in II is energetically favored. Other examples of this effect are known.[19]

The mass spectral results of lithium *t*-butoxide clearly demonstrate that the compound is a hexamer in the vapor phase. This is in consonance with the molecular weight data obtained in cyclohexane solutions,[13,14] but there remains some confusion regarding association in benzene. By freezing point measurements, we have determined the molecular weight in benzene solutions of II at various concentrations. The molalities (as monomer) of the solutions and the respective n values found were: 0.0867 (6.06); 0.129 (6.00); 0.178 (6.13).

Acknowledgment.—The assistance of Mr. George Sanzone in obtaining mass spectral data is greatly appreciated.

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