Studies on Chemical Thermodynamics of Hyperlithiated Molecules by Knudsen-Effusion Mass Spectrometry

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Experimental evidence for the existence of polylithiated molecules such as \( \text{C} \text{Li}_n \), \( \text{Li}_3 \text{O} \), \( \text{Li}_4 \text{O} \), \( \text{Li}_5 \text{S} \), \( \text{Li}_6 \text{S} \), and \( \text{Li}_7 \text{P} \) has been obtained by means of Knudsen-effusion mass spectrometry. These polylithiated molecules with nine or more of valence electrons are called hyperlithiated or hypervalent molecules; violating at least formally the octet rule. The dissociation energies, atomization energies and ionization energies of these hyperlithiated molecules were determined. The experimental values agreed fairly well with the theoretical values, and the theoretical prediction that hyperlithiated molecules were thermodynamically more stable than corresponding octet molecules such as \( \text{C} \text{Li}_4 \), \( \text{Li}_2 \text{O} \), \( \text{Li}_5 \text{S} \), and \( \text{Li}_7 \text{P} \) was verified through a series of experimental work.

1. Introduction

For the covalent bond of elements in the second- and third-row of the periodic table, the octet rule\(^{1,2}\) tells that the most stable molecule is formed by sharing with eight electrons in the valence shell. The typical example is seen in the formation of hydride molecules such as \( \text{CH}_4 \), \( \text{NH}_3 \), and \( \text{H}_2 \text{O} \). However, recent studies have revealed that replacement of hydrogen atoms by lithium atoms in these hydride molecules would change the feature of the chemical bond. \( \text{Ab initio} \) MO calculations by Schleyer et al.\(^{3-6}\), as well as experimental work by Kudo and Wu\(^{7-14}\), have shown the existence of stable polylithiated molecules with 9 or more of valence electrons. These molecules would violate, at least formally, the octet rule, and are called hyperlithiated or hypervalent molecules.

In 1978, Kudo, Wu and Ihle found \( \text{Li}_3 \text{O} \) molecules in the gas phase over \( \text{Li}_2 \text{O} \) crystals at elevated temperatures by means of Knudsen-effusion mass spectrometry.\(^{7,8}\) This was the first observation of the hyperlithiated molecule with 9 valence electrons. The observed ionization energy was as low as 4.5 eV and the dissociation energy of \( \text{Li}_3 \text{O} \) to give \( \text{Li}_2 \text{O} \) and \( \text{Li} \) was \( \Delta H^\circ = 212 \pm 42 \text{ kJ mol}^{-1} \). The results indicated that \( \text{Li}_3 \text{O} \) was thermodynamically more stable than \( \text{Li}_2 \text{O} \) of an octet molecule. Although the existence of this molecule was verified by other research groups\(^{5,6}\), it was hard to give a rational explanation to the formation of the stable \( \text{Li}_3 \text{O} \) molecule in a context of the octet rule. One can understand the presence of \( \text{Li}_3 \text{O}^+ \) in analogy with \( \text{H}_3 \text{O}^+ \), but formation of the stable \( \text{H}_3 \text{O} \) molecule is denied theoretically.

Existence of the stable \( \text{Li}_3 \text{O} \) molecule was theoretically confirmed by Schleyer

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Fig. 1. Optimized structures of Li$_3$O, Li$_3$O$^+$ and Li$_4$O deduced from ab initio MO calculations by Schleyer et al.\textsuperscript{3b} bond distances in Å.

Table 1. Dissociation Energy of Hyperlithiated Molecules

<table>
<thead>
<tr>
<th>Number of formal valence electrons</th>
<th>Molecules</th>
<th>$\Delta H_0^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theor.\textsuperscript{3a} 20, 31</td>
</tr>
<tr>
<td>9</td>
<td>CLI$_i$</td>
<td>226.4</td>
</tr>
<tr>
<td></td>
<td>Li$_i$N</td>
<td>231.8</td>
</tr>
<tr>
<td></td>
<td>Li$_i$P</td>
<td>141.8</td>
</tr>
<tr>
<td></td>
<td>Li$_i$O</td>
<td>228.4</td>
</tr>
<tr>
<td></td>
<td>Li$_i$S</td>
<td>150.2</td>
</tr>
<tr>
<td></td>
<td>Li$_i$F</td>
<td>207.1</td>
</tr>
<tr>
<td></td>
<td>CLI$_i$$_i$</td>
<td>59.4</td>
</tr>
<tr>
<td></td>
<td>[→CLI$_i$+Li$_i$]</td>
<td>275</td>
</tr>
<tr>
<td>10</td>
<td>Li$_i$N</td>
<td>71.1</td>
</tr>
<tr>
<td></td>
<td>Li$_i$O</td>
<td>120.9</td>
</tr>
<tr>
<td></td>
<td>Li$_i$S</td>
<td>123.2</td>
</tr>
<tr>
<td></td>
<td>Li$_i$F</td>
<td>41.1</td>
</tr>
<tr>
<td>11</td>
<td>Li$_i$O</td>
<td>65.7</td>
</tr>
<tr>
<td></td>
<td>Li$_i$F</td>
<td>85.4</td>
</tr>
</tbody>
</table>

\textsuperscript{3a} At the 3-21G level of ab initio MO calculations, they have been able to find the minimum for Li$_3$O of structure 1 (in Fig. 1) with $C_{2v}$ symmetry. The closely related $D_{3h}$ structure, 2, is only 2.1 kJ mol$^{-1}$ higher in energy but suggested to be a transition structure on the potential-energy surface. The Li–O bond lengths in 1 (average 1.661 Å) and 2 (1.662 Å) are shorter than in Li$_3$O$^+$ 3 (1.668 Å). For Li$_4$O 4 with a tetrahedral geometry ($T_d$), the Li–O bond length is calculated to be 1.728 Å. The dissociation energy calculated for Li$_3$O 1 to lose one lithium atom is $\Delta H_0^\circ=226.4$ kJ mol$^{-1}$, agreeing fairly well with the experimental value.

To our astonishment, the computational work by Schleyer et al.\textsuperscript{5} has predicted further the formation of a variety of stable polylithiated molecules with nine or more of valence electrons. Table 1 lists the theoretically predicted hyperlithiated molecules:
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Fig. 2. Optimized structures of CLi₅ and CLi₆ deduced from ab initio MO calculations by Schleyer et al.⁴⁶; bond distances in Å.

Fig. 3. A sketch of Knudsen-effusion mass spectrometer installed in a UHV chamber.

CLi₅, Li₄N, Li₃O, and Li₂F with 9 valence electrons, CLi₆, Li₃N, Li₃O, Li₃S, and Li₃F with 10 valence electrons, and Li₃O and Li₄F with 11 valence electrons.

Of these hyperlithiated molecules, CLi₅ and CLi₆ have attracted great interest from theoretical chemists as well as organic and organometallic chemists. Schleyer et al. have predicted that the molecular configurations of CLi₅(D₃h) and CLi₆(O₃) are highly symmetrical as shown in Fig. 2 and that both molecules are thermodynamically more stable than CLi₄ with eight valence electrons.⁴⁷ Namely, the following dissociation reactions

\[
\text{CLi}_5(g) \rightarrow \text{CLi}_4(g) + \text{Li}(g) \\
\text{CLi}_6(g) \rightarrow \text{CLi}_4(g) + \text{Li}_2(g)
\]  

are endothermic with \( \Delta H_0^\circ = 226 \text{ kJ mol}^{-1} \) and \( \Delta H_0^\circ = 273 \text{ kJ mol}^{-1} \).

To understand the nature of “hypervalent bonding” in polylithiated molecules, the present author has extended the experiments with Knudsen effusion mass spectrometry. We have accumulated thermochemical data of the CLi₆, Li₃O, Li₃S, Li₃S, and Li₄P molecules until now.⁹⁻¹⁴ This article describes details of the experimental work and discusses the nature of chemical bond in hyperlithiated molecules, focusing on CLi₆ of current interest.

2. Experimental

Knudsen-effusion mass spectrometry is used in the present experiments to meas-
ure equilibrium partial pressures of gaseous species vaporized from liquid and solid materials at elevated temperatures. Figure 3 shows a sketch of the mass spectrometer (Extrel C-80) consisting of a cross-beam ionizer (#041-2), a quadrupole mass filter (#270-9) and an electron multiplier with a conversion dynode (#051-92), which were installed in an ultrahigh-vacuum (UHV) system. The background pressure of the UHV system was kept below $6 \times 10^{-7}$ Pa at room temperature and $4 \times 10^{-5}$ Pa during the measurements even at elevated temperatures. Crystalline materials were loaded in a molybdenum Knudsen cell in the UHV system and heated by a radiofrequency generator (JEOL: 5 kW, 0.2 MHz). The cell temperature, controlled within $\pm 5$ K at 1,000 K, was measured with a thermocouple (R-type) embedded at the bottom of the cell and an optical pyrometer, which were calibrated in situ at the triple point of Al and Ag. The volume of the Knudsen cell was 1.5 cm$^3$ and the orifice diameter was 0.3 mm. Molecular species effusing from the cell were directly introduced into the ionizer. A shutter was inserted between the cell and the ionizer to discriminate the molecular beam from the residual gas; the beam was analyzed by the mass spectrometer only when the shutter was open.

The effusing gaseous species were ionized by electron impact at the energy around 5 eV higher than the ionization energy of molecules to be observed. Identification of the species was achieved from their mass-to-charge ratio, appearance energy, isotopic abundance and shutterability. The partial pressure $p_i$ of species $i$ was determined in the usual manner,\textsuperscript{17} based on the relation

$$p_i = \kappa I_i T / \sigma_i \beta_i \gamma_i,$$

where $\kappa$ is the proportionality constant, $I_i$ the ion intensity, $\sigma_i$ the relative ionization cross section, $\beta_i$ the isotopic abundance and $\gamma_i$ the multiplier gain of the detector. The proportionality constant $\kappa$ was obtained from comparison of the observed $I_{Li^+}$-to-$I_{Li^+}$ ratio with the equilibrium constant reported for the $Li_2(g) \rightarrow 2Li(g)$ reaction.\textsuperscript{18} The molecular ionization cross section was calculated by taking the sum of Mann's atomic cross sections.\textsuperscript{19} The multiplier's gain of the detector was obtained from a calibration curve.

3. Observation of CLi$_5$, CLi$_4$, and CLi$_6$ Molecules

In the equilibrium vapor over Li$_2$C$_2$ crystals, we have observed such gaseous species as Li(g), Li$_2$(g), Li$_3$(g), CLi$_4$(g), and CLi$_6$(g) at elevated temperatures.\textsuperscript{10,13,14} Of these CLi$_n$ species, CLi$_6$ has been observed for the first time. Previously, Lagow \textit{et al.} synthesized solid (CLi)$_n$ by the reaction of lithium vapor with CCl$_4$, and observed lithiated penta-coordinate carbocations like CLi$_5^+$, CHLi$_4^-$ and CH$_2$Li$_2^+$ by flash-vaporization mass spectrometry.\textsuperscript{20,21} Wu and Ihle observed CLi$_3$ in the lithium vapor permeating through graphite membranes at high temperatures.\textsuperscript{22} Figure 4 shows the mass spectrum of gaseous species in molecular beams effusing from the Knudsen cell containing Li$_2$C$_2$ crystals heated to 1,052 K. The gaseous species were ionized at 13.0 eV. The peak height in the spectrum represents the signal intensity of species observed when the beam shutter between the Knudsen cell and the cross-beam ionizer was open.

The mass peaks at $m/z$ 52, 53 and 54 seen in the mass spectrum indicated the presence of the CLi$_6$ molecule with natural isotopic abundance: $m/z$ 52 for $^{12}$C$^6$Li$_2^7$Li$_4^+$ and $^{13}$C$^6$Li$_2^7$Li$_4^+$, $m/z$ 53 for $^{12}$C$^6$Li$_2^7$Li$_3^+$ and $^{13}$C$^6$Li$_2^7$Li$_3^+$, and $m/z$ 54 for $^{12}$C$^6$Li$_2^7$Li$_2^+$ and $^{13}$C$^6$Li$_2^7$Li$_2^+$.
Fig. 4. Mass spectrum of gaseous species in molecular beams effusing from the Knudsen cell containing Li₃C₆(s) at 1,052 K. The gaseous species were ionized by electron impact at 13.0 eV.

Fig. 5. Ionization efficiency curves of Li⁺, CLi₃⁺, and CLi₄⁺ observed at 1,170 K.

\( ^{\text{13}}\text{C}^{\text{6}}\text{Li}^{\text{7}}\text{Li}_3 \)⁺. The observed pattern coefficient of these signals (0.1, 0.5, and 1.0) agreed with that calculated for a CLi₃ molecule with the natural isotopic abundances of lithium (7.5% \(^6\text{Li}, 92.5% \(^7\text{Li}\)) and carbon (98.9% \(^{12}\text{C}, 1.1% \(^{13}\text{C}\)). In addition, these signals were detected only when the shutter was open, indicating that these species effused from the cell. No distinct signals were observed for another interesting molecule of CLi₅. We suspect at present that the CLi₃ molecule, although thermodynamically stable, is not necessarily stable towards association or reaction with other molecules.
The ionization energies of CLi₃ were determined by the extrapolated voltage difference method from the observed ionization efficiency curves shown in Fig. 5. The ionization energies for the processes
\[
\begin{align*}
\text{CLi}_3 + e^- & \rightarrow \text{CLi}_3^+ + 2e^- , \\
\text{CLi}_4 + e^- & \rightarrow \text{CLi}_3^+ + \text{Li} + 2e^- , \\
\text{CLi}_4 + e^- & \rightarrow \text{CLi}_4^+ + 2e^- 
\end{align*}
\]
were 5.3 ± 0.3, 8.1 ± 0.3, and 8.2 ± 0.3 eV, respectively. The ionization energy of CLi₃ determined here was slightly higher than the experimental value (4.6 ± 0.05 eV) reported by Wu et al. and the theoretical value (4.65 eV) calculated by Schleyer. Quite a large difference is seen in the ionization energy of CLi₄ between the present experiment and the \textit{ab initio} MO calculation (3.86 eV). To discuss the discrepancy, further measurements should be required. The ionization energy of CLi₆ was not determined in a series of experiments, because of insufficient signal intensity, but the CLi₆ signals disappeared when the energy of the impact electrons was lowered below 9 eV or the emission current was turned off. The fact indicates that the ionization energy of CLi₅ is lower than 9 eV and the CLi₆ species must be a neutral molecule. The CLi₆ molecule would be a hypervalent molecule with 10 valence electrons.

4. Determination of Thermochemical Values for CLi₃, CLi₄, and CLi₆

From the signal intensities of the species observed by the Knudsen-effusion mass spectrometry, one can obtain the equilibrium partial pressures of molecules using Eq. (3). Figure 6 illustrates the partial pressures of Li(g), Li₂(g), CLi₃(g), CLi₄(g), and CLi₆(g) as a function of the reciprocal temperature. By adopting the partial pressures of CLi₆(g),
Table 2. Third-Law Enthalpies for the Reaction
\( \text{CLi}_6(\text{g}) \rightarrow \text{CLi}_4(\text{g}) + \text{Li}_2(\text{g}) \)

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>(- R \ln K_p )</th>
<th>(- \Delta(G^\ddagger - H^\ddagger)_{298}/T )</th>
<th>( \Delta H^\ddagger_{298}^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>961</td>
<td>130.6</td>
<td>149.54</td>
<td>269.2</td>
</tr>
<tr>
<td>973</td>
<td>136.4</td>
<td>149.46</td>
<td>278.2</td>
</tr>
<tr>
<td>987</td>
<td>138.2</td>
<td>149.37</td>
<td>283.8</td>
</tr>
<tr>
<td>1,052</td>
<td>112.7</td>
<td>149.10</td>
<td>275.5</td>
</tr>
<tr>
<td>1,075</td>
<td>112.4</td>
<td>148.93</td>
<td>281.0</td>
</tr>
<tr>
<td>1,083</td>
<td>103.5</td>
<td>148.85</td>
<td>273.3</td>
</tr>
<tr>
<td>1,168</td>
<td>95.6</td>
<td>146.97</td>
<td>283.3</td>
</tr>
</tbody>
</table>

Av. 277.7 ± 10.8

\( \Delta H^\ddagger_{298}^\circ = 273.9 ± 10.8 \)

*Second-law values: \( \Delta H^\ddagger_{100} = 237.5 ± 62.0 \) or \( \Delta H^\ddagger_{298} = 240.7 ± 62.0 \) kJ mol\(^{-1}\).

Table 3. Dissociation Energy of CLi\(_n\) Molecules \((n = 3-6)\)

<table>
<thead>
<tr>
<th>Process</th>
<th>( \Delta H^\ddagger_{298}/\text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CLi}_6(\text{g}) \rightarrow 3\text{Li}(\text{g}) + \text{C}(\text{g}) )</td>
<td>( 980 ± 40 )</td>
</tr>
<tr>
<td>( \text{CLi}_4(\text{g}) \rightarrow \text{Li}(\text{g}) + \text{CLi}_2(\text{g}) )</td>
<td>( 191 ± 18 )</td>
</tr>
<tr>
<td>( \rightarrow 4\text{Li}(\text{g}) + \text{C}(\text{g}) )</td>
<td>( 1,140 ± 56 )</td>
</tr>
<tr>
<td>( \text{CLi}_3(\text{g}) \rightarrow \text{Li}(\text{g}) + \text{CLi}_3(\text{g}) )</td>
<td>—</td>
</tr>
<tr>
<td>( \text{CLi}_3(\text{g}) \rightarrow \text{Li}(\text{g}) + \text{CLi}_3(\text{g}) )</td>
<td>—</td>
</tr>
<tr>
<td>( \rightarrow \text{Li}(\text{g}) + \text{CLi}_3(\text{g}) )</td>
<td>( 241 ± 31 )</td>
</tr>
<tr>
<td>( \rightarrow 6\text{Li}(\text{g}) + \text{C}(\text{g}) )</td>
<td>( 1,484 ± 73 )</td>
</tr>
</tbody>
</table>

CLi\(_3(\text{g})\) and Li\(_2(\text{g})\) observed in the range 961–1,168 K, the equilibrium constant \( K_p = \frac{p_{\text{CLi}_3} p_{\text{Li}_2}}{p_{\text{CLi}_6}} \) for the reaction
\( \text{CLi}_6(\text{g}) \rightarrow \text{CLi}_4(\text{g}) + \text{Li}_2(\text{g}) \) \hspace{1cm} (7)

were calculated, and then the third-law value of reaction enthalpy was evaluated to be \( \Delta H^\ddagger_{298} = 274 ± 11 \) kJ mol\(^{-1}\) from the relation \(- \Delta H^\ddagger_{298}/R = R \ln K_p + \Delta[(G^\ddagger - H^\ddagger)_{298}/T]\), as listed in Table 2. Here, the free energy functions, \((G^\ddagger - H^\ddagger)_{298}/T\), for Li\(_2(\text{g})\) and Li\(_2(\text{g})\) were taken from the JANAF tables. The second-law enthalpy of reaction, obtained from the relation \(- \Delta H^\ddagger/RT = d(\ln K_p)/d(1/T)\), was \( \Delta H^\ddagger_{298} = 241 ± 62 \) kJ mol\(^{-1}\). The third-law value agrees well with the theoretical value, \( \Delta H^\ddagger_{298} = 275 \) kJ mol\(^{-1}\), obtained by Schleyer et al. at higher levels of ab initio MO calculations with the 6–31 +G* basis set. The result indicates that the CLi\(_6\) molecule is thermodynamically more stable than CLi\(_4\) of the octet molecule, as predicted by Schleyer et al.

The dissociation energies of CLi\(_3\), CLi\(_4\), and CLi\(_6\) molecules evaluated in the same manner described above are summarized in Table 3, together with the theoretical values reported by Schleyer et al.\(^4\),\(^24\) Agreement of the experimental values with the theoretical values would make proof of the existence of these molecules. The molecular
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Fig. 7. Optimized structures of Cl$_{Li3}$ and Cl$_{Li4}$ deduced from ab initio MO calculations by Schleyer et al., bond distances in Å.

Fig. 8. Average Li–A bond energies (CBE) in Li$_n$A molecules as a function of the number of constituent Li atoms. The closed marks denote hyperlithiated molecules.

Table 4. Experimental Values of Atomization Energy ($D_0$), Contributing Bond Energy (CBE) and Ionization Energy (IP) of Li$_n$A Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$D_0$/kJ mol$^{-1}$</th>
<th>CBE/kJ mol$^{-1}$</th>
<th>IP/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_{Li3}$</td>
<td>918 ± 10</td>
<td>306 ± 10</td>
<td>5.3 ± 0.3</td>
</tr>
<tr>
<td>Cl$_{Li4}$</td>
<td>1,149 ± 24</td>
<td>287 ± 24</td>
<td>8.2 ± 0.3</td>
</tr>
<tr>
<td>Cl$_{Li6}$</td>
<td>1,529 ± 28</td>
<td>255 ± 28</td>
<td>&lt; 9</td>
</tr>
<tr>
<td>LiO</td>
<td>373 ± 14</td>
<td>373 ± 14</td>
<td>9.0 ± 0.2</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>745 ± 10</td>
<td>372 ± 10</td>
<td>6.4 ± 0.2</td>
</tr>
<tr>
<td>Li$_3$O</td>
<td>954 ± 23</td>
<td>318 ± 23</td>
<td>4.5 ± 0.2</td>
</tr>
<tr>
<td>Li$_4$O</td>
<td>1,155 ± 25</td>
<td>289 ± 25</td>
<td>&lt; 7.3</td>
</tr>
<tr>
<td>Li$_5$O</td>
<td>1,246 ± 27</td>
<td>255 ± 27</td>
<td>&lt; 8.5</td>
</tr>
<tr>
<td>Li$_6$P</td>
<td>450 ± 24</td>
<td>225 ± 24</td>
<td>7.9 ± 0.3</td>
</tr>
<tr>
<td>Li$_7$P</td>
<td>648 ± 26</td>
<td>216 ± 26</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>Li$_8$P</td>
<td>873 ± 35</td>
<td>218 ± 35</td>
<td>—</td>
</tr>
<tr>
<td>Li$_9$S</td>
<td>263 ± 10</td>
<td>263 ± 10</td>
<td>8.9 ± 0.3</td>
</tr>
<tr>
<td>Li$_3$S</td>
<td>534 ± 14</td>
<td>267 ± 14</td>
<td>7.9 ± 0.3</td>
</tr>
<tr>
<td>Li$_4$S</td>
<td>669 ± 21</td>
<td>221 ± 21</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>Li$_5$S</td>
<td>899 ± 38</td>
<td>225 ± 38</td>
<td>—</td>
</tr>
</tbody>
</table>

Structures of Cl$_{Li3}$ and Cl$_{Li4}$ deduced from theoretical consideration are shown in Fig. 7. At present, however, we have no experimental evidence for the Cl$_{Li5}$ molecule.

5. Bonding Situation of Hyperlithiated Molecules

Dissociation energies of the hyperlithiated molecules, Li$_n$A(A=C, O, S, P), determined in a series of experiments are summarized in Table 1, together with the theoretical values calculated by Schleyer et al. These values are the energy necessary to break a Li–A bond to give Li$_{n-1}$A and Li. For Cl$_{Li6}$, the dissociation energy to lose Li$_2$ is also

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listed. It is seen that all of the hyperlithiated molecules listed here are stable toward loss of a lithium atom, although the dissociation energy tends to decrease with an increase of the number of constituting lithium atoms.

Another value to be taken into account is the contributing bond energy (CBE), which is equivalent to an average bond energy in molecules. The CBE is derived from the atomization energy. Experimental values of the atomization energy as well as the average Li–A bond energy (CBE) in Li₄A molecules are summarized in Table 4. In Fig. 8, the CBES of Li₄A are plotted as a function of the number of Li atoms in the molecules. The CBE decreases with increasing number of Li atoms, but the average C–Li bond energy in CLi₆ (252±11 kJ mol⁻¹) is higher than the Cl–Cl bond energy (243.5 kJ mol⁻¹)²⁶ in Cl₂ of the covalent molecule. The average bond energies in Li₄P (Li–P, 218 ±35 kJ mol⁻¹) and Li₄S (Li–S, 225±38 kJ mol⁻¹) are still high compared with the F–F (157.7 kJ mol⁻¹), Br–Br (192.9 kJ mol⁻¹), and I–I (150.6 kJ mol⁻¹) bonding in the halogen molecules.²⁶

The C–Li bond distance in CLi₆ is calculated to be 2.245 Å; slightly longer than those in CH₃Li (2.001 Å) and CLi₄ (1.929 Å).⁴ For Li₄O molecules, the computed Li–O bond lengths increase with increasing number of lithium atoms: 1.583 Å in Li₂O, 1.661 Å (average) in Li₃O and 1.728 Å in Li₄O.⁹ From our preliminary calculation, the Li–P bond lengths are estimated to be 2.407 Å in Li₂P (C₂ᵥ), 2.250 Å in Li₃P (C₃ᵥ) and 2.302 Å (average) in Li₄P (C₂ᵥ). The Li–S bond lengths estimated are 2.109 Å in Li₂S (C₂ᵥ), 2.216 Å (average) in Li₃S (C₃ᵥ) and 2.296 Å in Li₄S (C₃ᵥ). As a whole, the bond lengths of hyperlithiated molecules are slightly longer than that of octet molecules.

For the configuration of valence electrons, theoretical considerations by Schleyer et al.⁴ indicate that the occupancy of the 10 valence electrons in CLi₆ is (3a₁g)²(2t₁u)⁶(4a₁g)². The 3a₁g and 2t₁u orbitals are analogous to the valence orbitals in T₄ or O₃ₙ symmetry. These orbitals are used for the C–Li bonding. The highest occupied molecular orbital (HOMO) in CLi₆ is totally symmetric (4a₁g) and possesses an additional
spherical node, although the C–Li contacts are antibonding. The HOMO is mainly comprised of the 2s atomic orbitals (AOs) of lithium, which is more diffuse than the 1s AOs of hydrogen. The Li–Li bonding character of this 4a_{1g} orbital would contribute significant stabilization to the whole system. The feature is illustrated in Fig. 9.

Schleyer et al. have also reported that the calculated charges on carbon do not increase appreciably as more lithium atoms are added; CLi_{3}(C, −0.81), CLi_{5}(C, −0.81), and CLi_{6}(C, −0.93). The same tendency is true for Li_{n}O molecules; the charges on oxygen are −0.81 in Li_{2}O, −0.87 in Li_{5}O, and −0.87 in Li_{6}O. These results lead to a consideration that the “extra” electrons in hyperlithiated molecules are not associated with carbon or oxygen, which remains content with its normal octet, but rather contribute to Li–Li bonding. Namely, the octet of valence electrons in Li_{n}A molecules is involved in Li–A bonding. The extra electrons in the hyperlithiated molecules are not associated with the central atom, but rather contribute to the formation of a metallic lithium “cage”. The overall structures can be described in terms of a negatively charged central atom embedded in a positively charged lithium clusters.

On the other hand, calculations based on the topological theory of molecular structure by Ritchie and Bachrach have indicated that the carbon atom in CLi_{6} is assigned a charge of −4.38, contrasting with a charge of −0.93 determined from Mulliken analysis and −3.44 determined by natural population analysis. No Li–Li bond paths have been observed for the CLi_{6} molecule, and the Li–Li bonding is revealed to play an minor role in determining the structures and energies. From the calculation it is deduced that polarization is the prime cause of the C–Li bond path and the ionic C–Li bonds likely contribute to the electrostatic stabilization of CLi_{6}.

It is also interesting to discuss the bonding situation of CLi_{6} based on the thermochemical data obtained in our experiments. The dissociation energy determined for the process

\[ \text{CLi}_{6}(g) \rightarrow \text{CLi}_{3}(g) + \text{Li}_{3}(g) \]  

is \( \Delta H_{\text{f}}^{\circ} (\text{CLi}_{6} - \text{Li}_{3}) = 395 \pm 13 \text{ kJ mol}^{-1} \). This value is larger than another dissociation energy, \( \Delta H_{\text{f}}^{\circ} (\text{CLi}_{4} - \text{Li}_{2}) = 274 \pm 11 \text{ kJ mol}^{-1} \), obtained for Reaction (7). Here, we can envisage a transition structure of the CLi_{6} molecule that would consist of CLi_{3} and Li_{3}; i.e., bonding of CLi_{3} (C_{2v}) to the surface of triangular plane of a Li_{3} (C_{2v}) cluster as depicted in Fig. 10. For this structure of CLi_{6} with CLi_{3}−Li_{3} bonding, the atomization energy is estimated to be a sum total of the enthalpy for Reaction (8) \[ \Delta H_{\text{f}}^{\circ} (\text{CLi}_{5} - \text{Li}_{3}) = \]
395 ± 13 kJ mol⁻¹] and the atomization energies of both CLi₃ (Δ₀° = 918 ± 10 kJ mol⁻¹) and Li₃ (Δ₀° = 173.6 ± 16.7 kJ mol⁻¹). However, the sum total of 1487 ± 23 kJ mol⁻¹ is smaller by 42 kJ mol⁻¹ than the atomization energy of CLi₆ (Δ₀° = 1529 ± 28 kJ mol⁻¹) determined for the process

\[ \text{CLi}_6(g) \rightarrow \text{C}(g) + 6\text{Li}(g). \]  

(9)

The fact implies that the potential well of CLi₆(O₆) is slightly deeper than that of CLi₆ with CLi₃-Li₃ bonding. Namely, the CLi₆ molecule has a simple octahedral (O₆) geometry in the equilibrium state, as predicted by \textit{ab initio} MO calculations.

There is increasing evidence for hyperlithiated or hypervalent molecules, but much more experimental work as well as theoretical considerations is needed to understand the whole nature of hypervalent bonding. With respect to ionization energies of hyperlithiated molecules, for example, there are large discrepancies between experimental and theoretical values.\(^{30,31}\) Experimental verification of vibration frequencies of the theoretically predicted molecules is also required to elucidate the definite molecular structures of hypervalent molecules.

We are extending the experimental studies to elucidate the thermochemical properties not only of hyperlithiated molecules but also of other interesting molecules like hypersodium, hyperpotassium, hyperberyllium, hypermagnesium and hyperaluminum molecules.\(^ {32-34}\) in collaboration with theoretical chemists.

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