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Observation of CLi_3 and CLi_4 in the Vapor over $Li_2C_2(s)$

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With Knudsen-effusion mass spectrometry, gaseous CLi_3 and CLi_4 species were observed for the first time in the vapor equilibrated with $Li_2C_2(s)$ above 900 K. The ionization potentials and atomization energies of these species as well as the heat of formation of $Li_2C_2(s)$ were determined.

Elements in the first row of the periodic table are normally surrounded with eight electrons. Carbon, for example, bonds to four hydrogen atoms to form a CH_4 molecule. What does happen when lithium atoms are replaced for the hydrogen atoms? One can expect that the CLi_4 molecule would be formed by the replacement, and molecular properties of CLi_4 are widely discussed in the theoretical study.$^{1)}$ However, experimental evidence of this molecule is very limited, although Wu and Ihle observed CLi_3 and CLi_4 in the gas phase by allowing lithium atoms to diffuse through graphite membranes at high temperatures.$^{2)}$

Recently, Schleyer et al. have reported from their ab initio calculation that CLi_5 and CLi_6 molecules are highly stable toward possible dissociation reactions to form CLi_4.$^{3)}$ The calculation shows that the formal charges on the carbon atoms in the CLi_5 and CLi_6 molecules are not much larger than that in CLi_4 and the carbon atoms remain content with its normal octet. The extra electron or electrons would contribute to Li-Li bonding and help to build a metal "cage" around the central carbon atom. These molecules are called as a "hyperlithiated" molecule or hypervalent species.

In order to understand further the nature of hypervalent species, it is of importance to observe the theoretically predicted molecules. This paper reports thermochemical properties of the CLi_3 and CLi_4 species observed in experiments for finding out the hyperlithiated species in the C-Li system.

Crystalline Li_2C_2 powders with the nominal purity of 96-98% were purchased from Cerac/Pure Inc. The material was loaded in a molybdenum Knudsen cell in an argon atmosphere and then placed in an ultra-high-vacuum apparatus ($<7 \times 10^{-6}$ Pa) equipped with a cross beam ionizer and an Extrel C-80 quadrupole mass filter system (Fig. 1). The volume of the Knudsen cell was 1.5 cm^3 and the orifice diameter was 0.6 mm. The cell was heated by an rf generator (5 kW, 0.2 MHz). The cell temperature, controlled within ± 1 K, was measured with a thermocouple (R type) and an optical pyrometer, calibrated in situ at the triple point of Al and Ag.

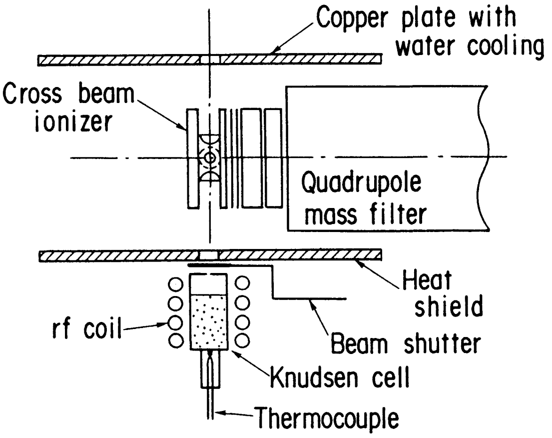

Fig. 1. A sketch of the apparatus.

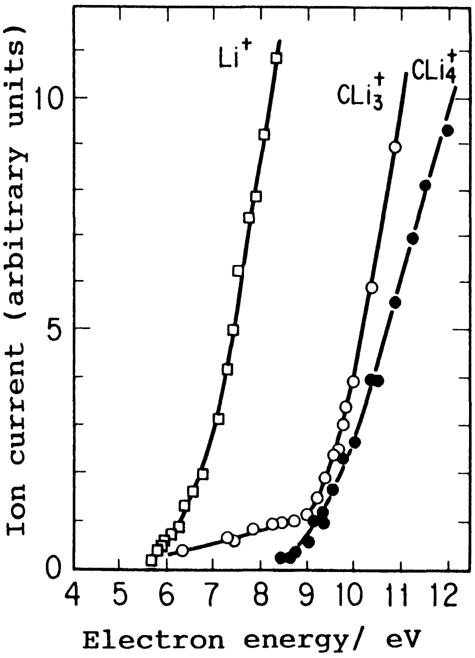

Fig. 2. Ionization efficiency curves of Li^+, CLi_3^+, and CLi_4^+ observed at 1170 K.

A shutter was installed between the Knudsen cell and the ionizer to discriminate the molecular beam from the residual gas. Identification of the ions was achieved from their mass to charge ratio, appearance potential, isotopic abundance, and shutterability. The partial pressure p_i of species i was determined in the usual manner[4)] based on the relation $p_i = k[I_iT/(\sigma_i \beta_i \gamma_i)]$, where k is the pressure calibration constant, I_i the ion intensity, σ_i the relative ionization cross section, β_i the isotope abundance and γ_i the multiplier gain. The pressure calibration constant k was obtained by measuring I_{Li}^+ and $I_{Li_2}^+$ for the vaporization of Li(s,l) at various temperatures.

The molecular species were ionized by electron impact at an energy 3.5-4.0 eV higher than the ionization potential of each species.[5)] The ionization potentials of CLi_3 and CLi_4 were determined in the present work with the extrapolated voltage difference method[6)] from the observed ionization efficiency curves shown in Fig. 2. The ionization potentials for the processes

$$CLi_3 + e^- \rightarrow CLi_3^+ + 2e^-, \qquad (1)$$

$$CLi_4 + e^- \rightarrow CLi_3^+ + Li + 2e^-, \qquad (2)$$

and

$$CLi_4 + e^- \rightarrow CLi_4^+ + 2e^- \qquad (3)$$

were 5.3± 0.3, 8.1± 0.3, and 8.2 ± 0.3 eV, respectively. The ionization potential of CLi_4 was determined for the first time. The ionization potential of CLi_3 was slightly higher than the value of 4.6 ± 0.05 that was reported by Wu et al.[2)]

The observed equilibrium vapor pressures of Li, Li_2, CLi_3, and CLi_4 over Li_2C_2(s) are plotted as a function of the reciprocal of temperature in Fig. 3. The equilibrium pressure of Li vapor at temperatures from 700 to 1000 K was expressed

Table 1. Standard heat of formation of $Li_2C_2(s)$

$-\Delta H_f{}^\circ{}_{298}$ kJ mol^{-1}	Method	Ref.
67.7 ± 4.3	Vaporization	This work
50.5 ± 4.1	Vaporization	7
65.3 ± 7.5	Vaporization	8
59.4 ± 8.4	Calorimetry	9
58.2	Calorimetry	10

by the equation

$$\log(p_{Li}/Pa) = -(9.46 \pm 0.05)\times10^3/T + (10.50 \pm 0.08). \qquad (4)$$

From the temperature dependence of p_{Li}, $d(\ln p_{Li}^2)/d(1/T) = -\Delta H^\circ/R$, the 2nd-law enthalpy of $\Delta H^\circ{}_{298} = 398.7 \pm 10.6$ kJ/mol was obtained for the reaction

$$Li_2C_2(s) \rightarrow 2C(s) + 2Li(g). \qquad (5)$$

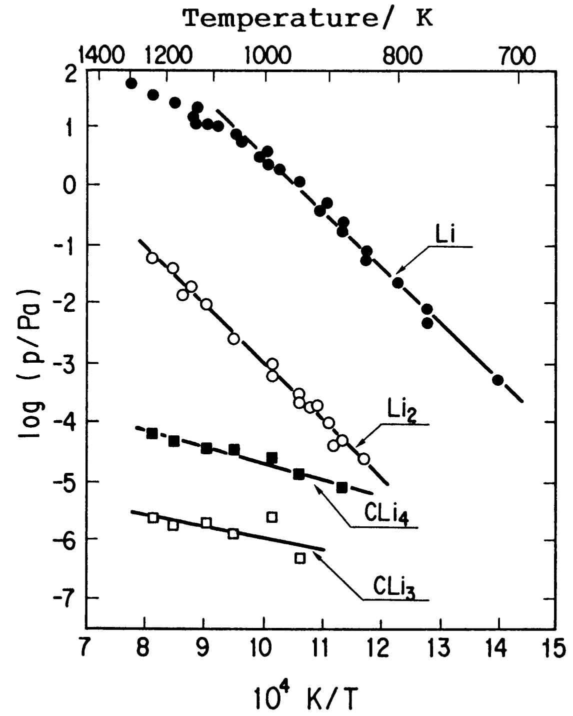

Fig. 3. Equilibrium vapor pressures of Li, Li_2, CLi_3, and CLi_4, over $Li_2C_2(s)$.

The 3rd-law enthalpy obtained from the relation $-\Delta H^\circ_{298}/T = R\ln K + \Delta[(G^\circ_T - H^\circ_{298})/T]$ was $\Delta H^\circ{}_{298} = 389.1 \pm 4.1$ kJ/mol and agreed well with the 2nd-law value within the experimental error. Hence, the standard heat of formation of $Li_2C_2(s)$ was evaluated to be $\Delta H_f{}^\circ{}_{298} = -67.7 \pm 4.3$ kJ/mol, as listed in Table 1 in comparison with the literature values.[7-10]

The equilibrium pressures of $CLi_3(g)$ and $CLi_4(g)$ over $Li_2C_2(s)$ observed in the temperature range between 950 and 1240 K were expressed in the equations

$$\log(p_{CLi_3}/Pa) = -(1.73 \pm 1.03)\times10^3/T - (4.20 \pm 0.96) \qquad (6)$$

and

$$\log(p_{CLi_4}/Pa) = -(2.58 \pm 0.24)\times10^3/T - (2.12 \pm 0.23). \qquad (7)$$

Combining these vapor pressures with p_{Li}, one can calculate the equilibrium constants $K_8 = p_{Li}^3/p_{CLi_3}$, $K_9 = p_{Li}^4/p_{CLi_4}$ and $K_{10} = p_{Li}\cdot p_{CLi_3}/p_{CLi_4}$ for the reactions

$$CLi_3(g) \rightarrow C(s) + 3Li(g), \qquad (8)$$

$$CLi_4(g) \rightarrow C(s) + 4Li(g) \qquad (9)$$

and

$$CLi_4(g) \rightarrow CLi_3(g) + Li(g). \qquad (10)$$

From the slope of plots of the equilibrium constants against the reciprocal of temperature, the enthalpies of reaction ($\Delta H^\circ{}_{1065}$) for these processes were calculated to be 334.3± 23.4, 478.9± 30.9, and 153.5± 14.2 kJ/mol, respectively. The enthalpy of reaction (10) corresponds to the energy required for loss of a lithium atom from CLi_4 or the bond dissociation energy (BDE) of gaseous CLi_4.

Table 2. Thermochemical values obtained for CLi_3 and CLi_4 at 1065 K

Molecule	Species lost	Atomization energy kJ mol^{-1}	Contributing bond energy (CBE) kJ mol^{-1}	Bond dissociation energy (BDE) kJ mol^{-1}
CLi_3	3Li	1060 ± 23	355 ± 23	
CLi_4	4Li	1219 ± 31	305 ± 31	
CLi_4	Li			153 ± 29

The atomization energies of gaseous CLi_3 and CLi_4 molecules were obtained by calculating the enthalpies of reaction for the processes

$$CLi_3(g) \rightarrow C(g) + 3Li(g) \tag{11}$$

and

$$CLi_4(g) \rightarrow C(g) + 4Li(g), \tag{12}$$

using $\Delta H^\circ_{298} = 715.0 \pm 1.9$ kJ/mol[9)] for the sublimation reaction $C(s) \rightarrow C(g)$. The atomization energies of CLi_3 and CLi_4 molecules at 1065 K are listed in Table 2. The BDE of CLi_4 was smaller than the contributing bond energy (CBE), which is equivalent to the average energy for the C-Li bond in CLi_4. This implies that the actual energy for dissociating either bond separately is not the same as the average bond energy of CLi_4. A discrepancy is seen in the CBE's between CLi_3 and CLi_4, but subtraction of the BDE of CLi_4 from the atomization energy of CLi_4 gives the same CBE as that of CLi_3 (355 kJ/mol).

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