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Formation and Stability of the Gaseous Species $LiAlCl_4$, Li_2AlCl_5 and $LiAl_2Cl_7$ – Mass Spectrometric and Quantum Chemical Studies

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The formation of the gaseous species LiCl, Li_2Cl_2, $AlCl_3$ and $LiAlCl_4$ was shown by mass spectrometric studies of the reaction of solid LiCl with gaseous $AlCl_3$ at 575 °C. Besides $AlCl_3$ and Al_2Cl_6, the gas complexes $LiAlCl_4$, Li_2AlCl_5 and $LiAl_2Cl_7$ were formed during the evaporation of liquefied $LiAlCl_4$. The structures of the molecules under discussion were computed by quantum chemical DFT studies. Thermodynamic data of these molecules were determined by experimental methods (mass spectrometry), and the results were confirmed by theoretical calculations.

Introduction

The existence of gaseous molecules, gas complexes, of the type $M^{I}M'^{III}X_4$ (X = halogen) has long been known. Other compositions of such complexes as $M^{I}_2M'^{III}X_5$, $M^{I}_3M'^{III}X_6$ and $M^{I}M'^{III}_2X_7$ are known in particular cases. Examples are Cu_2InCl_5, Cu_3InCl_6 and $CuIn_2Cl_7$. Gaseous halogen complexes are overviewed in ref.[1] They are formed through the heating of the appropriate metal halide mixtures or melts. Gas complexes containing alkali metal halides feature particularly high thermodynamic stabilities.[1]

However, thermodynamic data have been determined only for a few examples of those molecules. Compounds of this type, especially iodides, have recently become highly interesting for technical applications. Their formation is essential for the functionality of metal halide lamps, which contain lanthanide compounds like DyI_3, HoI_3 or TmI_3 besides alkali metal- or thallium iodides.[2] The predominantly empirical approach to the development of lamp fillings is being replaced to an increasing degree by a science-based approach that is based upon mathematical modelling of the course of reactions in such lamps.[3] Therefore, information on the reactions taking place in a lamp and the knowledge of thermodynamic data of each involved compound is required. Because the gas-phase composition over the solid phase is normally complex, classical methods for its determination fail. The experimental method of choice to solve this problem and hence to derive thermodynamic data of the gaseous species is the combination of Knudsen cell effusion technique with mass spectrometry.[4]

Such measurements can be performed and exploited in two different ways: Firstly, the intensities I_i of the detected ions are gauged in dependency of the temperature T. From the slope and the axis intercept of the log $I_i\,T/T^{-1}$ plot enthalpy and entropy values are obtained (second law analysis). Alternatively, the equilibrium constant of an investigated reaction is determined at *one* temperature and the reaction enthalpy is determined out of it upon implementation of the entropy (third law analysis). When reaction entropy is known, this method has the advantage of being less time consuming than the second law analysis with comparable accuracy.

Nowadays, quantum chemical methods allow the theoretical calculation of thermodynamic data.[5] Specifically, the standard entropy and the molar heat capacity can be computed reliably due to the comparability of experimentally and theoretically deduced vibrational spectra.

The aim of this work is the application of the above-mentioned method to the $LiCl/AlCl_3$ system; hence, a combined experimental and theoretical method was employed to derive reaction enthalpies by third law analysis, and subsequently, values for the heat of formation of the involved gaseous molecules were determined. To verify the accuracy of the applied method, the experimentally obtained enthalpies of formation were compared to those obtained by theoretical methods.

Results and Discussion

Mass spectrometric studies on the $LiCl/AlCl_3$ system show the formation of the gaseous molecules $LiAlCl_4$, Li_2AlCl_5 and $LiAl_2Cl_7$. These compounds were characterized by quantum chemical methods. The calculations provide structural information and thermodynamic data. The calculated standard entropies and heat capacities were used to

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Table 1. Computed energy difference between $LiAlCl_4$ (C_{2v}) and $LiAlCl_4$ (C_{3v}) at different theoretical levels.

Method	E ($LiAlCl_4$ C_{2v}) /Hartree	E ($LiAlCl_4$ C_{3v}) /Hartree	ΔE (C_{2v} – C_{3v}) [kJ mol^{-1}]
DFT/def-TZVPP	–2091.3897	–2091.3885	–3.1
MP2/def2-TZVPP	–2088.6726	–2088.6711	–3.9
HF/SCF 3-21G*[11]	–2078.0515	–2078.0488	–7.1
HF/SCF 6-31 G*[11]	–2087.6544	–2087.6501	–11.3

exploit the mass spectra by means of the third law method. The overall goal was to derive enthalpies of formation of the mentioned molecules from reaction enthalpies and to compare the values to the computed enthalpies.

Quantum Chemical Calculations

Ramondo et al. investigated[11] the energy difference between the bidentate isomer of $LiAlCl_4$ with C_{2v} symmetry and the tridentate isomer with C_{3v} symmetry (Figure 1) by Hartree–Fock self-consistent field calculations. By using basis sets of 3-21G* and 6-31G* quality, they reported an energy difference of 7 and 11 kJ mol^{-1}, respectively. In every case, the structure of the lowest energy corresponds to the molecule with C_{2v} symmetry (Table 1).

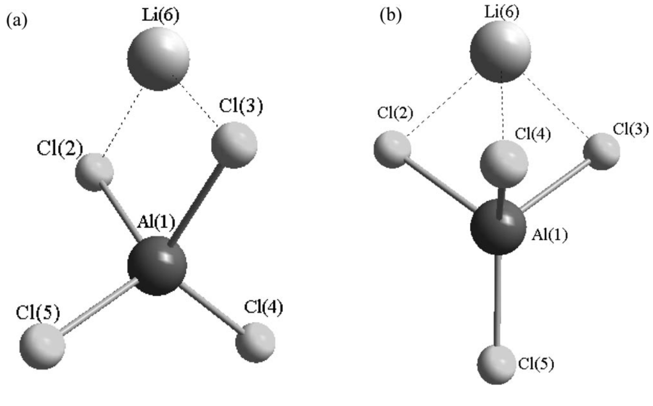

Figure 1. Two isomers of $LiAlCl_4$: (a) bidentate isomer (symmetry C_{2v}), $E_{rel.}$ = 0 kJ mol^{-1}; (b) tridentate isomer (symmetry C_{3v}), E_{rel} = 3.1 kJ mol^{-1}.

Improvement of these calculations is possible when taking into account the electron correlation. Determination of the structures and energies of the isomers by DFT calculations confirmed the former result: the energy difference was calculated to be 3.1 kJ mol^{-1}. The accuracy of the DFT method applied for this molecule was tested by the MP2 method by using basis sets of def2-TZVPP quality, which yielded an energy difference of 3.8 kJ mol^{-1}. Results are summarized in Table 1. Due to the strong ionic nature of the bonds connected to the Li^+ ion, the difference between these values is rather small (relative to the difference gained with the HF/SCF calculations in ref.[11]). Therefore, we decided to use the less computationally time consuming RI-DFT/BP86 method by applying def-TZVPP basis sets.

Three reasonable possible structures of Li_2AlCl_5 are shown in Figure 2. The Li_2AlCl_5 isomer with C_s symmetry (Figure 2a) with a fourfold coordinated Al centre resembles the ion pair $[Li_2Cl]^+[AlCl_4]^-$. It is energetically favoured with respect to the isomer with Al of coordination number 5 (Figure 2b, C_s symmetry) by 88 kJ mol^{-1}. The also fourfold-coordinated Al containing isomer with C_{2v} symmetry (Figure 2c) has energy of 117 kJ mol^{-1} (relative to that of the molecule shown in Figure 2a). In the case of $LiAl_2Cl_7$, the isomer shown in Figure 3a (C_s symmetry) is clearly the

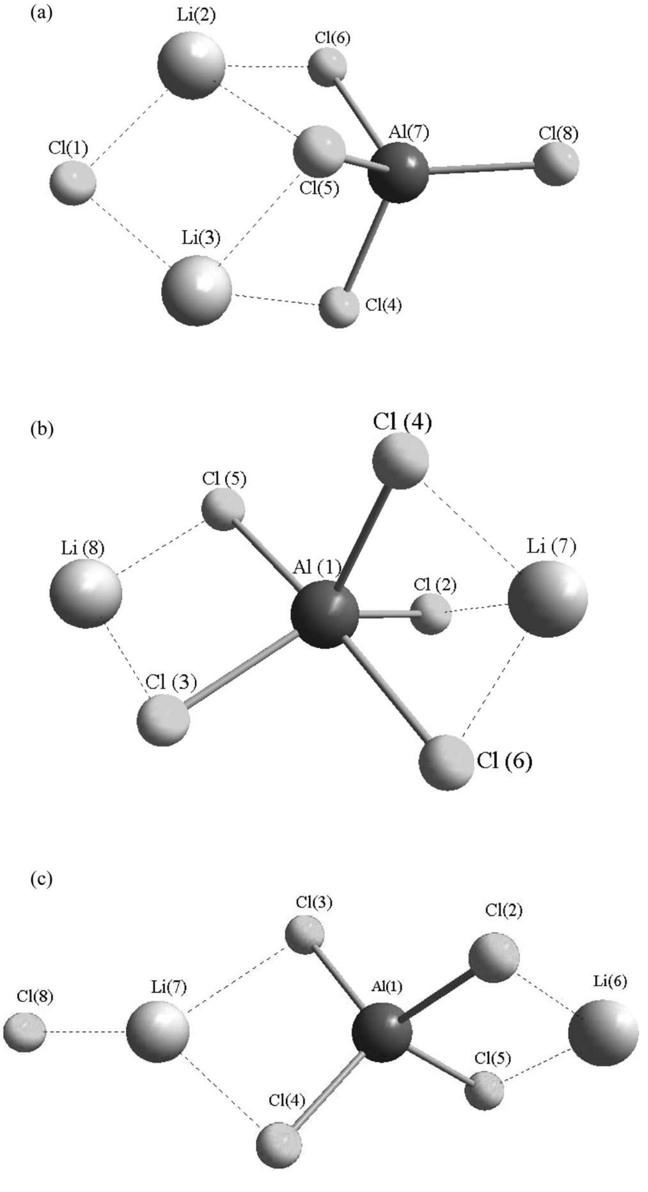

Figure 2. Three isomers of Li_2AlCl_5: (a) symmetry C_s, $E_{rel.}$ = 0 kJ mol^{-1}; (b) symmetry C_s, $E_{rel.}$ = 88 kJ mol^{-1}; (c) symmetry C_{2v}, $E_{rel.}$ = 117 kJ mol^{-1}.

energetically most stable one by 123.6 kJ mol^{-1}. The geometrical data of each energy minimum structure is summarized in Table 2.

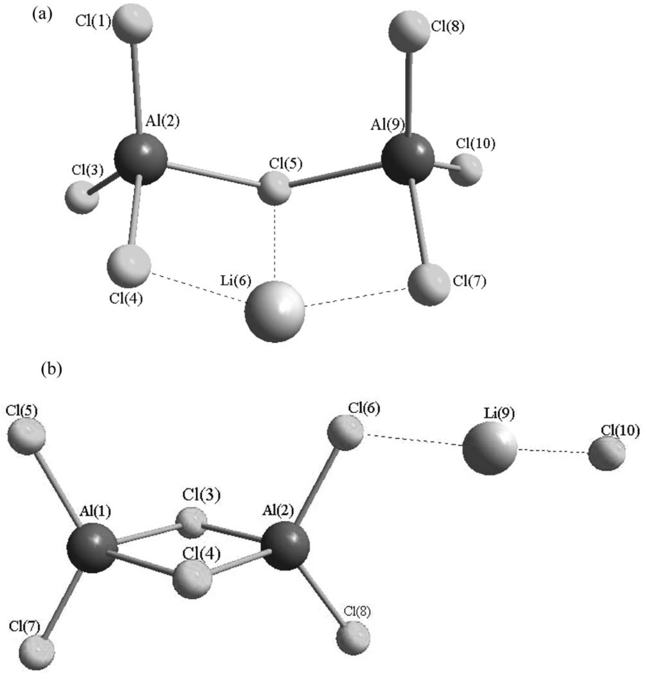

Figure 3. Two isomers of $LiAl_2Cl_7$: (a) symmetry C_1*, $E_{rel.}$ = 0 kJ mol^{-1} (*slightly distorted C_s symmetry); (b) symmetry C_s, $E_{rel.}$ = 123.6 kJ mol^{-1}.

Thermodynamic data (entropy, enthalpy and heat capacity each at 298 K as well as at the reaction temperature) were obtained by employing the FREEH module of the TURBOMOLE program package. With experience from other studies[15] the RI-DFT/BP86 method with the use of extensive basis sets leads to reliable structural, energetic and vibrational data. However, to estimate the accuracy of our method with regard to the type of reactions we explore by mass spectrometry, we determined theoretically the reaction enthalpy of the equilibrium in Equation (1) by both the RI-DFT/BP86/def-TZVPP and the MP2/def2-TZVPP methods. Considering the expected allowance for the calculation of the reaction enthalpies (±20 kJ mol^{-1}), the RI-DFT results are in excellent agreement with the experimental value (Table 3).

Table 2. Structural data for the most stable isomers of $LiAlCl_4$, Li_2AlCl_5 and $LiAlCl_7$.

Compound	Symmetry	*r*	[pm]	Angle	[°]
$LiAlCl_4$	C_{2V}	Al_1–$Cl_{4,5}$	212	Cl_2–Li_6–Cl_3	99
		Al_1–$Cl_{2,3}$	226	Cl_2–Al_1–Cl_3	97
		Li_6–$Cl_{2,3}$	223	Cl_2–Al_1–Cl_5	109.9
Li_2AlCl_5	C_s	Cl_1–$Li_{2,3}$	219.7	Li_2–Cl_1–Li_3	84
		Li_2–Cl_5	259	Li_2–Cl_5–Li_3	69
		Li_3–Cl_5	259.5	$Li_{2,3}$–Cl_5–Al_7	81
		Cl_5–Al_7	222.5	Cl_5–Al_7–$Cl_{4,6}$	100
		Al_7–$Cl_{4,6}$	219.9	Cl_5–Al_7–Cl_8	115
$LiAlCl_7$	C_1	Cl_1–Al_2	210.0	Cl_1–Al_2–Cl_3	121
		Cl_3–Al_2	211.2	Cl_1–Al_2–Cl_4	113
		Cl_4–Al_2	221.2	Cl_4–Al_2–Cl_5	97
		Cl_5–Al_2	238	Al_2–Cl_5–Al_9	124
		Li_6–$Cl_{4,7}$	227	Cl_4–Li_6–Cl_7	134
		Cl_5–Li_6	254.9		

To compute the standard heat of formation of $LiAlCl_4$, Li_2AlCl_5, and $LiAl_2Cl_7$, the reaction enthalpies and entropies for the equilibrium reactions depicted in Equations (1)–(3) were computed.

$$LiCl(g) + AlCl_3(g) \rightleftharpoons LiAlCl_4(g) \qquad (1)$$
$$\Delta_R H^0 = -175.6 \text{ kJ mol}^{-1}$$

$$Li_2Cl_2(g) + \tfrac{1}{2}\, Al_2Cl_6(g) \rightleftharpoons Li_2AlCl_5(g) \qquad (2)$$
$$\Delta_R H^0 = -92.8 \text{ kJ mol}^{-1}$$

$$LiAl_2Cl_7(g) + LiAlCl_4(g) \rightleftharpoons Li_2AlCl_5(g) + Al_2Cl_6(g) \qquad (3)$$
$$\Delta_R H^0 = -16.8 \text{ kJ mol}^{-1}$$

Equation (1) corresponds to the proposed reaction in the Knudsen cell (see above) and was used to derive the standard heat of formation for $LiAlCl_4$ upon analysis of the mass spectra. Contrary to the mass spectrometric studies (see above) we chose Equation (2) [instead of $2LiAlCl_4(g) \rightleftharpoons Li_2AlCl_5(g) + AlCl_3(g)$] to derive the heat of formation for Li_2AlCl_5, because it only consist of molecules with known heat of formation and thus does not entail the error of $LiAlCl_4$. We chose Al_2Cl_6 as a reactant instead of $AlCl_3$, because it features a halogen bridge. Equation (3) corresponds to the experiment (see above) and was used for the

Table 3. Comparison of computed reaction enthalpy and entropy at different levels of theory for the reaction $LiCl(g) + AlCl_3(g) \rightleftharpoons LiAlCl_4(g)$ at room temperature and at 848 K (experimental conditions).

	MP2/def2-TZVPP		DFT/def-TZVPP		Experimental
	T = 298.15 K	*T* = 848 K	*T* = 298.15 K	*T* = 848 K	*T* = 848 K
$\Delta_R H^0$ [kJ mol^{-1}]	–202.0	–195.2	–175.6	–168.7	–172.1[a]
$\Delta_R S^0$ [J K mol]	–137.7	–125.0	–134.8	–122.0	–
$\Delta_R G^0$ [kJ mol^{-1}]	–161.0	–89	–135.4	–65.5	–68.6[b]
K [bar^{-1}]	1.7×10^{28}	3.1×10^5	5.3×10^{23}	1.0×10^4	1.7×10^4[b]

[a] $\Delta_R H^0$(exp.) derived from third law analysis. [b] $\Delta_R G^0$(exp.) and *K*(exp.) derived from $\Delta_R H^0$(exp.) and $\Delta_R S^0$ (calculated by DFT/def-TZVPP method).

Table 4. Thermodynamic data of the involved molecules: standard heat of formation, standard entropy and the coefficients *a, b, c, d* of the molar heat capacity $C_p^0 = a + b \times 10^{-3}T + c10^6T^{-2} + d10^{-6}T^2$.

Compound	$\Delta_fH^0_{298}$ [kJ mol^{-1}] exp./calcd.	S^0_{298} [J K^{-1} mol^{-1}] exp./calcd.	a [J K^{-1} mol^{-1}] exp./calcd.	b [J K^{-2} mol^{-1}] exp./calcd.	c [J K mol^{-1}] exp./calcd.	d [J K^{-3} mol^{-1}] exp./calcd.
LiCl(s)	–408.6[14]/–	118.0[14]/–	42.15[14]/–	22.76[14]/–	–0.08[14]/–	0[14]/–
LiCl(g)	–195.7[14]/–	212.9[14]/212.9	36.56[14]/36.59	1.07[14]/0.77	–0.32[14]/–0.33	0[14]/–0.20
Li_2Cl_2(g)	–593.5[14]/–	288.8[14]/290.6	82.27[14]/81.97	0.54[14]/1.11	–0.91[14]/–1.03	0[14]/–0.28
$AlCl_3$(g)	–584.6[14]/–	314.5[14]/315.7	81.97[14]/81.72	0.63[14]/1.33	–0.99[14]/–0.89	0[14]/–0.34
Al_2Cl_6(g)	–1295.7[14]/–	475.0[14]/479.8	180.92[14]/180.69	1.05[14]/2.09	–2.04[14]/–1.84	0[14]/–0.53
$LiAlCl_4$(g)[a]	–959.9/–955.9	–/393.8	–/120.78	–/28.47	–/–1.0	–19.16
Li_2AlCl_5(g)[b]	–1345.9/–1334.2	–/467.9	–/167.69	–/35.39	–/–1.34	–23.83
$LiAl_2Cl_7$(g)[c]	–1655.6/–1637.7	–/570.94	–/211.67	–/48.91	–/–1.62	–32.82

[a] Calculated from LiCl(g) + $AlCl_3$(g) $\rightleftharpoons$ $LiAlCl_4$(g). [b] Calculated from Li_2Cl_2(g) + 0.5 Al_2Cl_6(g) $\rightleftharpoons$ Li_2AlCl_5(g). [c] Calculated from LiCl(g) + Al_2Cl_6 $\rightleftharpoons$ $LiAl_2Cl_7$.

derivation of the heat of formation of $LiAl_2Cl_7$, because it features an equal number of particles on both sides.

Taking into account the experimentally known values for the heat of formation [LiCl(g), $AlCl_3$(g), Li_2Cl_2(g), Al_2Cl_6(g)][14] and the reaction energy, the heat of formation for $LiAlCl_4$(g), Li_2AlCl_5(g) and $LiAl_2Cl_7$(g) was obtained. These values as well as the standard entropies $S_{298}{}^0$ and the heat capacities $C_p{}^0$ are summarized in Table 4.

Mass Spectrometric Studies

The reaction between LiCl and $AlCl_3$ in the gas phase was studied by mass spectrometry by employing a Knudsen cell in two ways: (1) LiCl was heated in a Knudsen cell[12] to 575 °C in order to detect the vapour by mass spectrometry. A flow of gaseous $AlCl_3$ was led over the solid/gas LiCl system, and the resulting vapour composition was analyzed. (2) Previously synthesized $LiAlCl_4$ was vapourized at 230 °C from a Knudsen cell, and the vapour was analyzed.

Step 1

LiCl (150 mg) was heated to 575 °C in the upper part of a double Knudsen cell. According to the literature,[14] the monomer LiCl(g) has a partial pressure of 3.5×10^{-6} bar at this temperature. At the bottom of the Knudsen cell, $AlCl_3$ was vapourized at 80 °C, and thus, it was subsequently brought to reaction with the gaseous LiCl at 575 °C. To make sure that during the measurement the solid phase in the upper part consists of pure LiCl (and not an undefined LiCl/$AlCl_3$ melt), the mass spectrum to be analyzed was recorded soon after a constant $AlCl_3$ vapour pressure was established. The following mass spectrum was registered from the *m*/*z* = 30 ion (absolute intensities in arbitrary units): $LiCl^+$ (1956), Li_2Cl^+ (5179), $AlCl^+$ (719), $AlCl_2^+$ (6659), $AlCl_3^+$ (1849), $LiAlCl_3^+$ (566). These ions indicate the formation of the gas molecules LiCl ($LiCl^+$), Li_2Cl_2 (Li_2Cl^+), $AlCl_3$ ($AlCl^+$, $AlCl_2^+$, $AlCl_3^+$) and $LiAlCl_4$ ($LiAlCl_3^+$).

From this measurement, the reaction enthalpies for the following reactions were derived:

$$2\,LiCl(g) \rightleftharpoons Li_2Cl_2(g)$$
$$LiCl(g) + AlCl_3(g) \rightleftharpoons LiAlCl_4(g)$$

By applying the third law method, the equilibrium constant was determined at one temperature and the reaction entropy was computed upon implementation of the quantum chemically calculated reaction entropy:

$$\Delta_R G^0 = -RT \ln K$$
$$\Delta_R G^0 = \Delta_R H^0 - T\Delta_R S^0$$

To calculate the partial pressure of the mother molecules from the recorded ion intensities, we made use of the following relation:

$$p_i = c\Sigma I_i T \tag{4}$$

p_i = partial pressure of ion i [bar]
c = proportional constant (has to be determined experimentally)
ΣI_i = sum of all ion intensities belonging to one mother molecule
T = equilibrium temperature [K]
The proportional constant results from the above-named values.

$$c = p_i/\Sigma I_i T = 2.1 \times 10^{-12}\ \text{bar K}^{-1}$$

By means of this factor, the following partial pressures and equilibrium constants can be calculated:
$p(AlCl_3) = 1.7 \times 10^{-5}$ bar
$p(LiAlCl_4) = 1.0 \times 10^{-6}$ bar
$p(Li_2Cl_2) = 9.3 \times 10^{-6}$ bar

$$2\,LiCl(g) \rightleftharpoons Li_2Cl_2(g) \tag{5}$$
$$K_p(5) = 7.6 \times 10^5\ \text{bar}^{-1}$$

$$LiCl(s) + AlCl_3(g) \rightleftharpoons LiAlCl_4(g) \tag{6}$$
$$K_p(6) = 1.7 \times 10^4\ \text{bar}^{-1}$$

Taking into account the known value for the reaction entropy for Equation (5) $\Delta_R S^0(5)_{848} = -129.6$ J K^{-1} mol^{-1},[13] the obtained reaction enthalpy is $\Delta_R H^0(5)_{848} = -205.5$ kJ mol^{-1}. The comparison to the literature (–203.2 kJ mol^{-1}[13]) evidences an excellent agreement.

To study and exploit Equation (6) in an analogous manner, the reaction entropy was calculated quantum chemically. For a reaction temperature of 575 °C, a reaction entropy of $\Delta_R S^0(6)_{848} = -122$ J K^{-1} mol^{-1} was obtained, resulting in a reaction enthalpy of $\Delta_R H^0(6)_{848}$ =

–172.1 kJ mol^{-1}. By using literature data[14] for the standard heat of formation and standard entropy of LiCl(g) and $AlCl_3$(g) and by taking into account the quantum chemically calculated molar heat capacity of the involved molecules, the result for the standard heat of formation of $LiAlCl_4$ is $\Delta_f H^0(LiAlCl_4)_{298}$ = –959.1 kJ mol^{-1}. This is in excellent agreement with the quantum chemically determined value of $\Delta_f H^0(LiAlCl_4)_{298}$ = –955.9 kJ mol^{-1}.

Step 2

From the vapour above a melt of $LiAlCl_4$ at 230 °C, the following mass spectrum from the m/z = 30 ion was registered [ion (absolute intensities in arbitrary units): Li_2Cl^+ (1505), $AlCl^+$(403), $AlCl_2^+$(7560), $AlCl_3^+$(10402), $LiAlCl_3^+$-(3308), $Li_2AlCl_4^+$(5562), $Al_2Cl_5^+$(3048), $LiAl_2Cl_6^+$(274)]. The Li_2Cl^+ ion seems to indicate the formation of Li_2Cl_2(g). Because the vapour pressure of LiCl at this temperature of 503 K lies beneath the detection limit of the measurement setup, the Li_2Cl^+ ion must originate from another mother molecule. The only other detected molecule containing two lithium atoms is Li_2AlCl_5. Thus we make the following assignment: $AlCl_3$: $AlCl^+$, $AlCl_2^+$, $AlCl_3^+$, ΣI = 18365; Al_2Cl_6: $Al_2Cl_5^+$, ΣI = 3048; $LiAlCl_4$: $LiAlCl_3^+$, ΣI = 3308; Li_2AlCl_5: Li_2Cl^+, $Li_2AlCl_4^+$, ΣI = 7067; $LiAl_2Cl_7$: $LiAl_2Cl_6^+$, ΣI = 274.

When analyzing a mass spectrum involving homogeneous gas equilibriums, thermodynamically it is reasonable – if possible – to choose such an equilibrium with equal numbers of molecules or particles on both sides of the equilibrium. In that case, the determination of the partial pressures from the recorded intensities is not necessary. Thus, the partial pressures in the law of mass action can be replaced by the intensities; this approach minimizes the mistake at evaluation and is to be preferred to the approach employing a separate calibration for the determination of c in Equation (4).

Firstly, we exploit the following equilibrium:

$$2\ LiAlCl_4(g) \rightleftharpoons Li_2AlCl_5(g) + AlCl_3(g)$$

$$K_p = \frac{p(Li_2AlCl_5)p(AlCl_3)}{p^2(LiAlCl_4)} = 11.9$$

With the quantum chemically calculated reaction entropy $\Delta_R S^0_{503}$ = –3.9 J K^{-1} mol^{-1}, a reaction enthalpy at 503 K of $\Delta_R H^0_{503}$ = –12.3 kJ mol^{-1} is obtained, and by considering the molar heat capacities, a reaction enthalpy at 298 K of $\Delta_R H^0_{298}$ = –12.3 kJ mol^{-1} is obtained. Taking into account the former determined heat of formation of $LiAlCl_4$ and the known heat of formation of $AlCl_3$ results in $\Delta_f H^0_{298}(Li_2AlCl_5) = [-12.3 - (-584.6) + 2\cdot(-959.1)]$ kJ mol^{-1} = –1345.9 kJ mol^{-1} for the heat of formation of Li_2AlCl_5. This value is in good agreement with the quantum chemically obtained value of $\Delta_f H^0_{298}(Li_2AlCl_5)$ = –1334.2 kJ mol^{-1}.

To determine the standard heat of formation of $LiAl_2Cl_7$, the following equilibrium was studied and exploited:

$$LiAl_2Cl_7(g) + LiAlCl_4(g) \rightleftharpoons Li_2AlCl_5(g) + Al_2Cl_6(g)$$

$$K_p = \frac{p(Li_2AlCl_5)p(Al_2Cl_6)}{p(LiAl_2Cl_7)p(LiAlCl_4)} = 23.8$$

With the quantum chemically determined reaction entropy $\Delta_R S^0_{503}$ = –17.0 J K^{-1} mol^{-1} a reaction enthalpy at 503 K of $\Delta_R H^0_{503}$ = –35.1 kJ mol^{-1} is obtained and a reaction enthalpy at 298 K of $\Delta_R H^0_{298}$ = –35.1 kJ mol^{-1} is obtained by considering the computed molar heat capacities. This value and the mass spectrometrically derived standard heat of formation of $LiAlCl_4$ and Li_2AlCl_5 as well as the known heat of formation of Al_2Cl_6 allow the calculation of the standard heat of formation of $LiAl_2Cl_7$:

$$\Delta_f H^0_{298}(LiAl_2Cl_7) = (35.1 - 1345.9 - 1295.7 + 955.9)\ \text{kJ mol}^{-1} = -1655.6\ \text{kJ mol}^{-1}$$

Considering the expected allowance of ±30 kJ mol^{-1}, this value is in good agreement with the quantum chemically computed value of $\Delta_f H^0_{298}(LiAl_2Cl_7)$ = –1637.7 kJ mol^{-1}. Thus, our mass spectrometric studies were able to detect and analyze hitherto unknown molecules.

Conclusions

The quantum chemical studies provide hints for the structural configuration of the molecules $LiAlCl_4$, Li_2AlCl_5 and $LiAl_2Cl_7$ found in the mass spectrometer. The structural determination of these molecules by conventional spectroscopic or diffraction techniques is almost impossible due to their nature as "high-temperature species".

Thus, the combination of Knudsen cell mass spectrometry and quantum chemical calculations proved to be an appropriate method for the qualitative characterization of high-temperature vapours.

Experimental Section

Sample Preparation: The synthesis of $LiAlCl_4$ was carried out in quartz glass ampoules (i.d. 15 mm, length 200 mm). To eliminate trace amounts of water, the ampoules were heated for about 10 min under vacuum with a heat gun. Afterwards, the ampoules were ventilated with argon and subsequently filled with lithium and aluminium chloride. The stoichiometric mixture of about 2 g was sealed in the ampoule under vacuum ($<5\times10^{-3}$ mbar). The following starting materials were used: LiCl (Merck, p.a. > 99.0%) and $AlCl_3$, (Sigma–Aldrich, powder, 98%). The mixture was slowly heated up to 240 °C and kept at this temperature for 5 h.

Analysis: Mass spectrometric investigations were carried out by using a mass spectrometer Finigan type 212. The ionization was carried out by electron bombardment with electron energy of 70 eV.

Quantum Chemical Calculations: The quantum chemical calculations on the molecules $LiAlCl_4$, Li_2AlCl_5 and $LiAl_2Cl_7$ were performed by employing the program package TURBOMOLE.[5] The determination of the electronic structure as well as the calculation of the total energies was carried out with the RI-DFT/BP86 method [b-p functional, type GGA, exchange: S + B88, correlation: VWN(V) + P86][6–10] by employing def-TZVPP basis sets.

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