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Publication Date

1970-06-01

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DETERMINATION OF ITS STABILITY

Harry B. Skinner and Alan W. Searcy

June 1970

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DEMONSTRATION OF THE EXISTENCE OF La_2F_6 GAS AND
DETERMINATION OF ITS STABILITY

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ABSTRACT

Intensities of ion peaks attributable to $\text{LaF}_3(\text{g})$ and $\text{La}_2\text{F}_6(\text{g})$ have been measured as functions of temperature in a mass spectrometer study of the equilibrium vapor of lanthanum trifluoride. The vaporization data for the monomer are in very good agreement with torsion-effusion data of Mar and Searcy. The heat of the reaction $\text{La}_2\text{F}_6(\text{g}) = 2\text{LaF}_3(\text{g})$ is 71.3 ± 1.9 kcal/mole at 1577°K . The apparent entropy of sublimation of the dimer is about 11 eu/mole lower than expected from studies of aluminum halides. It is argued that the principal ion fragment produced from $\text{La}_2\text{F}_6(\text{g})$ in the mass spectrometer is masked by that from $\text{LaF}_3(\text{g})$ and that the partial pressure of $\text{La}_2\text{F}_6(\text{g})$ is about 1% that of the monomer at 1575°K , a value about 100 times that calculated by conventional interpretation of the mass spectrometer data.

I. INTRODUCTION

Dimers are present at high concentrations in the vapors of aluminum trihalides but, although scandium, yttrium, and lanthanum trifluorides¹ and many lanthanide trifluorides²⁻⁴ have been studied with mass spectrometers, no dimers of these fluorides have been reported. By using effusion cells with multiple orifices of small diameter we have extended mass spectrometer measurements of lanthanum fluoride to higher temperatures and have measured as a function of temperature a low intensity peak that arises from dissociative ionization of La_2F_6 . This paper reports the measurements and compares the data obtained for $\text{La}_2\text{F}_6(\text{g})$ with data for aluminum trihalide dimers⁵⁻⁷ and for double chlorides of alkali metals and lanthanide metals.⁸ Analysis of the enthalpy and apparent entropy data for the dimer leads to the conclusion that the true pressure of the dimer is not four orders of magnitude lower than that of the monomer as suggested by conventional interpretation of intensity data, but only about two orders of magnitude lower.

II. EXPERIMENTAL

This study was carried out with a 60° sector, 1 foot radius, magnetic deflection mass spectrometer built by Nuclide Associates. The sample of lanthanum trifluoride obtained from Semi-Elements, Inc. was heated by electron bombardment in a molybdenum Knudsen cell with a graphite liner. The lanthanum fluoride of this study was a nominal 99.9% purity, and showed .015% iron as the principle impurity by spectrographic analysis. The same material was used for the torsion-effusion portion of the study of Mar and Searcy.⁹

Three small orifices were employed in each lid to increase the ion current signal without exceeding the mean free path to diameter ratio above which molecular flow equations become invalid. The limiting ratio for LaF_3 gas has been demonstrated to be about 0.4 as calculated from the hard sphere model.⁹ Two orifice sizes were used, .01 cm diam. and .04 cm. diam. drilled in graphite cell lids of thicknesses .025 cm and .1 cm respectively. It should be noted that while some measurements were made close to the upper pressure limit for molecular flow, other measurements were made well below the limit. The molecules of the beam could not, therefore, have undergone the kind of adiabatic cooling with the resultant cluster formation that has recently been described.^{10,11} No shutterable species were observed at the mass numbers of LaF_3^+ or La_2F_6^+ , but peaks at masses corresponding to LaF_2^+ and La_2F_6^+ were concluded to be produced solely by dissociative ionization of the monomer $\text{LaF}_3(\text{g})$ and the dimer $\text{La}_2\text{F}_6(\text{g})$ respectively.

Identification of the species La_2F_5^+ was made by use of the calibrated gauss indicator to establish the mass as correct for La_2F_5^+ . A cell

exhaustion experiment proved that the La_2F_5^+ intensity dropped in conjunction with the LaF_2^+ intensity. Agreement of data from a graphite-lined tantalum cell with that from the graphite-lined molybdenum cell proved that a foreign metal did not contribute to the mass peak. Thermodynamic calculations indicate that contributions to LaF_2^+ and La_2F_5^+ ion intensities by reactions other than the main vaporization reactions should be negligible.

The intensities of the LaF_2^+ and the La_2F_5^+ ions were followed as a function of temperature using 70 eV ionizing electrons. Many data points were taken during each run with temperatures varied up, then down. Temperatures were measured with a Pt/Pt-90% Rh 10% thermocouple clamped securely to the molybdenum cell. About 15 min. was allowed between measurements to ensure that equilibrium had been reached.

It was necessary at high temperatures to follow the LaF_2^+ that resulted from contributions from the low abundance isotope La^{138} because intensities from LaF_2^+ that contained La^{139} were so high that they flooded the detector. All data were divided by the appropriate isotopic fractional abundance.¹²

The $\text{LaF}_3(g)$ calculated from a least squares fit of the I T data of each run was made to coincide at the average temperature of the run with the lanthanum fluoride pressure of Mar and Searcy.⁹ The same factor, corrected for estimated relative cross sections and electron multiplier gain, was applied to the dimer intensity. The electron multiplier gain for the dimer was estimated to equal that of the monomer and the cross section for electron impact ionization for La_2F_6 was estimated to be 1.5 times the cross section of LaF_3 . This value is the approximate average found for dimers of alkali halides by Berkowitz et al.¹³

III. RESULTS AND DISCUSSION

Figure 1 shows the results of two mass spectrometer runs. Preliminary exploratory runs with the 0.01 cm diam. orifices gave data in reasonable agreement with the data of Fig. 1 but which were not included because instrumental variables were not as well controlled in the exploratory runs as in the subsequent runs.

Because the monomer data extend over a 500° range from 1221°K to 1736°K, the change in heat capacity for vaporization, ΔC_p , should not be neglected in calculation of enthalpies and entropies of vaporization. Mar and Searcy⁹ have estimated the heat capacity for the solid and monomer to be $C_p(s) = 19.796 + 8.42 \times 10^{-3} T - 5.90 \times 10^{-4} T^{-2}$ and $C_p(\text{monomer}) = 21.323 - 4.065 \times 10^{-4} T - 3.375 \times 10^{-5} T^{-2}$ respectively. The heat capacity difference for reactions, 2 monomer $\rightarrow$ dimer from JANAF⁵ for aluminum halides and iron chloride are all about 4 cal/deg.-mole of dimer. This constant 4 cal/deg.-mole of dimer was applied to give for sublimation of a mole of La_2F_6 $\Delta C_p = -11$ cal/deg. Second law enthalpies of sublimation were calculated for the monomer at 1487°K, the midpoint of the experimental range of Mar and Searcy⁹ and 1577°K, the midpoint of the range of measurements, to be 97.8±0.8 kcal/mole and 96.7±0.8 kcal/mole respectively. The enthalpy of sublimation at 1487°K for the monomer is in good agreement with the value of 99.3 kcal/mole of Mar and Searcy but only fair agreement with the value 92.0 kcal/mole reported by Kent et al.¹ at 1324°K. The calculated entropy of sublimation of the monomer at 1577°K is 42.03±.72 eu/mole.

From the least squares fit of the heat capacity-corrected data for the La_2F_6 molecule, the entropy and enthalpy of sublimation at 1577°K were calculated to be 38.4 ± 1.0 eu/mole and 122.1 ± 1.1 kcal/mole, respectively. The enthalpy and entropy of sublimation of monomers and dimers measured in this study yield a dimerization enthalpy for $\text{LaF}_3(\text{g})$ of -71.3 ± 1.9 kcal/mole and a dimerization entropy of -45.6 ± 1.8 eu/mole, where quoted error limits are standard deviations from the least squares fit.

Since temperature-dependent errors are easier to control in a torsion-effusion apparatus than in a mass spectrometer and since Mar and Searcy⁹ demonstrated careful temperature measurement by recording data on tin in good agreement with accepted values, their value of 99.3 kcal/mole at 1487°K should be accepted as the most reliable. Correction of our measured temperature dependences for the difference between this value and the value 97.8 that we measured at 1487°K yields a corrected value of 123.7 ± 5.0 kcal/mole for sublimation of the dimer at 1577°K . The same correction applied to the entropy of sublimation yields a value of 40.3 ± 3.0 eu/mole at 1577°K . The quoted error limits take into consideration uncertainties in measurement of relatively low pressures. These estimated limits yield probable error limits on the enthalpy and entropy of dimerization of ± 5.5 kcal/mole and ± 3.2 eu/mole, respectively.

Appearance potentials of ions observed in this work were determined by the method of extrapolated differences using Hg and are shown in Table 1. Our appearance potential data are in good agreement with that reported by Kent et al.¹ for fragments of the monomer.

The surprising result of this study is not that a dimer of a rare earth fluoride has been identified, but that its apparent concentration is so low -- the intensity of La_2F_5^+ is only about 10^{-4} times that of LaF_2^+ . In contrast Al_2F_6 is reported to constitute about 1.7% of the vapor of the aluminum trifluoride when the total vapor pressure is 10^{-5} atm. The aluminum chloride, bromide and iodide dimers vaporize at still higher relative concentrations. The enthalpy of dissociation of $\text{La}_2\text{F}_6(\text{g})$ to two $\text{LaF}_3(\text{g})$ molecules when the monomer pressure is 10^{-5} atm is 72.6 kcal compared to 48.8 kcal for $\text{Al}_2\text{F}_6(\text{g})$.⁷ The ratio of the enthalpy of sublimation of the monomer to the enthalpy of dissociation of the dimer to two monomers, which is usually critical in determining whether a dimer will be a major species,¹⁴⁻¹⁶ is 1.37 for the LaF_3 molecules compared to 1.38 for the AlF_3 molecules. The partial pressure calculated for La_2F_6 are anomalously low because of the exceptionally high entropy measured for dissociation of the La_2F_6 dimer to monomer. The exceptional entropy for La_2F_6 dissociation is apparent from Table II, which reports entropies for dissociation of the trihalide dimers and of alkali halide-metal trihalide molecules to the binary halides (for example, for $\text{KLaCl}_4(\text{g})$ dissociation to $\text{KCl}(\text{g})$ and $\text{LaCl}_3(\text{g})$).

In the absence of molecular structure and internal energy data which would permit calculation of entropies of the lanthanum fluoride vapor species by the methods of statistical mechanics, one cannot say with absolute certainty that the apparent entropy determined in this study is erroneous. But the anomalous entropy argues strongly that some systematic error was made either in measurement of $\text{La}_2\text{F}_5^+/\text{LaF}_2^+$ ion intensity ratios or in calculation of $\text{La}_2\text{F}_6/\text{LaF}_3$ pressure ratios from the measured intensities.

The most obvious possible source of such an error, failure to attain equilibrium for dimer vaporization, is ruled out by excellent agreement in intensity ratios measured with orifice areas that differed by a factor of 16.

The discrepancy could be explained by a breakdown in the proportionality rule:

$$P \propto I^+T$$

This possibility was suggested by Berkowitz et al.³ for lithium fluoride. The probable cause favored by those authors to explain the temperature trend in fragmentation of $\text{LiF}_{(g)}$ was the formation of Li^+ with excess kinetic energy. The very good agreement obtained in the present study for the temperature dependence of $\text{LaF}_{3(g)}$ pressures with that obtained by the torsion-effusion method implies that no such error exists for the monomer and, therefore, that such an effect would have to be an exclusive peculiarity of the dimer. To reconcile the measured intensity ratio with an expected entropy of ~ 35 for dimer dissociation to monomers would require that the efficiency of ionization at the highest temperature of measurement relative to that at the lowest temperature of measurement vary by a factor of about 5. Since significant temperature dependences for fragmentation have not been clearly established for any high temperature systems, such a large variation in ionization efficiency seems highly improbable. Furthermore, a less drastic explanation of the anomalous data is provided by comparison with fragmentation patterns for complex salt molecules.

Table III lists fragmentation patterns reported for several complex molecules for which the principal ion has been identified as a small fragment of the parent molecule. In each of these examples, the reaction that seems most reasonably to explain production of the observed ion from the singly ionized parent molecule is one that yields the observed ion, a

halogen atom, and a neutral monomer of one of the constituent salts.

For example,

It is well established¹⁷ that a sequence of monomolecular dissociation reactions can give rise to several fragments of the parent ion such as indicated in reaction 1. The analogous reaction for the lanthanum fluoride dimer would be

It is reaction 2, rather than $\text{La}_2\text{F}_6^+ = \text{La}_2\text{F}_5^+ + \text{F}$, which from behavior of related polymeric species under electron bombardment would be expected as the principal reaction of an excited La_2F_6^+ ion. But this reaction is masked by the higher LaF_2^+ intensity from LaF_3^+ fragmentation.

The appearance potential for LaF_2^+ from reaction 2 can be calculated from the enthalpy of dissociation of the dimer to monomer and from the appearance potentials of La_2F_5^+ and LaF_2^+ to be 14.9 eV compared to 11.8 eV for LaF_2^+ from the monomer. The occurrence of reaction 2, therefore, would not be revealed by measurement of LaF_2^+ intensities as a function of electron energies.

We conclude that reaction 2 is probably the principal reaction undergone by La_2F_6 when ionized by 70 eV electrons. The temperature dependence for vaporization of the dimer calculated from La_2F_5^+ intensity measurements and the enthalpy of dissociation of dimer to monomer and of sublimation of the dimer derived from that temperature dependence are correct. The partial vapor pressure of the dimer is best estimated by assuming the entropy

of dissociation of dimer to monomer to be about the same as for Al_2F_6 , 35 eu per mole of dimer, from which the partial pressure of La_2F_6 dimer is calculated to be 6.2×10^{-8} atm. when the partial pressure of the monomer is 10^{-5} atm. Figure 1 shows the estimated true pressure of the dimer.

We plan next to study $\text{Ce}_2\text{F}_{12}(\text{g})$. We anticipate that the extra electron of each cerium atom will give rise to a small increase in stability of the dimer relative to the monomer and will cause a change in fragmentation patterns¹⁸ for both monomer and dimer. A higher intensity of dimer would, and a changed fragmentation pattern could, make easier the problem of analysis of the monomer-dimer stability relationships. The cerium fluoride study should, therefore, not only be interesting in itself but should strengthen or weaken the credibility of the analysis we have presented of our lanthanum fluoride data.

Acknowledgement

This research was sponsored by the Metallurgy and Materials Branch of the U.S. Atomic Energy Commission.

TABLE I

Appearance potentials of ions in the mass spectra of $\text{LaF}_3(\text{g})$.

Ion	This work (eV)	Kent et al. (eV)
La^+	26.9	26.5
LaF^+	18.5	18.5
LaF_2^+	11.8	12.0
La_2F_5^+	12.4	

TABLE II Entropy changes for the reactions $2 \text{MX}_3(\text{g}) \rightarrow (\text{MX}_3)_2(\text{g})$ and $\text{NX}(\text{g}) + \text{MX}_3(\text{g}) \rightarrow \text{NMX}_4(\text{g})$ in the experimental temperature range.

Associated Compounds	$-\Delta S$ (eu)	Reference
$(\text{AlI}_3)_2$	33.9	5
$(\text{AlCl}_3)_2$	34.3	5
$(\text{AlBr}_3)_2$	37.4	5
$(\text{AlF}_3)_2$	35.0	6,7
$(\text{LaF}_3)_2$	45.6	this work
$(\text{FeCl}_3)_2$	33.9	5
NaLaCl_4	32.8 ± 1.8	8a
NaNdCl_4	33.3	8b
NaErCl_4	34 ± 5	8c
KLaCl_4	32 ± 9	8d
KCeCl_4	32.6 ± 3	8d
KPrCl_4	32.6 ± 3	8d
KNdCl_4	32.6 ± 3	8d
KErCl_4	32.6 ± 2	8e
CsNdCl_4	29.8	8b
CsErCl_4	30.8	8b

TABLE III Fragmentation patterns for some complex molecules

Parents	Observed Ions	Intensity	Reference
KCl-ErCl ₃ (30V electrons)	K ⁺	59	8f
	KCl ⁺	0.76	
	Er ⁺	0.63	
	ErCl ⁺	0.56	
	ErCl ₂ ⁺	1.9	
	KErCl ₂ ⁺	0.16	
	KErCl ₃ ⁺	1.0	
CsCl-ErCl ₃ (52V electrons)	Cs ⁺	67.6	8b
	CsCl ⁺	.88	
	Cs ₂ Cl ⁺	.96	
	ErCl ₂ ⁺	.79	
	CsErCl ₂ ⁺	.04	
	CsErCl ₃ ⁺	1.0	
CsCl-NdCl ₃ (51V electrons)	Cs ⁺	526	8b
	CsCl ⁺	5.84	
	Cs ₂ ⁺	.26	
	Cs ₂ Cl ⁺	4.58	
	Nd ⁺	1.05	
	NdCl ⁺	1.74	
	NdCl ₂ ⁺	6.05	
	NdCl ₃ ⁺	0.16	
	CsNdCl ₂ ⁺	0.05	
	CsNdCl ₃ ⁺	1	
LiBeF ₃ (60V electrons)	Li ⁺	2.9	19
	LiBeF ₂ ⁺	1	
	LiF ⁺	.06	
Li ₂ BeF ₄ (60V electrons)	Li ₂ F ⁺	40	19
	Li ₂ BeF ₃ ⁺	1	

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