International Journal of Mass Spectrometry 245 (2005) 90–93

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Formation of the negative cluster ions in a Knudsen cell at low temperatures

S.V. Abramov*, N.S. Chilingarov, J.V. Rau, A.Ya. Borschevsky, L.N. Sidorov

Chemistry Department, Thermochemistry Laboratory, Moscow State University, Leninskie Gory 1-3, 119992 Moscow, Russia

Received 11 April 2005; received in revised form 14 July 2005; accepted 14 July 2005
Available online 22 August 2005

Abstract

Mass spectrometric determination of absolute pressures of the positive Na^+, K^+, Cs^+ and the negative $NaAl_2F_8^-$, AlF_4^-, $Al_2F_7^-$, $NaAl_3F_{11}^-$, $Na_2Al_3F_{12}^-$ ions in the saturated vapor over the $Na_5Al_3F_{14}$–AlF_3 system was carried out at the temperature near 850 K. The measurements were made in a clean nickel effusion cell and in the same cell with the inner surface covered by cerium trifluoride. An increase of negative ion pressures at least three order of magnitude has been observed after CeF_3 treatment as compared with a clean cell. At that time the pressure of positive ions decreased slightly. The result is explained by F^- superionic conductivity of CeF_3.

Keywords: Thermal ionization; Thermionic emission; Ion-molecular equilibrium; Ion pressure; Hyolite; Aluminum fluoride; Cerium fluoride; Superionic conductor

1. Introduction

At now complex negative ions including multiply charged negative ions of organic materials are obtained mainly by ESI and MALDI methods [1,2]. In inorganic chemistry there are also some new examples of complex negative ions applications.

The negative $Me_nO_m^-$ (Me = Mn, Re) clusters were detected upon vaporization of manganese and rhenium in a Smalley type laser vaporization cluster source coupled with an ultrasonic device [3,4]. The negative Me_n^- clusters "cooled" in the gas-carrier pulse flow (He, 12 atm) were oxidized with molecular oxygen and further analyzed using a TOF-MS technique. The composition of $Me_nO_m^-$ was dependent on the operating conditions of a source of metal clusters, partial pressure of oxygen, and the time period during which these clusters stayed in the reaction zone.

The negative BO_2^- [5], ReO_4^- [6], OsO_3^- [7] and some other clusters have long been in use in the N-TIMS method for determination of isotope ratio of the corresponding elements. The methods of generating intense ReO_4^- beams for SIMS applications were studied by Delmore [8–10]. Usually, high emitter temperature and high concentration of thermal electrons are necessary for obtaining thermal negative ions, active metal (Ba, Ln) compounds being used to decrease the emitter work function. In [7], the formation of OsO_3^- was supposed to proceed through the resonance capture of thermal electrons by the OsO_3 molecules near emitter. It was established in [8,9] that the Eu_2O_3 matrix catalyzed oxidation of rhenium metal to form ReO_4^-. More intense ion beams were obtained, when $BaSO_4$ was used as an oxidizing agent [10]. The FeF_4^- ions were obtained with the matrix containing BaF_2, however, emission was low and tended to decay [11]. It should be noted that earlier, different oxygen- and fluorine-containing ions were generated in the Knudsen cell at relatively low temperature (for example [12]). The cited works were discussed in detail in [13].

The aim of this work was to elucidate the conditions for the predominant formation of negative ions below 1000 K. The $Na_5Al_3F_{14}$–AlF_3 system was used in the experiments, since reliable data on the composition of its saturated vapor are available in the literature: the formation of negative ions

---

* Corresponding author. Tel.: +7 095 9395463; fax: +7 095 9391240.
E-mail address: s_abramov@thermo.chem.msu.ru (S.V. Abramov).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.07.006

$NaAl_2F_8^-$, AlF_4^-, $Al_2F_7^-$ has been established in this system [14].

2. Experimental

2.1. Instrumentation

Mass spectrometric experiments were carried out using a MI-1201 magnetic sector mass spectrometer (single focusing, 90°, 200 mm) equipped by a combined ion source with an effusion cell. Such an ion source allowed for the study of positive, negative and neutral species in vapor within a single experiment. The mass resolution of this instrument was about 300 at the accelerating voltage of ±3 kV and the mass range was 2–1200 amu. The width of the outlet slit of the ion source was 0.3 mm. The pressures of the molecular components were determined by the standard procedure of Knudsen cell mass spectrometry [15]. The electron impact mass spectra were measured at the ionizing voltage of 65 V and at an emission current of 0.3 mA. The procedure of thermal ion measurements and their partial pressure calculations has been described in detail in [16].

A nickel Knudsen cell ($l = 16$ mm, $d = 12$ mm) covered with a fitted lid was used in the experiments. The effusion orifice had a diameter of 0.5 mm. The temperature was measured to within ±2 K using a Pt–Pt/Rh(10%) thermocouple. The junction was welded to the bottom of a cell.

2.2. Samples

NaF (>99.9% purity) and AlF_3 (>98% purity) were used as initial materials. The $Na_5Al_3F_{14}$–AlF_3 system was prepared by heating the NaF–AlF_3 (60 mol.%) mixture.

Two series of experiments were carried out. In one series the cell was washed with distilled water before experiment (in what follows, this cell is denoted as *a clean cell*). In another series the inner surface of the cell was preliminarily covered with a layer of CeF_3 using the following procedure: a sample of CeF_3 (>98% purity) was placed into the clean cell, which was further kept under vacuum at 1200 K for several hours (it is denoted as *the cell covered by* CeF_3). The nickel surface after CeF_3 evaporation have been analyzed using scanning electron microscopy (SEM) (a LEO 1450 VP, Carl Zeiss, Germany) coupled with energy dispersive X-ray microanalysis (EDS). The image is shown in Fig. 1. For areas picked out (1–4) the composition is presented in Table 1. It should be noted, that deep resolution in EDS analysis is about a few microns and in the case of less thin films the composition of the substrate should be taken into account. As can be seen from the table, the area 1 is practically CeF_3. The presence of Ce, F and O is detected in area 2. Most likely, the presence of oxygen is due to hydrolysis of the sample. The composition of areas 3 and 4 is determined as Ni, however, the presence of thin layer of CeF_3 is not excluded. It is obviously, the average thickness of CeF_3 layer is less than a few microns.

Table 1
The results of EDS analysis (wt.%)

Area	O	F	Na	K	Ni	Cs	Ce	Total
1	–	32	–	–	17	–	51	100
2	20	25	–	–	7	–	48	100
3	–	3	–	–	97	–	–	100
4	–	1	–	–	99	–	–	100

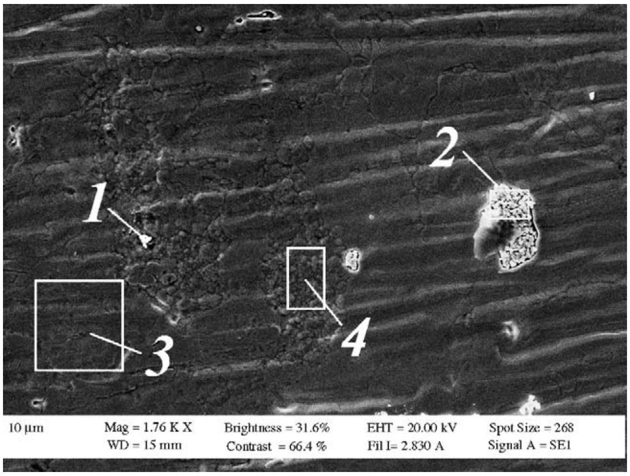

Fig. 1. The nickel surface after CeF_3 evaporation (SEM).

3. Results

3.1. Clean cell, $Na_5Al_3F_{14}$–AlF_3 system

3.1.1. Molecular composition of vapor

The EI mass spectrum of the gaseous phase at 886 K is presented in Table 2. The partial pressures of the main components of the saturated vapor, namely, $NaAlF_4$ and $Na_2Al_2F_8$, were calculated to be 2.7×10^{-5} and 4.8×10^{-6} atm, respectively.

3.1.2. Thermal positive ions

The mass spectrum of positive thermal ions and their partial pressures in the effusion cell at 842 and 873 K are given in Table 3. The data on the Na_2F^+ and $Na_2AlF_4^+$ ions are not presented because their intensities were close to the sensitivity limit of the instrument.

Table 2
Mass spectrum (EI) of the gas phase over the $Na_5Al_3F_{14}$–AlF_3 system at 886 K

Ion	I (%)
Na^+	100
AlF^+	10
AlF_2^+	38
$NaAlF_3^+$	18
$Na_2AlF_4^+$	20

Table 3
Measured currents of positive thermal ions and estimation of pressures in the effusion cell at 842 and 873 K (clean cell)

T (K)	Ion		
	Na^+	K^+	Cs^+
842			
I (fA)[a]	1	9	31
p (atm)	1×10^{-17}	1×10^{-16}	7×10^{-16}
873			
I (fA)	2	1	3
p (atm)	2×10^{-17}	1×10^{-17}	7×10^{-17}

[a] $f = 10^{-15}$.

3.1.3. *Thermal negative ions*

Negative ions were not detected within the 2–1200 amu mass range at 720–920 K. After $NaAlF_4$ was evaporated, the residue of AlF_3 was found in the cell.

The same results were obtained with addition of CeF_3 to the initial mixture of NaF and AlF_3 or to the $Na_5Al_3F_{14}$–AlF_3 system in the clean cell.

3.2. *Cell covered by CeF_3, $Na_5Al_3F_{14}$–AlF_3 system*

3.2.1. *Molecular composition of vapor*

The data obtained for this system are similar to those presented in Table 2.

3.2.2. *Thermal positive ions*

The mass spectrum of the positive thermal ions and their partial pressures in the effusion cell at 856 and 887 K are given in Table 4. As can be seen, positive ions registered in this system are similar to the ions formed in the clean cell, but their partial pressures are several times lower.

Table 4
Measured currents of positive thermal ions and estimation of pressures in the effusion cell at 856 and 887 K (cell covered by CeF_3)

T (K)	Ion		
	Na^+	K^+	Cs^+
856			
I (fA)	0.1	0.2	0.3
p (atm)	1×10^{-17}	3×10^{-17}	8×10^{-17}
887			
I (fA)	0.4	1	0.8
p (atm)	6×10^{-17}	2×10^{-16}	3×10^{-16}

3.2.3. *Thermal negative ions*

The mass spectrum of the negative thermal ions and their partial pressures in the effusion cell at 856 and 887 K are given in Table 5. It is evident that after the cell was treated with CeF_3, intensities of negative ions increased by at least 440 times. In addition to $NaAl_2F_8^-$, AlF_4^-, $Al_2F_7^-$, which were earlier detected in the system under study, the $NaAl_3F_{11}^-$ and $Na_2Al_3F_{12}^-$ ions were detected for the first time in our experiments. The intensities of negative ions remained unchanged as long as the partial pressure of $NaAlF_4$ was constant. When the pressure of $NaAlF_4$ decreased at the end of the experiment, the negative ions intensities also decreased. The residue in the cell was found to be AlF_3 with an admixture of CeF_3.

4. Discussion

$Na_5Al_3F_{14}$ salt is known to ensure a high partial pressure of $NaAlF_4$ molecules, which readily undergoes heterolytic dissociation by the following equation:

$$NaAlF_4\,(g) = Na^+\,(g) + AlF_4^-\,(g) \tag{1}$$

The ion pressure product $p(Na^+) \times p(AlF_4^-)$ calculated for equilibrium (1) at 873 K is 3.0×10^{-31} atm^2.

Let us consider the experiment with *a clean cell*. The Na^+ pressure at 873 K was measured to be 2×10^{-17} atm (Table 3); therefore, the pressure of AlF_4^- should have been 1.5×10^{-14} atm. If this had been the case, then the AlF_4^- ion current must necessarily have been measurable. However, negative ions were not really detected in the experiments with the clean cell over the temperature range studied (720–920 K). Since in the experiment the inner surface of effusion cell is covered by adsorption layer of volatile substance $NaAlF_4$, that the absence of AlF_4^- signal can be related to absence of sufficient ionic (electronic) conductivity of this layer. The circuit is broken.

In the case of *the cell covered by CeF_3* we have the high concentration of negative ions $NaAl_2F_8^-$, AlF_4^-, $Al_2F_7^-$, $NaAl_3F_{11}^-$, $Na_2Al_3F_{12}^-$. At the same time, as in the case of *a clean cell*, the inner surface of *the cell covered by CeF_3* is covered by adsorption layer of $NaAlF_4$, however, the circuit is closed that points at the presence of sufficient conductivity of the surface layer. The question about so abrupt difference in conductivity in both cases is open. It is known, that

Table 5
Measured currents of negative thermal ions and estimation of pressures in the effusion cell at 856 and 887 K (cell covered by CeF_3)

T (K)	Ion				
	AlF_4^-	$Al_2F_7^-$	$NaAl_2F_8^-$	$NaAl_3F_{11}^-$	$Na_2Al_3F_{12}^-$
856					
I (fA)	14	5	24	<0.5	<0.5
p (atm)	4×10^{-15}	2×10^{-15}	9×10^{-15}	–	–
887					
I (fA)	83	46	220	2	1
p (atm)	3×10^{-14}	2×10^{-14}	1×10^{-13}	1×10^{-15}	6×10^{-16}

CeF_3 is fluoride anion superionic conductor already at ambient temperature ($\sigma_{F^-} \approx 10^{-6}\,\Omega^{-1}\,cm^{-1}$ [17]). Also CeF_3 is not stoichiometric compound and has a wide homogeneous range: CeF_{3-x}, where x can take on both positive and negative values. Besides that CeF_3 does not lose the conductivity when doped by aluminum [18]. Experiment shows, that sputtering of $NaAlF_4$ layer on the surface of CeF_3 does not lead to loss of conductivity of surface layer. So, most likely, in particular the F^- conductivity and high concentration of chemically active F^- on the surface provides the working of effusion cell as the source of negative ions. As a matter of fact, we have two electrolytes: one is solid (CeF_3) with F^- conductivity and the second one is gaseous (saturated vapor over the heterogeneous field $Na_5Al_3F_{14}$–AlF_3) with anion conductivity ($NaAl_2F_8^-$, AlF_4^-, $Al_2F_7^-$, $NaAl_3F_{11}^-$, $Na_2Al_3F_{12}^-$). There are three interfaces:

1. Ni (inner surface of effusion cell)|CeF_3.
2. CeF_3|saturated vapor with anions.
3. Anions|detector (Faraday cup).

The following reactions take place:

- First interface (cathode):

$$CeF_3\,(s) + \bar{e}\,(s) = CeF_2\,(s) + F^-\,(s) \tag{2}$$

- Second interface:

$$NaAlF_4\,(g) + F^-\,(s) = AlF_4^-\,(g) + NaF\,(s) \tag{3}$$

$$Na_2Al_2F_8\,(g) + F^-\,(s) = NaAl_2F_8^-\,(g) + NaF\,(s) \tag{4}$$

$$NaAl_2F_7\,(g) + F^-\,(s) = Al_2F_7^-\,(g) + NaF\,(s) \tag{5}$$

- Third interface (anode):

$$AlF_4^-\,(g) - \bar{e}\,(s) = AlF_3\,(s) + F\,(s) \tag{6}$$

$$NaAl_2F_8^-\,(g) - \bar{e}\,(s) = NaAlF_4\,(s) + AlF_3\,(s) + F\,(s) \tag{7}$$

$$Al_2F_7^-\,(g) - \bar{e}\,(s) = 2AlF_3\,(s) + F\,(s) \tag{8}$$

The total reactions of electrolytes decomposition are:

$$CeF_3 = CeF_2\,(cathode) + F\,(anode) \tag{9}$$

$$NaAlF_4 = NaF\,(cathode) + AlF_3\,(anode) \tag{10}$$

An accelerating voltage power supply of mass spectrometer is a voltage source of a circuit. The current from the detector (Faraday cup) to cathode is provided by electrons. The current from cathode to the $CeF_3/NaAlF_4$ surface is provided by fluorine anions. The current from the $CeF_3/NaAlF_4$ surface to anode (in vacuum) is provided by beam of negative ions $NaAl_2F_8^-$, AlF_4^-, $Al_2F_7^-$, $NaAl_3F_{11}^-$, $Na_2Al_3F_{12}^-$.

5. Conclusion

Superionic conductor CeF_3 covering the inner surface of effusion cell provides sufficient ionic conductivity and surface concentration of fluorine anions and allows to obtain high intense beam of cluster negative ions.

Acknowledgment

This work was supported by the Russian Foundation for Basic Research, project 05-03-32916a.

References

[1] W. Chai, V.E. Piskarev, Y. Zhang, A.M. Lawson, H. Kogelberg, Arch. Biochem. Biophys. 434 (1) (2005) 116.

[2] J.L. Edwards, R.T. Kennedy, Anal. Chem. 77 (7) (2005) 2201.

[3] A. Pramann, K. Rademann, Int. J. Mass Spectrom. 185–187 (1999) 673.

[4] A. Pramann, K. Rademann, Int. J. Mass Spectrom. 209 (2001) 1.

[5] A. Sonoda, Y. Makita, K. Ooi, T. Hirotsu, J. Nucl. Sci. Technol. 39 (4) (2002) 295.

[6] K. Suzuki, Y. Miyata, N. Kanazawa, Int. J. Mass Spectrom. 235 (1) (2004) 97.

[7] K. Hattori, T.J.S. Cole, D.P. Menagh, Int. J. Mass Spectrom. 176 (1998) 189.

[8] J.E. Delmore, A.D. Appelhans, E.S. Peterson, Int. J. Mass Spectrom. Ion Proc. 146–147 (1995) 15.

[9] J.E. Delmore, A.D. Appelhans, E.S. Peterson, Int. J. Mass Spectrom. 178 (1998) 9.

[10] K.B. Johnson, J.E. Delmore, A.D. Appelhans, Int. J. Mass Spectrom. 229 (2003) 157.

[11] T. Walczyk, Int. J. Mass Spectrom. Ion Proc. 161 (1997) 217.

[12] S.V. Kuznetsov, M.V. Korobov, L.N. Sidorov, Int. J. Mass Spectrom. Ion Proc. 91 (1989) 283.

[13] L.N. Sidorov, Int. J. Mass Spectrom. Ion Proc. 118–119 (1992) 739.

[14] L.N. Sidorov, M.I. Nikitin, E.V. Skokan, I.D. Sorokin, Int. J. Mass Spectrom. Ion Phys. 35 (1980) 203.

[15] M.G. Inghram, J. Drowart, High Temperature Technology, McGraw-Hill, New York, 1959, p. 129.

[16] S.V. Abramov, N.S. Chilingarov, A.Ya. Borshchevskiy, L.N. Sidorov, Int. J. Mass Spectrom. 231 (1) (2004) 31.

[17] C. Hoff, H.-D. Wiemhöfer, O. Glumov, I.V. Murin, Solid State Ionics 101–103 (1997) 445.

[18] C. Tien, E.V. Charnaya, A.B. Sherman, Phys. Solid State 46 (9) (2004) 1578.