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Mass and FTIR Spectroscopic Investigations of Gaseous Manganese Tetrafluoride

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Introduction

This work is a part of an interlaboratory project aimed at the mass spectrometric and IR spectroscopic characterization of a number of transition metal tetrafluorides with unusually high oxidation state of the metal: CoF$_4$,[1] MnF$_4$, and FeF$_4$. The instability of these compounds brings about their synthesis and investigation in situ. The present study is mainly on the MnF$_4$ vibrational spectrum. Although MnF$_4$ was synthesized for the first time long ago,[2] reliable data on the IR characterization of this molecule so far are not available.

In the previous mass spectrometric study[3] solid MnF$_4$ was prepared in situ via fluorination of commercial MnF$_2$ at $\leq$750 K by molecular fluorine directly in the Knudsen effusion cell. Then it was evaporated and investigated. In the present research, gaseous MnF$_4$ was also produced in situ but employing an alternative solid-phase synthesis procedure, i.e., using a solid fluorinating agent. In many respects this procedure appears to be preferential in comparison with the fluorine admission technique because it does not require special assembly; it is simpler to reproduce it, and the ambient is less aggressive.

The TbF$_4$(s) fluorinating agent has been used in our studies to fluorinate MnF$_3$(s) in the Knudsen cell assembly coupled either with a mass spectrometer or with an FTIR interferometer. Knudsen cell mass spectrometry has been utilized to establish the optimum in situ conditions for manganese tetrafluoride generation in the gas phase. A suitable temperature interval and solid-phase composition leading to the highest MnF$_4$ partial pressure have been found. Subsequently, these conditions have been reproduced in the matrix isolation IR spectroscopy experiments, and the first spectroscopic data on MnF$_4$ have been obtained.

Experimental Methods and Samples

MnF$_3$ (>97% purity) was purchased from Aldrich Chemical Co. TbF$_4$ was prepared according to ref 4. X-ray powder diffraction analysis showed 95% purity for the TbF$_4$ sample. Both samples are very sensitive to traces of water, and the fluorinating ability of TbF$_4$(s) can be significantly reduced by moisture. Therefore, all the manipulations with samples in order to load the mixture of MnF$_3$(s) and TbF$_4$(s) (~1:10 by mass) into the effusion cells were performed in a drybox.

Table 1. Experimental Mass Spectrum of the Gas Phase over the MnF$_3$(s)−TbF$_4$(s) Mixture (Relative Abundances of the Ions)

temp, K	MnF$_4^+$	MnF$_3^+$	MnF$_2^+$	MnF$^+$	Mn$^+$
650	0.20	1	0.46	0.20	0.38
665	0.23	1	0.46	0.23	0.54
705	0.29	1	0.40	0.25	0.54
720	0.27	1	0.49	0.26	0.47
760	0.22	1	0.53	0.23	0.57
780	0.31	1	0.48	0.21	0.55
860		0.36	1	0.33	0.29
900		0.32	1	0.30	0.27

Nickel Knudsen effusion cells were used in our experiments. Preliminary fluorination of the cells was performed under the following conditions: $p(F_2) = 1$ atm, $T = 740$ K, $t = 15$ h. After fluorination a passivating layer of NiF$_2$(s) was formed on the surface of the cells, which prevented further loss of fluorine due to the reaction with the cell material.

(a) Mass Spectrometric Measurements. Mass spectrometric measurements were carried out with a magnetic mass spectrometer, model MI-1201, combined with a Knudsen cell. Details of the assembly and standard measurement procedures have been published elsewhere.[5] An effusion cell with an orifice/evaporation area ratio of 500 was used in the experiments. A movable shutter was installed in order to distinguish between the ions coming from the background gases and those originating from effusing species. Cell temperature was measured (±2 K) with a Pt−Pt/Rh thermocouple. The temperature scale was verified at the melting point of Ag.

Electron impact mass spectrometry conditions were as follows: electron ionization energy, 60 V; emission current, 0.4 mA; mass resolution, 700 (10% valley definition). Positive ions were accelerated to 2 keV and mass-analyzed in the magnetic field.

After the loading procedure, the system was evacuated and outgassed before the measurements. Background HF$^+$, H$_2$O$^+$, and O$_2^+$ signals were monitored during the entire course of the experiments. Their intensities initially increased with temperature and then progressively decreased in time; their shutterable profiles were those characteristic for the background signals.

The mixture of MnF$_3$ and TbF$_4$ was evaporated in the temperature range 650−900 K. Several repeated measurements were made at each temperature. All the detected ions were identified by mass-to-charge ratio (*m*/*e*) and their shutterable profiles. Atomic fluorine, F$_2$, and MnF$_4$ molecules were present in the gas phase. The MnF$_n^+$ ($n = 0-4$) ion intensities from MnF$_4$ were recorded as a function of temperature. Relative ion intensities of MnF$_n^+$ ($n = 0-4$) were constant in the temperature range 650−780 K.

Further temperature increase up to 860 K led to the decrease in the F$^+$ and F$_2^+$ intensities and the disappearance of the I(MnF$_4^+$) peak in the mass spectrum. At 860−900 K the mass spectrum was identical to that of pure MnF$_3$.[3] Experimental data are presented in Table 1.

According to the literature, TbF$_4$(s) cannot be evaporated without decomposition. Its decomposition accompanied by the elimination of fluorine takes place in the temperature range 600−800 K.[6] In our experiments the ratio of F$^+$ and F$_2^+$ signals detected during TbF$_4$ decomposition exceeded the value corresponding to the mass spectrum of the F$_2$ molecule. The conclusion of this work that an excessive

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Table 2. Individual Mass Spectrum of the MnF_4 Molecule (Relative Abundances of the Ions)

temp, K	U_{ion}, V	MnF_4^+	MnF_3^+	MnF_2^+	MnF^+	Mn^+	
650−780	60	0.25	1	0.47	0.23	0.51	our data
570−650	70	0.28	1	0.49	0.23	0.37	ref 3

amount of the F^+ ions originated from fluorine atoms is in the agreement with conclusions from our previous investigations.[7]

(b) FTIR Measurements. The apparatus consists of a cryotip (Displex, Air Products and Chemicals, 202 CSA) connected under rotary vacuum to a Bruker IFS 113v interferometer through a suitable IR-transparent window (CsI or polyethylene). The gold-plated coldfinger is allowed to rotate under high vacuum in a homemade stainless steel shroud equipped with a high-temperature furnace resistively heated. Details of the apparatus are described elsewhere.[8]

High-purity argon (Linde Gas Italia) was used as isolating gas with a flow rate of 1−1.5 mmol/h through a standardized needle valve. All samples were vaporized from Knudsen cells with orifices from 0.7 to 1.2 mm in diameter.

The vaporization temperature ranged from 600 to 1500 K for MnF_3, 650 to 1200 K for TbF_4, and 650 to 900 K for the MnF_3−TbF_4 mixture. Depositions lasted from 5 min to 1 h. For routine spectra 200 scans were accumulated with a resolution of 1 cm^{-1} or better.

Discussion

Mass Spectrometric Results. Manganese tetrafluoride was obtained according to the overall reaction

$$MnF_3(s) + TbF_4(s) = MnF_4(gas) + TbF_3(s) \qquad (1)$$

MnF_4 was the only manganese fluoride species present in the gas phase over the mixture at 650−780 K. In this temperature interval the vaporization of MnF_3 is negligible. The MnF_3-saturated vapor pressure [$P^0(MnF_3)$] is 2.2×10^{-10} and 5.9×10^{-8} atm at 700 and 800 K, respectively.[9] The individual mass spectrum of the MnF_4 molecule is presented in Table 2. The mass spectrum of MnF_4 obtained in our work is in good agreement with that obtained under different conditions and published in the literature.[3]

The ionization potential for the MnF_4 molecule, measured by us in a separate experiment using a Nuclide-Patco 12-60 magnetic mass spectrometer, was found to be 13.0 ± 0.7 eV, in excellent agreement with the value reported in ref 3.

It should be noted, however, that in our experiments MnF_4 was detected at much higher temperatures. The MnF_4-saturated vapor pressure [$P^0(MnF_4)$] was estimated by Ehlert[3] as $\sim 10^{-6}$ atm at 600 K. Other literature data[9] give $P^0(MnF_4) = 1.1 \times 10^{-5} - 2.8 \times 10^{-3}$ atm for 650−780 K. The MnF_4 vapor pressure [$P(MnF_4)$] determined in our work is 5.7×10^{-7} and 2.6×10^{-6} atm at 650 and 780 K, respectively. Therefore, one might conclude that under the conditions of our experiments the activity of MnF_4 was much less than unity; i.e., pure MnF_4(s) phase was not formed.

MnF_4 molecules were registered in the gas phase simultaneously with F_2 and F. After the disappearance of fluorine in the system, manganese tetrafluoride was no longer found. Atomic and molecular fluorine were products of the TbF_4 decomposition. It was shown in our previous studies[7] that TbF_4 can be used as a thermal generator of atomic fluorine and that the F atoms provide high oxidation ability of terbium tetrafluoride.

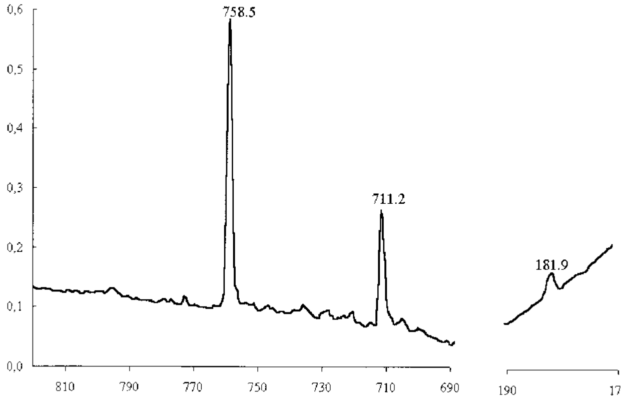

Figure 1. FTIR spectra of argon-isolated MnF_3 vaporized at 900 K.

To summarize, the optimum in situ conditions for the solid-phase synthesis of MnF_4(g) are the following: the mixture of initial MnF_3(s) and TbF_4(s) samples (~1:10 by mass), all the manipulations performed in a drybox, inert cell material, and temperature range 650−780 K.

FTIR Results. The spectroscopic investigation of the species present in the vapor over the MnF_3(s)−TbF_4(s) mixture required a preliminary study of both reactants in order to obtain blank spectra.

Trapping the vapor over TbF_4(s) at 650−900 K in excess argon, the matrix became less transparent, and no absorption peaks were detected, proving the purity of the sample. TbF_4 is known to decompose into TbF_3(s) and fluorine in the 600−800 K range.[7] In fact, when the temperature was increased to 1000 K, weak bands appeared at 550.8 and 523.0 cm^{-1} growing with the deposition temperature and they were assigned to TbF_3 according to the previous spectroscopic data.[10]

MnF_3 was carefully outgassed before deposition. On deposition of MnF_3 vaporized in the temperature range 900−1050 K, absorption peaks at 758.5 and 711.2 corresponding to Mn−F stretching modes and a peak at 181.9 cm^{-1} corresponding to F−Mn−F plane bending mode were observed (see Figure 1), in agreement with recent literature data.[11,12] The spectroscopic pattern suggests a planar C_{2v} symmetry structure for MnF_3 with two longer and a shorter Mn−F bond (Jahn−Teller effect). This geometry was recently supported by an electron diffraction analysis.[13] At a vaporization temperature over 1050 K a band appeared at 699.5 cm^{-1}, assigned to MnF_2 according to literature data.[14] Over 1200 K this was the only feature present in the spectra.

The MnF_3−TbF_4 mixture was vaporized in the 650−900 K temperature range. At 700 K, an intense band at 794.5 cm^{-1} and a weak doublet at 176.6/172.9 cm^{-1} were detected (see Figure 2 a). When the mixture was deposited at 830 K, Mn−F stretching modes of MnF_3 started to appear (see Figure 2b). On the grounds of mass spectrometric data and their behavior

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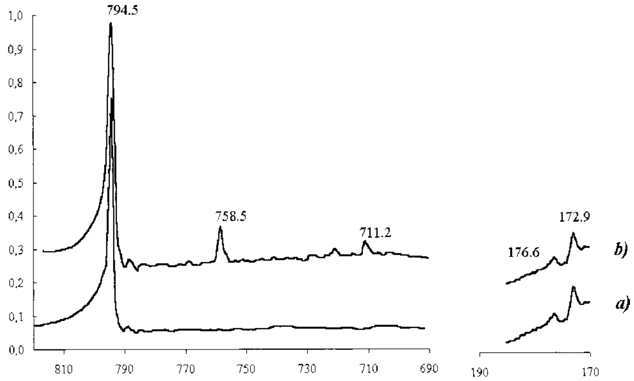

Figure 2. FTIR spectra of argon-isolated manganese fluorides: (a) MnF_4 obtained from the vaporization of the $MnF_3 + TbF_4$ mixture at 700 K; (b) MnF_4 and MnF_3 vaporized at 830 K over the same mixture.

with the vaporization temperature, the new features at 794.5 and 176.6/172.9 cm^{-1} could be attributed to the stretching and the bending modes of MnF_4, respectively. Moreover, this assignment is supported by coincidence by the ratio of Mn−F stretching modes of MnF_4 and MnF_3 obtained in this work to the corresponding modes observed in the case of CoF_4 and CoF_3.[1] A tetrahedral (T_d) or a square planar (D_{4h}) arrangement can be proposed for the MnF_4 molecule. Two infrared-active fundamentals are expected in the former symmetry and three in the latter one. On the grounds of the number of bands observed and their positions in the spectrum, the tetrahedral geometry is preferred for this molecule.

Osin et al.[11] speculated that a band absorbing at 768.7 cm^{-1} seems to correspond to the species richer in fluorine than to MnF_3 and MnF_2, which were produced in excess argon through the $Mn + F_2$ reaction. However, their suggestion that it might be MnF_4 was not confirmed by our data.

Conclusion

Knudsen cell mass spectrometry has been used to establish the optimum in situ conditions for the solid-phase synthesis of MnF_4(g) and to determine the vapor composition over the MnF_3(s)−TbF_4(s) mixture in the 650−900 K temperature range. MnF_4 has been obtained as the only gaseous manganese fluoride in the range 650−780 K. The same synthesis procedure was utilized to investigate the MnF_4 molecule by matrix isolation infrared spectroscopy. The infrared spectrum of argon-isolated MnF_4 molecules has been determined for the first time. The infrared pattern is in agreement with a T_d symmetry.

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