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Identification of Gaseous Cobalt Tetrafluoride: MS and FTIR Spectroscopic Studies

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The existence of gaseous CoF_4—a species with an unusually high degree of oxidation of the metal—has been demonstrated by means of Knudsen effusion mass spectrometry and FTIR spectroscopy. The Knudsen effusion mass spectrometry method has been applied to investigate the gas-phase composition over the $CoF_3(s)-TbF_4(s)$ system and to establish the optimum in situ conditions for CoF_4 synthesis. The electron impact mass spectrum of the CoF_4 molecule has been obtained. From the infrared spectrum of argon-isolated CoF_4 molecules, the Co−F stretching mode has been detected at 767.8 cm^{-1}.

Introduction

The existence of compounds with unusual valence states is of considerable scientific interest, because the achievement of unusual states of oxidation is connected to the theories of chemical valence and bonding. The theoretical and experimental aspects of this problem were discussed in the 1950s.[1] However, the synthesis and the investigation of compounds at the limits of thermodynamic stability are difficult to carry out without obtaining unambiguous results.

Synthesis of thermodynamically unstable fluorides in the solid state, such as NiF_4, NiF_3, and AgF_3, has been successfully performed.[2,3] The probable existence of unstable gaseous fluorides, with an unusually high degree of oxidation of the metal, was first predicted by Sidorov and Krasnov,[4,5] and indeed, CoF_4 was subsequently identified in the gas phase by mass spectrometry.[6,7]

$TbF_4(s)$ had been used to oxidize with $CoF_3(s)$, and $CoF_4(g)$ was found in small amounts[6] in $CoF_3(g)$ vapor at $T = 650-730$ K. Convincing evidence for the existence of $CoF_4(g)$ was provided by means of a fluorine admission technique.[7] In this technique, the interaction between atomic fluorine and the initial sample ($CoF_2(s)$) took place. However, CoF_4 was the only product of fluorination in a narrow temperature range of 620−640 K. Furthermore, the fluorine admission technique is difficult to combine with other methods, because relatively high concentrations of the aggressive gas may have a detrimental effect on the sensitive detectors of the instruments.

The aim of this research was to determine the optimum in situ conditions for the synthesis when cobalt tetrafluoride is the only product of fluorination so that other characterizational techniques could be applied with confidence. Solid-phase synthesis seemed to be best suited to this purpose. The $CoF_3(s)-TbF_4(s)$ system has been further investigated by mass spectrometry. Matrix isolation infrared spectroscopy has been applied to investigate cobalt tetrafluoride, and the first spectroscopic data on CoF_4 are presented here.

Experimental Methods

(a) Mass Spectrometric Measurements. Mass spectrometric measurements were carried out with a magnetic mass spectrometer combined with a Knudsen cell. Details of the apparatus and standard measurements procedure have been published elsewhere.[8] A nickel effusion cell with an orifice/evaporation area ratio of 500 was used for the experiments. Preliminary fluorination of the cell used the following conditions: $p(F_2) = 1$ atm, $T = 470$ C, $t = 10$ h. Cell temperature was measured (±2K) with a Pt−Pt/Rh thermocouple, which was verified at the melting point of Ag and KCl.

Electron impact mass spectrometry conditions were as follows: electron ionization energy 60 eV; emission current 0.3 mA; mass resolution 500 (10% valley definition). Positive ions were accelerated to 2 keV and mass analyzed in the magnetic field.

CoF_3 and CoF_2 (>97% purity) were supplied by Aldrich Chemical Co. TbF_4 was prepared according to the ref 9. X-ray powder diffraction analysis showed 95% purity for the TbF_4 sample. It should be pointed out that the fluorinating ability of TbF_4 depends heavily on its quality, and it can be significantly reduced by traces of water.

All samples were extensively outgassed in the instrument before the experiments. The mixture of CoF_3 and TbF_4 samples (∼1:10 by mass) was loaded into the prefluorinated nickel effusion cell in a drybox and evaporated in the temperature range 620−720 K. Two experimental runs were performed. All detected ions were identified by mass-to-charge ratio (m/e) and their shutterable profiles. CoF_n^+ ($n = 0-4$) ions were present in the mass spectrum for approximately 50 h in each run, and their intensities were recorded as a function of temperature. Relative

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(1) Kleinberg, J. *Unfamiliar Oxidation States and their Stabilization*, University of Kansas Publ.: Lawrence, 1950.

(2) Zemva, B.; Lutar, K.; Jesih, A.; Casteel, Jr.; Wilkinson, A. P.; Cox, D. E.; Von Dreele, R. B.; Borrmann, H.; Bartlett, N. *J. Am. Chem. Soc.* **1991**, *113*, 4192−4198.

(3) Zemva, B.; Lutar, K.; Chacon, L.; Fele-Beuermann, M.; Allman, J.; Shen, C.; Bartlett, N. *J. Am. Chem. Soc.* **1995**, *117*, 10025−10034.

(4) Sidorov, L. N. *Russ. J. Coord. Chem. Translated from Zh. Koordin. Khim.* **1977**, *3*, 1128−1139.

(5) Krasnov, K. S. *Russ. J. Phys. Chem. Translated from Zh. Fiz. Khim.* **1977**, *51*, N8, 3027−3031.

(6) Korobov, M. V.; Savinova, L. N.; Sidorov, L. N. *J. Chem. Thermodyn.* **1993**, *25*, 1161−1168.

(7) Chilingarov, N. S.; Skokan, E. V.; Rau, J. V.; Sidorov, L. N. *Russ. J. Phys. Chem. Translated from Zh. Fiz. Khim.* **1992**, *66* (10), 1389−1393.

(8) Sidorov, L. N. *High Temp. Sci.* **1990**, *29*, 153−170.

(9) Cunninghem, B. B.; Feay, D. C.; Rollier, M. A. *J. Am. Chem. Soc.* **1954**, *76* (13), 3361−3363.

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Table 1. Experimental Gas Phase Mass Spectrum (Relative Abundances of the Ions) over the $CoF_3(s) + TbF_4(s)$ System

T, K	*t*, h	CoF_4^+	CoF_3^+	CoF_2^+	CoF^+	Co^+
620	19	0.26	0.54	1	0.28	0.35
645	30	0.23	0.57	1	0.22	0.32
660	24	0.22	0.55	1	0.23	0.36
670	23	0.26	0.56	1	0.28	0.31
700	2	0.19	0.51	1	0.23	0.28
706	0.5	0.13	0.50	1	0.20	0.32
720	1.5		0.27	1	0.20	0.23

ion intensities of CoF_n^+ ($n = 0-4$) were constant in the temperature range 620−700 K. The $I(CoF_4^+) = I(m/e\ 135^+)$ peak was identified unambiguously. It was shutterable while the neighboring $I(m/e\ 134^+)$ and $I(m/e\ 136^+)$ peaks were not. The $I(CoF_4^+) = I(m/e\ 135^+)$ peak increased with the increase of temperature within the range of 620−700 K.

Further temperature increase up to 720 K led to the disappearance of the $I(CoF_4^+)$ peak in the mass spectrum. At $T = 720$ K the mass spectrum was identical to that of CoF_3.[10] TbF_n^+ ($n = 0-4$) ions that originated from TbF_4 and TbF_3 molecules were not registered under our experimental conditions. Experimental data are presented in Table 1.

(b) FTIR Measurements. The apparatus basically consists of a cryotip (Displex, Air Products and Chemicals 202 CSA) connected under a rotary vacuum to a Bruker IFS 113v interferometer through a suitable IR-transparent window (CsI or polyethylene). The gold-plated copper finger is free to rotate in a homemade shroud under high vacuum. Details of the assembly are described elsewhere.[11]

High-purity argon (Caracciolo) was used as isolating gas with a flow rate of 1−1.5 mmol/h through a standardized needle valve. Spectra of cobalt di- and trifluoride suspended in nitrogen (ultragrade, Caracciolo) were also obtained, but argon was preferred for its better transparency in the far-infrared.

All samples were vaporized from nickel Knudsen cells with effusion orifices from 0.7 to 1.2 mm in diameter. The vaporization temperature ranged from 900 to 1500 K for CoF_2, 600 to 1500 K for CoF_3, and 500 to 800 K for TbF_4 and for CoF_3 and TbF_4 mixtures. Depositions lasted from 5 min to 1 h. Spectra were taken in reflection, accumulating at least 200 scans at a resolution of 1 cm^{-1} or better.

Results and Discussion

Mass Spectrometric Determination of CoF_4(gas). Synthesis Conditions. The $CoF_3(s)-TbF_4(s)$ mixture was examined in our work in the temperature range 620−720 K. The distribution of ion intensities CoF_n^+ ($n = 0-4$) remained constant for a long time at $T = 620-700$ K (see Table 1). The intensities increased with the increase of temperature. The question is whether only CoF_4 or the mixture (CoF_4 and CoF_3) is present in the gas phase under our experimental conditions. According to literature data,[10,12,13] the CoF_3-saturated vapor pressure $[P^0(CoF_3)]$ is $\sim 3 \times 10^{-8}$ atm at 620 K. This value is below the sensitivity limit of our instrument. Therefore, all the measured ion intensities at 620 K might be attributed to the CoF_4 molecule. Furthermore, there is a 2 orders of magnitude increase in $P^0(CoF_3)$ in the range 620−700 K.[10,12,13] In this connection and taking into account the CoF_3 mass spectrum,[10] a decrease in the CoF_4^+/CoF_2^+ ratio was expected due to the anticipated appearance of a measured amount of CoF_3 in the vapor. However, no changes were observed in our mass spectrum up to 700 K (see Table 1). This may be a consequence of the activity of CoF_3 being much less than unity in the $CoF_3(s)-TbF_4(s)$ system (the CoF_3:TbF_4 ratio in the mixture was approximately 1:10). Therefore, one may conclude that under our experimental conditions CoF_4 is the only component of the gaseous product mixture in the temperature range 620−700 K. The CoF_4 partial pressure $[P(CoF_4)]$ lies in the range between 2.8×10^{-7} and 3.2×10^{-6} atm at 620−700 K. Our results for the individual mass spectrum of the CoF_4 molecule are the following (the relative abundances of the ions are given in parentheses): CoF_4^+ (0.2), CoF_3^+ (0.5), CoF_2^+ (1.0), CoF^+ (0.3), Co^+ (0.3).

There are differences between the present results and those reported elsewhere[6] for the same system $[CoF_3(s)-TbF_4(s)]$. The previous authors[6] reported a short lasting measurement of low concentration of $CoF_4(g)$ compared to $CoF_3(g)$. A reason for their less efficient fluorination could be the presence of water and the lower ratio of CoF_3 to TbF_4 in their mixture. Both $CoF_3(s)$ and $TbF_4(s)$ are destroyed by water. They quickly adsorb water at room temperature, and then hydrolyze as the temperature is increased.

FTIR Study of Argon-Isolated Cobalt Fluorides. (a) Cobalt Di- and Trifluorides. Cobalt trifluoride has been vaporized in a wide range of temperatures in order to characterize the spectral changes connected to the possible variation in the vapor composition with temperature. Since the vaporization process of CoF_3 involves also its decomposition to CoF_2,[10,13] a reinvestigation of CoF_2 with our apparatus was also required.

In our spectra the infrared fundamental modes of CoF_2 (ν_3 and ν_2) (Figure 1 a) have been detected at 722.5 and 150.8/148.9 cm^{-1}, respectively, in good agreement with literature data.[14,15] The absence of the symmetric stretching mode (ν_1) in the infrared, detected at 587 cm^{-1} in the Raman,[16] suggests a linear molecule. However, the quasilinear geometry, inferred from electron diffraction measurements, cannot be excluded owing to the low infrared intensity expected for the ν_1 mode.[17,18] An additional feature was observed at 706.3 cm^{-1} growing with deposition temperature likely faster than fundamental ones. This peak should correspond to the feature at 707.5 cm^{-1} tentatively assigned previously to dimeric or aggregate forms.[15] Even though mass spectrometric data[19] do not indicate the presence of a detectable amounts of dimeric CoF_2, its formation in the matrix cannot be excluded.

Recent investigations[10,13] of the vapor composition over cobalt trifluoride showed CoF_3 to be the main component in the 700−830 K temperature interval. The presence of a dimeric form (Co_2F_6) in the gas phase has also been proved in a recent mass spectrometric investigation.[20]

Fundamental bands of CoF_3 were detected in the FTIR spectra over cobalt trifluoride vaporized below 900 K (Figure 1 b). Above 900 K CoF_2 appeared in the matrix and increased with

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(10) Rau, J. V.; Chilingarov, N. S.; Sidorov, L. N. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1977−1979.

(11) Feltrin, A.; Guidi, M.; Nunziante Cesaro, S. *J. Phys. Chem.* **1992**, *97*, 8986−8989.

(12) IVTANTHERMO. Database on thermodynamic properties of individual substances. Developed in THERMOCENTER of the Russian Academy of Science. CRC Press: Boca Raton, 1993.

(13) Balducci, G.; Brunetti, B.; Piacente, V. *J. Alloys Compds.* **1997**, *260*, 56−58.

(14) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *J. Chem. Soc. D.* **1969**, 1452−1453.

(15) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.* **1969**, *1*, 76−85.

(16) Buchmarina, V. N.; Gerasimov, A. Yu.; Predtechenskii, Yu. B.; Shklyarik, V. G. *Optik. Spektrosc.* **1988**, *65*, 876−881.

(17) Girichev, G. V.; Subbotina, N. Yu.; Krasnov, K. S.; Ostropikov, V. V. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. (Russian)* **1985**, *28*, 12−16.

(18) Spiridonov, V. P.; Gershikov, A. G.; Lyutsarev, V. S. *J. Mol. Struct.* **1990**, *221*, 79−94.

(19) Kana'an, A. S.; Besenbruch, G.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1035−1037.

(20) Rau, J. V.; Chilingarov, N. S.; Sidorov, L. N. *14th International Mass Spectrometry Conference*, 25−29 August, Tampere, Finland, 1997, 64.

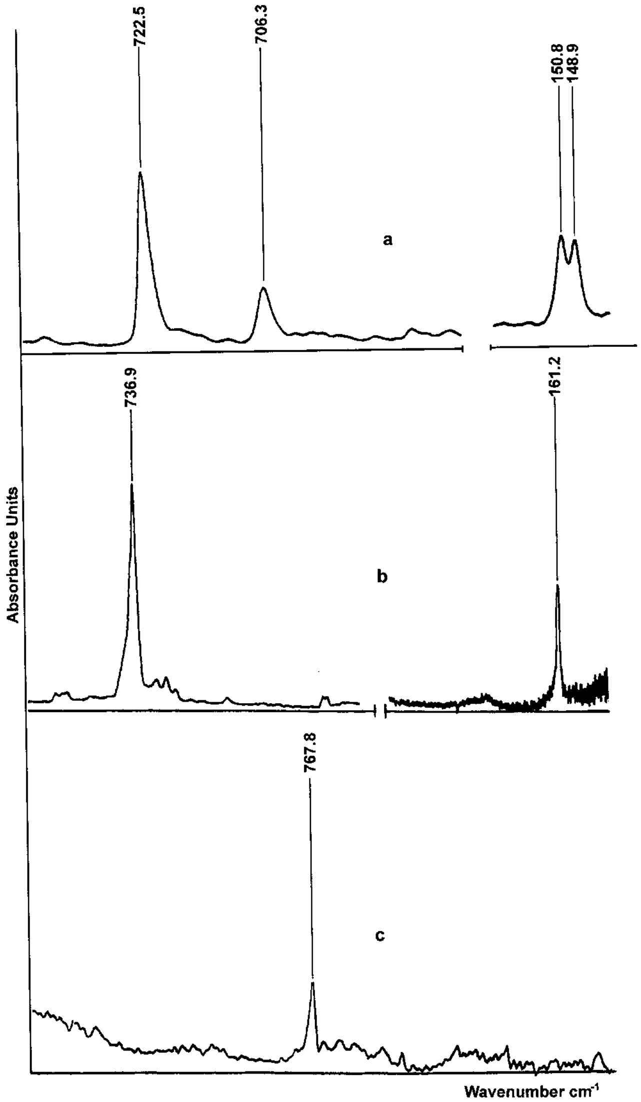

Figure 1. FTIR spectra of argon-isolated cobalt fluorides: (a) CoF_2 vaporized at 1000 K; (b) CoF_3 vaporized at 800 K; (c) CoF_4 obtained from the vaporization at 650 K of the CoF_3−TbF_4 mixture.

the vaporization temperature. From 1050 K on, it was the only species detected.

On deposition of CoF_3 in the 700−800 K range of temperature, a sharp band was observed at 736.9 and a medium one at 161.2 cm^{-1}, in agreement with literature data[21,22] and theoretical suggestions.[23] Electron diffraction measurements[24] have suggested a planar D_{3h} geometry for this molecule, supported by the lack of ν_1 in the infrared. Vaporization above 830 K led to the appearance of a weak band at 747.4 cm^{-1} and a medium intensity doublet at 728.7/724.9 cm^{-1}, which gained intensity with the vaporization temperature and therefore have been attributed to a dimeric form (Co_2F_6).

Observed vibrational levels are exactly reproduced by the following force constants (in mdyn/A): $F_r = 4.28$, $F_{rr} = 0.214$, $F_a = 0.27$, $F_{aa} = 0.2$, $F_{op} = 0.023$.

(b) $CoF_3(s)$−$TbF_4(s)$ Mixture. Vaporization of pure $TbF_4(s)$ was performed in the temperature range 300−1300 K, in order to obtain blank spectra. No bands were observed below 1000 K as expected. For higher temperatures, weak bands appeared at 550.8 and 523.0 cm^{-1}, indicating the presence of TbF_3 traces in the matrix, in agreement with literature data.[25]

Vaporization of the $CoF_3(s)$−$TbF_4(s)$ system was carried on in the 400−750 K range of temperature in order to reproduce the experimental conditions of the CoF_4 synthesis in situ in the mass spectrometric study described above. At 600 K a new band at 767.8 cm^{-1} was observed on deposition, which slowly gained intensity up to 700 K (Figure 1c). This new band is attributable to CoF_4 on the basis of our mass spectrometric measurements. Its spectral position reasonably supports this attribution. Since no other vibrational features could be confidently assigned to CoF_4, conclusions concerning the molecular geometry cannot be drawn. Any attempt to obtain a higher concentration of CoF_4 in the argon environment, with long-lasting depositions, unfortunately failed because of the deterioration of the transparency of the matrix.

It is necessary to note that CoF_3 bands were missing in our FTIR spectra of the $CoF_3(s)$−$TbF_4(s)$ mixture at 650 K (Figure 1c). This is in line with the conclusion of mass spectrometric experiments that CoF_4 was the only component of the gaseous product mixture at 620−700 K.

Conclusion

The results of this research demonstrate that gaseous cobalt tetrafluoride can be produced in sufficient amounts [$P(CoF_4) = (2.8 \times 10^{-7})-(3.2 \times 10^{-6})$ atm at 620−700 K] over the $CoF_3(s)$−$TbF_4(s)$ system. The solid-phase synthesis in situ procedure was utilized to investigate the CoF_4 molecule by Knudsen effusion mass spectrometry and matrix isolation infrared spectroscopy. The individual electron impact mass spectrum and the infrared spectrum of argon-isolated CoF_4 molecules were determined. The described synthesis procedure can be applied for further experimentation in order to investigate CoF_4 by other spectroscopic methods, for example, Raman spectroscopy and high-temperature gas electron diffraction, which could provide more information about the geometry and other characteristics of this molecule.

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(21) Davlyatshin, D. I.; Osin, S. B.; Shevel′kov, V. F. *Trudy V Vsesojuz. Sovešhan. po izuchen. structury molecul v gas. fase* (V meeting dedicated to the investigation of the molecular structure in the gas phase). Ivanovo, Russia, 1990, 60−65.

(22) Buchmarina, V. N.; Gerasimov, A. Yu.; Predtechenskii, Yu. B. *Vibrational Spectrosc.* **1992**, *4*, 91−94.

(23) Yates, J. H. and Pitzer, R. M. *J. Chem. Phys.* **1979**, *70*, 4049−4055.

(24) Girichev, G. V.; Giricheva, N. I.; Krasnova, O. G.; Krasnov, A. V.; Shlykov, S. A.; Rakov, E. G. and Khaustov, S. V. *Zh. Strukt. Khim.* **1992**, *33*, 84−90.

(25) Hauge, R. H.; Hastie, J. W. and Margrave, J. L. *J. Less-Common Met.* **1971**, *23*, 359−365.