Inorganica Chimica Acta, 64 (1982) L209–L210

Hepta-, Hexa- and Quinquevalent Rhenium Chalcogenide Fluorides: the Preparation and Characterization of ReF_5S, ReF_4S and ReF_3S

JOHN H. HOLLOWAY, DAVID C. PUDDICK, GARRY M. STAUNTON

Department of Chemistry, The University of Leicester, Leicester, LE1 7RH, U.K.

and DAVID BROWN

Chemistry Division, A.E.R.E. Harwell, Didcot, Oxfordshire OX11 0RA, U.K.

Received December 19, 1981

Several chalcogenide fluorides have been prepared [1, 2] and isolated [2] for the heavier metals of Group VIb of the Periodic Table. Apart from MoF_3S [3], they all contain the metal in oxidation state VI and have the general formula MF_4Y (M = Mo, W; Y = S, Se). We now report the preparation and isolation of the first thiofluorides of a Group VIIb metal, ReF_5S, ReF_4S and ReF_3S, in which the metal oxidation state ranges from VII to V.

Experimental

Rhenium heptafluoride was prepared by heating rhenium powder (99.9%; BDH) with an excess of fluorine [4]. The hexafluoride was prepared by the direct fluorination of a slight excess of rhenium powder [5]. Rhenium pentafluoride was obtained by reduction of ReF_6 with silicon in anhydrous hydrogen fluoride [6]. Commercial samples of Sb_2S_3 (Technical Grade; BDH) and B_2S_3 (99%; Ventron) were degassed and used without further purification. Anhydrous hydrogen fluoride (99.5%; I.C.I. Ltd.) was purified further by fluorination and distillation.

Thermal reactions were carried out in spun nickel-tube reactors attached to stainless-steel valves (Autoclave Engineers) via a nickel head sealed with gold rings. Solution reactions were carried out in ¼" o.d. FEP tubes fitted with Teflon 'Chemcon' (Production Techniques) valves.

Mass spectra and X-ray powder diffraction measurements were obtained as described previously [7]. Infrared spectra were recorded with a Perkin-Elmer 580 spectrophotometer using the powdered solids pressed between KBr plates.

Results and Discussion

The compounds ReF_5S, ReF_4S and ReF_3S are prepared by the reaction of an excess of the appropriate rhenium fluoride with either Sb_2S_3 (eqn. 1) or B_2S_3 (eqn. 2).

$$3ReF_x + Sb_2S_3 \rightarrow 3ReF_{x-2}S + 2SbF_3 \qquad (1)$$

$$(x = 5, 6, 7)$$

$$3ReF_x + B_2S_3 \rightarrow 3ReF_{x-2}S + 2BF_3 \qquad (2)$$

$$(x = 6, 7)$$

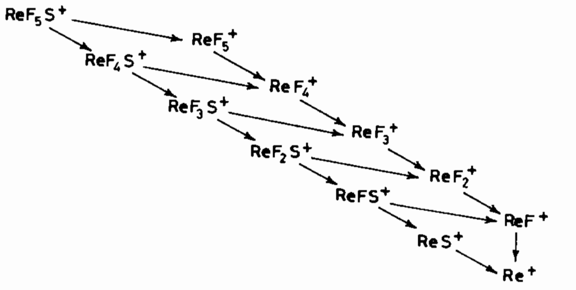
For ReF_5S and ReF_4S the preparations involve heating ReF_7 and ReF_6, respectively, with Sb_2S_3 or B_2S_3 in a nickel reactor at 300 °C, or reaction of Sb_2S_3 with the appropriate fluoride in anhydrous hydrogen fluoride. The quinquevalent compound cannot be prepared by thermal means since, at temperatures greater than 140 °C, ReF_5 disproportionates [8] and, at temperatures below this, in the absence of solvent, reaction with B_2S_3 or Sb_2S_3 does not take place. However, reaction of Sb_2S_3 with ReF_5 in anhydrous hydrogen fluoride occurs at room temperature.

Freshly prepared ReF_5S is a maroon solid, ReF_4S is red and ReF_3S is yellow. All three are exceedingly sensitive to traces of moisture and/or oxygen and deteriorate quickly even when handled in a dry nitrogen atmosphere (O_2, ~5 p.p.m.; H_2O, ~1 p.p.m.). The decomposition of ReF_3S is so rapid that unambiguous characterization is difficult. The slowest to decompose is ReF_4S yielding first a brown and then a black solid. When exposed to a moist atmosphere all three hydrolyse rapidly with evolution of H_2S and HF.

The mass spectra of the three compounds are related. The spectrum of ReF_5S shows the expected splitting pattern (Table I) together with peaks attributable to oxides and oxide fluorides of rhenium. The oxygen-containing species are presumably produced during the introduction of the sample to the mass spectrometer as well as being formed by the reactions of ReF_7 with oxide impurities in the other reactants. The spectrum of ReF_4S gain exhibits the expected patterns but the extent of contamination by oxygen species is less than in ReF_5S or ReF_3S, which is indicative of the relative stability of the hexavalent compound. In the case of ReF_3S, oxide and oxidefluoride species predominate, the isotopic abundance pattern for the parent ion, ReF_3S^+, is not observed and the most abundant rhenium-sulphur species in the spectrum is ReF_2S^+. This,

0020-1693/1982/0000-0000/$02.75

TABLE I. Observed Mass Spectrometric Splitting Pattern of ReF_5S.



along with the preparative and hydrolysis observations, is indicative of the low stability and high reactivity of the quinquevalent species. It is interesting to note, however, that disproportionation of ReF_3S is likely to produce either ReF_4S or ReF_6 and the absence of both in the mass spectrum of the yellow product suggests that, in solution in anhydrous HF, ReF_3S is stable.

The X-ray powder diffraction patterns of ReF_5S and ReF_4S confirm that they are structurally different and that they do not contain ReF_5. Comparison of the ReF_4S data with those of related species shows that it is not isostructural with ReF_4O, WF_4S or MoF_4S although the pattern resembles that of the last.

The main features of the infrared spectra of ReF_5S and ReF_4S include peaks in the regions associated with ν(Re–F) terminal and ν(Re···F) bridging in addition to bands which are tentatively assigned to ν(Re=S) (Table II). The peak at 583 cm^{-1} in the ReF_4S spectrum is close to the value for ν(Re=S) postulated for $ReCl_4S$ [11]. The results imply that both ReF_4S and ReF_5S are fluorine bridged polymers. In the case of ReF_4S the peaks are shifted by an average of 20 cm^{-1} from the corresponding peaks in ReF_4O [10] and this close similarity suggests that, in the solid state, ReF_4S may well have a structure related to the fluorine-bridged chain arrangement found in ReF_4O [12]. In the spectrum of ReF_5S the presence of small quantities of ReF_5O is indicated by a small peak at 960 cm^{-1} but, in the case of ReF_4S, ReF_4O is only a trace contaminant. In all samples where Sb_2S_3 has been used as a reactant the product contains SbF_3, the presence of which is indicated by an infrared band at 600 cm^{-1} [13]. Because of the extreme reactivity of ReF_3S, satisfactory infrared and X-ray diffraction data have, so far, not been obtained.

Acknowledgement

We thank Mr. P. R. Harrison for experimental assistance with part of this work.

TABLE II. Main Bands (cm^{-1}) in the Infrared Spectra of ReF_5S and ReF_4S Compared with those for Related Species.

ReF_5S	ReF_5O^a	ReF_4S	ReF_4O^b	Assignment
	998 990.8 984		1070	ν(Re=O)
695 670 664	747 737.7	705 698 657	680	$\nu(Re{-}F)_{sym}$
658 644 600	651 643 635	648 625	655	$\nu(Re{-}F)_{asym}$
562		583		ν(Re=S)
550 529		544 532	570 540	ν(Re····F)

[a] Data taken from the vapour phase spectrum; see Ref. 9. [b] See Ref. 10.

References

1 D. L. Hildenbrand, U.S. Nav. Tech. Inform. Serv., R. D. Rep. No. 757231, 1972;
Y. A. Buslaev, Y. V. Kokunov and Y. D. Chubar, *Dokl. Akad. Nauk SSSR, 213,* 912 (1973);
Y. V. Kokunov, Y. D.Chubar, V. A. Bochkareva and Y. A. Buslaev, *Koord. Khim., 1,* 1100 (1975);
Y. V. Kokunov, Y. D. Chubar, A. V. Kopytin and Y. A. Buslaev; *ibid., 2,* 796 (1976);
Y. V. Kokunov, Y. D. Chubar and Y. A. Buslaev, *Ibid.,* p. 1227;
Y. A. Buslaev, Y. V. Kokunov, M. P. Gustyakova, Y. D. Chubar and I. I. Moiseev, *Dokl. Akad. Nauk SSSR, 233,* 357 (1977).

2 M. J. Atherton and J. H. Holloway, *J. Chem. Soc., Chem. Commun.,* 424 (1977);
M. J. Atherton and J. H. Holloway, *Inorg. Nucl. Chem. Lett., 14,* 121 (1978);
J. H. Holloway and D. C. Puddick, *ibid., 15,* 85 (1979).

3 V. S. Perov, V. D. Butskii and L. G. Podzolko, *Russ. J. Inorg. Chem., (Engl. Transl.), 23,* 819 (1978).

4 J. G. Malm and H. Selig, *J. Inorg. Nucl. Chem., 20,* 198 (1961).

5 J. G. Malm and H. Selig, *J. Inorg. Nucl. Chem., 20,* 189 (1961).

6 R. T. Paine and L. B. Asprey, *Inorg. Synth., 19,* 137 (1979).

7 J. Fawcett, J. H. Holloway and D. R. Russell, *J. Chem. Soc., Dalton Trans.,* 1212 (1981).

8 R. D. Peacock, in Advances in Fluorine Chemistry, Vol. 7, Eds. J. C. Tatlow, R. D. Peacock and H. H. Hyman, Butterworths, London, 1973.

9 J. H. Holloway, H. Selig and H. H. Claassen, *J. Chem. Phys., 54,* 4305 (1971).

10 R. T. Paine, K. L. Treuil and F. E. Stafford, *Spectrochim. Acta, Part A, 29A,* 1891 (1973).

11 D. A. Rice, *Coord. Chem. Rev., 25,* 199 (1978).

12 A. J. Edwards, G. R. Jones and B. R. Steventon, *J. Chem. Soc., Chem. Commun.,* 462 (1967).

13 Yu. Ya. Kharitonov, R. L. Davidovich, V. I. Kostin, L. A. Zemnukhova and V. I. Sergienko, *Russ. J. Inorg. Chem. (Engl. Transl.), 17,* 682 (1972).