Journal of Fluorine Chemistry, *49* (1990) 167–169

Received: December 13, 1989; accepted: March 12, 1990

NEW SYNTHESIS OF IF_5O

C.J. SCHACK AND K.O. CHRISTE*

Rocketdyne, A Division of Rockwell International, Canoga Park, CA 91303 (USA)

SUMMARY

Phosphorus trifluoride oxide readily replaces two fluorine ligands in IF_7 for a doubly bonded oxygen atom, thereby providing a new and convenient synthesis for IF_5O. Attempts to extend this method to the syntheses of either IF_3O_2 or IFO_3 were unsuccessful due to competing deoxygenation reactions of the iodine oxyfluoride precursors. Furthermore, PF_3O does not undergo fluorine-oxygen exchange with the NF_4^+ cation.

INTRODUCTION

Recent work from our laboratory on fluorine-oxygen exchange reactions has shown that the nitrate ion is an excellent reagent for replacing two fluorine ligands by one doubly bonded oxygen atom in compounds such as BrF_5 [1, 2], XeF_6 [3], $XeOF_4$ [4], ClF_5, ClF_3 and ClF [5], and IF_5 [6]. However, IF_7 did not yield IF_5O but resulted in the formation of IF_5 and half a mol of oxygen [6]. This was unexpected since IF_7 is known to undergo fluorine-oxygen exchange with either silica at 100°C [7] or Cab-O-Sil [8], Pyrex [9, 10], I_2O_5 [10] or small amounts of water [9, 10] at ambient temperature. Recently, it was shown that PF_3O is also an effective reagent for accomplishing fluorine-oxygen exchange in XeF_6, UF_6, ClF_5, and BrF_5 [11]. It was, therefore, interesting to examine whether IF_7 and PF_3O undergo a fluorine-oxygen exchange reaction or are subject to deoxygenation as in the IF_7-NO_3^- case [6].

EXPERIMENTAL

Volatile materials were handled in a stainless steel vacuum line equipped with Teflon-FEP U-traps, stainless steel bellows-seal valves, and a Heise Bourdon tube-type gauge [12].

0022-1139/90/$3.50

All reactions were carried out either in stainless steel containers or sapphire tubes. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrometer using a 5-cm path length Teflon cell with AgCl windows for gases, and AgCl disks, pressed in an Econo press (Barnes Engineering Co.), for solids. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. Literature methods were used for the syntheses of IF_7 [8], PF_3O [13], IF_3O_2 [14], and NF_4BF_4 [15].

Synthesis of IF_5O

A 30 ml stainless steel cylinder was passivated first with ClF_3 and then with PF_3O. After evacuation and cooling to -196°C, the cylinder was loaded successively with IF_7 (1.04 mmol) and PF_3O (1.10 mmol) and allowed to warm to room temperature. After five days the volatile products were removed and separated by fractional condensation in U-traps cooled to -78, -126, and -196°C. Only a small amount of non-condensable gas was observed, presumably O_2. The -196°C trap contained PF_5 (1.03 mmol) and PF_3O (0.07 mmol). The -78°C trap contained IF_5 (0.08 mmol), while the -126°C trap contained IF_5O (0.91 mmol, 88% yield based on IF_7).

RESULTS AND DISCUSSION

Iodine heptafluoride and PF_3O readily undergo a fluorine-oxygen exchange reaction according to:

$$IF_7 + PF_3O \rightarrow IF_5O + PF_5$$

The reaction proceeds at room temperature and produces IF_5O in a yield of about 90%. In addition to IF_5O, small amounts of IF_5 and oxygen are formed due to some decomposition of IF_5O. Use of an excess of PF_3O does not result in further fluorine-oxygen exchange and the formation of either IF_3O_2 or FIO_3. This was confirmed by an examination of the IF_5O-PF_3O and the IF_3O_2-PF_3O systems. At room temperature, no fluorine-oxygen exchange was observed, while at elevated temperatures the iodine oxyfluoride starting materials underwent deoxygenation rather than fluorine-oxygen exchange with PF_3O.

Attempts to achieve fluorine-oxygen exchange in NF_4BF_4 with PF_3O did not produce any NF_3O. Instead, the NF_4BF_4 fluorinated the PF_3O to PF_5 and oxygen, followed by a partial displacement reaction of BF_4^- by PF_5.

$$NF_4BF_4 + PF_3O \rightarrow NF_3 + BF_3 + PF_5 + 0.5\,O_2$$

$$NF_4BF_4 + PF_5 \rightarrow NF_4PF_6 + BF_3$$

This result is not surprising in view of the previous findings that (+V) nitrogen exhibits a maximum coordination number of four toward fluorine [16] and PF_5 can displace BF_3 from NF_4BF_4 [17].

ACKNOWLEDGMENTS

The authors wish to thank Mr. R.D. Wilson and Dr. W.W. Wilson for their help, Dr. G.J. Schrobilgen for a sample of IF_3O_2 and the U.S. Army Research Office for financial support of the work at Rocketdyne.

REFERENCES

1 W. W. Wilson and K. O. Christe, Inorg. Chem., 26 (1987) 916.
2 W. W. Wilson and K. O. Christe, Inorg. Chem., 26 (1987) 1573.
3 K. O. Christe and W. W. Wilson, Inorg. Chem., 27 (1988) 1296.
4 K. O. Christe and W. W. Wilson, Inorg. Chem., 27 (1988) 3763.
5 K. O. Christe and W. W. Wilson, Inorg. Chem., 28 (1989) 675.
6 K. O. Christe, W. W. Wilson and R. D. Wilson, Inorg. Chem., 28 (1989) 904.
7 R. J. Gillespie and J. W. Quail, Proc. Chem. Soc., (1963) 278.
8 C. J. Schack, D. Pilipovich, S. N. Cohz, and D. F. Sheehan, J. Phys. Chem., 72 (1968) 4697.
9 L. G. Alexakos, C. D. Cornwell and S. B. Pierce, Proc. Chem. Soc., (1963) 341.
10 N. Bartlett and L. E. Levchuk, Proc. Chem. Soc., (1963) 342.
11 S. A. Kinkead and J. B. Nielsen, Paper 47 presented at the ACS Ninth Winter Fluorine Conference, St. Petersburg, FL (February, 1989).
12 K. O. Christe, R. D. Wilson, and C. J. Schack, Inorg. Synth., 24 (1986) 3.
13 W. Kwasnik in 'Handbook of Preparative Inorganic Chemistry,' 1 (1963) 193 (G. Brauer, Editor).
14 R. G. Syvret, Ph.D. Thesis, McMaster University (1987).
15 K. O. Christe, W. W. Wilson, C. J. Schack and R. D. Wilson, Inorg. Synth., 24 (1986) 39.
16 K. O. Christe, W. W. Wilson, G. J. Schrobilgen, R. V. Chirakal and G. A. Olah, Inorg.. Chem., 27 (1988) 879.
17 K. O. Christe, C. J. Schack and R. D. Wilson, Inorg. Chem., 15 (1976) 1275.