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Chlorine Trifluoride Dioxide, ClF_3O_2. Synthesis and Properties

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Chlorine trifluoride dioxide was prepared from FNO_2 and $ClF_2O_2^+PtF_6^-$, the latter being synthesized from $FClO_2$ and PtF_6. Physical properties and the ^{19}F nmr spectrum are reported. The nmr spectrum suggests the trigonal-bipyramidal structure I of symmetry C_{2v}. Chlorine trifluoride dioxide forms stable adducts with BF_3 and AsF_5 but not with FNO, FNO_2, or CsF.

Introduction

A brief note on the existence of ClF_3O_2 has recently been published by Christe.[1] In this paper we report details on its synthesis, purification, and properties. The infrared spectra of the gas, the solid, and the matrix-isolated species and the Raman spectra of the gas and the liquid together with a normal coordinate analysis and computation of thermodynamic properties will be published elsewhere.[2]

Experimental Section

Materials and Apparatus. The stainless steel Teflon FEP vacuum system,[3] the glove box, the ^{19}F nmr spectrometer and sampling technique,[4] and the syntheses and purification of PtF_6, $FClO_2$, FNO,[3] FNO_2, BF_3, and $ClF_2O_2^+BF_4^-$ [5] are described elsewhere. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. All equipment was passivated with ClF_3 and BrF_5 prior to its use.

Purification of ClF_3O_2. A sample of $ClF_2O_2^+BF_4^-$ (2.41 mmol), prepared and purified as previously reported,[5] was placed in a passivated Teflon FEP ampoule. Nitryl fluoride (6.83 mmol) was added at −196° and the mixture was kept at −78° for 12 hr with periodic agitation. Volatile products were removed at −78° and separated by fractional condensation through a series of traps kept at −95, −126, and −196°. The −95° trap contained only a very small amount of material which was discarded. The −126° trap contained 2.22 mmol of ClF_3O_2 which according to its infrared spectrum[2] at 700 mm of pressure showed as the only detectable impurity less than 0.1 mol % of $FClO_2$. This sample was used for the subsequent characterization studies. The −196° trap contained the unreacted FNO_2 (4.4 mmol) and a small amount of ClF_3O_2 (0.2 mmol). The solid residue was shown by its weight and infrared spectrum to be $NO_2^+BF_4^-$.

ClF_3O_2-CsF System. Two reactions between ClF_3O_2 (1.5 mmol) and CsF (1.0 mmol) were carried out in 10-ml stainless steel cylinders at 25 and 105°, respectively. At the lower temperature the cylinder was placed on a mechanical shaker for 5 days. The volatile material consisted of F_2, $FClO_2$, and some ClF_3O_2. The solid residue had gained 33 mg in weight and was identified by its infrared spectrum[6] as a mixture of $Cs^+ClO_2F_2^-$ and CsF. When the starting materials were heated to 105° for 68 hr, the ClF_3O_2 had quantitatively decomposed to $FClO_2$ and F_2.

Results and Discussion

Synthesis. The synthesis of ClF_3O_2 is best described by the following reaction sequence.

$$2FClO_2 + 2PtF_6 \rightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- \qquad (1)$$

Several side reactions compete with (1) and the yield of $ClF_2O_2^+$ varies greatly with slight changes in the reaction conditions.[3] The ClF_3O_2 is then displaced from its $ClF_2O_2^+$ salt according to

$$ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- + 2FNO_2 \rightarrow 2NO_2^+PtF_6^- + ClF_3O_2 + FClO_2 \qquad (2)$$

Chloryl fluoride is slightly less volatile than ClF_3O_2. Therefore, most of it can be removed from ClF_3O_2 by fractional condensation in a −112° trap. The remaining $FClO_2$, however, has to be removed by complexing with BF_3.

$$ClF_3O_2 + FClO_2 + 2BF_3 \rightarrow ClF_2O_2^+BF_4^- + ClO_2^+BF_4^- \qquad (3)$$

Since $ClF_2O_2^+BF_4^-$ is stable[5] at 20°, whereas $ClO_2^+BF_4^-$ is not,[7] the latter can be pumped away at 20°. The resulting pure $ClF_2O_2^+BF_4^-$ is then treated with an excess of FNO_2 and the evolved ClF_3O_2 and unreacted FNO_2 are readily separated by fractional condensation through a series of −126 and −196° traps.

$$ClF_2O_2^+BF_4^- + FNO_2 \rightarrow NO_2^+BF_4^- + ClF_3O_2 \qquad (4)$$

Whereas the overall yield of pure ClF_3O_2 based on the PtF_6 used in step 1 was found to be rather low (about 10 mol %), the method was satisfactory to provide enough material to characterize ClF_3O_2. Therefore, no effort was undertaken to search for alternate synthetic routes which might give higher yields of ClF_3O_2.

Properties. Pure ClF_3O_2 is colorless as a gas or liquid and white in the solid state. It melts at −81.2°. Vapor pressures were measured over the range −96 to −32° and the data for the range −64 to −32° were fitted by the method of least squares to the equation

$$\log P\,(\text{mm}) = 7.719 - 1217.2/T\,(^\circ\text{K})$$

with an index of correlation of 0.99998. The extrapolated boiling point is −21.58°. Measured vapor pressures at the noted temperatures are [T (°C), P (mm)]: −95.64, 7.3; −78.73, 25.5; −64.34, 77.5; −57.69, 117.5; −46.32, 226.5; −31.93, 470. The two lowest temperature points were not used for the computation of the vapor pressure equation because the lowest point was measured for solid ClF_3O_2 and the second lowest was too close to the melting point of ClF_3O_2. While at −78.73° the ClF_3O_2 sample was all liquid, the observed vapor pressure was reproducibly lower than expected from the above vapor pressure curve. This indicates that close to the melting point some ordering effect occurs in the liquid causing a decrease of the vapor pressure. The latent heat of vaporization of ClF_3O_2 is 5.57 kcal/mol and the derived Trouton constant is 22.13, indicating little association in the liquid phase. This is in agreement with the low boiling point and the good agreement between the Raman spectra of the gas and of the liquid.[2] The molecular weight was determined from the vapor density and found to be 122.1 (calcd for ClF_3O_2, 124.5). The good agreement in-

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(2) K. O. Christe and E. C. Curtis, unpublished results.

(3) K. O. Christe, *Inorg. Chem.*, in press.

(4) K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, 12, 84 (1973).

(5) K. O. Christe, R. D. Wilson, and E. C. Curtis, *Inorg. Chem.*, 12, 1358 (1973).

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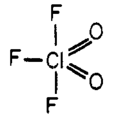
dicates little or no association in the gas phase at the pressures used ($P \sim 1$ atm).

Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It appears to be marginally stable in a well passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with $FClO_2$ formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of ClF_3O_2 was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing ClF_3O_2 resulted in the formation of $FClO_3$ and HF indicating the following reaction.

$$ClF_3O_2 + H_2O \rightarrow FClO_3 + 2HF \qquad (5)$$

^{19}F Nmr Spectrum. The ^{19}F nmr spectrum of liquid ClF_3O_2 was measured in the temperature range -20 to $-80°$. It showed at all temperatures one partially resolved signal centered at -413 ppm below the external standard $CFCl_3$. Figure 1 shows the details of the spectrum recorded at $-77°$. The observed signal is in excellent agreement with an AB_2 pattern[8] with $J/\nu_0\delta = 1.0$ (for the computed pattern, see Figure 1). From these data a value of $J_{FF} = 443$ Hz was calculated. The low chemical shift of -413 ppm for ClF_3O_2 is in excellent agreement with a heptavalent chlorine fluoride and compares favorably with those observed[4] for $FClO_2$ (-315 ppm), ClF_6^+ (-388 ppm), and $ClF_2O_2^+$ (-310 ppm). The fact that the resonance of the $ClF_2O_2^+$ cation was observed upfield from that of ClF_3O_2 is difficult to rationalize but seems to be quite general for chlorine fluorides.[4] The fluorine–fluorine coupling constant of 443 Hz observed for ClF_3O_2 is similar to that of 421 Hz observed for the structurally related ClF_3.[4]

Since the chlorine atom in ClF_3O_2 does not possess a free valence electron pair, it is pentacoordinated and the ligands should form a trigonal bipyramid. To account for an AB_2 pattern one has to assume two fluorine atoms in either the axial or the equatorial positions.



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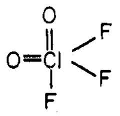

II

Of these two models, I has to be preferred for the following four reasons. (i) The B_2 part of the AB_2 pattern occurs downfield from the A part and in trigonal-bipyramidal species the resonance for the axial fluorines occurs at a lower field than that of the equatorial ones.[9,10] (ii) In trigonal-bipyramidal molecules the most electronegative ligands generally occupy the axial positions.[11] (iii) The vibrational spectrum[2] is consistent only with model I. (iv) In the structurally related ClF_3O[12] and ClF_3[13] molecules (in which the oxygen ligands are replaced by one and two sterically active free electron pairs, respectively), both axial positions are occupied by fluorine atoms.

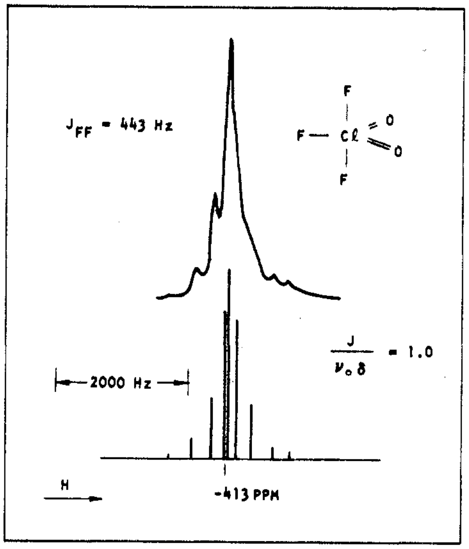

Figure 1. ^{19}F nmr spectrum of liquid ClF_3O_2 at $-77°$ recorded at 56.4 MHz. The chemical shift was measured relative to the external standard $CFCl_3$.

Adduct Formation. Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as BF_3, AsF_5, or PtF_5.[5] These adducts have ionic structures containing the $ClF_2O_2^+$ cation. A detailed discussion of the vibrational and nmr spectra of this cation will be given elsewhere.[5] The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal-bipyramidal structure of ClF_3O_2 to the more favorable tetrahedral $ClF_2O_2^+$ configuration.[14] Contrary to ClF_3,[15] but by analogy with ClF_3O,[14] it does not form stable adducts with FNO or FNO_2 at temperatures as low as $-78°$. This was demonstrated by the various displacement reactions where ClF_3O_2 and unreacted FNO or FNO_2 could be readily removed from the reactor at $-78°$. With the stronger base, CsF, it does not form a stable adduct but decomposes to $FClO_2$ and F_2 with CsF possibly catalyzing the decomposition.

Registry No. $(ClF_2O_2)BF_4$, 38682-34-7; FNO_2, 10022-50-1; ClF_3O_2, 38680-84-1; CsF, 13400-13-0.

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