Bromyl Fluoride and Bromosyl Trifluoride : Preparation and Chemical and Spectroscopic Properties

By Ronald J. Gillespie * and Paul H. Spekkens, Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

The preparation of bromyl fluoride BrO_2F by several methods is described as well as its reaction with KF to give $K[BrF_2O_2]$. The Raman spectrum of BrO_2F has been interpreted in terms of a pyramidal structure. The preparation of bromosyl trifluoride $BrOF_3$ by the reaction of $K[BrF_4O]$ with HF is described together with some of its properties. The ^{19}F n.m.r. spectrum of molten $BrOF_3$ and its solutions in SO_2ClF and SO_2F_2 have been recorded and interpreted in terms of fluorine exchange. The Raman spectrum is interpreted on the basis of association in the liquid, solid, and in HF solution. The hydrolysis of BrF_5 and the reactions of BrF_5 with IO_2F, IOF_3, and I_2O_5 produce BrO_2F but not $BrOF_3$, whereas the reaction of BrF_5 with IO_2F_3 produces a mixture of BrO_2F and $BrOF_3$. The compound BrO_2F is fluorinated to $BrOF_3$ and then to BrF_5 by KrF_2, but no bromine(VII) species are formed.

As part of our continuing investigation of the fluoride oxides of the halogens, we have examined the fluoride oxide compounds of Br^V. We have reported the Raman spectrum of bromyl fluoride in a communication,[1] and have recently described the preparation and Raman spectra of the anions $[BrF_2O_2]^-$ and $[BrFO_4]^-$.[2]

In this paper we give more complete Raman and ^{19}F n.m.r. spectroscopic data for BrO_2F, together with some of its reaction chemistry. We also report the preparation of $BrOF_3$ for the first time and its characterization by Raman and ^{19}F n.m.r. spectroscopy.

EXPERIMENTAL

Materials and Apparatus.—Potassium fluoride (B.D.H., 99%) was dried *in vacuo* at 250 °C for several days. Bromine pentafluoride (Ozark Mahoning Co.) was purified by bubbling fluorine through it until the liquid became colourless. It was then distilled on to dry NaF to remove trace amounts of HF. Anhydrous HF (Harshaw Chemical Co.) was used directly. Sulphonyl chloride fluoride (Baker and Adamson) was distilled on to SbF_5 and allowed to stand at room temperature for 1 h. The SO_2ClF was then distilled on to NaF where it was kept until use. Since the commercial product contained SO_2F_2 impurity, the most

volatile fraction of each distillate was discarded. The purity of the SO_2ClF was verified by its ^{19}F n.m.r. spectrum which showed only one line. Sulphonyl difluoride (Matheson Gas Products) was used directly. Krypton difluoride was provided by Dr. G. J. Schrobilgen and the preparation has been described elsewhere.[3] Di-iodine pentaoxide (Allied Chemical) was dried *in vacuo* at 150 °C for 2 or 3 d. The compounds IOF_3 and IO_2F were prepared by the method of Aynsley *et al.*;[4] IO_2F_3 was supplied by Dr. J. P. Krasznai and had been prepared by the method of Engelbrecht and Peterfy.[5] The preparation and purification of $K[BrF_2O_2]$ and $K[BrF_4O]$ have already been described in detail.[2]

Fluorine-19 n.m.r. spectra were generally recorded with a Varian DA-601L spectrometer operating at 56.4 or 58.3 MHz and modified as described previously.[3] Spectra of samples of $BrOF_3$ in SO_2ClF and SO_2F_2 were obtained with a Varian HA-100 spectrometer operating at 94.1 MHz. All the chemical shifts were measured from $CFCl_3$ as an external standard. Raman instrumentation has been described elsewhere.[3,6]

All the compounds were handled in a vacuum system or in the inert atmosphere of a dry-box. The vacuum systems, as well as the Teflon valves, have been described

[1] R. J. Gillespie and P. Spekkens, *J.C.S. Chem. Comm.*, 1975, 314.

[2] R. J. Gillespie and P. Spekkens, *J.C.S. Dalton*, 1976, 2391.

[3] R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 22.

[4] E. E. Aynsley, R. Nichols, and P. L. Robinson, *J. Chem. Soc.*, 1953, 623.

[5] A. Engelbrecht and P. Peterfy, *Angew. Chem. Internat. Edn.*, 1969, **8**, 768.

[6] R. J. Gillespie, P. Spekkens, J. B. Milne, and D. M. Moffett, *J. Fluorine Chem.*, 1976, **7**, 43.

in detail elsewhere.[7] The samples were generally contained in Kel-F or Teflon-FEP tubes. For the Raman spectrum of $BrOF_3$ in HF, a 5-mm quartz tube fused to a short length of 6-mm quartz tubing which was then connected to a Teflon valve was used. Sample tubes were conditioned with BrF_5 and HF before use.

Preparation of Bromyl Fluoride.—The preparation of BrO_2F by the reaction of $K[BrO_3]$ with BrF_5 has been described elsewhere.[2] This compound can also be prepared by dissolving $K[BrF_2O_2]$ in anhydrous HF. In a typical experiment, $K[BrF_2O_2]$ (0.087 g) was placed in a Teflon-FEP n.m.r. tube and HF (*ca.* 0.4 g) was distilled in. The mixture was warmed to -78 °C to melt the HF and then warmed further to dissolve the $K[BrF_2O_2]$. On cooling the solution to -78 °C, a white precipitate was formed which was identified as BrO_2F from its Raman spectrum. The HF was removed *in vacuo* at -78 °C, leaving a white solid. This solid was warmed to room temperature under dynamic vacuum and the volatile component was trapped at -48 °C and identified as BrO_2F by its Raman spectrum. The involatile residue was identified as $K[HF_2]$ from its Raman spectrum.

Decomposition of BrO_2F in HF.—When a solution of $K[BrF_2O_2]$ in HF was allowed to stand at room temperature for 30 min it became brown, suggesting Br_2 formation. When the solvent was removed *in vacuo* at -78 °C, and the remaining solid allowed to warm up to room temperature under dynamic vacuum, a white solid remained which was identified as $K[BrF_4]$ from its Raman spectrum.[8] Thus a decomposing solution of BrO_2F in HF produces Br_2 and BrF_3, and presumably O_2.

Preparation of N.M.R. Samples.—Bromyl fluoride was distilled dynamically into Teflon-FEP n.m.r. tubes and trapped at -48 °C, and the solvent was then added by distillation.

Reaction of BrO_2F with KF.—Potassium fluoride (0.133 g, 2.29 mmol) was shaken at room temperature with BrO_2F (0.592 g, 4.52 mmol) for 24 h in a Kel-F trap. Some decomposition occurred since Br_2 was liberated in the tube. The excess of BrO_2F was removed *in vacuo*, and a Raman spectrum of the white solid which remained showed it to be a mixture of $K[BrF_2O_2]$ and $K[BrF_4]$. The weight of the white solid in the tube had increased by 0.037 g (which corresponds to 0.28 mmol of BrO_2F or BrF_3).

Preparation and Properties of Bromosyl Trifluoride.—In a typical preparation, $K[BrF_4O]$ (0.219 g) was placed in a Teflon-FEP n.m.r. tube, and HF (*ca.* 0.6 g) was distilled in. The mixture was warmed to -78 °C to melt the HF, and then to a slightly higher temperature to dissolve the $K[BrF_4O]$. The HF was removed *in vacuo* at -78 °C, leaving a white solid whose Raman spectrum was consistent with $BrOF_3$. Bromine pentafluoride (1.3 g) was distilled in, and the mixture was warmed to -48 °C. This produced a clear solution with a translucent solid ($K[HF_2]$) floating on it (density[9] of BrF_5, 2.47 g cm^{-3}; $K[HF_2]$, 2.37 g cm^{-3}). It was possible to separate the solution from the solid by carefully manipulating the reaction vessel in such a way that the solution slowly flowed to one end of the n.m.r. tube while the solid adhered to the walls at the other end of the tube. The section of tube containing the solid was then sealed off and removed. The BrF_5 was removed *in vacuo* at -48 °C, and a white solid ($BrOF_3$)

resulted. The melting range of $BrOF_3$ was found to be *ca.* -5 to 0 °C and was determined by placing a solid sample of $BrOF_3$ contained in a Teflon-FEP n.m.r. tube in a glass Dewar which was kept cold by a flow of cold nitrogen through it. The temperature was varied by controlling the nitrogen flow and was measured using a copper–constantan thermocouple. In another experiment a sample of solid $BrOF_3$ in a Teflon-FEP tube was placed in a salt water–ice bath at -10 °C and the bath was slowly allowed to warm up to 0 °C over a period of 2 h while the temperature was monitored using a mercury thermometer. The melting range determined by this method was -4 to 0 °C. On standing at room temperature, liquid $BrOF_3$ began to bubble and became yellowish. After 2 h at room temperature the liquid was chilled to -196 °C, excess of KF was added, and the mixture was allowed to warm up to room temperature. A reaction took place which produced a white solid identified as $K[BrF_4]$ from its Raman spectrum.

Preparation of N.M.R. and Raman Samples of $BrOF_3$.—The Raman and ${}^{19}F$ n.m.r. spectra of liquid $BrOF_3$ were obtained from a sample prepared in a Teflon-FEP n.m.r. tube as described above. An HF solution of $BrOF_3$ for n.m.r. was obtained by dissolving $K[BrF_4O]$ in HF in a Teflon-FEP n.m.r. tube. An HF solution of $BrOF_3$ for Raman spectroscopy was prepared by dissolving $K[BrF_4O]$ in HF in a 5-mm quartz tube. These solutions often attack the quartz tube. (The solution rapidly turns brown, and the Raman spectrum of the solution shows large amounts of BrO_2F.) Raman spectra of $BrOF_3$ in HF were also recorded in Teflon-FEP and Kel-F containers, but in these cases the Raman lines associated with the container obscure many of the $BrOF_3$ lines. Fluorine-19 n.m.r. samples of $BrOF_3$ in SO_2ClF and SO_2F_2 were prepared by statically distilling $BrOF_3$ into a Teflon-FEP n.m.r. tube, and then distilling in the solvent. The mixtures were warmed to -78 °C to allow dissolution of the $BrOF_3$. Saturated solutions were used.

Reaction of $BrOF_3$ and $K[HF_2]$.—A mixture of $BrOF_3$ and $K[HF_2]$ (produced by dissolving $K[BrF_4O]$ in HF and removing the HF *in vacuo*) was allowed to warm up *in vacuo* to *ca.* -20 °C, and then chilled to -196 °C. The Raman spectrum showed the resulting solid to consist mostly of $K[BrF_4O]$, with only a small amount of $BrOF_3$ remaining. In another experiment, $K[BrOF_4]$ (0.012 g) was dissolved in HF, and the solvent removed *in vacuo* at -78 °C. The resulting $BrOF_3$–$K[HF_2]$ mixture was allowed to warm up to room temperature under reduced pressure. The remaining white solid weighed 0.010 g and was identified as $K[BrF_4O]$ from its Raman spectrum. Using a good dynamic vacuum, some $BrOF_3$ can be distilled out of a $BrOF_3$–$K[HF_2]$ mixture, but the residual $K[BrF_4O]$ still accounts for most of the $BrOF_3$ originally present.

Hydrolysis of BrF_5.—Bromine pentafluoride (0.213 g, 1.22 mmol) was distilled into a thin-walled Teflon-FEP tube (outside diameter, 0.25 in), and water (21.9 μl, 1.22 mmol) was syringed into the tube (kept at -196 °C) and formed a frozen bead above the level of the frozen BrF_5. Hydrogen fluoride (*ca.* 1.3 g) was then distilled in. The mixture was warmed to -78 °C to melt the HF, and then to -63 °C for 10 min giving a light yellow solution. On cooling the sample to -78 °C, a white solid was formed. The Raman spectrum of the solid was recorded at -196 °C and showed that it consisted of BrO_2F and BrF_5,[2] with no

[7] G. J. Schrobilgen, Ph.D. Thesis, McMaster University, 1973.

[8] T. Surles, H. Hyman, L. Quarterman, and A. Popov, *Inorg. Chem.*, 1970, **9**, 2726.

[9] 'Handbook of Chemistry and Physics,' 50th edn., The Chemical Rubber Company, Cleveland, Ohio, 1969.

BrOF$_3$ being present. The sample was left at -63 °C for 1 h and then at -78 °C for 2 d. The Raman spectrum of the solid in the bottom of the tube was again recorded and was still found to consist only of lines attributed to BrF$_5$ and BrO$_2$F. The solvent and excess of BrF$_5$ were removed *in vacuo* at -72 °C, leaving a yellow solid whose Raman spectrum showed lines attributable to BrO$_2$F with possibly a very small amount of BrF$_3$. No BrOF$_3$ was present.

Reaction of Iodine(v) *Oxides and Fluoride Oxides with* BrF$_5$.—(*a*) Iodyl fluoride (0.0571 g, 0.32 mmol) was placed in a Teflon-FEP n.m.r. tube, and BrF$_5$ (1.61 g, 9.2 mmol) was distilled in. The mixture was warmed to -48 °C and consisted of a clear solution with a white solid present. The mixture was allowed to react at room temperature for 15 min, and a solid was still present in the tube (BrO$_2$F·BrF$_5$ presumably, see Results and Discussion section). A ^{19}F n.m.r. spectrum at -45 °C showed only BrF$_5$,[10] IF$_5$,[10] and BrO$_2$F. The solvent was removed *in vacuo* at -48 °C and a white solid resulted whose Raman spectrum contained lines attributable to BrO$_2$F and IF$_5$,[11] but no BrOF$_3$. In another experiment a much larger (and unmeasured) excess of BrF$_5$ was used and complete dissolution occurred at -48 °C. The ^{19}F n.m.r. spectrum of this solution at -40 °C showed BrF$_5$, IF$_5$, and BrO$_2$F, and the integration of the spectrum gave the following results: BrO$_2$F : FIF$_4$: FIF$_4$ = 30 : 32 : 117 $\approx$ 1 : 1 : 4.

(*b*) I$_2$O$_5$. Di-iodine pentaoxide (0.114 g, 0.342 mmol) was placed in a Teflon-FEP n.m.r. tube, and BrF$_5$ (1.81 g, 10.3 mmol) was distilled in. The mixture was warmed to -48 °C and an orange solution was formed with a white solid still present in the tube. Decomposition seemed to occur since the solution was orange in colour and bubbles of gas were evolved. The solid dissolved when the sample was warmed to room temperature and a ^{19}F n.m.r. spectrum at this temperature showed signals due to BrF$_5$, IF$_5$, and BrO$_2$F. The solvent was removed *in vacuo* at -48 °C, and then at -30 °C. The Raman spectrum of the remaining material consisted of lines attributable to BrO$_2$F and IF$_5$, with no BrOF$_3$ being present.

(*c*) IOF$_3$. A large excess of BrF$_5$ was distilled on to IOF$_3$ and the mixture became brown on warming to -63 °C. Further warming to -35 °C caused complete dissolution and à darkening of the brown colour. The n.m.r. spectrum of the solution showed BrF$_5$, IF$_5$, and a relatively small amount of BrO$_2$F (BrO$_2$F : IF$_5$ < 1 : 10) to be present.

Reaction of IO$_2$F$_3$ *and* BrF$_5$.—Bromine pentafluoride (1.04 g, 5.95 mmol) was distilled on to IO$_2$F$_3$ (0.150 g, 0.694 mmol), and the mixture was warmed to -18 °C and then to room temperature for 40 min to obtain complete reaction. A Raman spectrum of the solution showed peaks attributable to BrF$_5$,[12] IOF$_5$,[13] BrO$_2$F, and a small amount of BrOF$_3$. The ^{19}F n.m.r. spectrum of this solution at -50 °C showed the characteristic multiplets of BrF$_5$ and IOF$_5$,[14] and a small amount of IF$_5$. No peaks other than those due to BrF$_5$ were observed in the F on Br^{V} region. The BrF$_5$ and IOF$_5$ were removed *in vacuo* at -48 °C, and the Raman spectrum of the remaining solid showed lines attributable to a large amount of BrO$_2$F, some BrOF$_3$, and very weak lines due to IF$_5$ and possibly BrF$_3$. Bromine

[10] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084.

[11] L. E. Alexander and I. R. Beattie, *J. Chem. Soc.* (*A*), 1971, 3091.

[12] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 1965, **42**, 2236.

pentafluoride was distilled into the tube and a more concentrated solution was prepared. The 94.1-MHz n.m.r. spectrum of this solution at -60 °C showed (in addition to BrF$_5$ and IF$_5$) a rather broad (*ca.* 200 Hz) weak peak at *ca.* -209 p.p.m. This signal broadened considerably as the temperature was increased (peak width *ca.* 375 Hz at -40 °C). The broadness and weakness of the peak is presumably why it was not observed in the ^{19}F n.m.r. spectrum of the original reaction mixture.
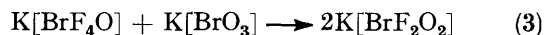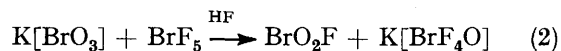
Reaction of BrO$_2$F *with* KrF$_2$.—Potassium difluorodioxobromate (*ca.* 0.1 g) was placed in a Teflon-FEP n.m.r. tube and excess of KrF$_2$ was distilled in. Hydrogen fluoride (*ca.* 0.5 g) was then distilled in and the mixture was warmed to -78 °C to melt the HF. All the solid in the tube dissolved at -45 °C. The tube was then warmed while the reaction was monitored by ^{19}F n.m.r. and Raman spectroscopy.

RESULTS AND DISCUSSION

Preparation of BrO$_2$F.—Schmeisser and Pammer [15] reported that K[BrO$_3$] and BrF$_5$ react at -50 °C according to equation (1). We have found, however,

$$K[BrO_3] + BrF_5 \longrightarrow BrO_2F + K[BrF_4] + \tfrac{1}{2}O_2 \quad (1)$$
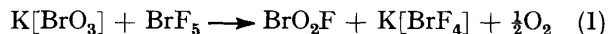
that when pure reagents are used K[BrO$_3$] and excess of BrF$_5$ do not react at -50 °C, and only a small amount of reaction occurs even after several hours at room temperature. When a small amount of HF is added the reaction is much more rapid and BrO$_2$F and K[BrF$_2$O$_2$] are the main products, with some K[BrF$_4$O] being formed as well.[2] The reactions occurring are (2) and (3).

$$K[BrO_3] + BrF_5 \xrightarrow{\text{HF}} BrO_2F + K[BrF_4O] \quad (2)$$

$$K[BrF_4O] + K[BrO_3] \longrightarrow 2K[BrF_2O_2] \quad (3)$$

The yield of BrO$_2$F is typically *ca.* 50% based on the amount of K[BrO$_3$] used. The reaction mixture also turns brown during the course of the reaction, so the low yield of BrO$_2$F is presumably due to its partial decomposition during the reaction. Another convenient method of obtaining small quantities of BrO$_2$F is to dissolve K[BrF$_2$O$_2$] in HF when reaction (4) takes place.

$$K[BrF_2O_2] + HF \longrightarrow K[HF_2] + BrO_2F \quad (4)$$

After removal of the HF *in vacuo*, the BrO$_2$F is separated from the K[HF$_2$] by allowing the mixture to warm up to room temperature under dynamic vacuum and trapping the BrO$_2$F at -48 °C.

Characterization of BrO$_2$F *by Raman and* ^{19}F *N.M.R. Spectroscopy.*—Figures 1 and 2 show the Raman spectra of solid and molten BrO$_2$F. Table 1 lists the frequencies obtained from these spectra, as well as those obtained from spectra of BrO$_2$F in various solvents. Also listed in Table 1 are the fundamental frequencies of the related species ClO$_2$F [16] and [SeFO$_2$]$^-$.[6] Bromyl fluoride is expected to have a pyramidal geometry (1) with C_s symmetry.

[13] D. F. Smith and G. M. Begun, *J. Chem. Phys.*, 1965, **43**, 2001.

[14] R. J. Gillespie and J. W. Quail, *Proc. Chem. Soc.*, 1963, 341.

[15] M. Schmeisser and E. Pammer, *Angew. Chem.*, 1957, **69**, 781.

[16] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 1964, **20**, 1763.

The six fundamentals ($\Gamma = 4A' + 2A''$) are all Raman active. Six lines are observed in the spectrum
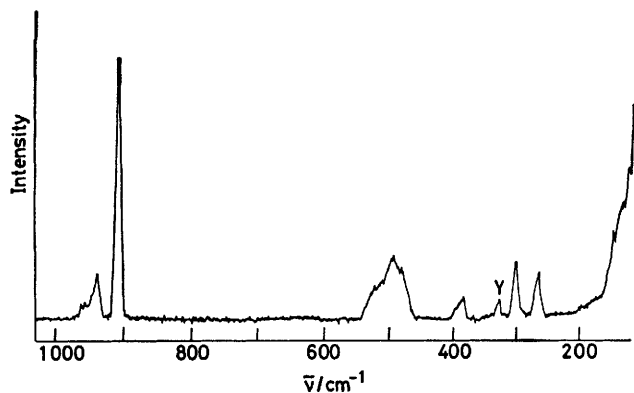

FIGURE 1 Raman spectrum of solid BrO₂F recorded in a Kel-F tube at −75 °C. The band marked Y is due to a small amount of Br₂ impurity
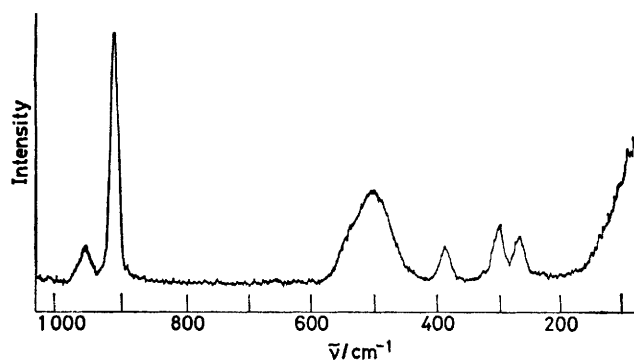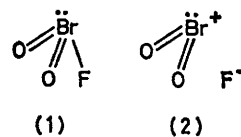

FIGURE 2 Raman spectrum of liquid BrO₂F recorded in a Kel-F tube at −9 °C

BrO₂F frequencies are lower than those of ClO₂F, which is consistent with the decrease in bond strength as the electronegativity of the central atom decreases. Direct

(1)   (2)

comparison with IO₂F is not possible since the latter is polymeric and gives a complex Raman spectrum.[17] The BrO₂F frequencies are slightly higher than those of the isoelectronic [SeFO₂]⁻ which reflects the bond-weakening effect of the negative charge on the anion.

The BrF stretching frequency in BrO₂F is relatively low when compared to other fluorine-containing bromine species. The frequency for BrO₂F (506 cm⁻¹) is similar to the mean of the BrF stretching frequencies in the anions [BrF₄]⁻ (531),[8] [BrF₆]⁻ (487),[18] and [BrF₄O]⁻ (498 cm⁻¹)[2] and considerably lower than that in the neutral molecules BrF₃ (613),[19] BrF₅ (615),[12] and BrO₃F (605 cm⁻¹).[20] A force-constant calculation for ClO₂F [16] has revealed an unusually low ClF stretching frequency. This has been disputed however on the basis of a more recent force-constant calculation.[21] A similar, unexpectedly low, stretching frequency has been found for the SeF bond in [SeFO₂]⁻.[6,22] Our results indicate that the BrF bond in BrO₂F is also rather weak, and presumably this may be attributed to a large contribution from the ionic resonance structure (2) in addition to the covalent structure (1).

The mean of the BrO stretching frequencies in liquid BrO₂F (931 cm⁻¹) is similar to that for BrO₃F (942 cm⁻¹)

TABLE 1

Raman spectra (cm⁻¹) of BrO₂F, ClO₂F, and [SeFO₂]⁻

Solution spectra of BrO₂F

ClO₂F [a]	[SeFO₂]⁻ [b]	in BrF₅ (Room temp.) [c]	in SO₂ClF (−100 °C) [d]	in HF (−20 °C) [e]	Liquid BrO₂F (−10 °C)	Solid BrO₂F (−75 °C)	Assignment
1 253dp (40) [f,g]	888 (45)	962 (8)	955 (13)	964 (15)	953dp (14)	963 (5) / 940 (20)	ν_5, ν_{asym}(BrO)
1 097p (100)	903 (100)	916 (100)	911 (100)	915 (100)	908p (100)	908 (100)	ν_1, ν_{sym}(BrO)
602p (20)	450 (sh) / 424 / 408 (sh) } (25) vbr		523br (20)	531 (25)	506p (36)	524 (sh) / 496 / 487 (sh) } (25) vbr	ν_2, ν(BrF)
533 (50)	324 (10)			395 (?)	394p (14)	400 (sh) / 386 } 10	ν_3, δ(OBrO)
398 (p?) (30)	283 (10)			310 (?)	305p (21)	305 / 294 (sh) } (20)	ν_4, δ_{sym}(OBrF)
351 (0+) [h]	238 (2)			276 (?)	271dp (16)	267 (15)	ν_6, δ_{asym}(OBrF)

[a] Ref. 16. [b] Ref. 6. [c] The BrO₂F spectrum below 900 cm⁻¹ is obscured by very strong BrF₅ lines. [d] Bending modes were obscured by lines of the Teflon-FEP tube. [e] The relative intensities of the three bending modes cannot be accurately measured due to the proximity of lines of the Teflon-FEP tube. [f] Numbers in parentheses are relative intensities. [g] dp = Depolarized, p = polarized, sh = shoulder, vbr = very broad. [h] Intensity too small to be measured.

of liquid BrO₂F and in the spectrum in HF solution. Of the six lines observed for molten BrO₂F, four are polarized and two are depolarized. They may be satisfactorily assigned to a monomeric BrO₂F molecule by analogy with the known spectrum of ClO₂F. The

but higher than those of other related species: [BrO₃]⁻ (829),[23] Br₂O₄ (893),[24] [BrF₂O₂]⁻ (895),[2] and [BrO₂]⁺

[17] H. Carter and F. Aubke, Inorg. Chem., 1971, 10, 2296.
[18] J. Shamir and I. Yaroslavsky, Israel J. Chem., 1969, 7, 495.
[19] H. Selig, H. H. Claassen, and J. H. Holloway, J. Chem. Phys., 1970, 52, 3517.

[20] H. H. Claassen and E. H. Appelman, Inorg. Chem., 1970, 9, 622.
[21] E. A. Robinson, P. S. Lavery, and S. Weller, Spectrochim. Acta, 1968, A25, 151.
[22] R. Paetzold and K. Aurich, Z. anorg. Chem., 1965, 335, 281.
[23] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1970.
[24] J. L. Pascal and J. Potier, J.C.S. Chem. Comm., 1973, 446.

(899 cm^{-1}).[25] As the stretching frequency for a bromine-(VII) compound is expected to be significantly higher than for a similar compound of Br^V, it appears that the BrO stretching frequencies in BrO$_2$ are abnormally high. This is also consistent with an important contribution from structure (2), which places a positive charge on bromine, thereby increasing the BrO stretching frequencies.

The spectra of BrO$_2$F in the solid and liquid phases and in solution are quite similar (Table 1). The molecule thus has the same pyramidal monomeric structure in all these phases. The BrF stretching frequency is significantly greater however in solution than in the solid or in the melt, indicating that there is possibly weak intermolecular fluorine bridging in the solid and in the melt. In ClO$_2$F, the ClF stretching frequency increases by 28 cm^{-1} on going from the liquid to the gas, indicating that fluorine bridging may be present in the liquid here also.

Bromyl fluoride is quite soluble in BrF$_5$, and the solutions are stable at room temperature for several hours. The ^{19}F n.m.r. spectrum of BrO$_2$F in BrF$_5$ at -35 °C consists of a sharp line at -210 ± 4 p.p.m. The chemical shift depends slightly on the composition and temperature of the solution. It lies between the chemical shifts of the two resonances of BrF$_5$ (-142 and -272 p.p.m.) and is thus in the F on Br^V region. During an attempt to prepare a concentrated solution of BrO$_2$F in BrF$_5$, a white solid was deposited in the tube at room temperature. Since BrO$_2$F melts at ca. -10 °C, the solid produced cannot be BrO$_2$F. It is presumably an adduct of BrO$_2$F and BrF$_5$. When the excess of BrF$_5$ was removed in vacuo at -48 °C, a white solid was produced which was identified as BrO$_2$F from its Raman spectrum. The adduct must, therefore, be a rather labile one since it dissociates even at -48 °C. The nature of this adduct is still under investigation.

Bromyl fluoride was also found to be soluble in SO$_2$ClF, even at very low temperatures (-120 °C). The ^{19}F n.m.r. chemical shift of BrO$_2$F in SO$_2$ClF at -78 to -123 °C was found to be -205 ± 2 p.p.m., in good agreement with the value found for the BrF$_5$ solution.

Bromyl fluoride is also quite soluble in HF at room temperature, but these solutions decompose with evolution of Br$_2$ and production of BrF$_3$, suggesting that the decomposition occurring is the same as the thermal decomposition [equation (5)] reported by Schmeisser

$$3BrO_2F \longrightarrow BrF_3 + Br_2 + 3O_2 \uparrow \qquad (5)$$
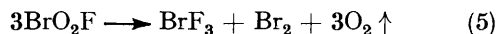
and Pammer.[15] The solubility of BrO$_2$F in HF is only slight at -78 °C, but at this temperature the solutions appear to be stable. At all the temperatures down to the freezing point of the HF solvent no separate ^{19}F n.m.r. signal was observed for BrO$_2$F, indicating that BrO$_2$F and HF undergo rapid fluorine exchange.

The Reaction of BrO$_2$F with KF.—This reaction at room temperature was found to give a mixture of

[25] E. Jacob, Angew. Chem. Internat. Edn., 1976, 15, 158.
[26] K. O. Christe, C. J. Schack, and D. Pilipovich, Inorg. Chem., 1972, 11, 2205.

K[BrF$_4$] and K[BrF$_2$O$_2$]. The K[BrF$_4$] is probably produced by decomposition of BrO$_2$F to BrF$_3$ [equation (5)] followed by reaction with KF. Only 12% of the available KF was consumed by reactions (6) and (7).

$$KF + BrO_2F \longrightarrow K[BrF_2O_2] \qquad (6)$$

$$KF + BrF_3 \longrightarrow K[BrF_4] \qquad (7)$$
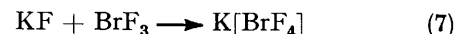
Thus the reaction of KF with BrO$_2$F proceeds only to a small extent ($<12\%$) after 24 h. This is probably due to kinetic reasons rather than inherent instability of the K[BrF$_2$O$_2$], since the latter can be obtained pure by other methods [2] and is stable indefinitely at room temperature.

Preparation and Properties of BrOF$_3$.—Bromosyl trifluoride is most conveniently prepared by dissolving K[BrF$_4$O] in HF at low temperature. Removal of the HF in vacuo at -78 °C leaves a white solid which was identified by Raman spectroscopy as a mixture of BrOF$_3$ and K[HF$_2$]. Reaction (8) thus occurs when excess of HF is present. When the BrOF$_3$-K[HF$_2$]

$$K[BrF_4O] + HF \longrightarrow BrOF_3 + K[HF_2] \qquad (8)$$
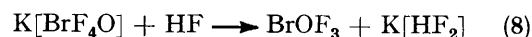
mixture is allowed to warm up to room temperature under dynamic vacuum, a rather small amount of volatile material (BrOF$_3$) can be collected in a trap at -78 °C. The Raman spectrum of the solid residue shows it to consist mostly of K[BrF$_4$O], indicating that the reverse of reaction (8) occurs in the absence of a solvent. Removal of the HF in vacuo as it is formed drives the reaction to the right even at -20 °C. This indicates that BrOF$_3$ is a stronger fluoride-ion acceptor than BrO$_2$F, just as ClOF$_3$ is a stronger fluoride-ion acceptor than ClO$_2$F.[26]

In order to isolate BrOF$_3$ from K[HF$_2$], the BrOF$_3$ is dissolved in BrF$_5$ and the insoluble K[HF$_2$] is removed. The BrF$_5$ can then be removed in vacuo at -48 °C leaving BrOF$_3$ as a white solid. Bromosyl trifluoride can be distilled statically by letting the solid warm up to room temperature. It has a melting range of ca. -5 to 0 °C and forms a clear colourless liquid. The liquid slowly decomposes at room temperature even in a well seasoned Teflon-FEP tube, turning slightly yellow and forming bubbles of gas. Treating the decomposed liquid with excess of KF produced K[BrF$_4$]. Thus the decomposition of BrOF$_3$ at room temperature appears to proceed according to equation (9). This is analogous

$$BrOF_3 \longrightarrow BrF_3 + \tfrac{1}{2}O_2 \qquad (9)$$

to the thermal decomposition of ClOF$_3$, which has been shown to proceed as follows: [27]

$$ClOF_3 \xrightarrow{\text{Heat}} ClF_3 + \tfrac{1}{2}O_2 \qquad (10)$$
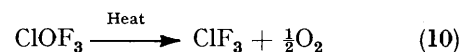
Characterization of BrOF$_3$ by Raman and ^{19}F N.M.R. Spectroscopy.—The Raman spectra of solid (Figure 3) and liquid (Figure 4) BrOF$_3$ and of a solution of BrOF$_3$ in HF (Figure 5) have been recorded, and the observed

[27] R. Bougon, J. Isabey, and P. Plurien, Compt. rend., 1970, C271, 1366.

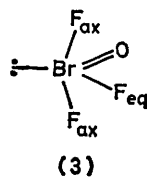peaks are listed in Table 2. A monomeric $BrOF_3$ molecule would be expected to have the structure (3)

$$
\begin{array}{c}
F_{ax} \\
| \quad \diagup \\
: — Br \Longleftrightarrow O \\
| \quad \diagdown \\
F_{ax} \quad F_{eq}
\end{array}
$$

(3)

TABLE 2

Raman spectra (cm^{-1}) of $BrOF_3$

HF solution (−78 °C)	Liquid (0 °C)	Solid (−196 °C)	Tentative assignment
1 011p (85) [a]	1 004p (90) [b]	1 010 (100)	$\nu(BrO)$
619p (100)	624p (100)	627 (60)	$\nu(BrF_{eq})$
		614 (70)	
557dp (15)		526 (sh)	
		510 (25)	
499p (25)	493p, vbr (100)	479 (70)	$\nu_{sym}(F_{ax}BrF_{ax})$
		460 (sh)	
435p (20)		447 (100)	
393dp (20)	396dp (20)	387 (35)	
353p (25)	351p (30)	350 (45)	
333dp (sh)	333(dp?) (sh)	315 (17)	
234 (?) (1)	243 (?) (4)	245 (2)	
200 (?) (7)	199p (?) (20)	206 (15)	
		123 (15)	
		74 (20)	⎬Lattice modes
		63 (25)	

[a] Numbers in parentheses give relative intensities. [b] p = Polarized, dp = depolarized, ? = uncertain degree of polarization.
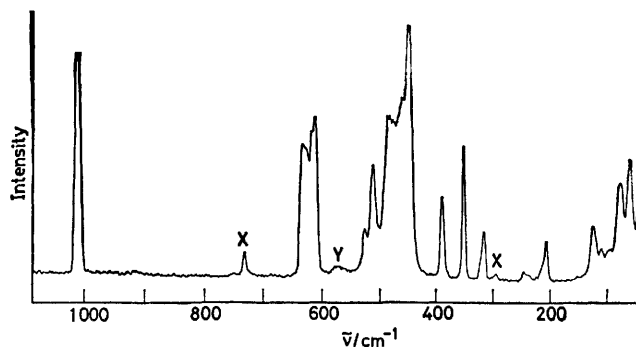

FIGURE 3 Raman spectrum of solid $BrOF_3$ at −196 °C. Peaks labelled X are due to the Teflon-FEP container, and that marked Y is due to an unidentified impurity
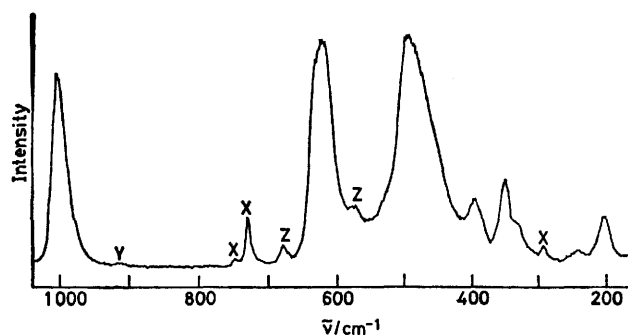

FIGURE 4 Raman spectrum of liquid $BrOF_3$ at room temperature. Peaks marked X are due to the Teflon-FEP container, Y is due to BrO_2F, and Z are due to a BrF_3 decomposition product

which has AX_4E geometry and C_s symmetry. Such a molecule would be expected to have nine fundamentals

$(\Gamma = 6A' + 3A'')$ which should all be Raman active. The spectrum of molten $BrOF_3$ has eight bands. However, the bands at 493 and 624 cm^{-1} are asymmetric and appear to consist of at least two overlapping lines which gives a total of at least 10 lines for liquid $BrOF_3$. That these two bands, and possibly others, consist of several overlapping peaks is supported by the fact that both split into several components in the solid-state spectrum. That the spectrum of molten $BrOF_3$ exhibits a greater number of lines than expected can only be readily explained by postulating that $BrOF_3$ is associated in the liquid state (and also in the solid state). A similar conclusion has been reached very recently by Bougon and Huy.[28] Since the nature of the association is unknown, it is not possible to make a complete assignment of the observed spectra but some useful conclusions can be drawn.

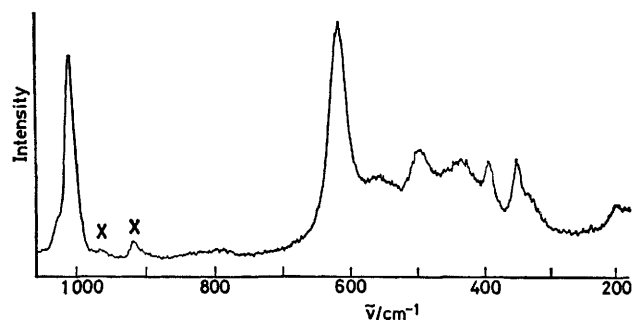It is clear that the highest-frequency band at 1 004 cm^{-1} must be assigned to the BrO stretching mode; this

FIGURE 5 Raman spectrum of $BrOF_3$ in HF at −78 °C in a quartz tube. Peaks marked X are due to BrO_2F produced by attack on the container

is in the normal Br=O stretching region and indicates that this bond is probably not involved (or at least not strongly involved) in the intermolecular association that we presume is present. The strong band at 624 cm^{-1} is too high in frequency to be a bending mode and can, therefore, be assigned to a terminal fluorine-stretching mode. Likewise, the strong band at 493 cm^{-1} can be assigned at least in part to a BrF stretching motion, and the lower frequency of this line suggests that it is associated with the fluorines involved in the bridging between molecules. This is supported by the appearance of the spectrum in HF solution. It might have been expected that, in HF solution, polymeric $BrOF_3$ would dissociate into monomers. However, this does not appear to be the case as although the spectrum changes it nevertheless remains rather complex. There are a number of broad overlapping bands in the 400— 600 cm^{-1} region which are not readily interpretable in terms of a monomeric structure, suggesting that some association is still present even in solution. The fact that this region of the spectrum is the one most markedly affected on going from solid to molten to a solution of $BrOF_3$ in HF supports the assignment of at least some of the peaks in this region to the BrF bridging stretching

[28] R. Bougon and T. B. Huy, *Compt. rend.*, 1976, **C283**, 461.

modes. Since the nature of the association, and hence the nature of the species present, is not known it was not possible to assign the remaining lines in the spectrum which must correspond to bending modes. If the association in $BrOF_3$ is similar to that which has been suggested for the related molecules $ClOF_3$,[29] and SF_4, BrF_3, and ClF_3,[30] then the association involves only the axial bonds. In this case the line at 624 cm^{-1} can be described as a BrF_{eq} stretch and one of the components of the line at 493 cm^{-1} can be assigned as a $v_{sym}(F_{ax}BrF_{ax})$ stretching motion, which would be expected to be lower in frequency than $v(BrF_{eq})$ due to the inherent weakness of the axial bonds and their further weakening by the bridging. This however is not totally satisfactory as it is not clear why the intensity of such a $v_{sym}(F_{ax}BrF_{ax})$ should decrease dramatically when $BrOF_3$ is dissolved in HF.

Although two signals of intensity ratio 2 : 1 would be expected for a $BrOF_3$ molecule with C_s symmetry, the [19]F n.m.r. spectrum of molten $BrOF_3$ at room temperature shows only a single line in the F on Br^V region at -152 p.p.m. There must be rapid exchange between the non-equivalent fluorines which may be a result of the association present in the liquid. Bromosyl trifluoride is quite soluble in HF even at low temperature, but no [19]F n.m.r. signal attributable to $BrOF_3$ could be observed, even down to the freezing point of the solution. The trifluoride was thus undergoing rapid fluorine exchange with the solvent. In SO_2ClF solution at -80 to -100 °C a single broad line (width ca. 600 Hz) appeared at -164 p.p.m., whereas at -120 °C the peak had shifted to -160 p.p.m. and the linewidth had increased to ca. 1 600 Hz. Similarly in SO_2F_2 at -136 °C only a single broad line was observed for $BrOF_3$ at -162 p.p.m. The small difference in chemical shift of $BrOF_3$ in the molten state and in solution in SO_2ClF and SO_2F_2 suggests that $BrOF_3$ is associated in a similar fashion in both states in these non-polar solvents. That only a single line is observed in these solvents indicates that exchange of non-equivalent fluorines is still occurring rapidly, probably intermolecularly, between the units of the associated cluster of $BrOF_3$ molecules.

Hydrolysis of BrF_5.—When equimolar amounts of BrF_5 and water are allowed to react at -63 °C, and the solution is cooled to -78 °C, a white precipitate is formed whose Raman spectrum consists of lines attributable to BrO_2F and BrF_5. Although the formation of BrO_2F presumably proceeds *via* the intermediate formation of $BrOF_3$ [equations (11) and (12)], no $BrOF_3$

$$BrF_5 + H_2O \longrightarrow BrOF_3 + 2HF \qquad (11)$$
$$BrOF_3 + H_2O \longrightarrow BrO_2F + 2HF \qquad (12)$$

was in fact observed. At -72 °C, HF and excess of BrF_5 can be removed *in vacuo*, and only BrO_2F and a very small amount of BrF_3 are left behind. It must be concluded that if $BrOF_3$ is indeed an intermediate, it

must hydrolyse considerably faster than BrF_5. The BrF_3 observed is produced by decomposition of either $BrOF_3$ or BrO_2F. These results are in agreement with mass-spectral data obtained by Sloth *et al.*,[31] who reported finding no evidence for $BrOF_3$ in the products of the neat hydrolysis of BrF_5.

Reaction of BrF_5 *with Iodine Oxides and Fluoride Oxides.*—Bromine pentafluoride rapidly fluorinates iodine(v) oxides and fluoride oxides and, as in the case of the hydrolysis of BrF_5, BrO_2F rather than $BrOF_3$ is the product.

Bromine pentafluoride reacts with IO_2F at -48 °C. If a large enough excess of BrF_5 is used a clear solution is obtained (otherwise the $BrO_2F \cdot BrF_5$ adduct precipitates out). A [19]F n.m.r. spectrum of this solution shows, in addition to the BrF_5 solvent peaks, the characteristic peaks due to IF_5 and BrO_2F, and integration of these signals showed that IF_5 and BrO_2F were present in equal amounts. Thus the overall reaction (13) can be written. On removing the excess of

$$BrF_5 + IO_2F \longrightarrow BrO_2F + IF_5 \qquad (13)$$

BrF_5 at -48 °C, a solid was produced whose Raman spectrum consisted of a mixture of BrO_2F and IF_5, containing no $BrOF_3$. The $BrOF_3$ which is presumably produced as an intermediate [equation (14)] must

$$BrF_5 + IO_2F \longrightarrow BrOF_3 + IOF_3 \qquad (14)$$

fluorinate the iodine(v) species present more rapidly than the BrF_5 solvent and be removed by rapid reactions such as (15) or (16).

$$BrOF_3 + IO_2F \longrightarrow BrO_2F + IOF_3 \qquad (15)$$
$$BrOF_3 + IOF_3 \longrightarrow BrO_2F + IF_5 \qquad (16)$$
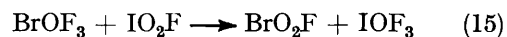
Similar results were obtained in the reactions of BrF_5 with I_2O_5 and IOF_3, except that some decomposition of a bromine species was evident from the formation of the characteristic brown colour of Br_2 and some gas evolution. In both cases, [19]F n.m.r. spectra of the resulting solutions showed only BrF_5, IF_5, and BrO_2F. Because of the decomposition which had occurred, integration of the BrO_2F and IF_5 signals showed amounts of BrO_2F that were less than would be required for equations (17) and (18). When the solvent

$$5BrF_5 + 2I_2O_5 \longrightarrow 5BrO_2F + 4IF_5 \qquad (17)$$
$$BrF_5 + 2IOF_3 \longrightarrow BrO_2F + 2IF_5 \qquad (18)$$
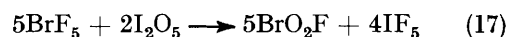
was removed *in vacuo* from the I_2O_5–BrF_5 reaction mixture, a solid was obtained whose Raman spectrum showed lines attributable to only BrO_2F and IF_5, but not to $BrOF_3$. As in the case of the IO_2F–BrF_5 reaction, the $BrOF_3$ presumably formed as an intermediate must be removed by rapid reaction with the iodine(v) species present.

When IO_2F_3 and BrF_5 react at room temperature the [19]F n.m.r. spectrum shows (in addition to the AX_4

[29] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 1972, **11**, 2196.
[30] R. Frey, R. Redington, and A. Aljibury, *J. Chem. Phys.*, 1971, **54**, 344.
[31] E. N. Sloth, L. Stein, and C. W. Williams, *J. Phys. Chem.*, 1969, **73**, 278.
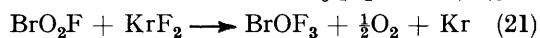
pattern of BrF_5) the AB_4 pattern of IOF_5 and a very weak AX_4 pattern assigned to IF_5. Removal of BrF_5 and IOF_5, *in vacuo* at −40 °C, produced a solid which consisted of mostly BrO_2F with some $BrOF_3$, IF_5, and possibly a very small amount of BrF_3. The BrF_3 may be produced by decomposition of either BrO_2F or $BrOF_3$, while the IF_5 is probably due to photochemical decomposition of IO_2F_3 to IOF_3,[5] followed by fluorination to IF_5 by the solvent. Thus the reaction of BrF_5 with IO_2F_3 can be written as in (19) and (20). Reaction (20)

$$BrF_5 + IO_2F_3 \longrightarrow BrOF_3 + IOF_5 \quad (19)$$

$$BrOF_3 + IO_2F_3 \longrightarrow BrO_2F + IOF_5 \quad (20)$$
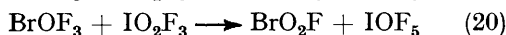
does not go to completion, which explains the mixture of BrO_2F and $BrOF_3$ which is observed. When the solid mixture of BrO_2F, $BrOF_3$, and IF_5 (and possibly some BrF_3) is redissolved in BrF_5, a ^{19}F n.m.r. spectrum of this solution shows BrF_5 and IF_5, and a very broad line at *ca.* 209 p.p.m. which is, presumably, due to BrO_2F undergoing fluorine exchange with $BrOF_3$ (and BrF_3 if any is present). The compounds BrF_5, IF_5, and IOF_5 cannot be involved in the exchange since the expected spin–spin coupling is observed for all these molecules.

Reaction of BrO_2F *with* KrF_2.—Bromyl fluoride can be fluorinated using the strong oxidizing agent KrF_2 with HF as a solvent. The ^{19}F n.m.r. spectrum of a solution or BrO_2F with excess of KrF_2 at −45 °C showed singlets at −52 and 183 p.p.m. which were assigned to KrF_2[32] and HF. The Raman spectrum of the solution at −45 °C showed only the single peak at 467 cm^{-1} due to KrF_2 and the BrO stretches of BrO_2F. Gas evolution occurred when the sample was warmed to 2 °C. The Raman spectrum of the solution showed BrO_2F and $BrOF_3$ to be present in comparable amounts, together with a small amount of BrF_5.[33] After 1 h at 2 °C, the $BrOF_3$ and BrF_5 lines had increased in intensity relative to those of BrO_2F. After another hour at 2 °C, no BrO_2F was observed. After 1 h at room temperature, the BrF_5 lines had grown in intensity. A ^{19}F n.m.r. spectrum showed KrF_2, HF, and BrF_5 to be present. Thus BrO_2F is fluorinated to $BrOF_3$ [equation (21)] which is in turn fluorinated to BrF_5 [equation (22)].

$$BrO_2F + KrF_2 \longrightarrow BrOF_3 + \tfrac{1}{2}O_2 + Kr \quad (21)$$

$$BrOF_3 + KrF_2 \longrightarrow BrF_5 + \tfrac{1}{2}O_2 + Kr \quad (22)$$

[32] F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Amer. Chem. Soc.*, 1965, **87**, 25.

[33] T. Surles, L. A. Quarterman, and H. H. Hyman, *J. Fluorine Chem.*, 1973—1974, **3**, 293.