

Preparation and Characterization of Potassium Difluorodioxobromate and Tetrafluoro-oxobromate

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The compounds $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$ have been prepared by the reaction of $K[\text{BrO}_3]$ with $K[\text{BrF}_6]$. The reaction of $K[\text{BrO}_3]$ with BrF_5 has been reinvestigated and $K[\text{BrF}_4\text{O}]$, $K[\text{BrF}_2\text{O}_2]$, and BrO_2F have been identified as the products. The Raman spectra of the $[\text{BrF}_2\text{O}_2]^-$ and $[\text{BrF}_4\text{O}]^-$ ions have been recorded and tentatively assigned on the basis of C_{2v} and C_{4v} symmetry respectively.

In a recent communication we reported the Raman spectrum of bromyl fluoride¹ which was prepared by the reaction of $K[\text{BrO}_3]$ with BrF_5 , which had been reported to proceed² at -50°C according to equation (1). We



have reinvestigated this reaction and have found that it generally does not occur as written in equation (1), but that the products are BrO_2F , $K[\text{BrF}_2\text{O}_2]$, and the previously unknown species $K[\text{BrF}_4\text{O}]$; $K[\text{BrF}_2\text{O}_2]$ had been reported by Mitra,³ but this claim was withdrawn when the results were found to be irreproducible.⁴ Independently of our work, Bougon and Tantot⁵ recently reported the preparation of $K[\text{BrF}_2\text{O}_2]$ and its Raman spectrum, together with a partial assignment. According to these workers, the reaction of $K[\text{BrO}_3]$ with BrF_5 proceeds according to equation (2). Bougon⁶ has



also prepared $K[\text{BrF}_4\text{O}]$ by the fluorination of $K[\text{BrO}_3]$.

In this paper we report the preparation of $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$ by the reaction of $K[\text{BrO}_3]$ with BrF_5 and by other methods. The Raman spectra of the anions $[\text{BrF}_2\text{O}_2]^-$ and $[\text{BrF}_4\text{O}]^-$ have been observed and tentative assignments of the spectra are given. The ^{19}F n.m.r. spectrum of $K[\text{BrF}_4\text{O}]$ has also been recorded.

EXPERIMENTAL

Materials and Apparatus.—The compounds $K[\text{BrO}_3]$ (Allied Chemical, 99.8%) and KF (B.D.H., 99%) were dried *in vacuo* at 250°C for several days. Bromine pentafluoride was obtained from Ozark Mahoning Co., and purified by bubbling fluorine through it until the liquid became colourless. It was then distilled on to NaF to remove trace amounts of HF . Anhydrous HF was obtained from Harshaw Chemical Co. and was used directly. Acetonitrile (Fisher Scientific Co.) was purified by distillation from P_4O_{10} , followed by distillation from dry $\text{K}_2[\text{CO}_3]$. The distilled material was stored over molecular sieves until used.

The Raman and ^{19}F n.m.r. instrumentation has been described elsewhere.^{7,8} The ^{19}F n.m.r. spectrum of $K[\text{BrF}_4\text{O}]$ was recorded on a Bruker WH90 n.m.r. spectrometer.

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 fluoroplastic valves and sample

¹ R. J. Gillespie and P. Spekkens, *J.C.S. Chem. Comm.*, 1975, 314 (see also ref. 8).

² M. Schmeisser and E. Pammer, *Angew. Chem.*, 1957, **69**, 781.

³ G. Mitra, *Z. anorg. Chem.*, 1965, **340**, 110.

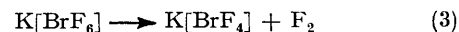
⁴ G. Mitra, *Z. anorg. Chem.*, 1969, **368**, 336.

⁵ R. Bougon and G. Tantot, *Compt. rend.*, 1975, **C281**, 271.

⁶ R. Bougon, personal communication.

tubes, have been described elsewhere.⁹ The fluoroplastic sample tubes were conditioned with HF and BrF_5 before use.

Preparation of $K[\text{BrF}_6]$.—Potassium fluoride (0.906 g, 15.71 mmol) and BrF_5 (11.06 g, 63.2 mmol) were stirred at room temperature for 1 week in a Kel-F tube; the excess of BrF_5 was then removed *in vacuo* leaving a white solid (3.570 g, 98% $K[\text{BrF}_6]$). The Raman spectrum of this solid showed only the three lines reported by Shamir and Yaroslavsky.¹⁰ Potassium hexafluorobromate is stable indefinitely when kept in well passivated Kel-F tubes. It is very soluble in MeCN, but decomposes slowly in this solvent. A white solid, identified as $K[\text{BrF}_4]$ from its Raman spectrum,^{10,11} was deposited. This decomposition proceeded in Kel-F, Teflon-FEP, glass, and quartz sample tubes so the decomposition is not due to attack on the walls of the container. The other products of the decomposition could not be positively identified. A ^{19}F n.m.r. spectrum of the decomposing solution did not show any peaks attributable to fluorinated solvent species. A gas was produced by the decomposing solution which darkened moist starch-iodide paper. Although it is perhaps somewhat surprising, the simplest explanation of our observations is that the decomposition proceeds according to equation (3). The rate of the decomposition can be



minimized by rigorously drying the MeCN, indicating that the above reaction may be catalyzed by trace amounts of moisture.

Preparation of Potassium Difluorodioxobromate and Tetrafluoro-oxobromate by the Reaction of $K[\text{BrO}_3]$ and $K[\text{BrF}_6]$.—Potassium bromate (0.216 g, 1.30 mmol) and $K[\text{BrF}_6]$ (0.250 g, 1.42 mmol) were shaken with MeCN (1.3 g) for 12 h in a Kel-F tube. The solvent was removed *in vacuo* and a white solid resulted which showed only lines attributable to $K[\text{BrF}_4\text{O}]$ and $K[\text{BrF}_2\text{O}_2]$. The reaction is thus as in (4). The separation of $K[\text{BrF}_4\text{O}]$ from $K[\text{BrF}_2\text{O}_2]$



relies on the slight solubility of $K[\text{BrF}_4\text{O}]$ in MeCN compared to the insolubility of $K[\text{BrF}_2\text{O}_2]$. A mixture (0.315 g) of $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$ and MeCN (2.4 g) were placed in ampoule A of the glass apparatus shown. The mixture was shaken for 2 h. The liquid was then filtered over to side B, through the glass frit F, and the MeCN distilled back to side A. A small amount of white solid was deposited in B. This operation was then repeated several

⁷ R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 22.

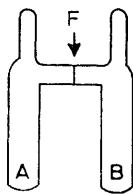
⁸ R. J. Gillespie, J. B. Milne, D. Moffett, and P. Spekkens, *J. Fluorine Chem.*, 1976, **7**, 43.

⁹ G. J. Schrobilgen, Ph.D. Thesis, McMaster University, 1973.

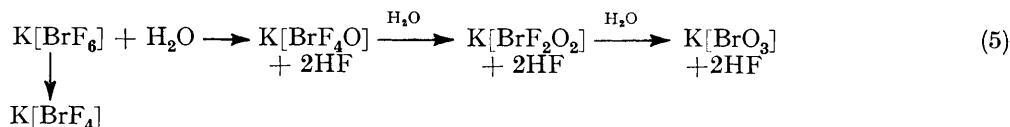
¹⁰ J. Shamir and I. Yaroslavsky, *Israel J. Chem.*, 1969, **7**, 495.

¹¹ T. Surlis, H. Hyman, L. Quarterman, and A. Popov, *Inorg. Chem.*, 1970, **9**, 2726.

times. The progress of the extraction can be monitored by Raman spectroscopy. The white material in B was $K[\text{BrF}_4\text{O}]$, sometimes contaminated with some $K[\text{BrF}_2\text{O}_2]$



(Found: Br, 37.45; F, 38.15; K, 18.9. Calc. for $K[\text{BrF}_4\text{O}]$: Br, 37.85; F, 36.0; K, 18.5%). The compound $K[\text{BrF}_2\text{O}_2]$ was obtained when a mixture of $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$



was extracted with MeCN, as described above, and all the $K[\text{BrF}_4\text{O}]$ was removed in this way (Found: Br, 42.55; F, 20.25; K, 20.4. Calc. for $K[\text{BrF}_2\text{O}_2]$: Br, 42.5; F, 20.1; K, 20.7%).

Reaction of $K[\text{BrO}_3]$ with BrF_5 .—In a typical reaction $K[\text{BrO}_3]$ (2.756 g, 16.5 mmol), BrF_5 (7.56 g, 42.0 mmol), and HF (0.0124 g, 0.6 mmol) were allowed to mix at room temperature for 3–5 h in a Kel-F tube. The resulting mixture was brown due to production of Br_2 by partial decomposition. The volatile products were then pumped through a trap at -48°C (n-hexyl alcohol slush bath). A white material (0.590 g, BrO_2F) was collected in the trap, which corresponds to 4.51 mmol of BrO_2F (55% yield based on the reaction scheme proposed below). The low yield is presumably due to decomposition of BrO_2F in the reaction mixture. A white solid remained in the reaction vessel which was identified from its Raman spectrum as consisting mostly of $K[\text{BrF}_2\text{O}_2]$ (with ca. 10% $K[\text{BrF}_4\text{O}]$). The weight of this solid was 3.11 g which corresponds to 16.4 mmol of $K[\text{BrF}_2\text{O}_2]$ (ignoring the presence of the $K[\text{BrF}_4\text{O}]$).

Analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

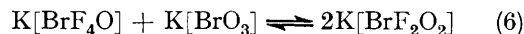
RESULTS AND DISCUSSION

(a) **Preparation and Properties of $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$.**—The compounds $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$ can be most conveniently prepared by the reaction of $K[\text{BrO}_3]$ and $K[\text{BrF}_6]$ in MeCN [equation (4)] and can then be separated by extraction of the mixture with MeCN. Both compounds are also produced in the hydrolysis of $K[\text{BrF}_6]$ in MeCN. The hydrolysis is, however, not a smooth reaction and mixtures of products are obtained. When water (ca. 0.02 mmol, dissolved in MeCN) was added to a solution of $K[\text{BrF}_6]$ (0.22 mmol in MeCN), and the solvent removed *in vacuo*, the resulting solid consisted of mostly unchanged $K[\text{BrF}_6]$ with small amounts of $K[\text{BrF}_4\text{O}]$ and $K[\text{BrF}_2\text{O}_2]$ present. When larger amounts of water were added the amounts of $K[\text{BrF}_4\text{O}]$ and $K[\text{BrF}_2\text{O}_2]$ increased but $K[\text{BrF}_4]$ also appeared as a major product {probably from the decomposition of $K[\text{BrF}_6]$ (see Experimental section)}. When

even more water was added $K[\text{BrO}_3]$ became the major product. These observations are consistent with the hydrolysis scheme (5). This hydrolysis cannot be used as a convenient source of $K[\text{BrF}_4\text{O}]$ or $K[\text{BrF}_2\text{O}_2]$ because of the relatively large amounts of $K[\text{BrF}_4]$ produced and because mixtures of products are always obtained. The ion $[\text{BrF}_4\text{O}]^-$ presumably hydrolyses more rapidly than $[\text{BrF}_6]^-$. The maximum co-ordination number of bromine appears to be six, so that attack by water on the $[\text{BrF}_6]^-$ ion would be slow. On the other hand $[\text{BrF}_4\text{O}]^-$ has a vacant co-ordination site and would probably be rapidly attacked by water. Both $K[\text{BrF}_4\text{O}]$ and $K[\text{BrF}_2\text{O}_2]$ are white solids that are stable at room temperature and can be kept indefinitely

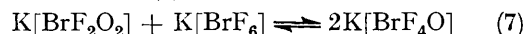
in dry FEP, Kel-F, or glass containers. They are, however, very sensitive to moisture and must be stored in rigorously dried vessels.

Some other reactions of the bromine(v) anions were also studied. When $[\text{BrF}_4\text{O}]^-$ was shaken with excess of $K[\text{BrO}_3]$ in MeCN overnight, the resultant contained no $K[\text{BrF}_4\text{O}]$, only $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrO}_3]$. This indicates that in MeCN equilibrium (6) lies to the right.



This may be due, in part, to the extremely small solubility of $K[\text{BrF}_2\text{O}_2]$ in MeCN. This means that when excess of $K[\text{BrO}_3]$ is used in the reaction of $K[\text{BrO}_3]$ with $K[\text{BrF}_6]$ a reduced amount of $K[\text{BrF}_4\text{O}]$ is obtained since the excess of $K[\text{BrO}_3]$ reacts with some of the $K[\text{BrF}_4\text{O}]$ produced in equation (2). In BrF_5 as a solvent, $K[\text{BrF}_4\text{O}]$ and $K[\text{BrO}_3]$ also reacted to give $K[\text{BrF}_2\text{O}_2]$ but not all the $K[\text{BrF}_4\text{O}]$ was consumed.

Although $K[\text{BrF}_4\text{O}]$ is stable in MeCN, and does not decompose to $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_6]$, it nevertheless cannot be prepared by the reaction of these two compounds, *i.e.* reaction (7) does not proceed to the right in



28 h. This again is probably due to the extremely low solubility of $K[\text{BrF}_2\text{O}_2]$ in MeCN.

(b) **Characterization of $K[\text{BrF}_2\text{O}_2]$ and $K[\text{BrF}_4\text{O}]$ by Raman Spectroscopy.**—Figure 1 shows the Raman spectrum of solid $K[\text{BrF}_2\text{O}_2]$ and Table 1 lists the observed lines and their assignments, together with those of some related molecules. The Raman spectrum corresponds well with that reported by Bougon and Tantot,⁵ but our assignments differ somewhat from their partial assignments. Because no solvent could be found for $K[\text{BrF}_2\text{O}_2]$ (BrF_5 , MeCN, SO_2ClF , and HF were tried), no polarization data are available. The assignments are thus made by comparison with the related molecules $[\text{IF}_2\text{O}_2]^-$,¹² $[\text{ClF}_2\text{O}_2]^-$,¹³ $[\text{SeF}_2\text{O}_2]^{2-}$,⁸ and

¹² A. Finch, P. N. Gates, and M. A. Jenkinson, *J. Fluorine Chem.*, 1972–1973, **2**, 111.

¹³ K. O. Christie and E. C. Curtis, *Inorg. Chem.*, 1972, **11**, 35.

XeO₂F₂.¹⁴ On the basis of VSEPR theory and the geometries of the related molecules, [BrF₂O₂]⁻ is expected to have a C_{2v} structure with the lone pair and two

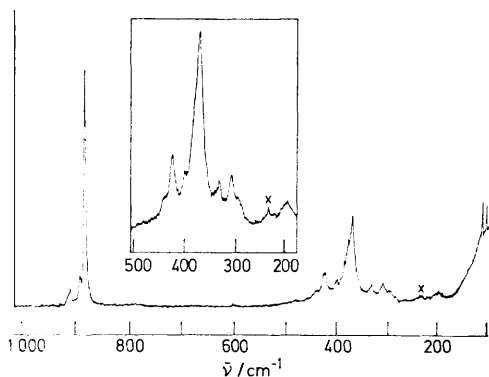
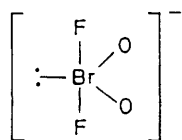


FIGURE 1 Raman spectrum of solid K[BrF₂O₂]. Peaks labelled × are due to an unidentified impurity (see text)

oxygen atoms occupying the equatorial positions of a trigonal bipyramid. The nine fundamentals ($\Gamma = 4A_1 + A_2 + 2B_1 + 2B_2$) for such a structure are all expected to be Raman active.



The three highest-frequency lines can readily be assigned to the BrO₂ symmetric and asymmetric

the fact that the negative charge on the anion decreases the amount of double-bond character in the BrO bonds. Finally, the BrO₂ frequencies in [BrF₂O₂]⁻ are higher than the SeO₂ frequencies in the isoelectronic [SeF₂O₂]²⁻, reflecting the additional bond weakening by the extra negative charge in the selenium compound.

In [IF₂O₂]⁻, [ClF₂O₂]⁻, and [SeF₂O₂]²⁻ there are two other motions which display strong Raman bands, *i.e.* $\nu_{\text{sym}}(\text{XF}_2)$ and $\delta(\text{rock})$. The two strongest remaining Raman lines of [BrF₂O₂]⁻ must be assigned to these motions. Since in all related molecules $\nu_{\text{sym}}(\text{XF}_2) > \delta(\text{rock})$, the peak at 424 cm⁻¹ is assigned to $\nu_{\text{sym}}(\text{XF}_2)$, while the peak at 369 cm⁻¹ (and the shoulder at 380 cm⁻¹) is assigned to $\delta(\text{rock})$. The lowest-frequency peak at 197 cm⁻¹ can be assigned to $\delta(\text{XF}_2)$, which occurs as the lowest-frequency fundamental in all the related molecules.

The remaining assignments are more arbitrary. The peak at 307 cm⁻¹ and the shoulder at 293 cm⁻¹ are assigned to $\delta(\text{wag})$ and are in the same region as the corresponding motions in [ClF₂O₂]⁻ and [IF₂O₂]⁻. Assignment of the peak at 400 cm⁻¹ to $\delta(\text{XO}_2)$ places it between [ClF₂O₂]⁻ and [IF₂O₂]⁻, and in the same region as the analogous motion in BrO₂F. {In [ClF₂O₂]⁻ (ref. 13) and ClO₂F,¹⁵ and in XeO₂F₂¹⁴ and [XeFO₂]⁺,¹⁶ the $\delta(\text{XO}_2)$ motions occur at similar frequencies.} The torsional mode ν_5 has been assigned to the peak at 333 cm⁻¹ and the shoulder at 442 cm⁻¹ to $\nu_{\text{asym}}(\text{XF}_2)$ which would be expected to be only very weakly active in the Raman spectrum. A small peak (<3% relative intensity) appeared in several spectra at *ca.* 230 cm⁻¹.

TABLE I
Raman bands (cm⁻¹) of [BrF₂O₂]⁻ and some related molecules

BrO ₂ F ^a	XeO ₂ F ₂ ^b	[SeF ₂ O ₂] ²⁻ ^c	[ClF ₂ O ₂] ⁻ ^d	[IF ₂ O ₂] ⁻	[BrF ₂ O ₂] ⁻	Assignment and approximate description $\nu_6(B_2)$ $\nu_{\text{asym}}(\text{XO}_2)$
953 (14) ^g	902w ^h	833 (25) 823 (sh)	1 221 (8)	838w	910 (7)	
			1 076 (100)			
908 (100)	845vs	868 (sh) 859 (100)	1 064 1 055	817vs 804w (sh) 456vw	892 (7) (sh) 884 (100) 442 (sh)	$\nu_1(A_1)$ $\nu_{\text{sym}}(\text{XO}_2)$ $\nu_6(B_1)$ $\nu_{\text{asym}}(\text{XF}_2)$
394 (14)	578w 490s 333ms	396 (15) 483 (<2) 445 (10) 304 (20)	363 (100) 559 (12)	479s 360m	424 (14) 400 (2)	$\nu_2(A_1)$ $\nu_{\text{sym}}(\text{XF}_2)$ $\nu_3(A_1)$ $\delta(\text{XO}_2)$
	313ms ^f		337 (80) ^f	323s	380 (sh) 369 (35)	$\nu_7(B_1)$ $\delta(\text{rock})$
	313ms		480 (10) 337 (80)	346w	338 (8) 307 (9) 293 (sh)	$\nu_5(A_2)$ Torsion $\nu_9(B_2)$ $\delta(\text{wag})$
	198w	241 (12)	198 (7)	194vw	197 (4)	$\nu_4(A_1)$ $\delta(\text{XF}_2)$

^a Ref. 1. ^b Ref. 14. ^c Ref. 8. ^d Ref. 13. ^e Ref. 12. ^f K[BrF₂O₂]. ^g Numbers in parentheses are relative intensities. ^h s = Strong, vs = very strong, m = medium, w = weak, vw = very weak, sh = shoulder, and br = broad. ⁱ The frequencies ν_7 and ν_9 are coincident in these molecules.

stretching frequencies, with $\nu_{\text{sym}}(\text{BrO}_2)$ being split by solid-state effects. The BrO₂ stretching vibrations are at lower frequency than those in [ClF₂O₂]⁻, and at higher frequency than those in [IF₂O₂]⁻, which reflects the decrease in bond strengths as the electronegativity of the central atom decreases. These BrO₂ frequencies are also lower than those in BrO₂F, which is consistent with

¹⁴ H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, 1968, **49**, 253.

However, since the relative intensity of this peak varied from one spectrum to the next and since it was absent in some spectra, it has been assigned to an unidentified impurity.

Figures 2 and 3 show the Raman spectrum of K[BrF₄O] at room temperature and liquid-nitrogen

¹⁵ D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 1964, **20**, 1763.

¹⁶ R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 1256.

TABLE 2
Raman bands (cm^{-1}) of $[\text{BrF}_4\text{O}]^-$ and some related molecules

I.r.	$[\text{BrF}_4]^-$ ^a Raman	XeOF_4 ^b 920 (20) ^h	ClF_5 ^b (liquid) 709 (30)	$[\text{ClF}_4\text{O}]^-$ ^c 1 211 (6)	IF_5 ^d (gas) 710 (5)	$[\text{IF}_4\text{O}]^-$ ^e 888vs ^f	BrF_5		Room temp. 930 (100)	$[\text{BrF}_4\text{O}]^-$ ^g -196 °C 930 (90)	Assign- ment
							liquid ^b 682 (70)	solid ^f 675 (50)			
530	567 (100)	538 (10)	461 (100)	614vs	533vs	570 (100)	603 (3) 578 (15) 555 (30)	523 (100)	529 (100)	$\nu_1(A_1)$ $\nu(\text{X}=\text{O})$	
570	[608] ^j	[732]	599 (1) 557 (4)	631 (sh)	475m (sh)	[644]		503 (50)	506 (47) 486 (55)(sh)	$\nu_2(A_1)$ $\nu_{\text{sym}}(\text{XF}_4)$ in phase $\nu_7(E)$ $\nu_{\text{asym}}(\text{XF}_4)$	
455	527 (40)	[480] ^k	350 (43) ^k	602 (sh)	485m	535 (100)	534 (25) 521 (100)	478 (70) 454 (70)	481 (75) 459 (75)	$\nu_4(B_1)$ $\nu_{\text{sym}}(\text{XF}_4)$ out of phase	
	365 (20)		416 (14) 395 (1)	370w	365ms	414 (10)	417 (5) 409 (5)	429 (60) 417 (sh) 403 (35) 392 (35)	434 (80) 421 (30) 409 (30) 399 (30)	$\nu_8(E)$ $\delta(\text{OXF})$	
302	285 (0+) ^l	480 (100)	[350]	318m	273m	365 (20)	368 (1) 360 (15)	310 (12)	314 (9)	$\nu_3(A_1)$ $\delta_{\text{sym}}(\text{XF}_4)$ out of plane	
242	233 (10)	375 (10)	285 (4)	318m	214w	312 (10)	314 (1) 308 (12)	241 (25)br	248 (20) 239 (sh)	$\nu_6(B_2)$ $\delta_{\text{sym}}(\text{XF}_4)$ in plane	
	161 (0+)	296 (4)	213 (16)	200w	144w, br	237 (0+)	240 (6) 231 (6)	187 (10)	196 (5) 184 (5)	$\nu_9(E)$ $\delta_{\text{asym}}(\text{XF}_4)$ in plane	
	[230]	[346]				[281]			161 (3)	$\nu_5(B_1)$ $\delta_{\text{asym}}(\text{XF}_4)$ out of plane Lattice mode ^m	

^a Ref. 11. ^b Ref. 17. ^c Ref. 19. ^d Ref. 20. ^e Ref. 18. ^f Unpublished work. ^g $\text{K}[\text{BrF}_4\text{O}]$. ^h Numbers in parentheses are relative intensities. ⁱ s = Strong, vs = very strong, m = medium, w = weak, br = broad, sh = shoulder. ^j Bands in square brackets were not observed directly in the Raman spectrum but were obtained from the i.r. spectrum or estimated from combination bands or force-constant calculations. ^k The frequencies ν_3 and ν_4 are coincident in these molecules. ^l Intensity too small to be measured. ^m Peaks below 150 cm^{-1} are assigned to lattice modes and are not listed (see text).

temperature respectively. The low-temperature spectrum is much better resolved and shows a few extra

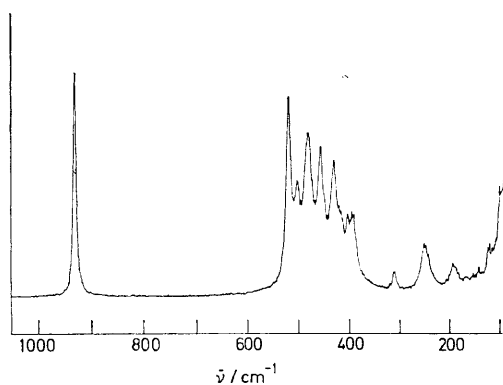


FIGURE 2 Raman spectrum of solid $\text{K}[\text{BrF}_4\text{O}]$ at room temperature

peaks. The room-temperature spectrum is very similar to the one obtained by Bougon.⁶ Table 2 lists the observed frequencies together with those of some related molecules and ions. Although $\text{K}[\text{BrF}_4\text{O}]$ is slightly soluble in MeCN, the solubility is not large enough to allow a solution spectrum of $\text{K}[\text{BrF}_4\text{O}]$ to be

¹⁷ G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 1965, **42**, 2236.

¹⁸ D. Moffett, Ph.D. Thesis, University of Ottawa, 1974.

obtained. The compounds BrF_5 , SO_2ClF , and HF were also unsuitable as solvents so no polarization data are available. The assignments in Table 2 are thus based only on comparison with the related molecules BrF_5 ,¹⁷ $[\text{IF}_4\text{O}]^-$,¹⁸ $[\text{ClF}_4\text{O}]^-$,¹⁹ XeOF_4 ,¹⁷ and $[\text{BrF}_4]^-$.¹¹ The assignments were also made so that the differences in frequency between BrF_5 and $[\text{BrF}_4\text{O}]^-$ were similar to differences between ClF_5 ¹⁷ and $[\text{ClF}_4\text{O}]^-$ and IF_5 ²⁰ and $[\text{IF}_4\text{O}]^-$. The $[\text{BrF}_4\text{O}]^-$ ion is expected to have C_{4v} symmetry. The nine fundamental modes are classified as $3A_1 + 2B_1 + B_2 + 3E$, and all are Raman active.

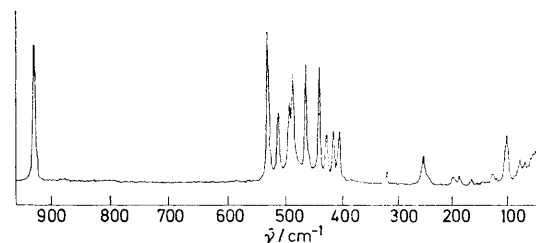


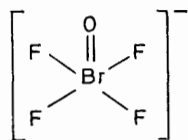
FIGURE 3 Raman spectrum of solid $\text{K}[\text{BrF}_4\text{O}]$ at -196 °C

The asymmetric XF_4 bending mode would, however, be expected to be very weak (this mode is inactive in D_{4h} symmetry), and has not been observed in any of the

¹⁹ K. O. Christie and E. C. Curtis, *Inorg. Chem.*, 1972, **11**, 2209.

²⁰ L. E. Alexander and I. R. Beattie, *J. Chem. Soc. (A)*, 1971, 3091.

related molecules. This mode is, therefore, assumed not to be observed for $[\text{BrF}_4\text{O}]^-$. The single line at 930 cm^{-1} is obviously the BrO stretching motion which, as expected, is intermediate in strength between those in



$[\text{IF}_4\text{O}]^-$ and $[\text{ClF}_4\text{O}]^-$. The fact that this frequency is very close to the mean of the BrO_2 stretching motions in BrO_2F (931 cm^{-1}) indicates that the bond-weakening effect of the negative charge is offset by the greater electron-withdrawing power of four fluorines in $[\text{BrF}_4\text{O}]^-$ as compared to the single fluorine and one oxygen in BrO_2F .

The strongest Raman band should be the BrF_4 symmetric stretch, ν_2 , and the line at 523 cm^{-1} in the room-temperature spectrum (529 cm^{-1} at -196°C) is assigned to this motion. This frequency is quite similar to that in $[\text{BrF}_4]^-$ (530 cm^{-1}) and lower than that in BrF_5 (570 cm^{-1}). The next strongest band should be the symmetric out-of-phase stretching mode ν_4 . This motion should appear in roughly the same region as the similar motion in $[\text{BrF}_4]^-$ (455 cm^{-1}), and the peaks at 478 and 454 cm^{-1} (room temperature) and 481 and 459 cm^{-1} (-196°C) are both possible. In solid BrF_5 this motion is split into two components (at 521 and 534 cm^{-1}). Both the bands at 478 and 454 cm^{-1} are, therefore, assigned to ν_4 in $[\text{BrF}_4\text{O}]^-$. The peak at 503 cm^{-1} in the room-temperature spectrum is assigned to $\nu_{\text{asym}}(\text{XF}_4)$. In the spectrum at -196°C a line at 486 cm^{-1} appeared in addition to the line at 506 cm^{-1} , and both lines are assigned to $\nu_{\text{asym}}(\text{XF}_4)$, with the E mode split into its two components by solid-state effects.

The five deformations remain to be assigned; $\nu_8(E)$ should be the highest-frequency deformation, since it involves motion of the doubly bonded oxygen atom, and it is assigned to the peaks at 429 (together with the shoulder at 417 cm^{-1}), 403 , and 392 cm^{-1} in the room-temperature spectrum. These lines were well resolved at -196°C and were at 434 , 421 , 409 , and 399 cm^{-1} . These values are close to those in BrF_5 (417 and 409), $[\text{IF}_4\text{O}]^-$ (365), and $[\text{ClF}_4\text{O}]^-$ (416 and 396 cm^{-1}), and it is assumed that the E mode is extensively split by solid-state effects. As in all the related molecules, ν_9 should have the lowest frequency of all and the broad line at 187 cm^{-1} in the room-temperature spectrum is thus assigned to it. In the spectrum at -196°C , this line was split into two components at 196 and 184 cm^{-1} . The frequency ν_3 can be assigned to the line at 310 cm^{-1} (314 cm^{-1} at -196°C) and ν_6 to the line at 241 cm^{-1} (a shoulder at 239 cm^{-1} appeared in the low-temperature spectrum). Both these assignments place the frequency found for $[\text{BrF}_4\text{O}]^-$ between those in $[\text{IF}_4\text{O}]^-$ and $[\text{ClF}_4\text{O}]^-$ and similar to the frequency in $[\text{BrF}_4]^-$. As mentioned earlier, ν_5 is assumed not to be observed.

A line was observed at 161 cm^{-1} in the low-temperature spectrum which was not observed at room temperature. This line is assigned to a lattice mode as it is too low in frequency to be a fundamental. Several other lattice modes (at 122 , 97 , 74 , 66 , and 46 cm^{-1}) were also observed but these are not listed in Table 2.

(c) *Fluorine-19 N.M.R. Spectrum of $[\text{BrF}_4\text{O}]^-$.*—The ^{19}F n.m.r. spectrum of a saturated solution of $[\text{BrF}_4\text{O}]^-$ in MeCN at room temperature showed a single peak at -104 p.p.m. relative to external CFCl_3 . This peak is in the F-on-Br ν region and is slightly upfield from the resonance due to the basal fluorines (-135 p.p.m.) of the isoelectronic molecule BrF_5 . The singlet was fairly broad (275 Hz), possibly due to partial coupling of the fluorines with the central Br atom.

(d) *Reaction of $[\text{BrO}_3]$ and BrF_5 .*—The reaction of $[\text{BrO}_3]$ and BrF_5 was reported by Schmeisser and Pammer² to occur at -50°C according to equation (1). Very recently Bougon and Tantot⁵ reported that the reaction, at room temperature, gives different products and proceeds according to equation (2). We found that when pure reagents were used $[\text{BrO}_3]$ and BrF_5 did not react at -50°C . Even after several hours at -50°C the white solid remaining, after the BrF_5 had been pumped off, was virtually all $[\text{BrO}_3]$ with a very small peak at 884 cm^{-1} (due to $[\text{BrF}_2\text{O}_2]$) appearing in the Raman spectrum. When BrF_5 and $[\text{BrO}_3]$ were allowed to react at room temperature for several hours a larger (but still relatively minor) amount of $[\text{BrF}_2\text{O}_2]$ was produced and a very small amount of BrO_2F can be obtained. The $\text{BrF}_5 : [\text{BrO}_3]$ ratio used in this work was higher than that used by Bougon, and Bougon noted that at $\text{BrF}_5 : [\text{BrO}_3]$ ratios greater than 1 the reaction is very slow. We found, however, that when a very small amount of HF was added the reaction was much more rapid and substantial amounts of BrO_2F were obtained and the solid product of the reaction consisted mostly of $[\text{BrF}_2\text{O}_2]$ with variable amounts of $[\text{BrF}_4\text{O}]^-$ being present (usually between 0 and 20%, as estimated from the Raman spectra). In most cases the $[\text{BrO}_3]$ was completely consumed. The amount of $[\text{BrF}_4\text{O}]^-$ produced varied considerably from one reaction mixture to the next. Our results are not consistent with the reaction scheme proposed by Schmeisser and Pammer as $[\text{BrF}_4]$ is not usually observed as a solid product. Our results are also not consistent with those of Bougon and Tantot as they did not observe BrO_2F as a product. Neither of the previously proposed reactions explain the formation of $[\text{BrF}_4\text{O}]^-$. Moreover, we did not find any evidence for large amounts of O_2 being liberated by the reaction as would be required by equations (1) or (2).

Our results can be explained by the following reaction scheme. The first steps, (8) and (9), are possible, and



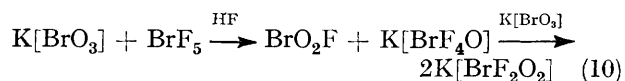
which of these steps occurs will depend on whether BrO_2F or BrOF_3 is the strongest fluoride-ion acceptor. In the related chlorine system, ClOF_3 is a stronger F $^-$

acceptor than ClO_2F .²¹ Also, when a mixture of $\text{K}[\text{BrF}_4\text{O}]$ and $\text{K}[\text{BrF}_2\text{O}_2]$ was treated with a deficit of AsF_5 in BrF_5 , all the $\text{K}[\text{BrF}_2\text{O}_2]$ reacted whereas some $\text{K}[\text{BrF}_4\text{O}]$ was left unchanged. Both these facts suggest that BrOF_3 is a stronger F^- acceptor than BrO_2F and that reaction (9) would be the preferred first step. Since $\text{K}[\text{BrF}_2\text{O}_2]$ is the main solid product, reaction (9) must be followed by another step. A reasonable reaction would be (6) which has earlier been shown to proceed to the right in BrF_5 . The fact that reactions (6) and (9) are occurring at the same time and that their rates may depend on the exact composition of the reaction mixture would account for the variable ratios of $\text{K}[\text{BrF}_2\text{O}_2]$ and $\text{K}[\text{BrF}_4\text{O}]$ formed in different reactions. The role of the HF in promoting the reaction is not clear, but it must be involved in the first step rather than in the second, since this second step [reaction (6)]

²¹ K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 1972, **11**, 2205.

has already been shown to occur in BrF_5 in the absence of HF.

Thus the overall reaction can be written as in (10).



If reaction (6) proceeds to completion then 1 mol of $\text{K}[\text{BrF}_2\text{O}_2]$ should be produced per mol of $\text{K}[\text{BrO}_3]$ used. Comparison of the weights of the $\text{K}[\text{BrF}_2\text{O}_2]$ product and the $\text{K}[\text{BrO}_3]$ used showed that this was indeed the case (see Experimental section). The percentage yield of BrO_2F typically obtained from the reaction of $\text{K}[\text{BrO}_3]$ with BrF_5 was *ca.* 50%. Also the reaction mixture usually turned quite dark brown due to evolution of bromine. Thus the low yield of BrO_2F can be attributed to its decomposition in the reaction mixture.

[6/630 Received, 2nd April, 1976]