35. *The Reaction of Bromine Trifluoride with Oxides and Some Oxy-acid Salts.*

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The reaction of bromine trifluoride with twenty-eight oxides was studied. With CuO, B_2O_3, Tl_2O_3, SiO_2, GeO_2, TiO_2, As_2O_3, Sb_2O_3, SeO_2, UO_3, and I_2O_5 oxygen evolution was quantitative: in other cases a mixture of oxide and fluoride resulted. Metaphosphates were converted quantitatively into hexafluorophosphates, but orthophosphates gave a mixture of fluorophosphate and bromofluoride. An ionic reaction mechanism involving the "acid" $BrF_2^+PF_6^-$ is postulated to explain the formation of hexafluorophosphate. Orthoarsenates resembled orthophosphates. Potassium persulphate and pyrosulphate gave fluorosulphonate, whereas the pyrosulphite, thiosulphate, and sulphate gave equimolecular mixtures of fluorosulphonate and bromofluoride. Sodium dithionite and sulphite gave only bromofluoride. The relationship between the products and the anion structure is discussed. Oxygen was liberated quantitatively from iodates and bromates but incompletely from chlorates and carbonates.

Qualitative observations on the reaction between bromine trifluoride and oxides were made by Ruff and his co-workers (*Z. anorg. Chem.*, 1931, **202**, 59; 1933, **214**, 91). Oxygen was found to be evolved, but a quantitative study of these reactions has shown that the reactivity of bromine trifluoride was over-emphasised, since for only twelve of the twenty-eight oxides examined was oxygen evolution complete. The reaction could not, therefore, be generally applied for the determination of oxygen in oxides. Certain of the quantitative reactions may, however, be of service in determining the heats of formation of bromine trifluoride and iodine pentafluoride. Thus in the case of silica the reaction is : $3SiO_2 + 4BrF_3 \longrightarrow 3SiF_4 + 3O_2 + 2Br_2$, all of the products being volatile. The same is true of arsenious oxide or the oxides of uranium. Similarly the reaction $6I_2O_5 + 20BrF_3 \longrightarrow 12IF_5 + 15O_2 + 10Br_2$, or the reaction with an iodate (see below) could be used in determining the heat of formation of iodine pentafluoride. The reaction of chlorine trifluoride with alkali-metal halides used by Schmitz and Schumacher (*Z. Naturforsch.*, 1947, **2a**, 362) to determine the heat of formation of chlorine trifluoride would not be applicable with bromine trifluoride or iodine pentafluoride because of the formation of complexes (Sharpe and Emeléus, *J.*, 1948, 2135). The criteria for ready reaction of an oxide with bromine trifluoride were that a volatile fluoride was produced, or that the fluoride formed was soluble in the reagent. Only in the reaction with vanadium pentoxide was an oxyfluoride formed ; in the other cases, when attack was incomplete, the proportions of fluoride and unchanged oxide varied with the experimental conditions and had no special significance.

Salts of oxy-acids reacted readily with bromine trifluoride but the products depended on the nature of the anion. Potassium metaphosphate yielded the hexafluorophosphate, in which the co-ordination number of phosphorus was increased from four to six. The mechanism was probably ionic, the anion being first converted into phosphorus pentafluoride, which reacted in bromine trifluoride solution as $BrF_2^+PF_6^-$. This would resemble the acid $BrF_2^+SbF_6^-$ (Woolf and Emeléus, *J.*, 1949, 2865) and could undergo the neutralisation reaction, $K^+BrF_4^- + BrF_2^+PF_6^- \longrightarrow KPF_6 + 2BrF_3$. Indirect evidence for such a mechanism was provided by the fact that bismuth orthophosphate was converted by bromine trifluoride into bismuth trifluoride with complete elimination of phosphorus and oxygen. This was due to the insolubility of the bismuth fluoride in the solvent which prevented an ionic reaction with the unstable intermediate $BrF_2^+PF_6^-$. The formation of hexafluorophosphates by the reaction of metallic halides and a small excess of phosphorus pentachloride may be explained in the same way. The dry reaction between excess of potassium or sodium fluoride and phosphorus pentachloride which produces hexafluorophosphates in much lower yields (Lange, *Ber.*, 1932, **65**, 1253) probably follows an essentially different course. Orthophosphates of metals which form bromofluorides also yielded hexafluorophosphates, but the product contained unchanged bromofluoride. Sodium orthophosphate, for example, gave two molecular proportions of sodium bromofluoride and one of sodium hexafluorophosphate. Sodium bromofluoride is relatively unstable and the analytical results showed a deficit of bromine trifluoride in the product. These reactions can also occur by an ionic mechanism, the products depending on the cation : phosphorus ratio. Pyrophosphates of univalent cations, for example, should give equimolecular proportions of bromofluorides and fluorophosphates. Silver orthoarsenate gave a similar result to sodium orthophosphate, the arsenic appearing in the product as silver hexafluoroarsenate with two molecular proportions of the stable silver bromofluoride.

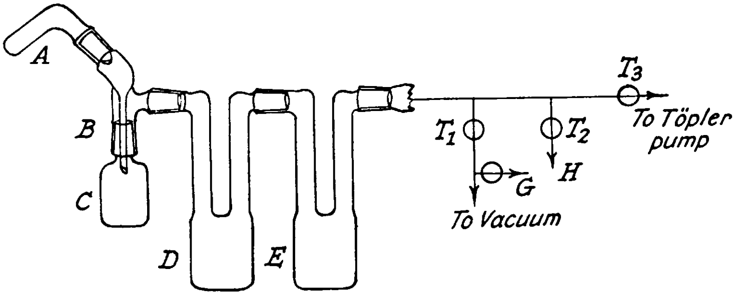
Salts of the sulphur oxy-acids reacted with bromine trifluoride in a way which was related directly to the anion structure. Potassium persulphate and pyrosulphate gave potassium fluorosulphonate, whereas potassium pyrosulphite, thiosulphate, and sulphate all gave equimolecular mixtures of the fluorosulphonate and potassium bromofluoride. The structures of these anions are known and in the case of both persulphate and pyrosulphate two S–O bonds are broken, oxygen in excess of that required to produce the SO_3F ion being eliminated. The oxygen evolution was not studied quantitatively, but it is unlikely that fluorine or bromine oxides were formed. In the bivalent pyrosulphite, thiosulphate, and sulphate ions the structures allow only one SO_3F ion to be formed and consequently one of the univalent cations was converted into the bromofluoride. The four-fold co-ordination round sulphur is retained because in an anion formed with oxygen or fluorine spatial considerations prevent a higher value being attained (Pauling, *J. Amer. Chem. Soc.*, 1933, **55**, 1895; 1927, **49**, 765). It is interesting that the pyramidal sulphite ion in sodium sulphite formed sodium bromofluoride and not sodium fluorosulphonate. Sodium dithionite also gave sodium bromofluoride as the only product. This evidence excludes the structure $[O_3S{-}S{\rightarrow}O]^{2-}$ proposed by Deines and Elstner (*Z. anorg. Chem.*, 1930, **191**, 340), since this would have given fluorosulphonate. It does not however distinguish between the structures $[O_2S{-}SO_2]^{2-}$ and $[O_2S{-}O{-}S{\rightarrow}O]^{2-}$, either of which could give bromofluoride.

EXPERIMENTAL.

Bromine trifluoride was prepared and purified as already described (Sharpe and Emeléus, *J.*, 1948, 2135). The oxides and salts used were whenever possible of AnalaR quality. The majority of the experiments were done in the apparatus shown in the figure, which was constructed of Pyrex glass except for the transparent silica reaction vessel *C*.

Tube *A* contained the bromine trifluoride and, together with the flask *C*, which held a weighed amount of oxide (or salt), was attached by standard ground joints to the dropping-tube *B*. Traps *D* and *E* were cooled in liquid air, and connections were made to the vacuum and Töpler pumps as shown.

Approx. 1—2 c.c. of freshly distilled bromine trifluoride were poured into *A*, which was then cooled in liquid air. Sufficient oxide to produce 50—70 c.c. of oxygen was weighed into *C* through a long funnel. While *A* was cooled and tap T_2 closed, the apparatus was evacuated slowly with T_1 and T_3 open. Traps *D* and *E* were cooled in liquid air, and *A* was allowed to reach room temperature for a short time, whereupon traces of volatile impurities in the bromine trifluoride distilled into *D*. Taps T_1 and T_3 were then closed and a known volume of pure nitrogen (*ca.* 25—30 c.c.) was passed into the reaction system from the calibrated manometer, *H*, by opening T_2; this served to prevent rapid distillation of bromine trifluoride into the cooled trap. The difference in level between *G* and *H* was observed, *C* was cooled in liquid air, and a few drops of liquid bromine trifluoride were introduced by rotating the tube *A* and partly melting its contents. The vessel *C* was warmed to initiate reaction, and further additions of bromine trifluoride were made in the same way, the completion of reaction being indicated by the manometer level. Some reactions occurred at room temperature, others required heat, and the remainder were incomplete after refluxing the oxide with liquid bromine trifluoride for periods up to 2 hours. It was essential to avoid contact of bromine trifluoride with the silicone grease used to lubricate the ground joints.



The oxygen–nitrogen mixture was drawn off with the Töpler pump and measured, excess of bromine trifluoride distilling from *C* to *D* during the process. The residue in *C* was weighed, and the equivalent weight of the reaction product was thereby determined.

Reaction of Bromine Trifluoride with Oxides.—The oxides from which a quantitative oxygen evolution was observed were: CuO, B_2O_3, Tl_2O_3, SiO_2, GeO_2, TiO_2, As_2O_3, Sb_2O_3, SeO_2, UO_3, I_2O_5. In the case of CuO, the product was CuF_2. B_2O_3, Tl_2O_3, SiO_2, GeO_2 and TiO_2 gave BF_3, TlF_3, SiF_4, GeF_4, and TiF_4 respectively. As_2O_3 and Sb_2O_3 were converted into AsF_5 and $SbBrF_8$. SeO_2 and UO_3 gave SeF_6 and UF_6, while I_2O_5 was converted into IF_5.

For the following oxides attack by bromine trifluoride was incomplete under the conditions used: BeO, MgO, ZnO, CdO, HgO, CaO,Al_2O_3, CeO_2, SnO_2, PbO, PbO_2, ZrO_2, ThO_2, MnO_2, Fe_2O_3. The product was a mixture of metal fluoride and oxide. V_2O_5 was converted into VOF_3, and BiOCl into BiF_3.

Reaction of Bromine Trifluoride with Phosphates and Arsenates.—Potassium metaphosphate was prepared by heating AnalaR potassium dihydrogen phosphate at 600° (Found: KPO_3/KH_2PO_4, 0·866. Calc.: 0·868). About 0·7 g. was refluxed with 10 c.c. of bromine trifluoride without dissolution occurring. The solid residue after removal of excess of reagent was soluble in cold water and gave no precipitate with silver nitrate; bromide and phosphate were thus absent. The hexafluorophosphate ion was determined as the nitron salt (Lange, *Ber.*, 1928, **30**, 799) (Found: PF_6, 79·2%; equiv., 182. Calc. for KPF_6: PF_6, 78·8%; equiv., 184. Found, for the nitron salt: C, 52·3; H, 4·0; N, 12·1. Calc. for $C_{20}H_{16}N_4,HPF_6$: C, 52·4; H, 3·7; N, 12·2%). For preparation of larger quantities of potassium hexafluorophosphate by this method, 5 g. of salt were obtained conveniently from 10 c.c. of reagent. Sodium metaphosphate reacted similarly, yielding the hexafluorophosphate (Found: PF_6, 85·6%; equiv., 165. Calc. for $NaPF_6$: PF_6, 86·2%; equiv., 166. Found, for the nitron salt: C, 52·3; H, 3·7; N, 12·0%).

Anhydrous sodium orthophosphate, made from AnalaR disodium hydrogen phosphate and excess of sodium hydroxide and dried at 400°, was insoluble in boiling bromine trifluoride. On evaporation of the latter in a vacuum, the residue was a mixture of sodium fluorophosphate and impure sodium bromofluoride in a 1 : 2 molecular ratio. The product was decomposed with dilute nitric and sulphurous acids in a stoppered bottle, and the bromine precipitated as silver bromide. Fluorophosphate was determined as the nitron salt, after the aqueous solution had been boiled with dilute acetic acid to remove hydrobromic acid formed in the decomposition. It was shown that nitron acetate gave no precipitate with M/6-potassium bromate. The comparative stability of hexafluorophosphate to hydrolysis by dilute sodium carbonate solution enabled the fluorine present as bromofluoride to be separately determined after hydrolysis of the mixture with this reagent [Found: Na, 14·0; Br, 29·9; PF_6, 30·5; F (as BrF_4), 31·6. Calc. for $NaPF_6 + 2NaF,0{\cdot}91BrF_3$: Na, 13·9; Br, 29·3; PF_6, 29·1; F(as BrF_4), 28·5%]. The high value found for fluorine is due to partial decomposition of the hexafluorophosphate. In a blank experiment 8·2% of the total fluorine in KPF_6 was hydrolised.

Bismuth orthophosphate, prepared by double decomposition of dilute nitric acid solutions of bismuth nitrate and sodium phosphate, gave the trifluoride as the only product of reaction with bromine trifluoride, the residue being free from bromine and phosphate. Fluorine was determined by fusion with sodium carbonate, extraction of sodium fluoride with water, and precipitation as calcium fluoride (Found : F, 21·7%; equiv., 263. Calc. for BiF_3 : F, 21·4%; equiv., 266). The oxygen evolved in the reaction was collected and measured, and corresponded to 106% of the theoretical value.

Silver orthoarsenate, prepared by double decomposition, was dried at 250° (Found : Ag, 69·7. Calc. for Ag_3AsO_4 : Ag, 69·9%). Reaction with excess of bromine trifluoride gave a clear solution from which excess of reagent was evaporated in a vacuum in the usual way. The residue gave a nitron precipitate and contained bromine and arsenic. The fluorine was determined as in the case of the product from sodium orthophosphate, silver hexafluoroarsenate being decomposed only slowly by sodium carbonate solution [Found : Ag, 40·0; Br, 19·5; F (as BrF_4), 20·0%; equiv., 822. Calc. for $AgAsF_6$ + $2AgBrF_4$: Ag, 39·3; Br, 19·4; F (as BrF_4), 18·5%; equiv., 825].

Reaction of Bromine Trifluoride with Metallic Halides and Phosphorus Pentachloride.—In preliminary experiments it was found that the product from potassium chloride and a small excess of phosphorus pentachloride was a mixture containing about 46% of hexafluorophosphate, the remainder being potassium bromofluoride. Silver chloride gave a similar result. Using pentabromide in place of pentachloride the yields of hexafluorophosphate were quantitative. These and certain related reactions are being more fully studied.

Reaction of Bromine Trifluoride with Salts of Sulphur Oxy-acids.—The reaction product from potassium persulphate was analysed by decomposition with boiling alkali for the fluorine determination. Fluorine was precipitated and weighed as calcium fluoride and then converted into sulphate to provide a correction for co-precipitated calcium sulphate. The sulphate formed on acid hydrolysis was precipitated with barium chloride, and fluorosulphonate was determined as the nitron salt (Traube, *Ber.*, 1919, **52**, 1272) (Found : S, 23·3; F, 12·7; SO_3F, 72·7%; equiv., 279. Calc. for $2KSO_3F$: S, 23·4; F, 13·8; SO_3F, 71·7%; equiv., 276). The nitron salt was also analysed (Found : C, 58·2; H, 4·1; N, 13·2. Calc. for $C_{20}H_{16}N_4HSO_3F$: C, 58·2; H, 4·1; N, 13·6%). The product from potassium pyrosulphate was analysed for potassium by conversion into sulphate and for fluorosulphonate as above (Found : K, 27·5; SO_3F, 72·3. Calc. for KSO_3F : K, 28·3; SO_3F, 71·7%. Found, for the nitron salt : C, 58·2; H, 4·4; N, 13·1%).

Potassium pyrosulphite gave a mixture consisting of an equimolecular mixture of potassium bromofluoride and potassium fluorosulphonate. Bromine was determined as silver bromide after decomposition with sulphurous acid in a stoppered bottle. Fluorosulphonate was determined as the nitron salt by the same procedure as for the determination of hexafluorophosphate in presence of bromofluoride. The high result was probably due to co-precipitation of nitron hydrobromide. Sulphur was determined as barium sulphate, after reduction of the aqueous solution of product with hydrazine hydrate, decomposition of the fluorosulphonate with hydrochloric acid, and a final heating at 100° for 24 hours to remove hydrogen bromide and fluoride (Found : Br, 23·8; SO_3F, 32·0; S, 9·7%; equiv., 334. Calc. for $KBrF_4$ + KSO_3F : Br, 24·0; SO_3F, 29·6; S, 9·6%; equiv., 333).

Potassium thiosulphate was dried at 150° before use (Found : S_2O_3, 58·7. Calc. for $K_2S_2O_3$: 58·9%). The product of reaction with bromine trifluoride was an equimolecular mixture of potassium bromofluoride and fluorosulphonate (Found : K, 22·8; Br, 23·1; S, 11·2; F, as BrF_4, 22·4%; equiv., 329. Calc. for $KBrF_4$ + KSO_3F : K, 23·5; Br, 24·0; S, 9·6; F, as BrF_4, 22·8%; equiv., 333). The bromofluoride was decomposed by sodium carbonate solution without appreciable decomposition of the fluorosulphonate. Potassium sulphate gave the same product (Found : Br, 24·1%; equiv., 331. Calc. for KSO_3F + $KBrF_4$: Br, 24·0%; equiv., 333). The product from silver sulphate was similar (Found : Ag, 46·7; Br, 17·4; S, 7·2%; equiv., 468. Calc. for $AgSO_3F$ + $AgBrF_4$: Ag, 45·9; Br, 17·1; S, 6·8%; equiv., 470).

Sodium dithionite on treatment with bromine trifluoride gave sodium bromofluoride as the only solid product (Found : Na, 13·0; Br, 44·1; F, 40·6. Calc. for $NaBrF_4$: Na, 12·9; Br, 44·7; F, 42·4%). The material used was only 85% pure with respect to the dithionite ion. The latter was determined by its reduction of ammoniacal silver nitrate to silver, which was converted into the bromide after filtration and dissolution in nitric acid. Sodium was determined as sulphate (Found : Na, 29·6. Calc. for $Na_2S_2O_4$: 26·4%), the high value being probably due to the presence of sodium sulphite and sodium chloride, the latter being used as a salting-out agent in manufacture. All of the sodium in the impure dithionite was converted into bromofluoride (Found : equiv., 408. Calc. for $NaBrF_4$ on the 29·6%-Na figure : equiv., 401). Sodium sulphite also gave the bromofluoride on reaction with bromine trifluoride, the product being free from sulphur (Found : Na, 13·7; Br, 44·1. Calc. for $NaF,0{\cdot}92BrF_3$: Na, 13·5; Br, 45·1%).

Qualitative Examination by X-Ray Powder Photography of the Reaction Products from Salts of Sulphur Oxy-acids.—Specimens were sealed in Pyrex capillaries and exposed to copper *Kα* radiation for approximately equal times, the filament current and voltage of the *X*-ray tube being maintained at constant values. The resulting films were compared by superposition. It was found that the lines obtained from the products from potassium persulphate and persulphate (Group A) were identical as regards position and relative intensity, the latter being judged visually. Those of the products from potassium thiosulphate, pyrosulphite, and sulphate (Group B) were also identical. A specimen of potassium bromofluoride was prepared from potassium chloride, and all of the lines of this compound were identified in the photographs from Group B, though all were absent in the photographs from Group A. The bromofluorides obtained from sodium carbonate and dithionite gave identical photographs.

Reaction of Bromine Trifluoride with Halogenates.—With potassium iodate the oxygen evolution was 97 and 101% of theory in duplicate experiments. The solid product was potassium bromofluoride (Found : K, 20·7; Br, 40·4; F, 38·2%; equiv., 197. Calc. for $KBrF_4$: K, 20·0; Br, 41·0; F, 39·0%; equiv., 195). Mercurous iodate, prepared by double decomposition of potassium iodate and mercurous nitrate in dilute nitric acid solution and dried at 120°, gave 100% oxygen evolution. The solid product was mercuric fluoride (Found : Hg, 83·2; F, 15·2%; equiv., 234. Calc. for HgF_2 : Hg, 84·0; F, 16·0%; equiv., 238). Thallous iodate gave an oxygen evolution of 104%. The white residue of thallic fluoride (Found : Tl, 77·9; F, 21·9%; equiv., 271. Calc. for TlF_3 : Tl, 78·3; F, 21·8%; equiv., 261) left on removal of excess of bromine trifluoride became brown in moist air and was decomposed by water to thallic hydroxide; when dried at 120° it gave the trioxide (Found: Tl, 88·4. Calc. for Tl_2O_3: 89·5%). This confirms the observation of Hannebohn and Klemm (*Z. anorg. Chem.*, 1936, **229**, 337) who prepared thallic fluoride by the action of fluorine on the oxide.

Bromine trifluoride liberated oxygen quantitatively from manganese iodate. The product was a mixture of the bi- and the tri-fluoride together with a small proportion of combined bromine trifluoride. A typical composition was: MnF_2, 37; MnF_3, 63; BrF_3, 5. Lead iodate gave a mixture of plumbous and plumbic fluorides free from other halides and containing in successive experiments 33 and 39% of PbF_4. Cobaltous iodate similarly lost all its oxygen and gave a mixture of 64% of CoF_3 and 36% of CoF_2. In the reaction with potassium bromate the evolution of oxygen was measured and found to be complete. For potassium chlorate, however, only one third was evolved as such. The solid residue in each case was potassium bromofluoride and it is possible that the chlorate yielded chlorine dioxide or even chlorine dioxyfluoride (Schmitz and Schumacher, *Z. anorg. Chem.*, 1942, **249**, 238). The reaction between bromine trifluoride and carbonates appears from preliminary experiments to be similar, since only one-third of the oxygen was liberated as molecular oxygen. The solid products from lithium and beryllium carbonate were reagent-insoluble fluorides contaminated with a trace of solvent (Found: Li, 23·2%; equiv., 59·9. Calc. for $2LiF,0{\cdot}03BrF_3$: Li, 23·3%; equiv., 59·9) (Found: Br, 8·1; F, 74·2. Calc. for $BeF_2,0{\cdot}06BrF_3$: Br, 8·7; F, 75·0%). Sodium carbonate, however, was soluble and the bromofluoride resulted (Found: Br, 43·1; F, 42·3%; equiv., 175. Calc. for $NaBrF_4$: Br, 44·7; F, 42·4%; equiv., 179).

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