tained for rubidium phosphate glasses with those for lithium, sodium, and potassium phosphate glasses shows that they are essentially similar; there are, nevertheless, slight but systematic differences. Thus, for example, in glasses with an $\bar{n}$ value of 4, it is observed that as the size of the alkali ion increases (Li^+ = 0.60 Å., Na^+ = 0.95 Å., K^+ = 1.33 Å., and Rb^+ = 1.48 Å.) the pyro- and hexapolyphosphates gradually decrease whereas tri-, tetra-, and pentapolyphosphates gradually increase (Fig. 2). At $\bar{n}$ values of 5 or higher similar trends exist except that pyro- and tripolyphosphates decrease whereas the others increase to some extent. At $\bar{n} = 3.5$ the changes are not systematic, as shown in Fig. 3.

According to the polymer theory of condensed phosphates, as presently developed, only the ratio cation/phosphorus decides the distribution of phosphorus among the various polymeric anion units. The results of this investigation point out that the effect of monovalent cations cannot be completely ignored in developing the polymer theory.

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Preparation of the Fluorosulfonates: $KI(SO_3F)_4$, $KBr(SO_3F)_4$, $SnCl(SO_3F)_3$, and $CrO_2(SO_3F)_2$

BY MAX LUSTIG AND GEORGE H. CADY

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It is known that peroxydisulfuryl difluoride, $S_2O_6F_2$, reacts with some chlorides to replace chlorine by the fluorosulfonate group.[1] This type of reaction now has been used to prepare $SnCl(SO_3F)_3$ from $SnCl_4$ and $CrO_2(SO_3F)_2$ from CrO_2Cl_2. It also has been shown that $S_2O_6F_2$ fails to replace the halogen in KBr or KI when reacting at about room temperature. Instead of this the complex salts, $KBr(SO_3F)_4$ and $KI(SO_3F)_4$, are formed.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared by the method of Dudley, *et al.*, by passing a stream of SO_3 containing a slight excess of F_2 through a "catalytic" reactor[1,2] (containing copper ribbon coated with silver fluoride(s)) at 165° using dry nitrogen as a carrier. The product was purified by pumping away fluorine fluorosulfonate and other volatile impurities while the material was held at −78°.[1] The potassium halogenides were of analytical quality. Stannic chloride and chromyl chloride were purified by vacuum distillation.

Potassium Tetrakis(fluorosulfonato)iodate(III).—An excess of peroxydisulfuryl difluoride was distilled into a weighed, cold bulb containing 0.271 mmole of KI. The bulb then was allowed to warm. A mildly exothermic reaction, evidenced by a slight warming of the reaction bulb, began to occur just below room temperature. At first the solid became brown in color. After several hours, however, it became white. The excess reagent was distilled out of the bulb, and the weight of the product was that of 0.267 mmole of $KI(SO_3F)_4$.

When a solution of sodium hydroxide was added, the product reacted according to the equation

$$3KI(SO_3F)_4 + 12OH^- \longrightarrow 2IO_3^- + 3K^+ + I^- + 12SO_3F^- + 6H_2O$$

rapidly and exothermically. Further hydrolysis of the fluorosulfonate to sulfate and fluoride ions took place by prolonged heating. The iodate was determined by iodometry using the "dead stop" potentiometric method.[3] The sulfate was determined as barium sulfate and the fluoride as triphenyltin fluoride.[4] *Anal.* Calcd.: iodate, 0.182 mmole; sulfate and fluoride, 1.08 mmoles. Found: iodate, 0.184 mmole; sulfate, 1.13 mmoles; fluoride, 1.09 mmoles.

Potassium tetrakis(fluorosulfonato)iodate(III) is a white solid which melts at 167–168° with slight decomposition yielding a green material which may be ISO_3F.[5] This salt does not react with F_2 at 100°.

Potassium Tetrakis(fluorosulfonato)bromate(III).—This salt was prepared in the same way as potassium tetrakis(fluorosulfonato)iodate(III) except that the reaction flask was closed by a break-seal rather than a stopcock. As the reactants warmed a chemical change started at about 0°. At first the solid became orange in color; then it slowly turned white. The flask was heated to 50° for several days to ensure complete reaction. KBr (4.697 mmoles) yielded a solid residue having the weight of 4.628 mmoles of $KBr(SO_3F)_4$.

The salt reacted with sodium hydroxide solution yielding oxygen and some bromine, the latter being quickly absorbed by the solution. The salt also produced some oxygen when it reacted with a solution containing a large excess of potassium iodide. In both cases the quantity of oxygen produced varied from one run to another. The solution from the alkaline hydrolysis was made acidic and then treated with $NaHSO_3$ to reduce BrO_3^- to Br^-. The sulfur dioxide then was removed by prolonged boiling. Bromide ion was determined as AgBr, sulfate as $BaSO_4$, and fluoride as triphenyltin

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(1) J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

(2) K. B. Kellog and G. H. Cady, *ibid.*, **70**, 3986 (1948).

(3) G. Wernimont and F. F. Hopkinson, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 308 (1940).

(4) N. Allen and N. H. Furman, *J. Am. Chem. Soc.*, **54**, 4625 (1932).

(5) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 352 (1960).

fluoride. *Anal.* Calcd.: Br, 15.51; S, 24.89; F, 14.75. Found: Br, 15.4; S, 24.7; F, 14.3.

Potassium tetrakis(fluorosulfonato)bromate(III) is a white solid which begins to decompose at 100° giving a dark red liquid having the appearance of $BrSO_3F$.[5]

Chlorotris(fluorosulfonato)tin.—This compound was prepared by contacting tin(IV) chloride with a large excess of peroxydisulfuryl difluoride in a sealed tube equipped with a break-seal attachment. A mild reaction took place just below room temperature and was complete within a few minutes. The reaction proceeded as indicated.

$$2SnCl_4 + 3S_2O_6F_2 \longrightarrow 2SnCl(SO_3F)_3 + 3Cl_2$$

It was found that heating the reactants at 100° for several days achieved no further replacement of the chlorine. $SnCl_4$ (0.518 mmole) yielded a weight of the above compound corresponding to 0.517 mmole.

The volatile material remaining after the reaction was distilled away. This material was fractionated into three products: chlorine, determined by molecular weight and color; $S_2O_6F_2$, determined by molecular weight and infrared spectrum; and a trace of an unidentified product. After hydrolysis of the solid material in sodium hydroxide solution, chloride and sulfate were determined gravimetrically as AgCl and $BaSO_4$, respectively. *Anal.* Calcd.: Cl, 7.87; S, 21.3. Found: Cl, 7.84; S, 21.0.

Chlorotris(fluorosulfonato)tin is a white solid decomposing at about 167°.

Dioxobis(fluorosulfonato)chromium(VI).—Chromyl chloride was found to react with excess $S_2O_6F_2$ at room temperature.

$$CrO_2Cl_2 + S_2O_6F_2 \longrightarrow CrO_2(SO_3F)_2 + Cl_2$$

CrO_2Cl_2 (0.362 mmole) yielded a solid having the weight of 0.345 mmole of $CrO_2(SO_3F)_2$. *Anal.* Calcd.: Cr, 14.74; S, 18.17; Cl, 0.00. Found: Cr, 14.23; S, 17.8; Cl, 0.99. Chromium was determined by iodometric analysis involving the chromate ion formed by alkaline hydrolysis of the solid. Chloride and sulfate were determined as AgCl and $BaSO_4$, respectively.

Dioxobis(fluorosulfonato)chromium(VI) is a dark brown, slightly volatile solid which decomposes very slowly at room temperature into a greenish compound. Hydrolysis of an aged sample yielded a yellow solution and a small amount of green flocculent precipitate resembling chromium(III) hydroxide.

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Nitrosodifluoramine (F_2NNO)

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It has been reported by Johnson and Colburn[1] that when tetrafluorohydrazine is handled by conventional vacuum line techniques it possesses a light to dark blue-purple color in the liquid phase. This color originally was attributed to trace impurities and was found to be a function of the concentration of NF_2 radicals in the gas phase prior to condensation. In the present work evidence for the existence of nitrosodifluoramine and evidence that the purple color of condensed tetrafluorohydrazine is due to trace amounts of this compound are presented. It is estimated that as little as 0.1% NF_2NO in liquid N_2F_4 will give a pronounced purple color to the solution.

Preparation

When a mixture of tetrafluorohydrazine[2] (N_2F_4) and nitric oxide is passed through a coil at elevated temperatures (300°) and then allowed to impinge upon a Pyrex finger at liquid nitrogen temperature, a dark purple deposit is formed. The intensity of the color of this material is (within limits) proportional to the temperature (concentration of NF_2 radicals) of the incoming stream of gas and to the concentration of NO in the incoming stream.

In order to get maximum conversion of N_2F_4 into NF_2NO it is necessary to use excess NO. In a typical preparation a stream of gas consisting of 10 parts NO and 1 part N_2F_4 is passed through a coil at 300° and allowed to condense on a Pyrex finger at liquid nitrogen temperature. Purification is accomplished by substituting liquid oxygen for the nitrogen in the finger, and pumping off the excess NO (vapor pressure 3 mm. at $-183°$). Quite pure NF_2NO can be prepared in this way as shown below.

Characterization of NF_2NO

If a relatively pure sample of NF_2NO prepared as described above is allowed to warm up to room temperature, the gases produced have in a typical case the composition (as determined by mass spectrometric analysis): 32.4% N_2F_4, 65.0% NO, 1.8% N_2O, 0.6% SiF_4. This is the composition which would be expected if NF_2NO decomposed according to the equation

$$2NF_2NO \rightleftharpoons N_2F_4 + 2NO \qquad (1)$$

We have as yet been unable to prepare NF_2NO completely free of N_2O and SiF_4. This is not surprising, however, as in Pyrex systems many NF compounds react with glass at elevated temperatures to form N_2O and SiF_4.

In addition to the analysis of NF_2NO given above, the following observations have been made on NF_2NO. The F^{19} n.m.r. spectrum of a mixture of NF_2NO and N_2F_4 has been observed. Two absorption peaks are observed; the peak on

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[1] F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

[2] C. B. Colburn and A. Kennedy, *ibid.*, **80**, 5004 (1958).