

632. *Alternative Syntheses of Peroxodisulphuryl Difluoride.*

By F. B. DUDLEY.

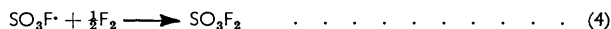
Peroxodisulphuryl difluoride, $S_2O_6F_2$, can be prepared by (a) direct reaction of sulphur trioxide and fluorine in the presence of silver difluoride at 180–200°, (b) oxidation of metal fluorosulphates by elementary fluorine, or (c) anodic oxidation of solutions of alkali fluorosulphates in fluoro-sulphuric acid.

THE powerful oxidising agent peroxodisulphuryl difluoride, $S_2O_6F_2$, was first prepared by Dudley and Cady,¹ by reaction of fluorine and sulphur trioxide at 180° on a catalytic surface of silver difluoride. When the vapour of this compound is carried by a non-reactive gas, such as nitrogen, through a glass tube heated at one spot to about 120°, an intense brown colour is produced at that spot (no trace of colour exists at a distance of ~1" on either side of it). After passing the heated area, the condensable material proves to be the original substance. This behaviour strongly suggests cleavage of the peroxo-linkage to form fluorosulphate free radicals, further evidence for their existence being provided by the work of Roberts and Cady,² who prepared a variety of fluorosulphates by treating peroxodisulphuryl difluoride with halogens, nitrogen dioxide, sulphur dioxide, thionyl fluoride, sulphur tetrafluoride, etc.

Traube³ has shown that sulphur trioxide reacts with ammonium and alkali fluorides to form fluorosulphates although Lange⁴ states that free sulphur trioxide will not react with fluorides in a commercially useful manner. The fact that some reaction occurs between metal fluorides and sulphur trioxide suggests that the function of the silver fluoride surface in the original preparation is the intermediate formation of silver fluoro-sulphate, there being subsequent displacement of fluorosulphate radicals by fluorine:



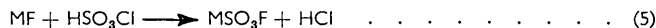
In the presence of an excess of fluorine, the reaction



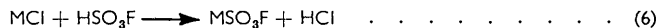
would result in formation of hypofluorite in preference to peroxo-compound. This type of mechanism would also serve to explain the formation of other hypofluorites, such as trifluoromethyl hypofluorites from carbonyl fluoride and fluorine, or of pentafluorosulphur hypofluoride from fluorine and thionyl tetrafluoride, and of course the alternative formation of the corresponding peroxo-derivatives. Addition compounds such as perfluoromethoxysilver, $CF_3 \cdot OAg$, and silver pentafluorosulphur oxide, $Ag \cdot O \cdot SF_5$, would then be the expected intermediates.

The plausibility of the above arguments suggested that peroxodisulphuryl difluoride could be prepared by oxidation of fluorosulphates either by the use of elementary fluorine or by anodic oxidation of cold solutions at high anodic current densities.

General methods used in the preparation of salts of fluorosulphuric acid are discussed by Lange.⁴ One of the simplest is the reaction of a metal fluoride with chlorosulphuric acid, thus:



An analogous procedure, first employed by Ruff,⁵ involves addition of a metal chloride to anhydrous fluorosulphuric acid:



¹ Dudley and Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 513.

² Roberts and Cady, *J. Amer. Chem. Soc.*, 1960, **82**, 353, 354.

³ Traube, *Ber.*, 1913, **46**, 2513.

⁴ Lange, *Ber.*, 1927, **60**, 962.

⁵ Ruff, *Ber.*, 1914, **47**, 656.

This method was particularly useful in preparing a solution of potassium fluorosulphate in fluorosulphuric acid, giving a solution of reasonably high conductivity and containing fluorosulphate anions only.

Electrolytic Preparation of S₂O₆F₂.—Woolf⁶ reported that electrolysis of fluorosulphuric acid resulted in the liberation of gas at the cathode only. He claimed that 0.5 mole of hydrogen was liberated per faraday of electricity. He also reported that the liquid at the anode became strongly oxidising. The explanation offered was the formation of an oxidising peroxodisulphuryl dichloride ion:



Since the powerfully oxidising agent, peroxodisulphuryl difluoride, is readily reduced to fluorosulphate ions, it appears very probable that the reverse process occurs during the electrolysis of fluorosulphuric acid. Moreover, the non-existence of a peroxodisulphuryl dichloride ion is also indicated by Woolf's observation that conductivity data provide no evidence of a second acid in the HF-SO₃ system.

When a diaphragm cell was used in our work, phenomena not reported by Woolf were observed at the cathode. Although it was not possible to devise a technique to establish clearly the changes occurring at the cathode, colour changes and deposition of sulphur on the cathode indicated the formation of sulphur sesquioxide, a bluish-green solid which decomposes spontaneously at room temperature to sulphur, sulphur dioxide, and sulphur trioxide. When prepared by addition of finely powdered, pure, dry sulphur to freshly distilled, water-free sulphur trioxide, the sesquioxide is insoluble in the free trioxide, but in the presence of sulphuric acid it gives a greenish solution.

The necessity for avoiding, or at least minimising, the reduction of fluorosulphate by nascent hydrogen suggested the construction of a cell whereby any gaseous products could be removed as soon as possible after their formation. This required that the electrolysis be conducted under a vacuum and at a low enough temperature for the fluorosulphuric acid not to be distilled over into the traps. The lower temperature results in a greater solubility of the desired product in fluorosulphuric acid, and of course greater diffusion into the cathode compartment where reduction to this acid may occur. A temperature of -23° permitted peroxodisulphuryl difluoride to be removed from the anolyte to give yields corresponding to a current efficiency of about 55%. The use of a diaphragm to separate anolyte and catholyte was discarded because of an electro-osmotic effect which resulted in a mass transfer of electrolyte from anolyte to catholyte.

EXPERIMENTAL

Preparation of Peroxodisulphuryl Difluoride by Oxidation of Metal Fluorosulphates.—(1) The metal fluorosulphates used were prepared by a modification of Traube's method.³ Anhydrous fluorides of nickel and copper were prepared by fluorination of the anhydrous chloride in apparatus similar to that described by Priest.⁷ The golden-yellow anhydrous nickel chloride yielded nickel fluoride as a pale yellow homogeneous powder, and the dark brown cupric chloride yielded cupric fluoride as a white powder. In each case 20 g. of the metal fluoride powder were spread on stainless-steel trays made from ¾" tubing cut lengthwise. These were then placed in the reactor at 200° and sulphur trioxide vapour was carried by a stream of nitrogen over the powdered salt. The unchanged gases were passed through a cold trap and hence to the fume cupboard. Passage of gas was continued until sulphur trioxide began to condense in the cold trap, and for a further 2 hr. A stream of dried nitrogen was allowed to pass through the reactor overnight to ensure complete removal of unchanged sulphur trioxide. The trays were then reweighed, to ascertain the conversion into fluorosulphate; 20 g. of nickel fluoride gave 27 g. of product, corresponding to a 22% conversion. Cupric fluoride gave 20% conversion.

No analyses were attempted as it was desired only to show qualitatively that the product

⁶ Woolf, *J.*, 1954, 2840; 1955, 433.

⁷ Priest, *Inorg. Synth.*, 1950, 3, 173.

would react with fluorine to yield fluorosulphate free radicals or products such as fluorine fluorosulphate or peroxydisulphuryl difluoride.

Each of the two products was exposed to a slow stream of fluorine at 200°, a flow rate of ~1 l./hr. being maintained for 24 hr. A condensable product was obtained fairly rapidly at first, about 75% of the final yield of about 7 g. being obtained within the first 2 hr. After 24 hr. the weight of salt in each case corresponded to ~99% reconversion into the metal fluoride. The products in each case were readily separated into two fractions by trap-to-trap distillation under a vacuum. That which was volatile at 78° was essentially fluorine fluorosulphate contaminated with sulphuryl fluoride; the residue was essentially peroxydisulphuryl difluoride. The first fractions gave molecular weights averaging 115 and 114, respectively, and liberated an average of 1.8 and 1.75 equivalents of iodine per mole, respectively, from a potassium iodide solution. The second fractions gave molecular weights averaging 202 and 204, respectively, and liberated an average of 1.85 and 1.75 equivalents of iodine per mole, respectively.

(2) Alternatively, sulphur trioxide was added to a nickel reaction vessel 8" high, 5" in diameter, and packed tightly with 7½" lengths of nickel tubing (⅜" outside diameter), the reactor having been previously fluorinated at high temperature for about a week. Addition of the trioxide to the vessel at 200° was followed by a continuous pressure decrease, fairly rapid at first, but settling to a fairly steady pressure decrease of 1—1.5 mm. per min. The weight of trioxide added was obtained by difference, a total of 3.2 g. being added. The amount reacting with the nickel fluoride surface, however, would be somewhat less, as the reactor was evacuated when the pressure had dropped to 100 mm. 0.527 g. of fluorine fluorosulphate, SO_2F_2 , was then admitted to the reactor, the pressure finally attained corresponding to *ca.* twice that which would have normally been expected. This corresponded to a reaction $\text{SO}_3\text{F}^- + \text{SO}_2\text{F}_2 \longrightarrow 2\text{SO}_3\text{F} \cdot + \text{F}^-$. On evacuation 30 min. later, the product was essentially peroxydisulphuryl difluoride, as shown by molecular-weight determinations and reaction with potassium iodide.

An excess of fluorine was then added to the reactor; the product obtained 30 min. later was essentially fluorine fluorosulphate, presumably formed by reaction of fluorine with the remainder of the fluorosulphate ions: $2\text{SO}_3\text{F}^- + 2\text{F}_2 \longrightarrow 2\text{F}^- + 2\text{SO}_3\text{F}_2$. The products were again identified by molecular-weight determinations and by reaction with potassium iodide.

(3) "AnalaR" sodium fluoride (20 g.) was converted into the fluorosulphate as in the first experiment, by subjecting the solid to sulphur trioxide vapour at 200°. The final product weighed 60 g., corresponding to complete conversion. An aqueous solution of the product gave a copious precipitate with nitron.

The finely powdered salt was subjected to fluorine at 200° as before. The reaction was slower than in case (1), but 50 g. were eventually reduced in weight by 20 g., corresponding to a 60% displacement of fluorosulphate by fluorine. To achieve this, however, it was necessary to crush the salt at intervals and redistribute it in the trays.

(4) Ammonium fluorosulphate was prepared by dropwise addition of freshly distilled chlorosulphuric acid to dry ammonium fluoride (20 g.) in a porcelain evaporating basin under moisture-free conditions. A vigorous exothermic reaction resulted and hydrogen chloride was evolved. To complete the reaction the pasty mass was heated on a sand-tray. The resulting salt was dissolved in water, and the theoretically required weight of potassium hydroxide added. The solution was then heated on a water-bath to remove the ammonia and to concentrate the solution. The crystals which separated gave a copious precipitate when nitron solution (10% in 5% acetic acid) was added to their aqueous solution. The yield of dried potassium fluorosulphate was 35 g. (58%).

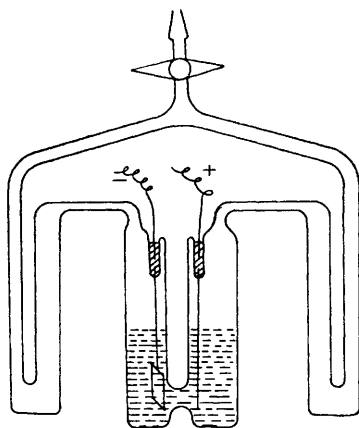
The powdered salt was treated with fluorine at 200° as before. Difficulty was again experienced in getting further reaction once the surface ions had been displaced, and frequent powdering was again necessary. Only 12 g. of reactive material were obtained. This proved to be essentially fluorine fluorosulphate, the slowness of the reaction presumably keeping the partial pressure of fluorosulphate free radicals so low that further fluorination resulted before dimerisation could occur.

Electrolytic Preparation.—Electrolysis of fluorosulphuric acid was carried out in a variety of cells before peroxydisulphuryl difluoride was isolated in appreciable quantity. In all cases the electrolyte was prepared by subjecting commercial fluorosulphuric acid to a high vacuum at room temperature to remove the more volatile impurities, and fractionating the residue in a column packed with Fenske helices. Only the central fraction, b. p. 161.5°, was retained.

This was redistilled into an electrolytic cell containing sufficient dry potassium chloride to give an initially 0.1M-solution of potassium fluorosulphate in fluorosulphuric acid. The object of using such solutions was to increase the conductivity and yet have only fluorosulphate anions present. Any dissolved hydrogen chloride was then removed under a vacuum at room temperature. Small quantities of fluorosulphuric acid were also removed in the process.

(a) The first cell tried contained a sintered-glass diaphragm to separate anolyte from catholyte, and to prevent mechanical mixing of electrolytic products left in solution. U Tubes leading to the vacuum-line were connected to the vapour phases. The most noteworthy phenomena to occur during passage of a 30 mA current were: (1) an electro-osmotic effect resulting in the mechanical transfer of solution from anolyte to catholyte; (2) evolution of hydrogen from the cathode; and (3) formation of a bluish deposit on the cathode. This deposit gradually dissolved and diffused into the surrounding liquid giving it a blue colour which slowly became green and finally honey-coloured. By stopping the electrolysis and carefully reducing the pressure over the anolyte, the liquid in the two compartments could be restored to a common level, but a sharp colour boundary existed at the diaphragm. Any of the coloured solution which moved from catholyte to anolyte compartments was immediately decolorised.

(b) A second diaphragm cell was designed to prevent the electro-osmotic effect. The anode compartment had a B14 socket attached at its highest point. The anode was sealed to the



Electrolytic vacuum cell.

base of a B14 cone. The latter was fitted with a Teflon sleeve to ensure a vacuum-tight seal without the use of lubricants. Only one U tube was used in this cell, and it was attached to the upper portion of the cathode compartment. A potassium fluorosulphate solution was generated in the cell as before, the anode compartment being completely filled so that even when a high vacuum was applied above the catholyte there was no tendency for liquid to move from anolyte to catholyte compartment, and no vapour phase was apparent above the anolyte.

Electrolysis was then effected as before at room temperature but at ~ 80 mm. This pressure was maintained above the catholyte by means of a Cartesian manostat. Although no mechanical transfer of liquid now occurred, the colour changes referred to above were observed. After 48 hr. a firmly adherent deposit of sulphur covered most of the cathode. More still had apparently flaked off and settled at the bottom of the cathode compartment. The catholyte was a pronounced honey colour whilst the anolyte was colourless, a sharp colour boundary existing at the diaphragm. Any attempt to lower the pressure over the catholyte below about 70 mm. resulted in mechanical transfer of liquid from anolyte to catholyte. This was accompanied by instantaneous discharge of the colour in the catholyte compartment near the diaphragm and the development of a vapour phase above the anolyte. About $\frac{1}{2}$ c.c. of peroxodisulphuryl difluoride was obtained by vacuum-fractionation of the anolyte.

(c) A third cell (see Figure) was designed, having an anode consisting of two 26-gauge platinum wires twisted together. The smaller surface area of the anode thus permitted a higher anodic current density to be attained. The cathode consisted of thin platinum sheet as before. The electrode compartments consisted of Pyrex tubing ($\frac{3}{8}$ " outside diameter) joined by a $\frac{3}{8}$ " horizontal length of tubing ($\frac{1}{4}$ " internal diameter), the electrodes being vertically

placed opposite the connecting holes, and as close together as possible. Each compartment was connected to a common vacuum-line by means of separate U tubes in which any volatile substances generated at the electrodes would be condensed if the electrolysis was conducted *in vacuo*. A solution of potassium fluorosulphate in fluorosulphuric acid was prepared as before. To minimise transfer of fluorosulphuric acid, whilst not prohibiting the transfer of peroxydisulphuryl difluoride if formed, the cell was maintained at -22° by a mixture of solid and liquid carbon tetrachloride.

Electrolysis was conducted at a high vacuum, a copper coulometer being again used to determine the quantity of electricity passed. After the passage of 2.604×10^{-2} equivalent of electricity, about 3.2 g. of condensed material had been collected from the anolyte and about 1.5 g. from the catholyte. From the anolyte condensate a fraction (1.689 g.) was separated by trap-to-trap distillation in the range -55° to -45° . This had m. p. -55.3° ($S_2O_8F_2$ has m. p. -55.4°), gave an average molecular weight of 201, and liberated an average of 1.96 equiv. of iodine per mole (4 determinations). The vapour, on being swept through a glass tube heated locally, gave rise to the brown colour observed with peroxydisulphuryl difluoride prepared by other methods. The weight of difluoride obtained corresponded to a current efficiency of 55%.

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