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The safe and convenient preparation of bis(fluorosulfuryl)peroxide ($S_2O_6F_2$) on a large scale

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Abstract

The design and construction of a catalytic reactor (AgF_2 on copper turnings as support) for the fluorination of SO_3 in a flow reaction to produce bis(fluorosulfuryl)peroxide ($S_2O_6F_2$) are described in detail. An operating procedure is developed that allows the production of $S_2O_6F_2$ in substantial quantities (80–120 g h^{-1}) and avoids the accidental production of fluorine fluorosulfate ($FOSO_2F$) as a hazardous byproduct. Also described are purification methods and disposal procedures for highly reactive byproducts (F_2 or $FOSO_2F$) in a safe and environmentally friendly manner, as well as the long-term storage of $S_2O_6F_2$.

Keywords: Catalytic fluorination; Flow reactor design; Bis(fluorosulfuryl)peroxide synthesis; AgF_2 catalysis.

1. Introduction

Bis(fluorosulfuryl)peroxide ($S_2O_6F_2$) was first reported in 1955 as a minor byproduct formed during the electrical discharge of an SOF_2–O_2 mixture [1]. Only approximate physical, and no chemical, properties were described at that time. Following the detection of a small amount of $S_2O_6F_2$ during the synthesis of $FOSO_2F$ [2], the compound was subsequently isolated and characterized by Dudley and Cady [3] in 1957. The direct fluorination of SO_3 catalyzed by AgF_2 between 100 and 170 °C in a flow reaction was found to be an effective synthetic route [3]. In the meantime, a number of alternate routes to $S_2O_6F_2$ have become known [4]; however, the use of a catalytic reactor as described in [5] has remained the method of choice for the preparation of substantial amounts of $S_2O_6F_2$. A possible exception is the anodic oxidation of SO_3F^- in HSO_3F [6], which also offers the added advantage that elemental fluorine is not involved either in the synthesis itself or in the preparation of starting materials. However, following anodic oxidation it is difficult to cleanly separate $S_2O_6F_2$ from a small amount of HSO_3F even when the electrolysis is performed in an evacuated cell [6]. In addition, as SO_3F^- ions are consumed during the hydrolysis, the solubility of $S_2O_6F_2$ in HSO_3F increases with increasing acidity of the solvent system according to a recent study [7], which will reduce the yield.

On the contrary, the solvolysis of XeF_2 in HSO_3F [8] and subsequent thermal decomposition of the product according to

$$XeF_2 + 2HSO_3F \xrightarrow[-2HF]{} Xe(SO_3F)_2 \longrightarrow Xe + S_2O_6F_2 \quad (1)$$

will produce $S_2O_6F_2$ with a very high purity and free of HSO_3F. However, this method will necessarily require elemental fluorine.

The possible presence of a potentially explosive byproduct, suspected to be fluorine fluorosulfate ($FOSO_2F$) in materials prepared by catalytic fluorination of larger amounts of SO_3, has led to serious concerns. A published warning by Cady [9a] has cast some doubt on the suitability of the catalytic fluorination process.

Our own interest in bis(fluorosulfuryl)peroxide ($S_2O_6F_2$), its use in synthesis and its preparation by the catalytic fluorination of SO_3 go back almost 30 years and are well documented [10–12]. During this time a number of serious flaws in the reactor design, the SO_3 delivery system and the trapping system have become apparent and have resulted in a number of radical changes to all aspects of the catalytic fluorination processes as described previously [5].

A number of these changes are dictated by safety concerns. The construction material, copper, is insufficiently resistant to fluorine at elevated temperatures. Both puncturing of the reactor wall and a melt-down of the copper-wool-supported

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AgF_2 catalyst have occurred in our laboratory and have presented serious problems. The use of glass-inlet (SO_3–N_2) and glass-outlet systems attached to a rather rigid and large metal reactor leads easily to fracture at the metal–glass juncture, resulting in the escape of highly reactive and toxic gases such as F_2, SO_3 or $S_2O_6F_2$, frequently at elevated temperatures. Asbestos, used originally as an insulating material [5], is no longer tolerable, and the lack of any disposal tower for highly volatile effluent gases such as F_2 and $FOSO_2F$ in the original design presents serious and unnecessary environmental hazards.

More importantly, many of the safety hazards can be reduced by operating the reactor more efficiently, less frequently and for shorter periods of time. Bis(fluorosulfuryl) peroxide can be stored at room temperature in sealed glass ampoules for years. Greater efficiency is achieved by an accelerated reactant flow, which in turn requires a more flexible and responsive heating system, more accurate temperature monitoring and a more efficient product-trapping system. To avoid the trapping of substantial amounts of $FOSO_2F$, only dry ice is used as coolant.

Many of the changes to the original reactor design and the mode of operation [5], which are described below, have been introduced gradually over the last 25 years. The improved reactor was designed and built by the Mechanical Engineering Service and the Electronic Engineering Service of the Department of Chemistry at the University of British Columbia in 1985. The operating procedure described was last employed by us in the fall of 1994.

2. Experimental details

2.1. Chemicals

Fluorine gas (technical grade) was supplied by Air Products, Long Beach, CA, contained in an A-size cylinder (4.9 lb contents). Stabilized sulfur trioxide (Sulfan B) was supplied by DuPont de Nemours Co., Wilmington, DE, contained in stainless steel containers. Fluorocarbon oils used in bubble counters were supplied by Halocarbon Products Corp., Hackensack, NJ. Sodium hydrogen fluoride tablets of the type NA-0101T $\frac{1}{8}$ in (Harshaw Chemicals) were heated to 800 °C inside the HF-removal tower for 2 h in a stream of dry nitrogen shortly before use. Copper turnings were obtained from Johnson Matthey. Silver nitrate (AR grade), potassium cyanide (AR grade) and soda–lime in granular form (technical grade) were obtained from commercial sources. Only fluorocarbon greases were used (Halocarbon Products Corporation) as lubricants for ground-glass joints.

2.2. Materials used in the construction of the reactor

Construction details of the reactor are shown in Fig. 1. A Monel-K (Inco trademark) tube (47 in long, of 4 in outside diameter and $\frac{1}{4}$ in wall thickness) was used. Monel-K tubing, of $\frac{3}{8}$ in outside diameter was used also for the gas-inlet tubes and the fluorine line. For the nitrogen line, copper tubing of $\frac{1}{4}$ in outside diameter was employed, fitted with Swagelock fittings. The upper parts of the SO_3 flask and of the four collection traps were machined from solid brass to fit into B34 ground-glass sockets. Inlet and outlet tubes, made from $\frac{1}{4}$ in copper tubing, were soldered to the brass cones (Johnson and Matthey Easyflo 45 silver solder was used). Copper flanges (of 5 min outside diameter and $4\frac{1}{2}$ in inside diameter) were custom made. A Teflon gasket was used as seal between the reactor and the removable copper lid (see Fig. 1). Ultratemp 3000 ceramic paper (Cotronics Corporation), Eisenglass (sodium silicate solution from Fisher Scientific) and fiberglass (Corning Glass) were obtained from the sources indicated. Tungsten inert gas (TIG) welding was used to fit the bottom plate to the reactor body. Chromel-A (Hoskens Co.)—20 ga was used as heating wire and a Fluke 51 K/J digital thermometer was employed for temperature measurements with chromel–alumel thermocouples.

The valves used are indicated in Fig. 2 and were supplied by Columbia Pipe Fitting Co. The glass traps (length, about 12 in; outside diameter, $1\frac{3}{4}$ in), were fitted with B34 ground-glass sockets. The SO_3 flask shown in Fig. 2 was made from a 500 ml round-bottomed flask, and a B34 ground-glass socket was attached to the upper section. All metal-ground glass connections were sealed with halocarbon grease.

2.3. Selected physical properties of bis(fluorosulfuryl)-peroxide and some related compounds (see also [9b])

(I) $S_2O_6F_2$; colorless to pale-yellow liquid; boiling point (b.p.), 67.1 °C; melting point (m.p.), −55.4 °C; density at 35.5 °C, 1.645 g cm^{-3}; vapor pressure, $\log_{10} P_{mm} = 5.49916 - 1.2925 \times 10^2/T - 2.5291 \times 10^5/T_2$ (all from [3]. IR [3] and Raman spectra [13] are known.

(II) $FOSO_2F$; colorless gas at 25 °C; b.p., −31.3 °C; m.p., −158.5 °C; density at 74 °C, 1.784 g cm^{-3}; vapor pressure, $\log_{10} P_{mm} = 6.56476 - 6.2687 \times 10^2/T - 6.3906 \times 10^4/T_2$ (all from [2]). IR [2] and Raman [13] spectra are known.

(III) $S_2O_5F_2$; colorless liquid; b.p., 51.0 °C; m.p., −48 °C; density at 20 °C, 1.75 g cm^{-3}; vapor pressure, $\log_{10} P_{mm} = 8.015 - 1662/T$ [9b].

3. Discussion of the catalytic fluorination of SO_3

3.1. The catalytic reactor

The flow reactor used in the synthesis of bis(fluorosulfuryl)peroxide is shown in Fig. 1. A glossary of the terms and abbreviations used in the drawing and a list of suppliers are found in Section 2. Except for copper flanges, the Teflon seal, and silver solder, Monel-K is used as construction material throughout, including inlet and outlet tubes and the two thermocouple wells at the top and the bottom of the reactor. Both inlet and outlet tubes are fitted at the ends

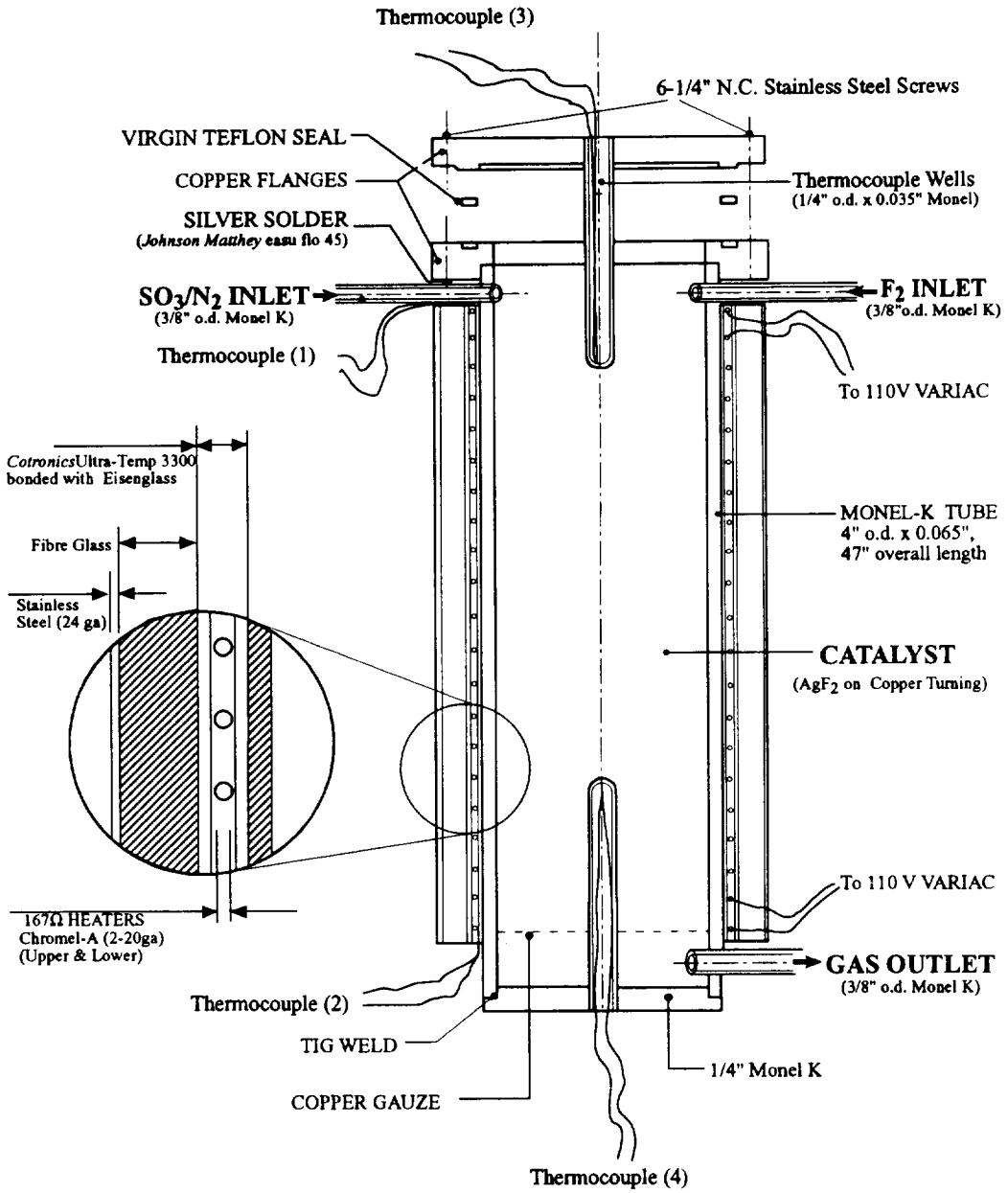

Fig. 1. The catalytic reactor employed in the large-scale synthesis of bis(fluorosulfuryl)peroxide ($S_2O_6F_2$).

with brass Swagelock junctions, which allow sealing off the reactor with solid copper plugs when the reactor is not in use. The overall dimensions of the reactor differ slightly from the original size; the length is increased from 90 to 119.4 cm and the width is 10 cm rather than 7.6 cm in the original reactor.

To fit the slightly larger reactor to the fluorine line, the SO_3 flask and the trapping system, the horizontal rather than vertical inlet and outlet tubes are silver soldered into holes drilled into the reactor body. To prevent debris from the catalyst preparation or molten copper from clogging the outlet tube, a fine copper screen is attached to the reactor wall by spot welding and fitted into the bottom section of the reactor.

The reactor top is detachable to allow exchange or refill of the catalyst. For efficient gas mixing and protection of the Teflon gaskets used, the top section of the reactor is kept empty, about 10 cm from the top, and the reactor is not heated in this zone. The top thermocouple well is not in contact with the catalyst, with the end of the well about 2 cm above the filling level of the catalyst. In our experience, overheating of the reactor during operations is due to metal combustion in F_2, which starts in the upper section and is often caused by incomplete mixing of the gases. The empty space on top permits effective mixing of F_2 and SO_3. With the reactor at a normal operating temperature of about 150 °C, the temperature in the head space should be 65–70 °C, unless an F_2 fire in the upper section causes a sudden temperature increase.

A second thermocouple well is placed in the reactor bottom, to measure the reactor temperature in the lower third of the reactor. Two additional thermocouple leads are attached to the outside of the reactor: one in the upper section and one

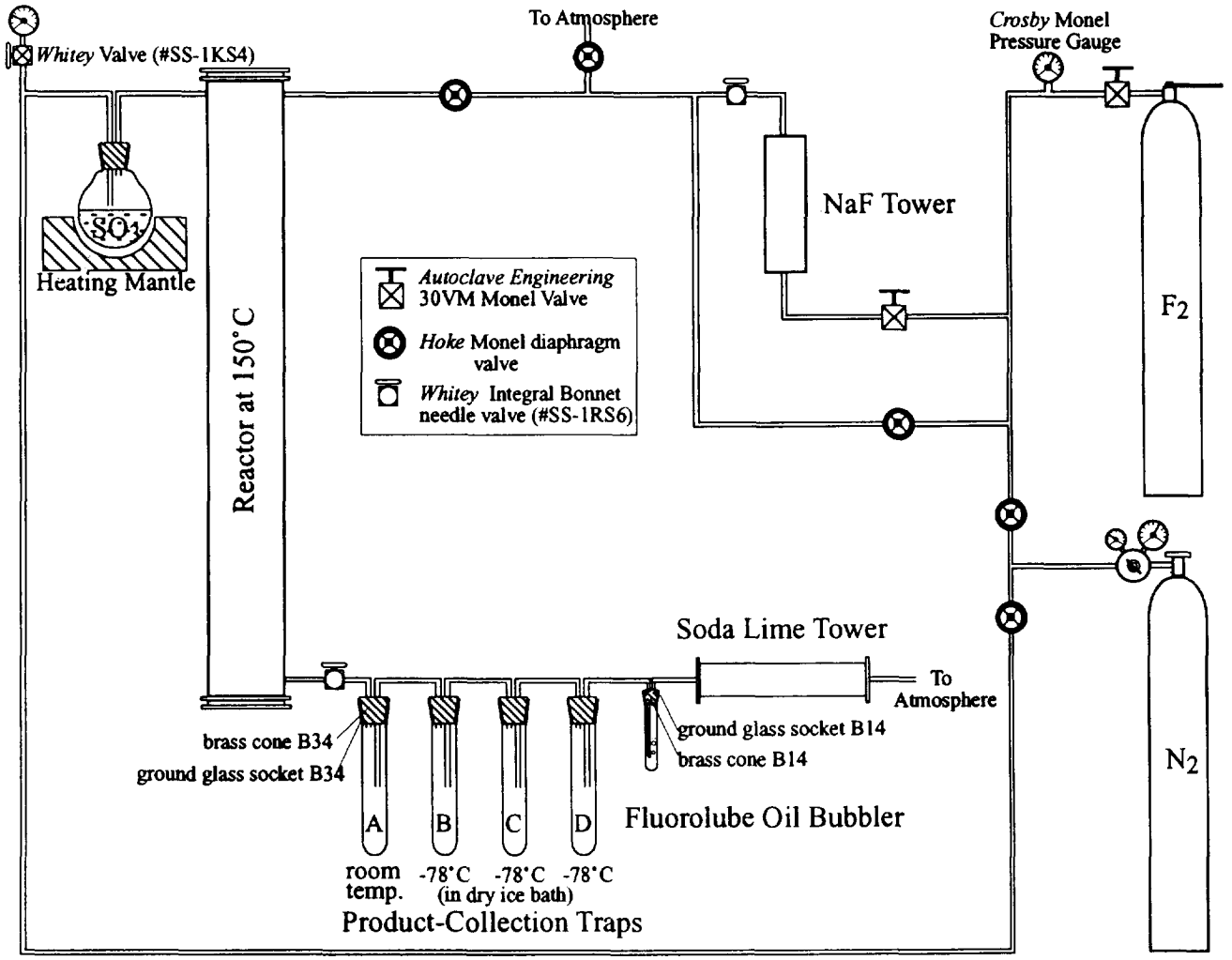

Fig. 2. A schematic diagram of the preparation of bis(fluorosulfuryl)peroxide ($S_2O_6F_2$).

at the gas outlet to measure the temperature of the exiting product. Two independently controlled heating circuits are employed. As shown in Fig. 1, the reactor is wrapped from the outside with ceramic paper (Cotronic Ultra-Temp 3300) bonded with sodium silicate (Eisenglass). A 20 ga Chromel-A heating wire is wrapped tightly and covered with a second layer of ceramic paper–sodium silicate. Heat insulation is accomplished with fiberglass, and a 24 ga stainless steel sheet is wrapped around the reactor as shown. The catalytic reactor, supported by an iron tripod, is placed in a vertical position (as shown in Fig. 2) inside a well-ventilated fumehood and held in place by two large chain clamps which, in turn, are affixed to a lattice work mounted inside the fumehood. The fumehood cabinet is dimensioned to house the F_2 tank, the fluorine and SO_3 delivery lines, the product traps and the NaF and soda–lime towers.

The catalyst is prepared as described previously [5] by self-plating of silver from an aqueous $[Ag(CN)_2]^-$ solution onto copper. The copper wool chore balls [1] used previously [5] are now commercially available with a plastic liner, which makes them unsuitable for the purpose. We have subsequently employed copper turnings, which results in a slightly looser packing of the catalyst. About 3 kg of copper turnings are used, and about 100 g of silver are plated evenly on the surface. The turnings are degreased by repeated washing with trichloroethylene and dried at 100 °C in an oven prior to silver plating. The plating reaction is instantaneous with the surface of the turnings becoming black. The silver plating solution is left in contact with the pre-catalyst overnight at room temperature. After repeated washings with cold water, the silver-plated turnings are dried for 24 h in an oven, set at 105 °C and then packed into the reactor from the top opening. Drying is continued for 6 d in a slow stream of nitrogen with the reactor at about 150 °C and the top plate closed tightly with six stainless steel screws.

With both the SO_3 inlet system and the product traps detached, the reactor is heated to 200 °C and a slow stream of undiluted fluorine is admitted. The temperature rises immediately and the heating is switched off, first in the upper circuit and then, as the reaction front proceeds through the reactor, in the lower section. It is important that the temperature dur-

[1] Chore balls is a term used by the late G.H. Cady and refers to copper wool in the form of balls used for kitchen chores.

ing the fluorination step does not increase beyond 300 °C. Besides reducing outside heating, a reduction in the fluorine flow and, if necessary, a shut-off of the F_2 tank, permit control of the reactor temperature. The end of the fluorination is indicated by a drop in the reactor temperature and the detection of fluorine in the exiting gases by the use of KI paper. To remove excess fluorine from the reactor, a slow stream of nitrogen is maintained for several hours. The reactor is allowed to cool down to 150 °C overnight. The SO_3 inlet flask and the collection traps are now attached to the reactor.

It is advisable to repeat the fluorination procedure, when the reactor has not been in use for several years. Commonly, small amounts of pure $S_2O_6F_2$ are collected at −78 °C during refluorination. Since the amounts of $S_2O_6F_2$ formed during refluorination are small, cooling of the third trap only is sufficient. This, and keeping the temperature below 150 °C, will ensure that little $FOSO_2F$ is formed at this stage and will not be trapped. When the reactor is not in use, the SO_3 delivery and the trapping system are removed and all inlet and outlet tubes are sealed by Swagelok caps to prevent degradation of the catalyst.

3.2. The SO_3 and F_2 inlet systems

To increase the efficiency of the catalytic fluorination, undiluted F_2 is used, after HF is removed by passing F_2 through the NaF tower. The SO_3 flow is increased by keeping the temperature of the SO_3 flask at 55–60 °C, with N_2 used as the carrier gas. It is found difficult under these circumstances to obtain accurate flow rate measurements. The use of calibrated manometers filled with fluorocarbon oil requires fragile glass-to-metal seals. Rotaflow meter readings become inaccurate when polymeric SO_3 condenses. We have therefore used the exit bubbler for approximate qualitative flow rate measurements and a sensitive pressure gage at the SO_3 inlet tube (see Fig. 2) to indicate any pressure build-up due to clogging. The two Autoclave Engineering needle valves are employed for adjustment of the F_2 flow. The Hoke 413 diaphragm valves are used as shut-off valves to seal the reactor off. A handle is attached to the fluorine tank, to permit immediate shut-down in an emergency situation.

There is an additional advantage of heating the SO_3 flask with a heating mantle. In addition to liquid SO_3, either polymeric SO_3 or fuming sulfuric acid may be used.

3.3. The product collection system

Owing to the faster reactant flow rate, four traps are needed for efficient product collection. The first is air cooled, and the remaining three are cooled to −78 °C by dry ice. For each trap, the inlet tube is about $\frac{1}{4}$ in long with the exit tube, made of $\frac{1}{4}$ in copper tubing, about 4 in long. Any excess SO_3 is now detected in the air-cooled trap as a solid film or as a flaky precipitate in the second trap. During normal operations a small amount of very pure $S_2O_6F_2$ will collect in the first air-cooled trap. The product level is frequently checked in the second and occasionally in the third trap. The majority of the product is collected in the second and third traps either as a solid or as a liquid, depending inter alia on the purity of the product. Very occasionally, when a large excess of fluorine is employed, the liquid collected at −78 °C has a pale-yellow–green color, which fades when a vacuum is applied. The color is attributed to very small amounts of dissolved F_2.

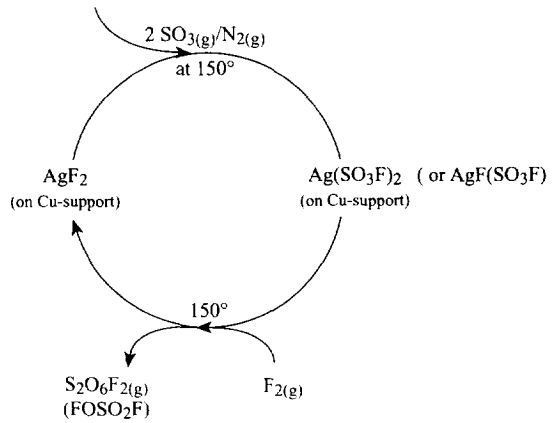

Fig. 3. A proposed catalytic cycle for the catalytic fluorination of SO_3.

Even under optimal conditions, some of the crude product will collect over several days in the fourth trap, which in turn may suggest that in a rapid gas stream (F_2 and N_2) some of the product may be carried through all four traps and will be eventually destroyed in the soda–lime trap. Fluorine fluorosulfate can be obtained by cooling the third and fourth trap with liquid oxygen [9a], and by raising the reactor temperature to 200 °C. We have in the past used this procedure to obtain small quantities of $FOSO_2F$ for occasional use in synthesis [14] but have found that the risks outweigh the advantages. In our experience, the use of finely crushed dry ice as solid coolant is perfectly sufficient and also safe for the efficient trapping of $S_2O_6F_2$.

3.4. Operations of the catalytic reactor — the catalytic fluorination of SO_3

The previously reported synthesis of $Ag(SO_3F)_2$ by the reaction of AgF_2 with SO_3 at 50 °C and the generation of $S_2O_6F_2$ by reaction of $Ag(SO_3F)_2$ at 130 °C with F_2 [15], as well as the formation of $S_2O_6F_2$ (at 160 °C) and $FOSO_2F$ (at 220 °C) from F_2 and SO_3 with AgF_2 as catalyst in a static system [15] have allowed some understanding of the catalytic process. The formation of an intermediate of the composition $AgF(SO_3F)$ cannot be ruled out. Likewise the thermal decomposition of $Ag(SO_3F)_2$ to $AgSO_3F$ and $S_2O_6F_2$, which is fast at 215 °C [15], followed by re-oxidation of $AgSO_3F$, to $Ag(SO_3F)_2$ may play a role in the process. The chemical conversions that take place are summarized in a catalytic cycle shown in Fig. 3.

With the system described here, it is possible to produce about 80–120 g of crude $S_2O_6F_2$ per hour, or to convert about 300–350 ml of SO_3 into mainly $S_2O_6F_2$ in a day's operation

of five to six hours. All traps, excluding the first, are found to contain small amounts of $FOSO_2F$, best detected by ^{19}F nuclear magnetic resonance (NMR) [8,13] because the vibrational spectra of $FOSO_2F$ and $S_2O_6F_2$ are very similar [16]. The recommended purification procedure of crude $S_2O_6F_2$ [5], prolonged pumping with the product trap at −78 °C, is in our view insufficient to remove all $FOSO_2F$, and we have found that a completely pure product is only obtained by careful trap-to-trap distillation with bis(fluorosulfuryl)-peroxide collected at between −50 and −60 °C. The purity of the product obtained can now also be detected by vapor pressure measurements, since the vapor pressure curves of $S_2O_6F_2$ and $FOSO_2F$ are known [3] and small amounts of $FOSO_2F$ will result in higher vapor pressure. Small amounts of $FOSO_2F$ obtained by trap-to-trap distillation are safely disposed of by reaction with soda–lime.

Formation of $FOSO_2F$ is largely avoided by operating the reactor at 140–150 °C. It is commonly observed that, during the catalytic fluorination of SO_3, the temperature in the upper part of the reactor will rise quickly. This is counteracted by reducing heating in the upper section, and we have on occasion operated the catalytic reactor for several hours with external heating in the upper reactor zone switched off. To prevent overheating, the F_2 flow has to be reduced on occasion or the reactant flow has to be stopped until the temperature in the upper half of the reactor has stabilized. Once adjusted to 140–150 °C, the temperature in the lower part of the reactor remains steady and it appears that the exothermic fluorination reaction of SO_3 takes place primarily in the upper part of the reactor.

On occasion, some unreacted sulfur trioxide collects in the first three traps as a flaky precipitate. We have not been able to remove SO_3 completely by repeated trap-to-trap distillation. Some (albeit incomplete) separation is achieved by washing the impure product with concentrated H_2SO_4, where $S_2O_6F_2$ is not appreciably soluble [8]. Vigorous shaking of the two liquids in a separatory funnel is highly dangerous and not recommended. Some mixing of the two layers is achieved by manual stirring with a glass rod. An acid-absorbent gas mask should be worn during this procedure. Some flaky SO_3 remains in the upper layer (crude $S_2O_6F_2$). Since the separation is carried out in an open system, and the separatory funnel is placed in a well-ventilated fumehood, some decomposition of $S_2O_6F_2$ occurs (evident from a slight evolution of O_2), and the resulting product contains small amounts of bis(fluorosulfuryl)oxide ($S_2O_5F_2$) which is reportedly highly toxic [17] and impossible to separate by trap-to-trap distillation owing to the very similar vapor pressures [9b]. In our opinion the above-described washing procedure is dangerous and not recommended. The procedure will not remove all SO_3 and will introduce additional impurities ($S_2O_5F_2$ and SiF_4).

More successful is a repeat of the catalytic fluorination process by distilling the crude product into the round-bottomed SO_3 flask in vacuo and reattaching the flask to the reactor. To avoid formation of $FOSO_2F$, the reactor temperature is lowered to 110–120 °C and the F_2 flow is drastically limited. We have been able to convert about 1 lb of crude product with a high SO_3 content to pure $S_2O_6F_2$ within a few hours. Alternatively small amounts of SO_3 may be tolerated for exploratory reactions in HSO_3F.

The accidental trapping of unreacted SO_3 has three main causes: (1) a gradual drop in the F_2 flow rate occurs, usually when the F_2 cylinder is nearly empty; (2) when the amount of SO_3 in the round-bottomed flask decreases to such an extent that the remainder is now heated to 80–100 °C unless external heating is reduced gradually as the volume of SO_3 decreases; (3) when SO_3 is rapidly introduced into the reactor by an increased N_2 flow.

As discussed above, there are many unexpected problems that may arise during the catalytic fluorination of SO_3. Many of these problems can be anticipated and avoided when the reactor is constantly watched during operations and temperature readings are made at frequent intervals (about every 10 min). At no point should the reactor be left unattended during operation. It is, however, safe and advisable to purge the reactor overnight with a slow stream of dry nitrogen and to operate the reactor only during the day. When shutting the reactor down overnight, it is advisable to continue a slow fluorine flow for another 15 min after the SO_3 flow has been stopped to allow most of the product to condense and then to establish a slow N_2 flow overnight, while traps 2, 3 and 4 are continuously cooled with dry ice and the reactor temperature is maintained at 150 °C.

A last comment concerns the storage of purified $S_2O_6F_2$. Since $S_2O_6F_2$ will react slowly with fluoro-chloro-carbon grease, resulting in the formation of $ClOSO_2F$, long-term storage in 80–100 ml sealed-off ampoules is recommended. The use of an "ampoule key" [18] allows opening in vacuo and resealing of the ampoule. The sealed ampoules are fitted into poly(vinyl chloride) tubes that are sealed with rubber stopcocks to prevent accidental breakage.

4. Summary and conclusions

In most of the major developments from our laboratory over the last 25 years, bis(fluorosulfuryl)peroxide ($S_2O_6F_2$) has played a key role. Some of these developments, like the study of superacids in HSO_3F [10], the generation of unusual cations in superacids [11], and the syntheses and structural studies of metal carbonyl cations [12], are expected to continue in the future. It appears likely, however, that the catalytic reactor at the University of British Columbia will not be operated again. Hence the purpose of this publication at this time is to describe the equipment and the process in such detail that a reconstruction of the reactor and continued safe operation is possible elsewhere. In addition, we hope that this description will replace the original detailed synthesis [5] as a more efficient and safe synthetic procedure.

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