

## Short Communication

### The photochemical preparation of peroxydisulfuryl difluoride, fluorine fluorosulfate and peroxysulfuryl difluoride

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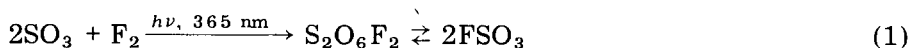
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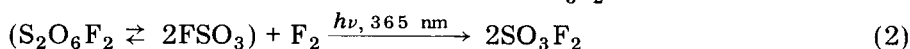
The methods usually employed to prepare  $\text{S}_2\text{O}_6\text{F}_2$  and  $\text{SO}_3\text{F}_2$  are based on the thermal reaction between fluorine and sulfur trioxide [1 - 4]. According to the literature [1, 4], by-products such as  $\text{S}_2\text{O}_5\text{F}_2$  and  $\text{SO}_2\text{F}_2$  are formed in considerable amounts. In addition, Cady [5] has observed the formation of an explosive substance during the preparation of  $\text{S}_2\text{O}_6\text{F}_2$ .

If photochemical methods are employed, however, the final products can be obtained quite simply and with a high degree of purity.

The photochemical reaction between fluorine and sulfur trioxide [6] leads to the formation of  $\text{S}_2\text{O}_6\text{F}_2$  with the quantum efficiency  $\Phi_{\text{S}_2\text{O}_6\text{F}_2} = 1.0 \text{ molecule } h\nu^{-1}$



and the corresponding reaction between  $\text{F}_2$  and  $\text{S}_2\text{O}_6\text{F}_2$  [7, 8] to form  $\text{SO}_3\text{F}_2$  proceeds with the quantum efficiency  $\Phi_{\text{SO}_3\text{F}_2} = 2 \text{ molecules } h\nu^{-1}$



At room temperature the dissociation of  $\text{S}_2\text{O}_6\text{F}_2$  only occurs to a small extent, and hence on illuminating a mixture of  $\text{SO}_3$  with excess of  $\text{F}_2$ ,  $\text{SO}_3\text{F}_2$  only appears when almost all the  $\text{SO}_3$  has been converted to  $\text{S}_2\text{O}_6\text{F}_2$ .

In the photochemical reaction between oxygen difluoride and sulfur trioxide [9, 10], peroxysulfuryl difluoride is produced with a quantum efficiency  $\Phi_{\text{FSO}_4\text{F}} = 1 \text{ molecule } h\nu^{-1}$



When the near-UV absorption spectra of these different sulfur compounds are studied, it is found that  $\text{S}_2\text{O}_6\text{F}_2$  exhibits no appreciable absorption in this region whereas  $\text{SO}_3\text{F}_2$  exhibits a continuous spectrum with  $\epsilon = 0.12$  and  $1.46 \text{ mol}^{-1} \text{ cm}^{-1}$  at 365 and 313 nm, respectively.

Absorption of light by  $\text{SO}_3\text{F}_2$  in the above spectral region leads to a reversible dissociation similar to that at 254 nm [11]



However, this dissociation does not interfere with the course of the reaction between  $\text{F}_2$  and  $\text{S}_2\text{O}_6\text{F}_2$ .

The spectrum of  $\text{FSO}_4\text{F}$  is also continuous in this region, with the absorption increasing strongly with decreasing wavelength, giving  $\epsilon = 0.27$  and  $2.01 \text{ mol}^{-1} \text{ cm}^{-1}$  at 365 and 313 nm, respectively.

At 313 nm, sulfur trioxide exhibits only a very weak absorption, the primary process [12] probably being



Franz and Neumayr [13] have reported a preparative method for  $\text{FSO}_4\text{F}$  based on reaction (3) in a Pyrex reactor with a high-pressure mercury lamp and using a plate of window glass as a light filter (transmission above 350 nm). The reactor was charged with  $\text{SO}_3$  (100 Torr) and excess  $\text{F}_2\text{O}$ , and the mixture was illuminated until all the  $\text{SO}_3$  had been consumed. The authors claim to have obtained pure  $\text{FSO}_4\text{F}$  in this way but unfortunately their results could not be confirmed.

On irradiating  $\text{FSO}_4\text{F}$  in a quartz cell at constant temperature ( $25^\circ\text{C}$ ) with light of wavelength 365 nm, an irreversible dissociation was observed with  $\text{SO}_2\text{F}_2$  being the main product formed; no  $\text{S}_2\text{O}_5\text{F}_2$  could be detected. Solomon *et al.* [14] have obtained similar results. If the temperature is not maintained constant, then as the temperature increases the reaction becomes more complicated and other products are formed. This might explain the data reported by Neumayr and Vanderkooi [15].

The latter authors have detected  $\text{FSO}_2$  and  $\text{O}_2\text{F}$  radicals during the UV decomposition of  $\text{FSO}_4\text{F}$  in a  $\text{CFCl}_3$  matrix. The primary process proposed to explain this observation appears to agree with our results [16], *i.e.*



In the method used for the preparation of  $\text{FSO}_4\text{F}$  discussed below, an excess of  $\text{SO}_3$  is always present so that the  $\text{O}_2\text{F}$  radicals produced by reaction (6) are scavenged *via* reaction (7). The  $\text{FSO}_3$  radicals thereby formed react with  $\text{FSO}_2$  to yield  $\text{S}_2\text{O}_5\text{F}_2$  [reaction (8)]



$\text{FSO}_4\text{F}$  is rather unstable and dissociates thermally in the gaseous phase. This decomposition has been studied [16] above  $60^\circ\text{C}$ , and it has been shown that the overall reaction is



The reaction is in fact a chain process which is strongly inhibited by oxygen.

In the presence of  $\text{SO}_3$ , the thermal decomposition of  $\text{FSO}_4\text{F}$  yields  $\text{S}_2\text{O}_5\text{F}_2$  and  $\text{O}_2$  as in the photolysis reaction. Any unreacted  $\text{FSO}_4\text{F}$  is readily separated from the  $\text{S}_2\text{O}_5\text{F}_2$  generated.

From the data given it can be deduced that Pyrex glass of thickness *ca.* 4 mm enables complete cut off of light of wavelength  $< 300$  nm, and can therefore be used as a suitable light filter for the photochemical preparation of all three substances.

### *Experimental*

IR spectra were recorded on a Perkin-Elmer 221 spectrophotometer. UV spectra were recorded on a Beckman DK-2 and a Cary Model 14 spectrophotometer. Fluorine (Allied Chemical) and oxygen were passed through cold traps at  $-183^{\circ}\text{C}$  and  $\text{OF}_2$  (Allied Chemical) through a trap at  $-78^{\circ}\text{C}$  before entering the reaction system. Sulfur trioxide was obtained by heating oleum (60%) at low pressure.

The static reactor ( $7000\text{ cm}^3$ ) consisted of a cylindrical Pyrex jar with a double-walled water-cooled finger (total thickness of glass 4 mm) inserted into its upper end. A 500 W medium-pressure mercury lamp (Heraeus Q 700) was placed inside the finger and the reactor was tightly wrapped with aluminium foil. The pressure in the reactor was controlled by means of a quartz spiral manometer connected to the main vacuum line to prevent back diffusion of gases during the process of charging the reactor. The flow of fluorine and oxygen difluoride was controlled by means of a miniature Monel needle valve fitted with a Teflon gasket. Stopcocks were lubricated with Halocarbon grease.

#### *Preparation of $\text{S}_2\text{O}_6\text{F}_2$*

The temperature of the water circulating through the glass finger was maintained between  $25^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ . Sulfur trioxide (150 Torr, 0.056 mol) and excess fluorine (150 Torr) were added to the evacuated reactor, and the mixture was irradiated until no further change of pressure with time occurred, indicating that reaction (1) was complete (in our case after 75 min). To be absolutely sure that complete conversion of  $\text{SO}_3$  had occurred, the irradiation was continued for a further 2 - 3 min. The resulting  $\text{S}_2\text{O}_6\text{F}_2$  was condensed at  $-78^{\circ}\text{C}$  and small amounts of  $\text{SO}_3\text{F}_2$  were removed as a head fraction by trap-to-trap distillation at  $-50^{\circ}\text{C}$ .

#### *Preparation of $\text{SO}_3\text{F}_2$*

The reaction conditions were similar to those employed above. A mixture consisting of  $\text{SO}_3$  (150 Torr) and  $\text{F}_2$  (225 Torr) is irradiated until no further change of pressure with time occurred (after 45 min) and then irradiated further to convert the  $\text{S}_2\text{O}_6\text{F}_2$  formed to  $\text{SO}_3\text{F}_2$ . As this step occurs without any pressure change, a longer irradiation time than that employed above (75 min) was used in this case.

The reaction product was condensed at  $-196^{\circ}\text{C}$  and a small portion of substance contaminated with  $\text{SiF}_4$  was removed by trap-to-trap distillation at  $-130^{\circ}\text{C}$ . The volatile fraction at  $-110^{\circ}\text{C}$  (pure  $\text{SO}_3\text{F}_2$ ) was retained.

In order to study the effect of limited photo-activation of  $\text{SO}_3$  at 313 nm

on the reaction and on the purity of  $\text{SO}_3\text{F}_2$ , one preparation was undertaken using the maximum pressure attainable of  $\text{SO}_3$  (270 Torr) and  $\text{F}_2$  (400 Torr). The only detectable impurity was a very small amount of  $\text{S}_2\text{O}_5\text{F}_2$  (0.2%). Hence it must be concluded that  $\text{S}_2\text{O}_6\text{F}_2$  prepared in this manner could also be contaminated by traces of  $\text{S}_2\text{O}_5\text{F}_2$  (0.4%).

Since the formation of  $\text{S}_2\text{O}_5\text{F}_2$  depends on the relative amounts of  $\text{SO}_3$  and  $\text{F}_2$ , it appears advisable to work with large excess of  $\text{F}_2$ . In this way the extent of contamination by  $\text{S}_2\text{O}_5\text{F}_2$  can be reduced still further.

#### *Preparation of $\text{FSO}_4\text{F}^*$*

In this case the reaction conditions were controlled very carefully. The temperature of the water circulating through the glass finger was maintained between 20 °C and 25 °C, and when necessary the reactor temperature was kept below 30 °C by the use of a forced air stream. After evacuation, 50 Torr of  $\text{SO}$ , (0.02 mol), 20 Torr of  $\text{O}_2$  and 700 Torr of  $\text{OF}$ , were introduced into the reactor. The mixture was irradiated for 57 min when it was calculated that *ca.* 80% of the  $\text{SO}$ , had reacted on the basis of an average change of pressure with time of 0.7 Torr  $\text{min}^{-1}$ . The mixture was fractionally condensed at -130 °C (removing  $\text{SO}$ , +  $\text{S}_2\text{O}_5\text{F}_2$  +  $\text{FSO}_4\text{F}$ ) and at -196 °C (removing  $\text{OF}_2$  and some  $\text{O}$ ). A residual pressure of *ca.* 10 Torr in the reactor had no effect on the preparation of a second batch of products. In this case after a new portion of  $\text{SO}$ , had been introduced into the reactor, the mixture of  $\text{OF}_2$  and  $\text{O}_2$  removed from the first batch at -196 °C was recycled, being allowed to evaporate into the reactor under controlled conditions.

The product was again purified by trap-to-trap distillation. A small amount of substance obtained as a head fraction at -115 °C was discarded and the volatile residue remaining at -95 °C (pure  $\text{FSO}_4\text{F}$ ) was retained.

The vapor pressure equation previously reported [9] for  $\text{FSO}_4\text{F}$  is incorrect. The correct equation which is valid for temperatures between -75 °C and -25 °C is  $\log p(\text{Torr}) = 7.851 - 1340/T$ . The extrapolated boiling point is -3.5 °C and the Trouton constant is 22.7.

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**\*Caution:  $\text{FSO}_4\text{F}$  is a strong oxidizing agent and the compound should be handled very carefully. In the course of our studies we have had two explosions: One was caused by reaction of  $\text{FSO}_4\text{F}$  with organic matter and the other when solid  $\text{FSO}_4\text{F}$  at -196 °C was suddenly warmed up to -20 °C.**

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