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DATA ON THE FORMATION AND DECOMPOSITION OF BIS(PENTAFLUOROSULFUR) TRIOXIDE, BIS(PENTAFLUOROSULFUR) DIOXIDE, BIS(PENTAFLUOROSULFUR) MONOXIDE AND OF THE RADICALS SF_5O_2 AND SF_5O. A REVIEW OF EARLIER KINETIC INVESTIGATIONS

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ABSTRACT

A method is described for the preparation of pure bis(pentafluorosulfur) trioxide. The mechanisms of formation and decomposition of $SF_5O_3SF_5$ and $SF_5O_2SF_5$ are described by reference to previous kinetic studies. The dissociation energies of these oxides and of the radicals SF_5O_2 and SF_5O are given and some reactions of $SF_5\cdot$, $SF_5O\cdot$, and $SF_5O_2\cdot$ are described.

INTRODUCTION

We have recently reported the preparation of bis(pentafluorosulfur) trioxide [1]. Having studied the kinetics of the thermal decomposition of this molecule in the presence of oxygen [2] and of carbon monoxide [3] we have been able to establish the best conditions for its preparation. This work with studies of the kinetics of the thermal decomposition of the dioxide with and without the presence of carbon monoxide [4,5] together with investigations of the photochemical decomposition of pentafluorosulfur chloride and bis(pentafluorosulfur) dioxide in the presence of oxygen and of carbon monoxide [6] gave valuable information on the mechanisms of the formation and decomposition of the various oxides and radicals containing SF_5 groups.

1. BIS(PENTAFLUOROSULFUR) TRIOXIDE

$SF_5O_3SF_5$ decomposes according to the following mechanism:

$$\begin{array}{llllll}
SF_5O_3SF_5 & & \longrightarrow SF_5O & + & SF_5O_2 & (1) \\
SF_5O & + \; SF_5O_2 & \longrightarrow SF_5O_3SF_5 & & & (1') \\
SF_5O_2 & & \longrightarrow SF_5 & + & O_2 & (2) \\
SF_5 & + \; O_2 & \longrightarrow SF_5O_2 & & & (2') \\
SF_5O_2 & + \; SF_5O_2 & \longrightarrow 2SF_5O & + & \underline{O_2} & (3) \\
SF_5O & + \; SF_5O & \longrightarrow \underline{SF_5OOSF_5} & & & (4) \\
SF_5O & + \; SF_5 & \longrightarrow \underline{SF_5OSF_5} & & & (5) \\
SF_5 & + \; SF_5 & \longrightarrow S_2F_{10} & & & (6)
\end{array}$$

At temperatures below 25 $^\circ$C and in the presence of oxygen pressures above 200 Torr, the concentration of SF_5 radicals is extremely small, therefore reactions (5) and (6) are of no importance and can be ignored. The only products formed are therefore SF_5OOSF_5 and O_2, i.e.

$$SF_5O_3SF_5 \longrightarrow SF_5O_2SF_5 \quad + \quad 1/2\ O_2 \qquad (a)$$

In the absence of oxygen and at high temperatures the concentration of SF_5O_2 will be small compared with that of SF_5 and consequently it is now the monoxide which is formed preferentially.

$$SF_5O_3SF_5 \longrightarrow SF_5OSF_5 \quad + \quad O_2 \qquad (b)$$

It can be concluded that $k_5 > k_4$ (where k denotes the forward rate of reaction n).

S_2F_{10} appears only in the absence of oxygen and at high temperatures therefore $k_5 \gg k_6$.

The activation energy of reaction (1) was found to be 25.3 0.5 kcal and $k_{1\infty} = 10^{16.32\pm0.40} \exp[-(25300\pm500\ \text{cal})/RT]\ \text{sec}^{-1}$. Therefore the half lifes of the trioxide are $t_{\frac{1}{2}(0^\circ C)} = 105$ min and $t_{\frac{1}{2}(25^\circ C)} = 2.1$ min.

The energy of dissociation $D_{SF_5O-O_2SF_5}$ is 25.3±0.5 kcal.

The trioxide is formed by the combination of the two radicals SF_5O and SF_5O_2.

$$SF_5O \quad + \quad SF_5O_2 \longrightarrow SF_5O_3SF_5 \qquad (1')$$

Therefore, in order to obtain it in a high yield, the concentratio of the SF_5O_2 must be high and the concentration of the SF_5 as low as possible. Therefore, the oxygen pressure must be high and the reaction temperature low ($T < 0^\circ C$).

Preparation of $SF_5O_3SF_5$

The trioxide was prepared by the photochemical decomposition of SF_5Cl in the presence of high O_2 pressures at approximately $- 15^\circ C$. The apparatus used was similar to the one described by Witucki [7] for the preparation of $SF_5O_2SF_5$.

The photochemical reactor consisted of a 2 l pyrex bulb with a quartz center tube containing the light source (a low pressure Mercury Lamp, type TNK 6/20, Quarzlampen G.m.b.H. Hanau). The lamp emitted essentially the 2537 Å line.

The circulating system was composed of the reactor, a trap, a quartz spiral manometer which served as zero-instrument, and a glass circulating pump. It was connected with the vacuum line and the storage bulbs of SF_5Cl and O_2

Before starting the preparation, the whole system was evacuated. Later the cooled trap was filled with about four cm^3 of SF_5Cl and then oxygen introduced up to a pressure of about 500 Torr. The temperature of the photochemical reactor was held between -12 and $-16^\circ C$, by allowing a current of alcohol at the appropriate temperature stream over its outer surface. The temperature of the trap was held at $-78^\circ C$ and the total pressure in the system at about 500 Torr. When no further pressure decrease could be observed, the trap was cooled with liquid air and the oxygen pumped off. The reaction products were then destilled into a trap outside of the circulation system to allow a new charge of reactants to

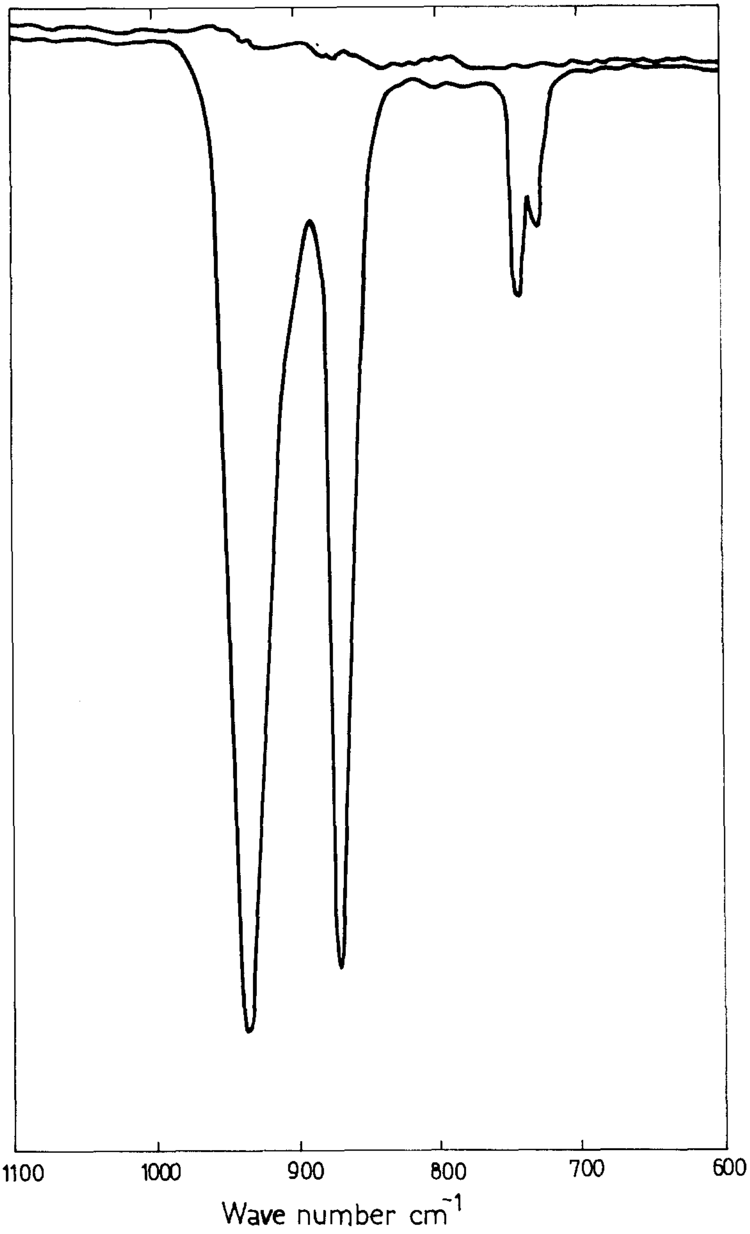

Fig. 1. Infrared spectrum of SF_5OOOSF_5 in the 600 - 1100 c
region using a 10 cm cell. Pressure 0.9 Torr. Temperature 0

be irradiated. The illumination time for each charge was approximately 60 h. The products, after removal of chlorine, were separated by a low temperature destillation with a Podbielniak. Yield of trioxide was about 80%, the rest dioxide with smaller amounts of monoxide.

$SF_5O_3SF_5$ is colourless. Its vapour pressure, measured between -53° and $0^\circ C$ can be represented by the following equation

$$\log p_{(Torr)} = -\frac{1852}{T} + 8{,}529$$

The boiling point, obtained by extrapolation, is 54.9°C and the observed freezing point -55°C. The IR spectrum, taken with a Perkin Elmer 325 Spectrometer, (Fig. 1) shows two characteristic very strong bands at 936 and 872 cm^{-1}, and further weak bands at 743 cm^{-1} and 730 cm^{-1}.

2. BIS(PENTAFLUOROSULFUR) DIOXIDE

$SF_5O_2SF_5$ is much more stable than the trioxide. It only begins to decompose with a measurable velocity at temperature above 200°C |5|. The final products are F_4SO and F_5SOF. The primary process is the dissociation into two SF_5O radicals.

$$SF_5OOSF_5 \longrightarrow SF_5O^\bullet + SF_5O^\bullet$$

$$k_{\infty(SF_5O_2SF_5)} = 10^{15.26\pm0.13}\exp[(-37200\pm300\ cal)/RT]\ sec^{-1}. \quad [4]$$

The energy of dissociation of the O-O bound in the peroxyde is $D_{SF_5O-OSF_5} = 37.2\pm0.3$ kcal [4].

The dioxide is formed by the reaction of two SF_5O radicals ($SF_5O + SF_5O \longrightarrow SF_5OOSF_5$) in a very fast bimolecular reaction, $E \approx 0$.

3. BIS(PENTAFLUOROSULFUR) MONOXIDE

The monoxide is thermally stable up to 300°C. Until now there have been no reports on the primary process of its homogeneous decomposition. SF_5OSF_5 is formed by combination of the radicals SF_5 and SF_5O.

$$SF_5 + SF_5O \longrightarrow SF_5OSF_5$$

a very fast bimolecular reaction, $E \approx 0$.

4. THE RADICAL SF_5O_2

SF_5O_2 is formed by the addition of O_2 to SF_5.

$$SF_5 + O_2 \longrightarrow SF_5O_2$$

in a very fast reaction, $E \approx 0$.

The SF_5O_2 radical is rather unstable. The rate of its decomposition could not be measured. However the energy of dissociation can be estimated.

$$D_{F_5S-O_2} = 13 \pm 2 \text{ kcal (estimated value)}.$$

There is also a fast bimolecular reaction between two SF_5O_2 radicals forming SF_5O and oxygen.

$$SF_5O_2 + SF_5O_2 \longrightarrow 2\ SF_5O + O_2, \quad E = 2 \pm 1 \text{ kcal } |3|.$$

5. THE RADICAL SF_5O

SF_5O is relatively stable. Its thermal decomposition leads to the formation of OSF_4 and F.

$$OSF_5 \longrightarrow OSF_4 + F.$$

$$k_{\infty(OSF_5)} = 10^{13.2} \exp[(-28800 \pm 1200 \text{ cal})/RT] \text{ sec}^{-1} \text{ [4]}$$

$$D_{OSF_4-F} = 28.8 \pm 1.2 \text{ kcal.}$$

$OSF_5^{\bullet}$ is formed in a fast bimolecular reaction between two SF_5O_2 radicals.

As mentioned previously, $2SF_5O$ combine rapidly to form the dioxide, whereas the addition of an SF_5 radical to SF_5O leads to the formation of the monoxide. SF_5O also reacts very rapidly with carbon monoxide producing CO_2 and the radical $SF_5^{\bullet}$ [3, 4, 8]

$$SF_5O \quad + \quad CO \longrightarrow CO_2 \quad + \quad SF_5$$

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