

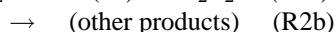
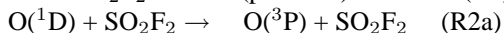
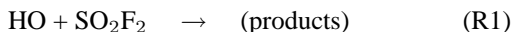


On the atmospheric chemistry of sulphuryl fluoride

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Sulphuryl fluoride, SO_2F_2 , is increasingly used as a crop fumigant, replacing CH_3Br (banned under the Montreal protocol). There is little photochemical data in the literature regarding the atmospheric chemistry of SO_2F_2 . In this work the technique of pulsed laser photolysis, coupled to laser induced fluorescence detection of HO was used to determine rate coefficients for the reactions (R1) and (R2), which control the gas-phase loss of SO_2F_2 , in the atmosphere.



The upper limit obtained of $k_1(298 \text{ K}) < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ suggests that SO_2F_2 may have a lifetime of > 30 years in the troposphere and that transport to the stratosphere, and reaction with $\text{O}(^1\text{D})$ would therefore be an important atmospheric loss process for SO_2F_2 . Reaction (R2) was therefore studied in more detail, resulting in $k_2(220 - 300 \text{ K}) = (1.3 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The relative importance of the physical quenching (R2a) and chemical reaction (R2b) product channels was determined in two ways. By direct detection of $\text{O}(^3\text{P})$, the product yield $\alpha_{2a}(220 - 300 \text{ K}) = (0.55 \pm 0.04)$ was determined. In separate static experiments, the rate of SO_2F_2 destruction by $\text{O}(^1\text{D})$ (R2b) was monitored relative to the well-characterised reaction $\text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow (\text{products})$. The result obtained of $\alpha_{2b}(298 \text{ K}) = (0.45 \pm .06)$, indicates that a significant loss process for SO_2F_2 is destruction by $\text{O}(^1\text{D})$.

In the course of this work the reactions of $\text{O}(^1\text{D})$ with a series of straight-chain alkanes, $\text{C}_n\text{H}_{2n+2}$, were studied:



Bimolecular rate coefficients were determined to be independent of temperature (220 - 300 K) as (in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{n=1} = (1.8 \pm 0.1)$; $k_{n=2} = (3.4 \pm 0.2)$; $k_{n=3} = (4.3 \pm 0.3)$; $k_{n=5} = (5.1 \pm 0.3)$; $k_{n=6} = (6.0 \pm 0.3)$. For $n = 2$ (ethane) and $n = 3$ (propane) these values are considerably smaller (by a factor of 2) than those found in the existing literature.