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The atmospheric chemistry of sulphuryl fluoride, SO₂F₂

T. J. Dillon, A. Horowitz, and J. N. Crowley Max Planck Institute for Chemistry, Mainz, Germany

Abstract. The atmospheric chemistry of sulphuryl fluoride, SO₂F₂, was investigated in a series of laboratory studies. A competitive rate method, using pulsed laser photolysis (PLP) to generate $O(^{1}D)$ coupled to detection of OH by laser induced fluorescence (LIF), was used to determine the overall rate coefficient for the reaction $O(^{1}D) + SO_{2}F_{2} \rightarrow \text{products}$ (R1) of k_{1} $(220-300 \text{ K}) = (1.3 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Monitoring the O (^{3}P) product (R1a) enabled the contribution (**a**) of the physical quenching process (in which SO_2F_2 is not consumed) to be determined as a (225–296 K) = (0.55 ± 0.04) . Separate, relative rate measurements at 298 K provided a rate coefficient for reactive loss of O(¹D), k_{1b} , of (5.8 ± 0.8) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ in good agreement with the value calculated from $(1-a) \times$ $k_1 = (5.9 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Upper limits for the rate coefficients for reaction of SO₂F₂ with OH (R2, using PLP-LIF), and with O₃ (R3, static reactor) were determined as k_2 (294 K)<1 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ and k_3 (294 K)<1 × 10⁻²³ cm³ molecule⁻¹ s⁻¹. In experiments using the wetted-wall flow tube technique, no loss of SO2F2 onto aqueous surfaces was observed, allowing an upper limit for the uptake coefficient of $y(pH 2-12) < 1 \times 10^{-7}$ to be determined. These results indicate that SO_2F_2 has no significant loss processes in the troposphere, and a very long stratospheric lifetime. Integrated band intensities for SO_2F_2 infrared absorption features between 6 and 19 μm were obtained, and indicate a significant global warming potential for this molecule. In the course of this work, ambient temperature rate coefficients for the reactions $O(^{1}D)$ with several important atmospheric species were determined. The results (in units of 10^{-10} cm³ molecule⁻¹ s⁻¹, $k_{(0}1_{D + N_2)} = (0.33 \pm 0.06)$; $k_{(0}1_{D + N_20}) = (1.47 \pm 0.2)$ and $k_{(0}1_{D + H_20}) = (1.94 \pm 0.5)$ were in good agreement with other recent determinations.

■ Final Revised Paper (PDF, 910 KB) ■ Discussion Paper (ACPD)

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