THE PRODUCTION OF SO(${}^{3}\Sigma^{-}$) BY FLASH EXCITATION OF SULPHUR DIOXIDE

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The spectrum of SO(X³ Σ ⁻) has been observed following the flash excitation of sulphur dioxide with radiation above 250 nm. Sulphur monoxide is produced via an excited molecule mechanism involving triplet SO₂. The rate constant for the reaction ³SO₂ + SO₂ was measured as (3.1 ± 1) × 10⁸ M⁻¹ sec⁻¹.

Triplet sulphur dioxide has been shown to be produced following light absorption in the first allowed band [1-3]

 $SO_2(X^1A_1) + h\nu (240 - 340 \text{ nm}) \rightarrow SO_2(A^1B_1), (1)$ $SO_2(X^1A_1) + SO_2(A^1B_1) \Rightarrow SO_2(A^2B_1) + SO_2(2)$

$$SO_2(A^-A_1) + SO_2(A^-B_1) \rightarrow SO_2(a^-B_1) + SO_2$$
 (2)
and it has also been produced [4] directly following

and it has also been produced [4] directly, following light absorption in the forbidden $a^3B_1 - X^1A_1$ system (340-390 nm) [5]. There is also some evidence that triplet sulphur dioxide is the photochemically active species which is responsible for the production of SO₃ and SO [6].

The rate constants for the reactions

$${}^{3}\mathrm{SO}_{2} + \mathrm{SO}_{2} \to 2\mathrm{SO}_{2}, \tag{3}$$

$${}^{3}\mathrm{SO}_{2} + \mathrm{SO}_{2} \rightarrow \mathrm{SO} + \mathrm{SO}_{3} \tag{4}$$

(as well as for radiative and non radiative decay processes) have been measured in phosphorescence decay studies where the triplet state was populated through reactions (1) and (2) by flash excitation (240-320 nm) [3] or, was populated directly by a frequency doubled Raman shifted ruby laser pulse [4]

$${}^{1}\text{SO}_{2}(X^{1}\text{A}_{1}) + h\nu (382.88 \text{ nm}) \rightarrow {}^{3}\text{SO}_{2}(a^{3}\text{B}_{1}).$$
 (5)

Although the chemical reaction (4) is faster [3] than physical quenching (3), neither of the presumed products have been directly observed. The evidence for SO_3 formation is that SO_4^{2-} is formed by reaction

of irradiated SO₂ with water (see footnote 7 in ref. [6]), while SO has been produced from SO₂ flash photolysis only under conditions where direct photodissociation was possible ($\lambda < 220$ nm) [7, 8].

We report here the spectroscopic observation of $SO(X^3\Sigma^-)$ following flash excitation of SO_2 with radiation above 250 nm and the direct measurement of the rate constant for its production in reaction (4).

Preliminary experiments were performed on the conventional flash photolysis apparatus previously described in detail [9]. A mixture of SO₂ (53 N m⁻²) with argon or helium (13.3 kN m⁻²) in a 0.5 m reaction vessel was subjected to a 1 kJ flash through a Corning 7-54 filter which transmits radiation between ca. 240 and 400 nm. Results were recorded on Ilford HP3 photographic plates through a 3.4 m spectrograph. The spectrum of the SO radical was observed by the 6,0 and 7,0 bands of the $B^3\Sigma^- - X^3\Sigma^-$ system. It increased to a maximum at approximately 100 µsec and then decayed slowly over a period of several msec by the reactions.

$$2SO \rightarrow SO_2 + S, \tag{6}$$

$$SO + SO_3 \rightarrow 2SO_2,$$
 (7)

for which the rate constants are $< 5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ [10]. In these experiments, quantitative kinetic measurements on the formation of SO were not possible because of severe interference from the strong C-X system of SO₂ below 235 nm.

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Hence, similar experiments were performed on an apparatus designed for kinetic spectroscopy in the vacuum ultraviolet [8]. In these, a 0.1 m long doublewalled reaction vessel was used, with the 5 mm annular space filled with CCI_{Δ} liquid, transmitting only radiation above ca. 250 nm [11]. Spectra were recorded on sodium salicylate-sensitised Ilford HP4 film using a 2 m Czerny-Turner vacuum spectrograph. The SO radical was detected by the strong bands of the $D^3\Pi - X^3\Sigma^-$ and $E^3\Pi - X^3\Sigma^-$ Rydberg systems at 180 and 149 nm, which were not obscured by SO_2 at pressures below ca. 133 N m⁻² [8]. It was thus possible to study the rate of formation of SO over a narrow range of conditions. The results were plotted as $\log (OD_{max} - OD_t)$ versus t (fig. 1), where OD is the optical density of SO. Assuming Beer's law holds, the sum of all first and pseudo-first order rate constants for the decay of 3SO_2 could then be calculated. The

slope of this plot was not affected by a change in the helium pressure over the range 40-106 N m⁻² and since Calvert et al. [3, 4] have shown that the pressure dependent decay of ${}^{3}SO_{2}$ by SO_{2} is more important than the radiative decay or internal conversion, the rate constant measured is actually $k_{3} + k_{4}$. From five experiments, we obtain $k_{3} + k_{4} = (3.1 \pm 1.0) \times 10^{8} \text{ M}^{-1}$ sec⁻¹, in good agreement with the values $(3.68 \pm 0.28) \times 10^{8} \text{ M}^{-1} \text{ sec}^{-1}$ and $(3.9 \pm 0.1) \times 10^{8} \text{ M}^{-1} \text{ sec}^{-1}$ given by Calvert et al. [3, 4].

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