# CHEMICAL AND PHYSICAL QUENCHING OF EXCITED SULPHUR DIOXIDE

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SO and vibrationally excited SO<sub>2</sub> have been detected as transient products of the quenching of electronically excited SO<sub>2</sub>. The SO is produced through self-quenching of a non-emitting meta-stable triplet state of SO<sub>2</sub>, believed to be the  ${}^{3}A_{2}$  state and not the phosphorescent  $\tilde{a}^{3}B_{1}$  state as was previously thought.

## 1. Introduction

The photochemical reactions of SO<sub>2</sub> at wavelengths >218 nm must involve 'excited molecule' mechanisms since the absorbed energy is insufficient to promote direct photodissociation. The identification of these mechanisms has proved far more difficult than at first anticipated since there are six low-lying excited states of SO<sub>2</sub>,  ${}^{1,3}B_1$ ,  ${}^{1,3}B_2$  and  ${}^{1,3}A_2$  (correlating with electronic states derived from the  $1\pi_g \rightarrow 2\pi_u$  transition in a linear molecule). Thus the phosphorescent  $\tilde{a}^3 B_1$  state, which can be populated through collisionally induced intersystem crossing from the  $\tilde{A}^1B_1$  state or alternatively, by direct absorption ca. 380-390 nm, is perturbed by a neighbouring  ${}^{3}A_{2}$  state and probably by  $a^{3}B_{2}$  state as well [1]. It has been suggested that the quenching of the phosphorescence by 'inert' gases such as Ar, N2, CO, etc., involves collisionally induced radiationless transitions into one or other of these states [2]. In the singlet manifold there is a Renner interaction of the zero order X<sup>1</sup>B<sub>1</sub> state and iso-energetic vibronic levels of the ground state [3].

It has become apparent that the chemical reactivity of excited SO<sub>2</sub> need not reside solely in the optically accessible, emitting states initially populated by UV light absorption; for example, the photooxidation of CO by excited SO<sub>2</sub> is thought to involve two or perhaps three distinct electronically excited states, both singlet and triplet [4]. In contrast the self-photooxidation of SO<sub>2</sub> is believed at the present time, to proceed through self-quenching of the  $\tilde{a}^{3}B_{1}$  state alone [5, 6]

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$$SO_2(\tilde{a}^3B_1) + SO_2 \rightarrow SO(\tilde{X}^3\Sigma^-) + SO_3.$$
 (1)

We report here the results of flash photolysis experiments with SO<sub>2</sub> at wavelengths > 225 nm, in the presence of large excesses of Ar, or CH<sub>4</sub> which, together with a re-appraisal of earlier results [6], establish the involvement of other non-emitting triplet state(s) in the self-photooxidation. In addition transient over-populations of vibrationally excited SO<sub>2</sub> have been photographed for the first time, produced through the quencl ing of electronically excited (probably singlet) molecules. The experiments may be divided as follows:

- (i) spectrographic detection of SO in the vacuum UV,
- (ii) spectrographic detection of vibrationally excited SO<sub>2</sub>, and
- (iii) photoelectric monitoring of their formation and decay.

## 2. Results and discussion

(i) Mixtures of SO<sub>2</sub> (1 torr) and argon or methane (200 torr) were exposed to a flash dissipating 810 J in a conventional flash photolysis system incorporating a McPherson 216.5 vacuum spectrograph; all light at wavelengths < 235 nm was filtered from the flash by inserting a sheet of Chance OX7 glass between the sil-

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Fig. 1. Transient absorption bands of vibrationally excited SO<sub>2</sub> produced following flash excitation under isothermal conditions: delay, 20  $\mu$ sec, flash energy, 2.06 kJ,  $\lambda > 225$  nm. (a)  $p_{SO_2} = 5$  torr,  $p_{A_1} = 500$  torr; (b)  $p_{SO_2} = 5$  torr,  $p_{O_2} = 500$  torr.

Table 1 Transient band assignment in the isothermal flash photolysis of SO<sub>2</sub>:  $\lambda > 225 \text{ nm}^{3}$ 

<i>v<sub>obs</sub>(cm<sup>-1</sup>)</i>	v <sub>calc</sub> (cm <sup>-1</sup> )	Assignment
41870	41880	$SO_{2}(\tilde{C} \leftarrow \tilde{X}); (1, 1, 0) \leftarrow (1, 1, 0)$
41999	41998	$SO_{2}(\tilde{C} \leftarrow \tilde{X}); (1,0,0) \leftarrow (1,0,0)$
42265	42256	$SO_2(\hat{\mathbb{C}} \leftarrow \hat{\mathbb{X}}); (1,2,0) \leftarrow (1,1,0)$
42408	42404	$SO_{2}(\hat{C} \leftarrow \hat{X}); (1,1,0) \leftarrow (1,0,0)$
42773	42766	$SO_2(\tilde{C} \leftarrow \tilde{X}); (1,2,0) \leftarrow (1,0,0)$
43146	43142	$SO_2(\tilde{C} \leftarrow \tilde{X}); (1,3,0) \leftarrow (1,0,0)$
43510	43512	$SO_2(\bar{C} \leftarrow \bar{X}); (1,4,0) \leftarrow (1,0,0)$
54260	54260	
54420	54420	S⊖(Ď ← X); (0,0)
54620	54600	

a) Data taken from ref. [12] for SO2, ref. [13] for SO.

ica flash tube and the reaction cell. Transient absorption bands of SO were detected via the intense  $\vec{D} \leftarrow \vec{X}$ Rydberg system at 180 nm.

(ii) Transient absorption bands due to vibrationally excited SO<sub>2</sub> were photographed in the near UV using a quartz-Littrow spectrograph (Rank Precision, type E742), following flash excitation of SO<sub>2</sub> (5 torr) mixed with Ar, He or O<sub>2</sub> (500 torr), see fig. 1. In this system light of wavelength < 225 nm was filtered from the flash (2.06 kJ) by a double thickness of polythene sheet. Table 1 summarises the identified band heads. The majority is associated with absorption by molecules carrying one quantum of the symmetric stretching frequency  $\nu_1$ , though if the polythene filter were removed faint absorption from molecules carrying an additional quantum of the bending frequency  $\nu_2$  could be detected near the peak of the photolysis flash. The 'hot' bands decayed rapidly and could not be detected photographically after delay times > 50  $\mu$ sec.

(iii) The rate of formation and decay of  $(SO_2)_{\nu_1=1}$  was followed photoelectrically in an SO<sub>2</sub> (6 torr): Ar (300 torr) mixture, via the  $\tilde{C}(1,2,0) \leftarrow \tilde{X}(1,0,0)$  band head at 233.8 nm, using the split-beam kinetic spectrophotometer described elsewhere [7]. A band-pass of 0.12 nm was necessary to ensure adequate resolution and to eliminate interference from scattered light during the period of the photolysis flash. Fig. 2 shows that the transient population in  $\nu_1 = 1$  reaches a maximum ca. 14 µsec after the peak of the flash intensity.



Fig. 2. Formation and decay of  $(SO_2)_{\nu_1=1}$  produced through quenching of electronically excited  $SO_2$ .  $p_{SO_2} = 6$  torr,  $p_{Ar} = 300$  torr, flash energy, 2.06 kJ.

If its time dependence followed the simple expression

$$d[v_1 = 1]/dt = \phi I(t) - k_{v_1 = 1 \to 0} [SO_2] [v_1 = 1]$$

this delay would correspond to a value for  $k_{\nu_1=1 \rightarrow 0} \approx 1.4 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{sec}^{-1}$  which is considerably smaller than the literature value [8]. However, the observation of a transient absorption from the (1,1,0)level suggests that molecules in the (1,0,0) state are not only being relaxed through collisional energy transfer but are also being populated at a significant rate by relaxation from higher vibrational levels. The absence of detectable absorption from the lower lying (0,1,0)and (0,2,0) levels must be due to their rapid relaxation under the conditions employed; SO<sub>2</sub> is one of the few molecules to display the phenomenon of double relaxation [9]. If the triplet yield in  $SO_2$  in the range 250-320 nm is as small as has been suggested ( $\leq 10\%$ ) [5] the vibrational excitation is more likely to be associated with quenching from the excited singlet state. Experiments using a variety of foreign gases with different quenching efficiencies should help to confirm this.

The rate constants for quenching of the SO<sub>2</sub>( $\tilde{a}^{3}B_{1}$ ) by 'inert' gases are all unusually large, in the range (5-12) × 10<sup>10</sup> cm<sup>3</sup>mole<sup>-1</sup>sec<sup>-1</sup>, with activation energies ca. (2.6-3.0) kcal mole<sup>-1</sup> [2]. Since SO<sub>2</sub>( $\tilde{a}^{3}B_{1}$ ) molecules in this energy range are perturbed by interaction with neighbouring <sup>3</sup>A<sub>2</sub> and possibly <sup>3</sup>B<sub>2</sub> states [1], it has been suggested that quenching involves collisionally induced radiationless transfer into one, or perhaps both of these [2]. The rate constant for selfquenching of SO<sub>2</sub>( $\tilde{a}^{3}B_{1}$ ) is rather larger,  $3.8 \times 10^{11}$  cm<sup>3</sup>mole<sup>-1</sup>sec<sup>-1</sup> and it has a slightly smaller activation energy, (2.0 ± 0.2) kcal mole<sup>-1</sup> [2].

Self-quenching of electronically excited SO<sub>2</sub> is known to produce SO<sub>3</sub> [5] and at the present time it is believed that the phosphorescent  $3^{3}B_{1}$  state is involved [5, 6]. There are two types of experiment on which this assertion is based:

(i) Both the yield of  $SO_3$  and the phosphorescence of  $SO_2$  are quenched by the addition of biacetyl [5].

(ii) The transient absorption spectrum of SO, produced following flash photolysis of SO<sub>2</sub> at wavelengths longer than the dissociation threshold, continues to develop after extinction of the flash. The kinetics correspond to a bimolecular rate constant of  $(3.1 \pm 1.0)$  $\times 10^{11}$  cm<sup>3</sup>mole<sup>-1</sup>sec<sup>-1</sup>, which is in close agreement with that found for self-quenching of the  $\tilde{a}^{3}B_{1}$  state [6]. Self-quenching of the SO<sub>2</sub>( $\tilde{A}^{1}B_{1}$ ) initially populated by absorption of the flash, has a rate constant at least two orders of magnitude greater (depending on its vibrational energy content [3]).

The first experiment is inconclusive since later investigations have shown that much of the phosphorescence of biacetyl is sensitised through energy transfer from other, non-emitting triplet state(s) of SO<sub>2</sub> [10]. The interpretation of the flash photolysis experiment is invalid since the  $SO_2$  was diluted with Ar or He at molar ratios  $\geq$  100:1. Under these conditions almost all the  $SO_2(\tilde{a}^3B_1)$  would suffer physical quenching by the inert gas rather than self-quenching. The argument applies with equal force in the experiments reported here, since the Ar or  $CH_4$ :SO<sub>2</sub> ratios were 250:1. The production of SO under these conditions must be associated with the self-quenching of some other triplet state of SO<sub>2</sub> which is not quenched at a competitive rate by Ar, He or  $CH_4$ . There are two candidates,  ${}^{3}A_2$  and  ${}^{3}B_2$ ; the following discussion suggests that the former is the most likely.

If the phosphorescence of  $SO_2$  is quenched through collisional transfer into one or other of these states, the lowest triplet cannot be  $a^3B_1$  [2]. If it were  ${}^3B_2$  it is difficult to understand why it does not phosphoresce or why it has not been observed in absorption: the  ${}^3A_2$ state however, would be metastable. Direct intersystem crossing from  $\tilde{A}^1B_1 \rightarrow a^3B_1$  is forbidden in the absence of a vibronic perturbation but there is no restriction on the spin-orbit coupling of  ${}^1B_1$  with  ${}^3B_2$  or  ${}^3A_2$ . A possible scheme which accommodates these competing demands is shown in fig. 3. Intersystem crossing from the  $\tilde{A}^1B_1$  state initially populates the  ${}^3B_2$  state and subse-



Fig. 3. Possible state diagram for the quenching of electronically excited SO<sub>2</sub>.

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quently the phosphorescent  $\tilde{a}^{3}B_{1}$  state via a collisional process. (The latter transition is vibronically forbidden and Calvert has shown [11] that population of the  $\tilde{a}^{3}B_{1}$  state through intersystem crossing requires a collisional mechanism.) Finally, the quenching of  $\tilde{a}^{3}B_{1}$ populates the lowest triplet state,  ${}^{3}A_{2}$ ; its electronic configuration will include a major contribution from structures of the type tO-S-Ot which should favour the disproportionation

$$SO_2(^3A_2) + SO_2 \rightarrow SO(\tilde{X} \ ^3\Sigma^-) + SO_3.$$
 (2)

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