

## TEMPERATURE DEPENDENCE OF THE COLLISIONAL QUENCHING OF SINGLET MOLECULAR OXYGEN ( $O_2(a^1\Delta_g)$ AND $O_2(b^1\Sigma_g^+)$ ) BY $SO_2$

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(Received March 5, 1985; in revised form May 2, 1985)

### Summary

Between 600 K and 1150 K the rate constant for the collisional quenching of  $O_2(a^1\Delta_g)$  by  $SO_2$  was found to be

$$k_q^{SO_2} (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = (8.6 \pm 0.1) \times 10^6 \exp\left(-\frac{2400 \pm 100}{T}\right) \quad (T \text{ in kelvins})$$

Extrapolation to 295 K gives a value of  $(2.5 \pm 0.8) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , which is consistent with limits obtained from measurements made at room temperature.

At 295 K the rate constant for the quenching of  $O_2(b^1\Sigma_g^+)$  by  $SO_2$  is  $(2.5 \pm 0.5) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . It does not increase appreciably with temperature up to 1150 K, so that  $SO_2$  provides an exception to our classification of the quenchers of  $O_2(b^1\Sigma_g^+)$  according to their efficiency at room temperature and their temperature dependence. The lack of temperature dependence has enabled us to verify our previous results with  $O_2$  itself.

### 1. Introduction

Despite the importance of both  $SO_2$  and the singlet excited states of molecular oxygen as constituents of natural and polluted atmospheres, there has only been one estimate [1] of the quenching of  $O_2(b^1\Sigma_g^+)$  at room temperature, and none at all of  $O_2(a^1\Delta_g)$ .

The value obtained by O'Brien and Myers [1] for the quenching of  $O_2(b^1\Sigma_g^+)$  by  $SO_2$  suggests that it is a relatively poor quencher at 295 K, and is thus anomalous, since triatomic and polyatomic molecules are generally efficient quenchers [2] of this state. Our recent work [3, 4] on the temperature dependence of collisional quenching reactions has shown that quenchers of  $O_2(b^1\Sigma_g^+)$  can be roughly divided into two classes: poor quenchers at room temperature for which the rate constant shows a positive temperature dependence, and the efficient quenchers for which the rate constant is nearly independent of temperature.

SO<sub>2</sub> thus provides an interesting case for study. The results reported here show that the quenching of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is in fact anomalous, in that its quenching is nearly independent of temperature; however, this has allowed us to confirm our previous results for the quenching of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) by oxygen itself.

Also, the experiments showed that O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) is quenched by SO<sub>2</sub> at high temperatures, and so we have been able to estimate the rate constant for this quenching reaction.

## 2. Experimental details

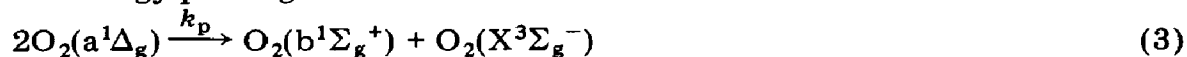
The measurements were made with a combined discharge flow-shock tube apparatus which has been described in detail previously [3]. O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) is generated by passing O<sub>2</sub> through a 2450 MHz discharge; mercury and mercury (II) oxide are used to remove oxygen atoms. SO<sub>2</sub> is added to the oxygen which contains up to 5 wt.% O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>), and the mixture is passed into a shock tube of diameter 50 mm. The normal flow rate was 1.1 mmol s<sup>-1</sup>, which corresponds to a linear flow rate of about 1.5 m s<sup>-1</sup> at 295 K.

In the pre-shock flow, O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) is deactivated both by collisions within the tube and at the wall.

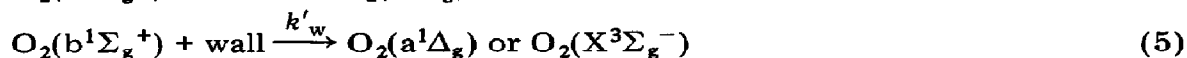


so there is a concentration gradient along the tube. By monitoring the variation of the dimol emission from O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) at 634 nm using a movable photomultiplier and interference filters, the quenching rate constant at room temperature was estimated.

O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is generated in the flow itself from O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) which undergoes the energy pooling reaction.



O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is also deactivated:



so that at any point in the tube there is a steady-state concentration which depends on the concentration of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>). Thus the emission from O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) at 762 nm can also be used to monitor the concentration gradient of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>). The rate constant for the quenching of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) by SO<sub>2</sub> was measured by observing the change in the ratio of the emissions from O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) and O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) at a single point in the tube when SO<sub>2</sub> was added [5].

The high temperatures are generated by propagating a shock wave into the gas flow by bursting an aluminium diaphragm with either helium

or nitrogen or a mixture of the two. The shock velocity is measured with laser light screens. The emissions at 634 nm and 762 nm are observed simultaneously with two photomultipliers, the outputs from which are captured by transient recorders. The digital output is subsequently analysed by a combination of interactive computer graphics and non-linear least squares [6] to yield the rate constants. The temperature range available was approximately 550 - 1500 K, but work above about 1200 K was often hindered by the growth of additional emission.

### 3. Quenching of $O_2(a^1\Delta_g)$

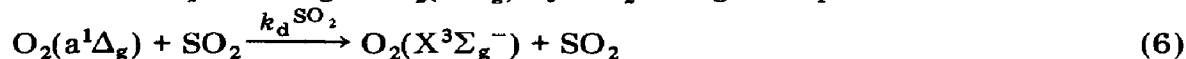
In the pre-shock flow at room temperature, it was found that the concentration gradient along the tube of both  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  was almost unaffected by the addition of  $SO_2$  up to 20 vol.%. At such high concentrations of additive, variations in diffusion to the wall and wall deactivation become significant, so our result simply indicates that  $SO_2$  is similar to  $O_2$  itself in quenching  $O_2(a^1\Delta_g)$ . Unfortunately it does not permit us to obtain a precise estimate of the rate constant, but we conclude that the rate constant must lie between 500 and 3000  $dm^3 mol^{-1} s^{-1}$ .

At high temperatures the 634 nm dimol emission is similar in form to that observed previously [3] with a sharp initial rise at the shock front followed by a fall-off with no intermediate relaxation zone. The traces could be fitted to the equation

$${}^{634}I_2 = {}^{634}I_{psg} \left( \frac{\rho_2}{\rho_1} \right)^2 \left( \frac{T_2}{T_1} \right)^{0.5} \frac{K}{t_s} \int_{t-t_s}^t \exp(-At) dt \quad (I)$$

where  ${}^{634}I_2$  and  ${}^{634}I_{psg}$  are the post- and pre-shock emission intensities,  $\rho_2/\rho_1$  and  $T_2/T_1$  are the post- to pre-shock density and temperature ratios,  $A$  is a constant which describes the fall-off in emission after the initial rise,  $K$  is an enhancement factor to allow for the change in emissivity with temperature, and  $t_s$  is the integration time which allows for the finite slit width at the observation station.

In contrast to our previous results [3, 4, 7] with  $O_2$ ,  $N_2$ ,  $N_2O$ ,  $CO_2$  and  $NH_3$ , it was found that the fall in concentration of  $O_2(a^1\Delta_g)$  was faster than that predicted from the measured pre-shock concentration gradient. The behaviour is similar to that observed [8] with  $NO$ , and we attribute this to the quenching of  $O_2(a^1\Delta_g)$  by  $SO_2$  at high temperatures.



The fall-off constant  $A$  is thus composed of two terms.

$$A = k_d^M [M] + \alpha \quad (II)$$

where  $k_d^M$  is the second-order rate constant for the quenching of  $O_2(a^1\Delta_g)$  by the gases present, and  $\alpha$  is given by

$$\alpha = u\alpha_q \left( \frac{\rho_2}{\rho_1} - 1 \right) \quad (\text{III})$$

$u$  is the shock speed and  $\alpha_q$  is the parameter which describes the pre-shock concentration gradient along the tube. It was found previously that  $k_d^{O_2}$  was too small to measure at high temperatures in our system so  $k_d^M$  gives  $k_d^{SO_2}$  directly.

The experimental traces were fitted by non-linear least squares to evaluate  $A$ ,  $K$  and  $t_s$ . As will be indicated, it was also possible to determine  $A$  from the emission due to  $O_2(b^1\Sigma_g^+)$  at 762 nm.

Figure 1 shows an Arrhenius plot of the measured rate constant  $k_d^{SO_2}$ . The results from the three mixtures coincide and, within the scatter of the results, a satisfactory linear plot is found which is described by the equation

$$k_d^{SO_2} (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = (8.6 \pm 0.1) \times 10^6 \exp\left(-\frac{2400 \pm 100}{T}\right) \quad (T \text{ in kelvins})$$

Since the extrapolated line passes through the estimated limits for the rate constant at room temperature, the equation appears to be valid from 295 to 1100 K and the value of the rate constant at 295 K is  $(2.5 \pm 0.8) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

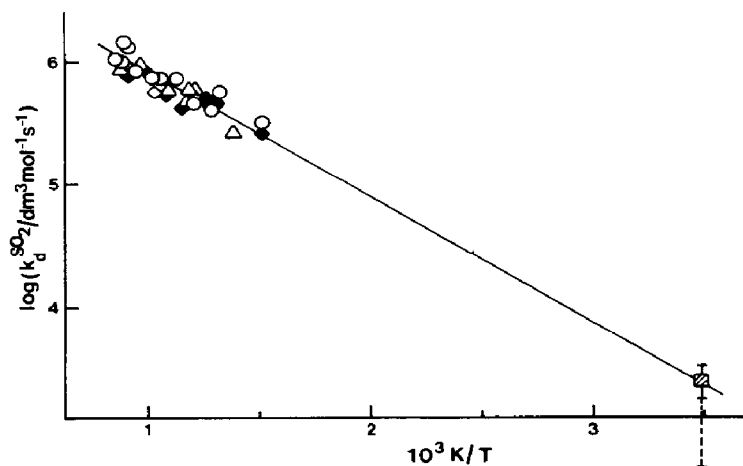


Fig. 1. An Arrhenius plot for the quenching rate constant  $k_d^{SO_2}$  of  $O_2(a^1\Delta_g)$  by  $SO_2$ . The mole fractions of  $SO_2$  are:  $\circ$ , 0.1;  $\blacklozenge$ , 0.15;  $\triangle$ , 0.2.  $\boxtimes$  is the value at 295 K extrapolated from the high temperature results. The full error bar relates to the extrapolation; the broken extension shows the limits from the room temperature estimate.

#### 4. Quenching of $O_2(b^1\Sigma_g^+)$

The rate constant  $k_q^{SO_2}$  for the quenching of  $O_2(b^1\Sigma_g^+)$  by  $SO_2$  at 295 K

$$O_2(b^1\Sigma_g^+) + SO_2 \xrightarrow{k_q^{SO_2}} O_2(a^1\Delta_g) + SO_2 \quad (7)$$

was measured using our technique [5] in which the relative change in emission from  $O_2(b^1\Sigma_g^+)$  and  $O_2(a^1\Delta_g)$  at 634 nm and 762 nm is observed for differing concentrations of  $SO_2$ . A good straight line plot was obtained [5] which gave  $k_d^{SO_2} = (2.5 \pm 0.5) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

At high temperatures the forms of the time traces of the emission from  $O_2(b^1\Sigma_g^+)$  at 762 nm were similar to those observed with the poorer quenchers [3]  $N_2$  and  $O_2$ , rather than the more efficient [4, 7]  $N_2O$ ,  $CO_2$  and  $NH_3$ . After the rapid rise at the shock front there is a relatively slow relaxation to an enhanced level of emission and then a fall-off similar to that observed with the 634 nm emission from  $O_2(a^1\Delta_g)$ . The relaxation zone was noticeably longer than that seen when, for instance,  $CO_2$  is added; also the emission enhancement factor  $K$ , which is the ratio of the post- to pre-shock emission, was much smaller.

One notable difference from the previous studies was that the fall-off at longer times was more rapid than that expected from the pre-shock concentration-gradient measurements. The difference was the same as that observed with the 634 nm emission from  $O_2(a^1\Delta_g)$ . A similar effect was seen previously in our study of NO quenching [8] and is caused by the appreciable deactivation of  $O_2(a^1\Delta_g)$  at high temperatures. Following the analysis developed for the NO system [8], the emission is described by

$${}^{762}I_2 = {}^{762}I_{psg} \frac{\rho_2}{\rho_1 t_s} \times \int_{t-t_s}^t [ \{ K \exp(-k_d^M[M]t) + (1 - K) \exp(-k_q^M[M]t) \} \exp(-At) ] dt \quad (IV)$$

The enhancement factor  $K$  can be expressed as

$$K = \frac{\{k_p/(k_q^M - k_d^M)\}_{T_2}}{\{k_p/(k_q^M - k_d^M + k'_w/[M])\}_{T_1}} \quad (V)$$

where  $k_d^M$  and  $k_q^M$  are the sums of the second-order rate constants for the quenching of  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  respectively by  $SO_2$  and  $O_2$ , and  $k_p$  is the rate constant for the energy-pooling reaction [3].

The experimental traces were fitted to eqn. (IV) to evaluate the four constants  $k_q^M$ ,  $k_d^M$ ,  $K$  and  $t_s$ . In each case  $t_s$  could be compared with an estimated value and  $k_d^M$  with the value obtained from the 634 nm emission. Combining  $k_q^M$  and  $K$  gave  $k_p$  which could be compared with previous results, so there were several consistency checks on the results from each experiment. In contrast to the work with  $NH_3$ ,  $CO_2$  and  $N_2O$ , the relaxation time  $(k_q^M[M])^{-1}$  was readily distinguished from the integration time  $t_s$  and so the analysis gave reliable values for both quantities.

The results obtained with three mixtures (mole fraction  $x_{SO_2}$ : 0.1, 0.15 and 0.20) showed that the relaxation was slower when  $SO_2$  was added, so that  $SO_2$  acts essentially as an inert diluent in the quenching of  $O_2(b^1\Sigma_g^+)$  by  $O_2$  itself. Thus we were able to calculate  $k_q^{O_2}$  from

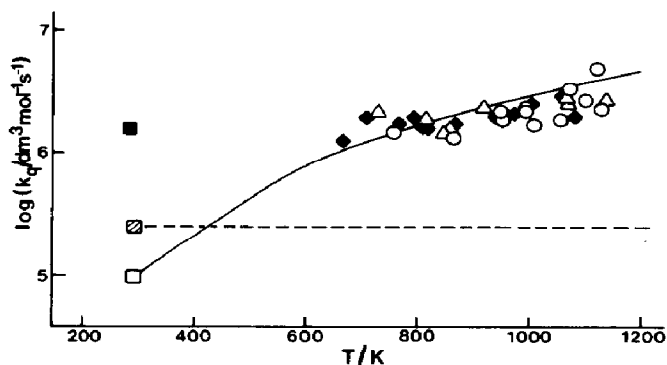


Fig. 2. A plot of the rate constant for the quenching of  $O_2(b^1\Sigma_g^+)$  by  $O_2$  determined from mixtures with  $SO_2$ ; the points denote the same mixtures as in Fig. 1. The full line is our previous result for  $O_2$ ;  $\square$ , the rate constant for the quenching by  $SO_2$  at 295 K;  $- - -$ , room temperature value used at other temperatures to give consistent results for  $O_2$ ;  $\blacksquare$ , the early determination by O'Brien and Myers.

$$k_q^{O_2} = \frac{\{k_q^M - k_q^{SO_2}(T_1)x_{SO_2}\}}{1 - x_{SO_2}} \quad (VI)$$

where  $k_q^{SO_2}(T_1)$  is the room temperature value for the quenching of  $O_2(b^1\Sigma_g^+)$  by  $SO_2$ ; it is assumed that the quenching constant does not change appreciably with temperature. The results for  $O_2$  are plotted against temperature in Fig. 2; within the scatter of the experiments, the results agree quite well with our previous results for  $O_2$  which are indicated by the full line and were obtained from experiments on  $O_2-N_2$  mixtures.

## 5. Discussion

Although it was not possible to measure directly the rate constant for the quenching of  $O_2(a^1\Delta_g)$  by  $SO_2$  at 295 K, the limits obtained show that the value from the extrapolation of the high temperature results is reasonable. This rate constant has not been determined previously; it shows that  $SO_2$  is similar to  $O_2$  itself as a quencher and that it is much more efficient than the linear triatomic quenchers  $CO_2$  and  $N_2O$  for which only upper limits have been obtained. However  $SO_2$  is a poorer quencher than the polar molecules  $NO$ ,  $HCl$ ,  $HBr$  and  $NH_3$ .

At high temperatures the rate constant is given by

$$k_q^{SO_2} (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = (8.6 \pm 0.1) \times 10^6 \exp\left(-\frac{2400 \pm 100}{T}\right)$$

where the error limits are the statistical  $2\sigma$  values. Arrhenius behaviour for the quenching constant has also been found with  $NO$  [8] and  $HCl$  [9], and also over a limited range at lower temperatures with  $O_2$  itself [10], but we have found no measurable temperature dependence with  $NH_3$ ,  $N_2$ ,  $CO_2$  and  $N_2O$ . However, with the last three the absolute values of the rate constants at room temperature are so small that, for an increase to be observed using our method, the activation energy would need to be unreasonably large.

The activation energy for quenching is  $19.9 \text{ kJ mol}^{-1}$  which is similar to that found for NO ( $16.9 \text{ kJ mol}^{-1}$ ) and also for HCl. The temperature dependence suggests that there is a barrier to a higher energy channel for deactivation, but this hardly seems reasonable for  $\text{SO}_2$  which possesses a large number of vibrational levels into which the energy released could be channelled. Also on this basis there is no real distinction between  $\text{SO}_2$  and  $\text{NH}_3$ ; both are polar and have several vibrational modes.

No attempt was made to detect chemical products in our experiments, so that a reaction channel cannot be excluded; however a molecular reaction between  $\text{SO}_2$  and  $\text{O}_2(\text{a}^1\Delta_g)$  is unlikely, and the temperature and time scales do not favour a free-radical reaction which consumes  $\text{O}_2(\text{a}^1\Delta_g)$ . So no real explanation can be offered for either the different quenching abilities or the temperature dependencies observed in these systems.

$\text{SO}_2$  is a poor quencher of  $\text{O}_2(\text{b}^1\Sigma_g^+)$  at 295 K; the only previous measurement of the rate constant was by O'Brien and Myers [1] who removed  $\text{O}_2(\text{b}^1\Sigma_g^+)$  from the flow with aluminium wire and studied the re-establishment of the steady state. Their value is greater than ours but we prefer the present result in the light of our previous experience with these systems [5] and because possible impurities make any value found an upper limit for a particular quencher.

While  $\text{SO}_2$  is more efficient than  $\text{O}_2$  itself at 295 K this is not so at higher temperatures. The results indicate that  $\text{SO}_2$  is similar to intermediate quenchers of  $\text{O}_2(\text{b}^1\Sigma_g^+)$  such as NO and HCl where the rate constant for quenching is nearly independent of temperature. It was disappointing not to be able to measure the rate constant precisely at higher temperatures; however the results do provide useful confirmation of our early results for  $\text{O}_2$  and for the energy pooling reaction which form the basis for our measurements in these systems.

## Acknowledgments

We would like to thank Dr. Kevin Grant for the suggestion that  $\text{SO}_2$  might be an anomalous case. R.B. would like to thank the University of Keele for the award of a departmental studentship; this work, surprisingly, was supported by the Science and Engineering Research Council!

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