

A COMBINED DISCHARGE FLOW/SHOCK TUBE STUDY OF THE REACTIONS OF OXYGEN
($^1\Delta_g$ and $^1\Sigma_g^+$) AT HIGH TEMPERATURES

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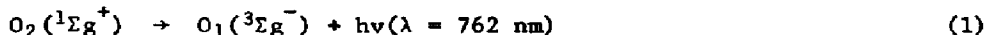
Oxygen is unique in having two low lying excited electronic states: the singlet delta $O_2(^1\Delta_g)$ at 95 kJ mol^{-1} , 0.98 eV; and singlet sigma $O_2(^1\Sigma_g^+)$ at 157 kJ mol^{-1} , 1.63 eV relative to the ground state $O_2(^3\Sigma_g^-)$.¹

While the collisional reactions of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ have attracted many studies², the detailed mechanisms of these reactions are still not well understood but recent theoretical studies^{3,4,5} have begun the path to understanding. Thrush has suggested that to distinguish the roles of the various interactions in the quenching process it is necessary to determine the temperature dependence of the quenching rate and the distribution of energy among the product molecules. It was to this end that a study of the rate constants of several reactions of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ over a wide temperature range was made, both in pure O_2 and O_2/N_2 mixtures.

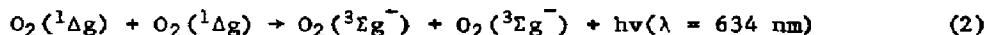
Experimental

The shock tube/discharge flow apparatus was developed in this laboratory and is similar to that used by several other workers.⁶⁻⁹ Singlet molecular oxygen is generated by passing purified oxygen over a clean mercury surface and then through a microwave discharge; the excited species then flow down the shock tube.

The excited states are observed using photomultiplier/filter combinations. $O_2(^1\Sigma_g^+)$ is observed by the 0.0 transition



$O_2(^1\Delta_g)$ is most easily seen using the dimol emission¹⁰



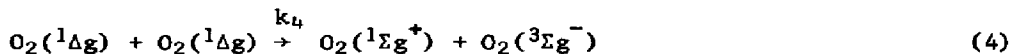
The concentration of excited species decreases as the gas flows along the tube; this decay is monitored using a mobile photomultiplier, before the gas is shocked. After measurements of the pre-shock emission levels have been made a shock is passed into the gas. The shock speed is determined using laser light screens and time interval meters; from this and the initial pressure, the experimental conditions can be calculated. The post-shock photomultiplier outputs are fed into transient recorders and are analysed using an interactive graphics programme we have developed, taking into account vibrational relaxation and the rise time of the system.

Results

A room temperature rate constant for the deactivation of $O_2(^1\Delta_g)$ by $O_2(^3\Sigma_g^-)$ of $0.9 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ has been determined^{11,12}, the absence

of any further deactivation during the shock allows an upper limit at the highest temperature, 1470 K, of $3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ to be set.

In the post-shock emission from $\text{O}_2(^1\Sigma_g^+)$ there is an initial rise which varies with the density ratio as expected for a single molecule transition. This rise is followed by a relaxation zone, after which the actual level of $\text{O}_2(^1\Sigma_g^+)$ emission is greater than that due solely to compression. $\text{O}_2(^1\Sigma_g^+)$ is formed predominantly by the energy pooling reaction^{13,14}



and is removed by collisional quenching



and by wall deactivation. When the shock passes through the gas the steady state concentration of $\text{O}_2(^1\Sigma_g^+)$ changes; analysis of the relaxation zone allows k_5 to be determined at the shock temperature and the ratio of the observed to expected emission gives a function of k_4/k_5 , allowing k_4 to be calculated. Figures 1 and 2 show $\log k_4$ and $\log k_5$ plotted against temperature for various mixtures, all lines drawn through a minimum of 20 experimental points for each composition.

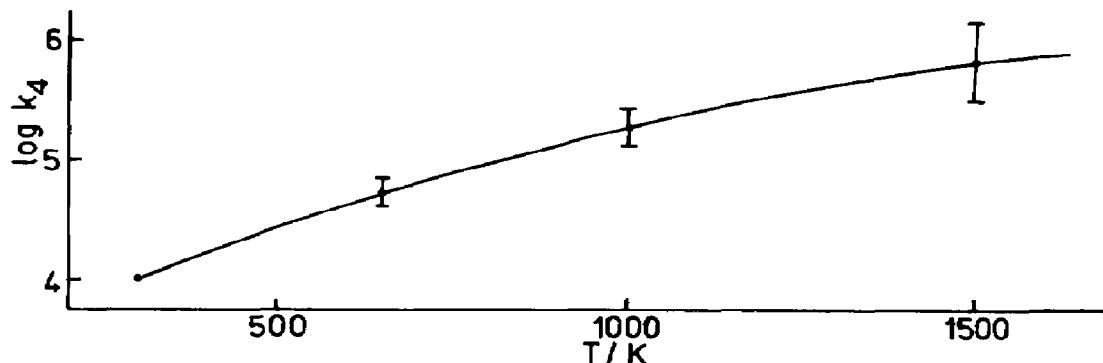


Figure 1. A plot of $\log k_4$ against temperature, values for all compositions fall within error bars shown. Room temperature value from ref. 15.

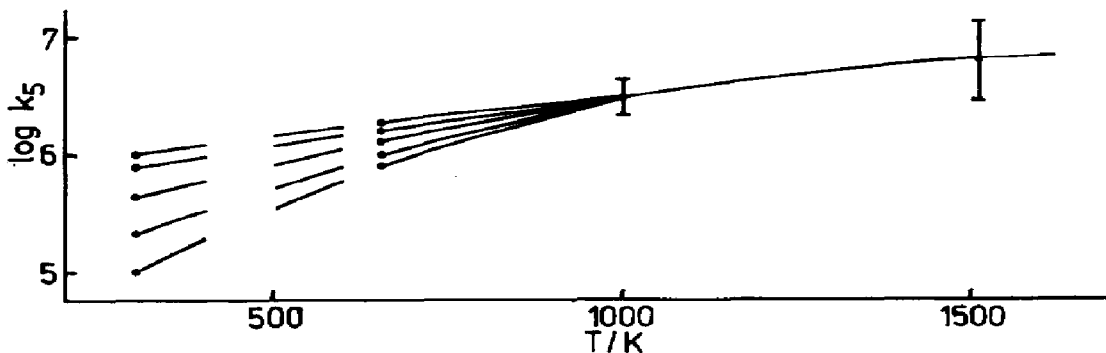


Figure 2. A plot of $\log k_5$ against temperature. At 300 and 650 K values are shown, from the lowest, for 100, 90, 75, 50 and 25% O_2 .

From figure 1 it can be seen that the energy pooling reaction shows no composition dependence. The exact mechanism remains uncertain; however the temperature dependence is not that of a simple collisional process in which the rate should vary with $T^{1/2}$, nor is the Arrhenius plot linear suggesting a bound complex is not formed.

The quenching rate constants, k_5 , show discernable composition dependence up to 850 K, the lowest shock temperature that can be achieved in our equipment being about 650 K; the lines are extrapolated to the room temperature values^{2,16}. Above 850 K all values fall on the same line within the limits of experimental error. Kear and Abrahamson³ have calculated the quenching rate constants for $O_2(^1\Sigma_g^+)$ by various molecules assuming that short range repulsive forces control the process, while Ogryzlo and coworkers⁴ have considered long range interactions. Both models stress near resonance between energy lost by $O_2(^1\Sigma_g^+)$ in going to $O_2(^1\Delta_g)$ and the vibrational energy acquired by the quencher and oxygen molecule. Thomas and Thrush⁵ however, using a statistical theory of energy distribution suggest that though energy is primarily taken up in vibration of the products, resonance is not generally important in the quenching of both species. The close similarity we have found in the temperature dependence of the quenching of $O_2(^1\Sigma_g^+)$ and energy pooling does suggest a common mechanism.

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