

HIGH TEMPERATURE QUENCHING REACTIONS OF SINGLET MOLECULAR OXYGEN[†]

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Summary

In this paper recent experimental work on the collisional quenching reactions of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ at high temperatures is reviewed. The results were obtained with a combined discharge flow-shock tube technique in which singlet oxygen is generated in a microwave discharge, mixed with a quencher and raised to a high temperature in a shock tube. The factors which contribute to the reliability of the technique are discussed.

Results from previous studies for both $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ are presented, together with some preliminary results for quenching of both species by SO_2 and HCl . Taken together, the results present a complex picture of quenching efficiencies and temperature dependences which cannot be correlated with any single physical property. The present theoretical approaches do not appear to be capable of explaining the results in a quantitative way.

1. Introduction

Despite the large number of studies of the quenching reactions of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ at room temperature, there were few studies of the temperature dependence of the quenching reactions before our contributions. Findlay and Snelling [1] had studied the quenching of $O_2(a^1\Delta_g)$ by O_2 , and Ogryzlo and coworkers [2, 3] had measured the quenching of $O_2(b^1\Sigma_g^+)$ by H_2 and HBr . Since then Kohse-Hoinghaus and Stuhl [4] have measured rate constants for the quenching of $O_2(b^1\Sigma_g^+)$ with several quenchers at lower temperatures.

Attempts have been made to correlate the quenching rate constants at a single temperature with the vibrational energy spacing in diatomic quenchers [5] but the results were quite scattered. Suprisal analysis of the results for both $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ suggested that, while a proportion of energy

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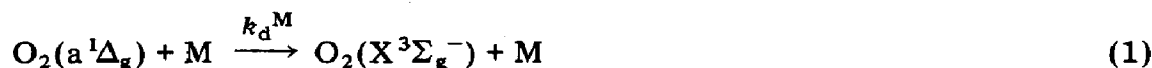
released certainly appeared as vibrational energy in the quencher, near resonance between the spacings and the energy gap between $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ was not important, and that there was little evidence for specific interactions [6, 7]. Several researchers pointed to the need for studies of the temperature dependence of these reactions.

Our contribution has been to measure the temperature dependence of the reactions of $O_2(b^1\Sigma_g^+)$, and lately $O_2(a^1\Delta_g)$, with several quenchers. A variety of effects have been observed. The purpose of the present paper is to review these, to report some preliminary results with two more quenchers and to discuss the reliability of our method of measuring the rates.

2. Experimental details

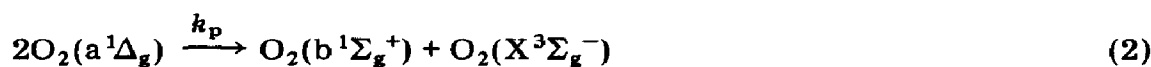
The technique used is a development of a method first used by Hartunian *et al.* [8], by Gross and Cohen [9, 10] and later by Glass and coworkers [11, 12]. In our experiments [13] $O_2(a^1\Delta_g)$ is generated in a microwave discharge. Mercury is added to the oxygen before the discharge to remove oxygen atoms, and in this way a flow of about 9 mmol s^{-1} containing about 5% of $O_2(a^1\Delta_g)$ is generated at 6 Torr pressure.

The flow, together with the added quenching gas, is passed along the shock tube in the opposite direction to that in which the shock wave is propagated. An important feature of the method is to make a thorough analysis of the concentration gradient of $O_2(a^1\Delta_g)$ which exists in the pre-shock flow, by studying the decrease in the "dimol" emission [14] at 634 nm along the length of the tube. From this the rate constants for the quenching of $O_2(a^1\Delta_g)$

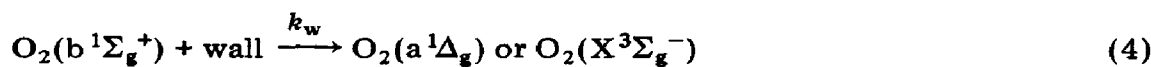


can be measured at room temperature.

$O_2(b^1\Sigma_g^+)$ is generated in the flow itself by the energy pooling reaction [15]



and it is removed by quenching either in the gas phase or at the wall:



Thus at any point in the tube a steady state concentration of $O_2(b^1\Sigma_g^+)$ exists, and so it is possible to measure k_q^M at room temperature by studying the relative changes in the $O_2(b^1\Sigma_g^+)$ emission at 762 nm, and the dimol emission at 634 nm, as a function of added gas pressure.

A bonus in this work is to make measurements at room temperature [14] in a regime which, because of the size of the apparatus, is relatively free from spurious effects from the discharge and from impurities.

When the preshock measurements are complete, a shock wave is propagated into the flowing gas by bursting an aluminium diaphragm with helium or N_2 at high pressure. The shock velocity is measured with laser light screens and the emissions at both 634 nm and 762 nm are followed as a function of time and recorded digitally for later computer analysis, using interactive graphics and fitting by non-linear least squares.

The two emissions exhibit quite different behaviour. Figure 1 shows a trace at 634 nm from $O_2(a^1\Delta_g)$. At the shock front the emission level jumps from its preshock level I_1 to a new level I_2 determined by the compression ratio ρ_2/ρ_1 and the temperature ratio T_2/T_1 :

$$\left(\frac{I_2}{I_1}\right)_{\text{initial}} = \left(\frac{\rho_2}{\rho_1}\right)^2 \left(\frac{T_2}{T_1}\right)^{0.5} \quad (5)$$

The values of I_2/I_1 found (20 - 70) are those expected from simple collision theory, but they do increase still further with temperature [16]. There then follows a simple exponential decay in emission, so that allowing for the optical rise time t_s , the emission at time t is given by

$$\left(\frac{I_2}{I_1}\right)_t = \left(\frac{\rho_2}{\rho_1}\right)^2 \left(\frac{T_2}{T_1}\right)^{0.5} \int_{t-t_s}^t \exp(-At) dt / t_s \quad (6)$$

where A is the decay constant [13].

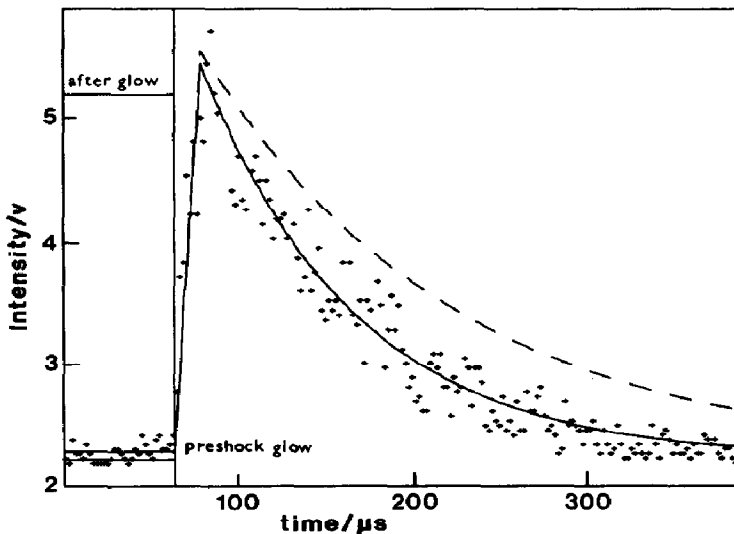


Fig. 1. Quenching of $O_2(a^1\Delta_g)$ by HCl: +, digitized record of the emission; —, fit using eqn. (6); - - -, decay predicted from the preshock concentration gradient.

In the earlier work with N_2 , O_2 , CO_2 and N_2O as quenchers [13, 17], it was realized that the decay was simply a reflection of the preshock concentration gradient along the tube as the gas upstream is swept past the observation station in the postshock flow. Thus A could be predicted from the preshock measurements:

$$A = U\alpha \left(\frac{\rho_2}{\rho_1} - 1 \right) \quad (7)$$

where α is the preshock decay constant with length, and U is the shock velocity. Thus in each experiment we obtain a check on the shock behaviour by comparing the preshock and postshock decays. As Fig. 1 shows for HCl and also with NO [18], and SO_2 , the postshock decay is found to be steeper than that predicted from the preshock decay. The extra contribution is from the quenching of $O_2(a^1\Delta_g)$ at high temperature, and so k_d^M can be estimated from the difference between the observed and the predicted decay constants:

$$k_d^M = \frac{A - \{U\alpha(\rho_2/\rho_1) - 1\}}{[M]} \quad (8)$$

The form of the emission from $O_2(b^1\Sigma_g^+)$ is more complex, as Fig. 2 shows. First the initial jump is not so great as for the $O_2(a^1\Delta_g)$ emission since here the emission is from a single molecule transition for which it would be expected that

$$\left(\frac{I_2}{I_1} \right)_{\text{initial}} = \frac{\rho_2}{\rho_1} \quad (9)$$

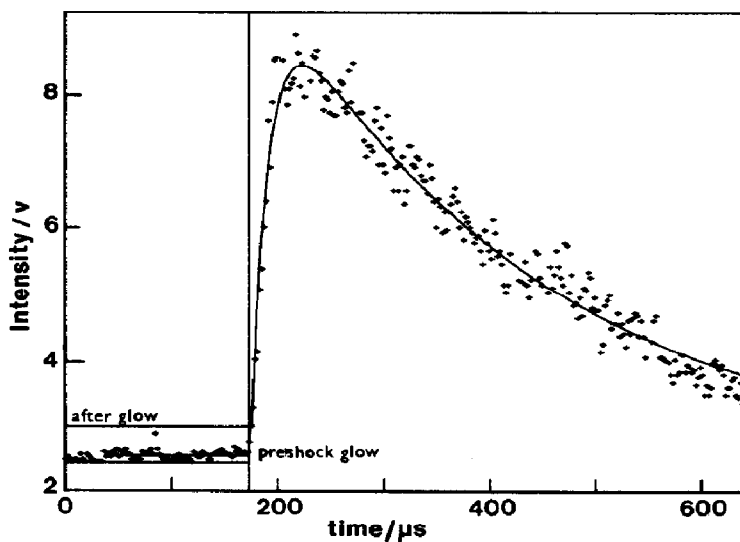


Fig. 2. Quenching of $O_2(b^1\Sigma_g^+)$ with CO_2 : +, digitized record of the emission; —, fit using eqn. (10).

However, the rise to the peak is more than that predicted from eqn. (9); the enhancement varies from a factor of about 3 for pure oxygen to factors as high as 70 when NH_3 is an additive. After the peak there is a decay which again can be attributed to the preshock concentration gradient. The emission can be described by [13]

$$\left(\frac{I_2}{I_1}\right)_t = \frac{\rho_2}{\rho_1} \int_{t-t_s}^t \{K + (1-K) \exp(-k_q^M t)\} \exp(-At) dt / t_s \quad (10)$$

where k_q^M is the quenching constant for the mixture and K is the enhancement factor given by

$$K = \frac{(k_p/k_q^M)_{T_2}}{\{k_p/(k_q^M + k_w/[M])\}_{T_1}} \quad (11)$$

Thus the enhancement in emission observed is due to the change with temperature in the steady state reactions which form and remove $\text{O}_2(\text{b}^1\Sigma_g^+)$. Analysis of the traces gives both k_q^M and k_p .

Equation (11) was derived assuming that $\text{O}_2(\text{a}^1\Delta_g)$ is not deactivated at high temperatures. If it is, as with NO as a quencher, then the equation must be modified [18]:

$$\left(\frac{I_2}{I_1}\right)_t = \frac{\rho_2}{\rho_1} \int_{t-t_s}^t \{K \exp(-k_d^M[M]t) + (1-K) \exp(-k_q^M[M]t)\} \exp(-At) dt / t_s \quad (12)$$

For both eqns. (11) and (12) the decay constant is the same as that for the emission from $\text{O}_2(\text{a}^1\Delta_g)$ at 634 nm, so there is a check on the consistency both of the traces and of the model used.

The analysis of the $\text{O}_2(\text{b}^1\Sigma_g^+)$ traces gives a value for the pooling constant, reaction (2), and since this should be independent of the quencher there is an additional consistency check on every experiment.

Thus it can be seen that by comparing preshock and postshock decays for both $\text{O}_2(\text{b}^1\Sigma_g^+)$ and $\text{O}_2(\text{a}^1\Delta_g)$ emissions, and the values of k_p obtained in a single run with the known values, a series of checks on the reliability of individual runs is obtained.

3. Results

3.1. Quenching of $\text{O}_2(\text{a}^1\Delta_g)$

Figure 3 shows the results for the quenching of $\text{O}_2(\text{a}^1\Delta_g)$ by NO as a function of temperature [18], together with some preliminary results for one mixture each for SO_2 and HCl. They each show an Arrhenius dependence of rate constant with temperature within the range studied, and the lines extrapolate well to encompass the room temperature results. The activation energies are in the range from 15 to 20 kJ mol^{-1} . Also shown are the results

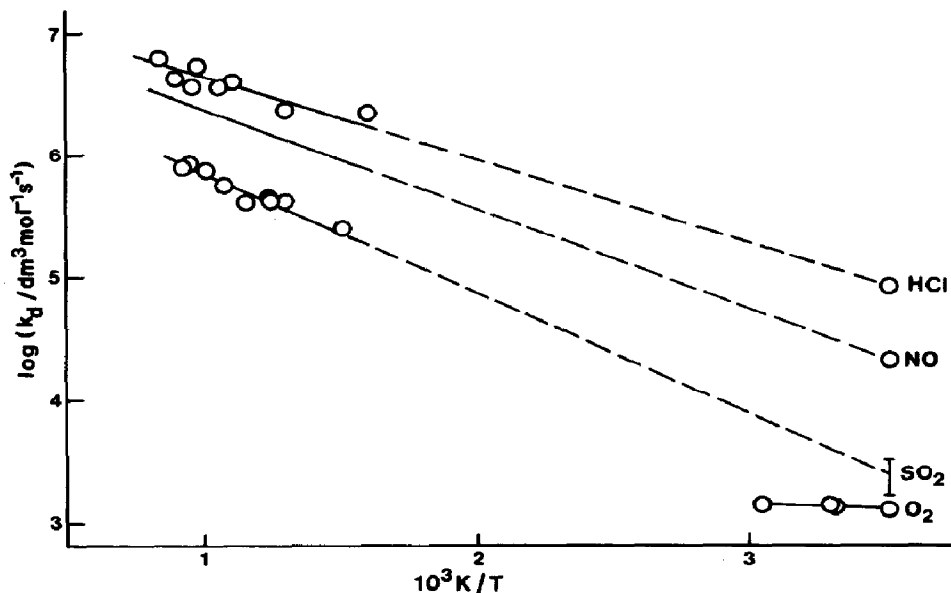


Fig. 3. An Arrhenius plot of the rate constants for the quenching of $O_2(a^1\Delta_g)$ by HCl, NO, SO_2 and O_2 . The results for O_2 are those of Findlay and Snelling [1].

of Findlay and Snelling [1] who found that the rate constant for quenching by O_2 itself increased with temperature. The approximate activation energy is 1.8 kJ mol^{-1} . Unfortunately the extrapolated values would be too small for us to measure at high temperatures.

Similarly, it was not possible for us to estimate the rate constants for N_2 and NH_3 [13, 19], but clearly an increase in rate constant with temperature cannot be excluded. It is only possible to put an upper limit to the activation energy of about 8 kJ mol^{-1} if the increase is in fact Arrhenius in behaviour.

With CO_2 , N_2O and argon [17] there was also no detectable increase, but here the rate constants are small at room temperature so that it is not possible to put a meaningful upper limit to the activation energy.

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

Figure 4 shows the results for the rate constants for the quenching of $O_2(b^1\Sigma_g^+)$ with a variety of molecules. Each of the sets of results is represented by an empirically drawn best line. The broken portions represent extrapolations to encompass the room temperature measurements which are shown as points. The results for SO_2 and HCl are still preliminary. Also included are the results of Kohse-Hoinghaus and Stuhl [4] who studied several systems using a vacuum UV H_2 laser for excitation. They found that their results could be fitted to Arrhenius plots with small activation energies. When the results for N_2 and NH_3 are compared with ours at higher temperatures it appears that the rate constant is nearly independent of temperature below about 700 K in these systems.

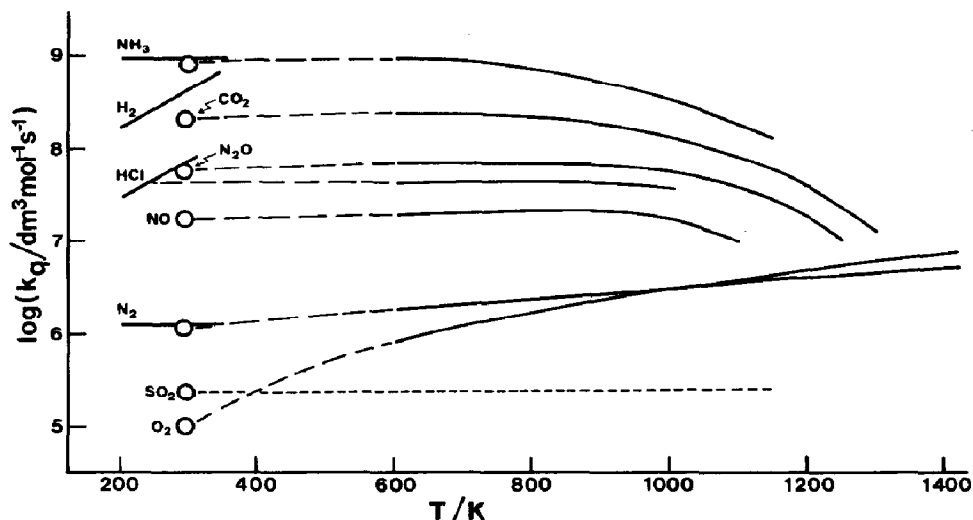


Fig. 4. A logarithmic plot of the rate constants for the quenching of $O_2(b^1\Sigma_g^+)$ with various quenchers against temperature: —, best lines; ---, interpolations. The room temperature values are taken from ref. 14. The results below room temperature are from Kohse-Hoinghaus and Stuhl [4].

The temperature dependence can be roughly divided into three types. Poor quenchers such as N_2 and O_2 have a positive temperature dependence, whereas for relatively efficient quenchers such as NH_3 , CO_2 and N_2O the rate constant actually decreases at higher temperatures. In between, the rate constants for NO and HCl appear to be nearly independent of temperature. SO_2 may be an anomaly in this classification; it is a poor quencher, but its effect at high temperatures is negligible in comparison with O_2 itself, so it appears that the rate constant is nearly independent of temperature.

4. Discussion

The theoretical approaches to understanding the mechanism of quenching of $O_2(b^1\Sigma_g^+)$ can be characterized as "short-range" and "long-range" interactions. In the work of Kear and Abrahamson [20], the energy transfer is imagined to occur at close intermolecular distances on the repulsive part of the intermolecular potential energy curve, in a similar way to vibration-translation transfer. Thus an increase in rate constant with temperature should be observed for short-range transfer. Long-range transfer is imagined to occur on the attractive part of the intermolecular curve, or in the neighbourhood of the Lennard-Jones minimum. Braithwaite *et al.* [3] treated this problem, and found that for HBr as a quencher the rate constant should decrease with temperature. Unfortunately, the predicted rate constants were too low, but they found better agreement by combining their work with the short-range calculations and concluded that both mechanisms may be operating with HBr .

An alternative long-range approach is that of Parmenter and Seaver [21, 22] who, in a general treatment of energy transfer, correlated the quenching cross section with the depth of the minimum in the intermolecular potential. Their model also predicted a decline in rate constant with temperature with a negative "activation energy" equal to the well depth.

We tried [17, 19] to apply this approach to the negative temperature dependences observed in quenching of $O_2(b^1\Sigma_g^+)$ with CO_2 , N_2O and NH_3 but approximate fits could only be obtained with unreasonably large well depths. However, Parmenter's model was only intended for very efficient quenchers, and so it was perhaps optimistic to expect it to fit the $O_2(b^1\Sigma_g^+)$ system, where even the best quenchers are relatively inefficient.

The variety of temperature dependences which can be observed in the quenching of $O_2(b^1\Sigma_g^+)$ point to the conclusion that at least two mechanisms are operating here. The poorer quenchers perhaps relax by the short-range mechanism, and the efficient quenchers by the long-range mechanism. If this is so, then the rate constant, for say NH_3 , could be expected to turn and begin to increase at still higher temperatures. Unfortunately we cannot investigate this because O_2 itself becomes efficient and would mask the effect of NH_3 .

Another point worth experimental investigation is whether there is actually a maximum in the rate constant for NH_3 , CO_2 and N_2O . Comparison with the results of Kohse-Hoinghaus and Stuhl [4] suggests that there might be, and at present we are setting up an experiment to explore this point.

While the long-range and short-range classification provides a rough rationalization of the temperature dependence, it does not explain the detailed differences in quenching ability between molecules. For example, among the triatomic quenchers, why should CO_2 and N_2O be efficient while SO_2 is a relatively poor quencher? Clearly the polarity does not have a simple effect if, for example, N_2O is compared with CO_2 ($k_q(N_2O) < k_q(CO_2)$) and NO is compared with N_2 ($k_q(NO) > k_q(N_2)$). It was proposed at an early stage that there is a rough correlation of efficiency with the vibrational energy spacing in the quencher, and recently this has been suggested [7] in the quenching of $SO(b^1\Sigma_g^+)$. However, this picture does not fit well with the polyatomic quenchers, particularly here with SO_2 , where there should be sufficient near-resonant levels for efficient transfer.

Altogether it seems as if we are observing a process which is very sensitive to the detailed nature of the intermolecular potentials, so that the efficiency varies sharply with small differences in the chemical nature of the quencher. This will be a difficult problem to treat theoretically.

Only positive temperature dependences, as observed in the quenching of $O_2(a^1\Delta_g)$, point to the mechanism being dominated by energy exchange at short range. The Arrhenius behaviour measured with NO , and also possibly with SO_2 and HCl , may point to some specific reaction channel which can only be entered by passing over a barrier, but alternatively it may be that the temperature dependence observed for short-range interaction fits the Arrhenius equation only over this range. The detailed differences between

molecules are again difficult to rationalize. The triatomic molecules CO₂ and N₂O are extremely poor quenchers while SO₂ is relatively efficient. In one or two cases, *e.g.* NH₃, it may be that the deactivation observed is in fact due to chemical reaction which our experiments cannot exclude.

Overall our work so far has shown that the temperature dependence is an important feature, but unfortunately the results do not admit of any easy explanation.

Acknowledgments

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