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DEACTIVATION OF SINGLET MOLECULAR OXYGEN, $O_2(^1\Delta_g)$, BY OXYGEN

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The value for the rate constant, k_q, for the deactivation of $O_2(^1\Delta_g)$ by molecular oxygen has been measured with the discharge flow technique using the elongated measurement section of our discharge flow/shock tube. The value, $k_q = (0.94 \pm 0.03) \times 10^3$ ℓ mol^{-1} s^{-1} at 294 K is lower than the previously accepted value but has been determined with a better precision.

1. Introduction

In our present work [1], we are using a combined shock tube and discharge flow system [2–5] to study the reactions at high temperature of the singlet excited states of oxygen, $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$. In doing so we have remeasured the rate constant for the deactivation of singlet molecular oxygen, $O_2(^1\Delta_g)$, by O_2 itself at room temperature. Since we obtained, with measurements of greater precision, a lower value than that normally accepted [6–9], it seemed worthwhile to report our new value of the rate constant for this important reaction.

2. Experimental

Singlet molecular oxygen was produced by passing highly purified oxygen saturated with mercury vapour through a microwave discharge and over a mercuric oxide film; the Hg and HgO serve to remove atomic oxygen from the system [10]. The gas was passed along a 5 m cylindrical pyrex shock tube (5 cm diameter) and the measurements were started 150 cm from the discharge; the decay was then studied over a distance of 250 cm. The pressure, measured with Edwards dial gauges checked by a diethyl phthalate manometer, was varied between 260–1900 Pa (2–14 mm Hg); the flow rate of oxygen was generally 17.5 cm^3 s^{-1} at 101.35 kPa (760 mm Hg), but measurements made at lower and higher flow rates showed that there was no variation of the rate constants with flow rate.

The changes in concentration of $O_2(^1\Delta_g)$ were measured with the dimol emission at 634 nm

$$2O_2(^1\Delta_g) \rightarrow 2O_2(^3\Sigma_g^-) + h\nu\ (\lambda = 634\ \text{nm}), \qquad (1)$$

or more usually by the comparatively intense emission from $O_2(^1\Sigma_g^+)$ at 762 nm, using an EMI 9658B photomultiplier together with a suitable filter (Baltzer Ltd.).

The walls of the shock tube were cleaned periodically with diethyl ether, followed by thorough pumping.

3. Results

In the discharge-flow system, $O_2(^1\Sigma_g^+)$ is formed entirely by energy pooling [11]

$$2O_2(^1\Delta_g) \xrightarrow{k_p} O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-) \qquad (2)$$

and deactivated by gaseous collision (k_1) or at the walls (k'_w). It follows from the rate equations and steady state approximation that

$$[O_2(^1\Sigma_g^+)] = k_p[O_2(^1\Delta_g)]^2/(k_1[O_2] + k'_w)\,.$$

Thus the emission of $O_2(^1\Sigma_g^+)$ may be used to follow the concentration of $O_2(^1\Delta_g)$. Fig. 1 shows first order plots of the decay of $O_2(^1\Delta_g)$ along our tube by observing both the $O_2(^1\Sigma_g^+)$ and the dimol emissions, which illustrate their equivalence. To obtain the first

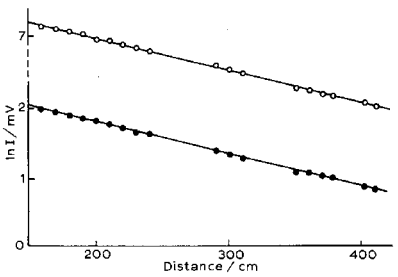

Fig. 1. First order plots for the decay of $O_2(^1\Delta_g)$ against distance from the discharge; dimol emission, •; $O_2(^1\Sigma_g)$ emission, ○; flow rate 10.5 $cm^3\ s^{-1}$, corrected to S.T.P.; concentration of O_2, 1.53×10^{-4} mol ℓ^{-1}; temperature, 294 K.

order constant for the decay, k_{obs}, the slopes of the plots are divided by 2 to account for the square dependence of the emissions on the concentration.

$O_2(^1\Delta_g)$ is removed from the system by reactions (1) and (2) and also by the following processes:

$$O_2(^1\Delta_g) + O_2(^3\Sigma_g^-) \xrightarrow{k_q} 2O_2(^3\Sigma_g^-)\,, \qquad (3)$$

$$O_2(^1\Delta_g) + \text{wall} \xrightarrow{k_w} O_2(^3\Sigma_g^-)\,, \qquad (4)$$

$$O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + h\nu\ (\lambda = 1270\ \text{nm})\,. \qquad (5)$$

Of these reactions, only (3) and (4) are rate determining, for reactions (5) and (1) are very slow [10] and the energy pooling reaction (2) only becomes significant in comparison with (3) and (4) at high concentrations of $O_2(^1\Delta_g)$. In our system the observation section is sufficiently far from the discharge to ensure that the concentration of $O_2(^1\Delta_g)$ is too low for (2) to contribute appreciably; as a check, a few runs were made using Wayne's technique [6] of adding 90% of the oxygen after the discharge to ensure low concentrations of $O_2(^1\Delta_g)$; the results were in excellent agreement with the rest.

Fig. 2 shows the good straight line obtained for a plot of the first order constants against concentration. At pressures below 0.7 kPa (6 mm Hg) where the flow rate was very high, it was found at first that k_{obs} was significantly larger than expected at a discharge power of 100 W, perhaps because under these conditions the Hg/HgO technique for removing atomic oxygen is less effective [9]; satisfactory results were obtained by reducing the discharge power.

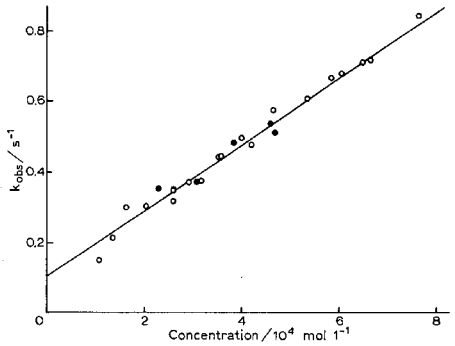

Fig. 2. First order rate constants plotted against concentration of oxygen. Points marked • are for runs with 90% of O_2 added after the discharge.

These results give values of $k_q = (0.936 \pm 0.029) \times 10^3\ \ell\ mol^{-1}\ s^{-1}$ and $k_w = 0.106 \pm 0.013\ s^{-1}$ for our system. Our value of k_q is lower than those of earlier authors (table 1), but of higher precision. The improvement, we believe, is brought about by making measurements over a long length of tube and by studying the $O_2(^1\Sigma_g^+)$ emission rather than that at 1270 nm (5), which is an extremely difficult region of the spectrum to detect. Another reason for preferring our lower value is that in deactivation processes the measured rate constant is usually increased by the presence of impurities; which might well have been present in earlier measurements, as for example Thomas and Thrush [12] recently found for the deactivation of $O_2(^1\Sigma_g^+)$.

The wall deactivation efficiency, γ (= $(1.23 \pm 0.14) \times 10^{-5}$), calculated from k_w is lower than that reported by other authors, but similar to that obtained by Wayne [6] using a reaction tube freshly rinsed in HF.

Table 1
Rate constants and wall deactivation efficiency for quenching of $O_2(^1\Delta_g)$

$k_q \times 10^{-3}$ ($\ell\ mole^{-1}\ s^{-1}$)	k_w (s^{-1})	$\gamma \times 10^5$	Wavelength studied (nm)	Ref.
0.94 ± 0.03	0.11 ± 0.02	1.2 ± 0.2	762/634	this work
1.33 ± 0.30	0.07 ± 0.03	2.1	1270	[6]
1.31 ± 0.07	0.3 ± 0.1	4	1270	[7]
1.23 ± 0.14	0.13 ± 0.06	1.3	1270	[8]
1	0.2	1	634	[9]

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