Short Communication

A direct determination of the rate constant for the quenching of O(^{1}S) by O$_2$(a $^1\Delta_g$)

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It has recently been reported [1] that all the experimentally determined rate constants for the quenching of O(^{1}S) by O(^{3}P) are in error because of extremely effective quenching by O$_2$($^1\Delta_g$) which is always present in systems containing oxygen atoms. The mutual annihilation of O(^{1}S) and O$_2$($^1\Delta_g$) in an energy pooling reaction has been reported by Slanger and Black [1] to have a rate constant of $(1.7 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Using an indirect method Kenner *et al.* [2] obtained a value of 5.5×10^{-10} cm^3 molecule^{-1} s^{-1}. In this paper we describe an independent method of directly determining the rate constant for this reaction at room temperature.

The use of the surface-catalysed recombination of O(^{3}P) to produce the A $^3\Sigma_u^+$ state of molecular oxygen for kinetic studies has already been described [3]. We have found that this same technique can also be used to prepared O(^{1}S) (as well as O$_2$(c $^1\Sigma_u^-$) and O$_2$(A$'$ $^3\Delta_u$)) in a conventional fast flow system. A stream of O(^{3}P) is produced by passing a dilute mixture of oxygen in argon through a 2.45 GHz microwave discharge. This stream is then directed through a fine mesh nickel screen which is placed across the diameter of the flow tube. The oxygen atoms are efficiently recombined at the nickel surface and the electronically excited molecules and atoms produced can be seen as a blue cone downstream of the screen. The emission spectrum of these excited species in the vicinity of the 557.7 nm line of O(^{1}S) is shown in Fig. 1.

The discharge flow apparatus consisted of a quartz discharge tube followed by two light traps, a Pyrex flow tube 2.5 cm in diameter (40 cm long), a flow tube 10 cm in diameter (1 m long) and a pumping system (1000 l min^{-1}). The flow rate under the conditions used in these experiments was 26.5 m s^{-1} in the small flow tube. The pressure was measured using a capacitance manometer at the midpoint of the small flow tube. The nickel screen was placed 10 cm downstream from the discharge tube. The argon carrier gas was passed through an 800 °C furnace filled with titanium sponge to remove nitrogen-containing impurities. Linde ultrahigh purity oxygen was used without further purification.
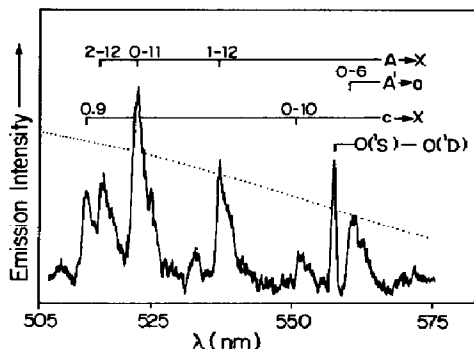
Fig. 1. The emission spectrum of the nickel-catalysed recombination of $O(^3P)$ between 505 and 575 nm: $\cdots\cdots$, the relative detector sensitivity. The transitions $O(^1S) \to O(^1D)$, $O_2(c\ ^1\Sigma_u^-)_{v=0} \to O_2(X\ ^3\Sigma_g^-)$, $O_2(A'\ ^3\Delta_u)_{v=0} \to O_2(a\ ^1\Delta_g)$ and $O_2(A\ ^3\Sigma_u^+)_{v=0-2} \to O_2(X\ ^3\Sigma_g^-)$ are labelled. The spectrum was recorded with a spectral bandpass of 0.8 nm at the position of maximum intensity on the downstream side of the nickel screen.

The $O_2(a\ ^1\Delta_g)$ concentration was determined by scanning the 1.27 μm line with a 0.25 m monochromator looking along the axis of the large diameter flow tube. The 1.27 μm emission was modulated at 100 Hz and was detected with a cooled intrinsic germanium detector coupled to a lock-in amplifier and chart recorder. The germanium detector was calibrated using the O + NO afterglow [4].

The decay of the $O(^1S)$ concentration along the reaction tube was followed with a movable 0.25 m monochromator operating in the second order and looking across the diameter of the small flow tube. The photomultiplier was coupled to a photon counter which was interfaced to a computer. The monochromator and the photomultiplier were moved using a stepping motor controlled by the computer. The resulting decay curves were corrected for background radiation and were fitted using a non-linear regression program (adapted from ref. 5). Several curves were collected for each $O_2(^1\Delta_g)$ concentration and averaged.

A plot of the reciprocal lifetime $1/\tau$ as a function of the $O_2(a\ ^1\Delta_g)$ concentration is shown in Fig. 2. The error bars are the standard deviations of the repeated measurement of $1/\tau$, the inverses of which are used as weighting factors in the regression analysis. The line is the weighted linear regression fit. The slope of the line gives $k_1 = (2.6 \pm 1.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K where the error is the 90% confidence limit.

The data points shown have been corrected for axial diffusion [6] but not for radial diffusion which could reduce the rate constant by about 15% [7]. Correction for the pressure drop along the small tube is negligible. Correction for parabolic flow is also unnecessary because the nickel screen disrupts its formation in the observation area.

The small intercept in Fig. 2 indicates that any other $O(^1S)$ quenching process (including that by $O(^3P)$) is very much slower than the $O_2(^1\Delta_g)$
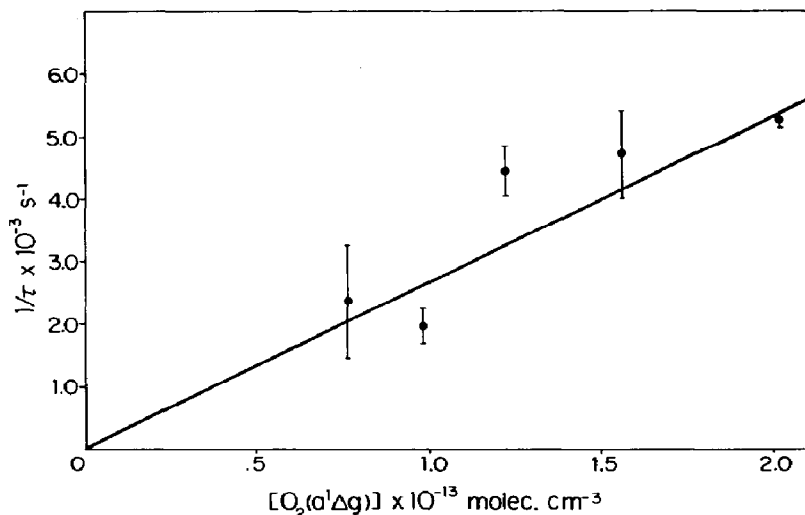
Fig. 2. The reciprocal of the lifetime of $O(^1S)$ as a function of $[O_2(a\ ^1\Delta_g)]$. The error bars are the standard deviation of repeated measurements of $1/\tau$ and the line is the weighted linear regression fit to the points.

TABLE 1

k_1 (cm^3 molecule^{-1} s^{-1})[a]	Source
$(1.7 \pm 0.3) \times 10^{-10}$	[1]
5.5×10^{-10}	[2]
2×10^{-10}	[9]
$(2.6 \pm 1.2) \times 10^{-10}$	This work

[a]All measurements were made at room temperature.

quenching. However, in view of the uncertainty in the intercept no useful upper limit can be placed on the quenching rate constant for $O(^1S)$ by oxygen atoms. The theoretical value of 2×10^{-14} cm^3 molecule^{-1} s^{-1} [8] therefore remains the only reasonable estimate of this rate constant.

The experimentally determined rate constants for the quenching of $O(^1S)$ by $O_2(^1\Delta_g)$ are collected in Table 1. Our value agrees with that of Slanger and Black [1] within experimental error. Ogryzlo and Wassell [9] have repeated the earlier measurements of Kenner *et al.* [2] and have obtained a lower value $(2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) in excellent agreement with the results of Slanger and Black [1] and of the present study.

1 T. G. Slanger and G. Black, *Geophys. Res. Lett.*, *8* (1981) 535.
2 R. D. Kenner, E. A. Ogryzlo and P. T. Wassell, *Nature (London)*, *291* (1981) 398.
3 R. D. Kenner and E. A. Ogryzlo, *Int. J. Chem. Kinet.*, *12* (1980) 501.
4 M. Sutoh, Y. Morioka and M. Nakamura, *J. Chem. Phys.*, *72* (1980) 20.
5 S. J. Gumbley, Kinetic studies of redox and related reaction of some new iso-alloxazines, *D. Phil. Thesis*, University of Waikato, New Zealand, 1976.
6 C. J. Howard, *J. Phys. Chem.*, *83* (1979) 3.
7 F. Kaufman, *Prog. React. Kinet.*, *1* (1961) 3.
8 M. Krauss and D. Neuman, *Chem. Phys. Lett.*, *36* (1975) 372.
9 E. A. Ogryzlo and P. T. Wassell, to be published.