Short Communication

A kinetic study of O(2^3P_J) by atomic absorption spectroscopy following the flash photolysis of ozone

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We describe a kinetic investigation of the aeronomically significant reactions:

$$O(2^3P_J) + O_3 \rightarrow 2O_2 \tag{I}$$

$$O_2(a^1\Delta_g) + O_3 \rightarrow 2O_2 + O(2^3P_J) \tag{II}$$

Schiff[1] has stressed the need for direct measurements of the rate of reaction (I), which has been investigated by a number of workers[1-3] and whose value ranges over an order of magnitude. The data for the rate of reaction (II) have been obtained principally by direct observation of $O_2(a^1\Delta_g)$ using both infra-red emission[2] and photoionization[3,4] and supports a value of $k_2 = 3 \pm 0.5 \times 10^{-15}$ cm³ molecule⁻¹ sec⁻¹, an order of magnitude lower than that initially suggested by Schiff *et al.*[5]. In the present studies, $O_2(a^1\Delta_g)$ and $O(2^3P_J)$ have been generated following the flash photolysis of ozone, and a kinetic analysis of the time-dependence of $O(2^3P_J)$ has been used to obtain a value for k_1-k_2 together with an upper limit for k_2, thus yielding a direct measurement of k_1. Vacuum ultra-violet spectrographic observation of $O_2(a^1\Delta_g)$ in this system has been reported previously[6].

Experimental

The general arrangement for time-resolved, photoelectric monitoring of $O(2^3P_J)$ in a static system following flash photolysis by absorption of the resonance triplet at 130 nm ($3^3S_1^0 \rightarrow 2^3P_J$) from a microwave-powered flow lamp has been described in detail previously[7,8]. Ozone, prepared by the method of Clough and Thrush[9], was pulse irradiated in a coaxial lamp and Spectrosil vessel assembly, permitting photolysis to a lower wavelength limit of $\lambda > 170$ nm. As some decomposition of the ozone before use was unavoidable, the concentration in each experiment was measured using the extinction coefficients at 130 and 121.6 nm reported by Tanaka *et al.*[10]. The purity of ozone samples used in these experiments

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was generally in the range 80–90%. The decomposition of ozone in the reaction vessel due to photolysis by the flow lamp used for spectroscopic detection was kept as low as possible by minimizing the total residence time of each mixture in the reaction vessel to a few seconds. The initial and final concentrations of ozone were recorded as well as the kinetic trace monitoring $O(2^3P_J)$.

Results and discussion

For attenuation of the resonance triplet at 130 nm by the transient concentration of $O(2^3P_J)$ present following photolysis, the absorption law:

$$I_{tr} = I_0 \exp[-\varepsilon(lc)^\gamma] \tag{1}$$

was employed, where the symbols have their usual significance[7]. The value of γ was taken to be 0.5 as found in a previous investigation under comparable conditions within the same range of absorption[7]. For a first-order kinetic decay of the oxygen atoms, a plot of log $[\log(I_0/I_{tr})]$ against time yields a straight line of slope $-\gamma k'/2.303$ where k' is the pseudo first-order decay coefficient. In the present system, the photolysis of ozone will occur primarily in the wavelength region $\lambda > 200$ nm[11] where the primary process has been established in recent studies as[12,13]:

$$O_3 + h\nu \rightarrow O_2(a^1\Delta_g) + O(2^1D_2)$$
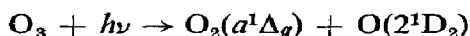
The present experiments were performed in the presence of a large excess of molecular nitrogen to ensure rapid collisional deactivation of $O(2^1D_2)$ to $O(2^3P_J)$[14] and to prevent any significant reaction of $O(2^1D_2)$ with either O_2 or O_3 which would give rise to excited states of O_2 with high quantum yields[14]. The initial degree of the low energy ($E = 160$ J) photodissociation of ozone was found to be *ca.* 10%. Under these conditions, the contribution to the overall decay of $O(2^3P_J)$ by the recombination of $O + O$ and $O + O_2$ $[O = O(2^3P_J)]$ is small[15,16] and ozone is in excess over $O(2^3P_J)$ and $O_2(a^1\Delta_g)$. Thus, to a good approximation, we may write:

$$-d[O]/dt = K[O] + k_1[O][O_3] - k_2[O_2(a^1\Delta_g)][O_3] \tag{2}$$

where the removal of $O(2^3P_J)$ by diffusion to the walls of the vessel and by collisional decay by any trace impurities at a given pressure is treated as a first-order process of coefficient K. Immediately following photolysis, $[O] = [O_2(a^1\Delta_g)]_{t=0}$. Thus:

$$-d[O]/dt_{(t=0)} = \left[K + (k_1 - k_2)\,[O_3] \right] [O] \tag{3}$$

The *initial* slope of the first-order plot for $[O]$ will therefore be given by:

$$k' = K + (k_1 - k_2)[O_3] \tag{4}$$

Figure 1 shows a typical oscilloscopic trace for the decay of $O(2^3P_J)$. The horizontal traces illustrate the initial and final values of I_0 due to the decomposition of ozone by photolysis and subsequent chemical reaction. Thus I_0 is effectively a func-
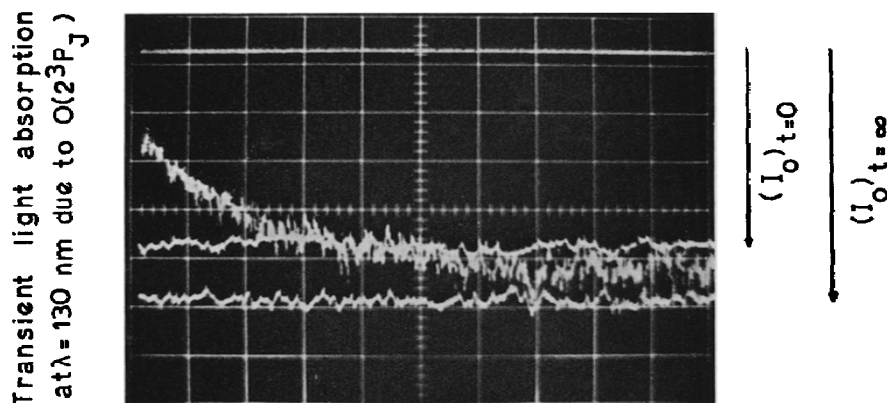
Fig. 1. Typical oscilloscopic traces indicating the decay of $O(2^3P_J)$ by monitoring the light absorption at 130 nm following the flash photolysis of ozone. p_{0_3} (initial) = 37.8 N m^{-2}; p_{0_3} (final) = 29.1 N m^{-2}; p(total with N$_2$) = 19.95 kN m^{-2}; E = 160 J; Time scale: 5 msec per division.

tion of time. Whilst the magnitude of this effect was minimized by using the lowest possible photolysis energy consistent with the production of measureable quantities of $O(2^3P_J)$ and empirical corrections made, the time variation of I_0 remains the limiting source of error in these experiments. Figure 2 shows some semi-logarithmic plots derived from such oscilloscopic traces. Values of k' obtained from these plots are plotted against the corresponding estimated ozone pressure immediately following the photoflash (Fig. 3). The slope of this plot yields the value of k_1-k_2, which, after small computerized correction ($\sim$ 10%) for the recombination of O + O and O + O$_2$ with N$_2$, was found to be 1.0 $\pm$ 0.5 $\times$ 10^{-14} cm^3 molecule^{-1} sec^{-1} (300 K).

The shape of the latter portions of the semi-logarithmic plots (Fig. 2) is essentially a function of the magnitude of k_2 as well as of the difference k_1-k_2. Computerized curve fitting for log $[O(2^3P_J)]$ using Runge–Kutta–Gill numerical integration of eqns. (2) and (3) for various values of k_2 and the values of k_1-k_2 and K derived from the slope and intercept, respectively, of Fig. 3 was carried out. The computed curves were correct in general form over a wide range of ozone pressures studied; however, the reproducibility was limited due to the more significant effect of the uncertainty of I_0 in the latter portions of the trace (Fig. 1). Therefore, it was only possible to place an upper limit of 10^{-14} cm^3 molecule^{-1} sec^{-1} (300 K) on k_2 and, in general, a much lower value was indicated. This thus supports the lower literature value of 3 $\pm$ 0.5 $\times$ 10^{-15} cm^3 molecule^{-1} sec^{-1} [2-4] and using this we obtain for k_1 a value of 1.3 $\pm$ 0.5 $\times$ 10^{-14} cm^3 molecule^{-1} sec^{-1} (300 K). This compares favourably with the most recent direct[17] measurement of k_1 of 1.46 $\times$ 10^{-14} cm^3 molecule^{-1} sec^{-1} which was obtained in a flow system free from electronically excited molecular oxygen, and is somewhat higher than many of the more recent indirect measurements[1,3]. This agreement further supports the use of the primary
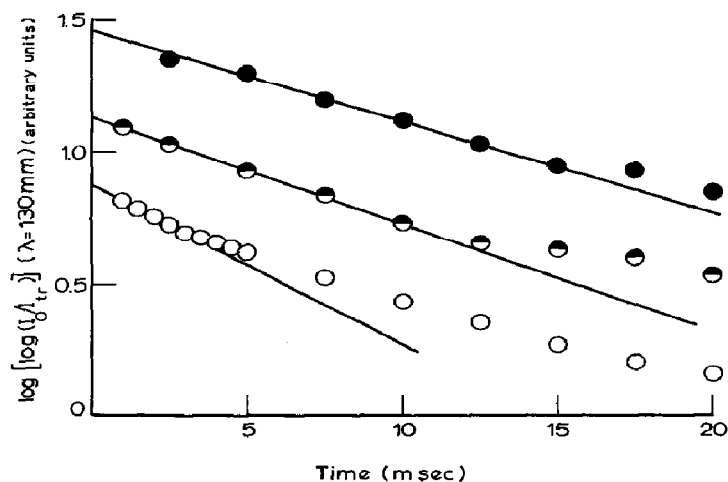
Fig. 2. Semi-logarithmic plots for the decay of $O(2^3P_J)$ following the flash pohotlysis of ozone. p(total with N_2) $= 19.95$ kN m^{-2}; $E = 160$ J. ●, $p_{O_3} = 10.6$ N m^{-2}; ◒, $p_{O_3} = 29.4$ N m^{-2}; O, $p_{O_3} = 66.1$ N m^{-2}.
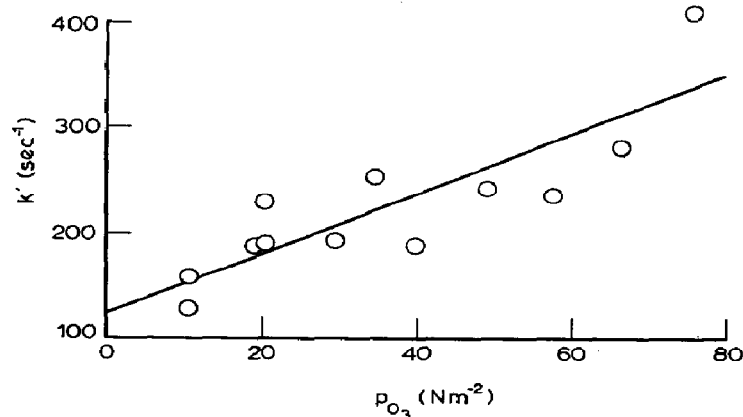

Fig. 3. Plot of the initial first order rate coefficient (k') for the decay of $O(2^3P_J)$ versus the mean pressure of ozone. p total with $N_2 = 19.95$ kN m^{-2}; $E = 160$ J.

process leading to $O_2(a^1\Delta_g)$[12,13]. The primary generation of $O_2(b^1\Sigma_g^+)$ and its subsequent rapid chemical reaction with O_3[18] would lead to a higher value of k_2 and a consequently higher value for k_1 from the kinetic analysis. Further, we have been unable so far to detect $O_2(b^1\Sigma_g^+)$ in absorption in this system[6,19].

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