Reactions of Oxygen Atoms

Part 3.—Reaction of $O(2^3P_J)$ and $O(2^1D_2)$ with CO and CO_2 .

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Direct measurements of $O(2^3P_J)$ by kinetic absorption spectroscopy in the vacuum ultra-violet have been used to investigate the rate of the reaction

 $O(2^{3}P_{J}) + CO + M \rightarrow CO_{2} + M \tag{6}$

The results obtained were :

$$k_6(M = Ar) = 1.4 \pm 0.7 \times 10^{-35} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

 $k_6(M = He) = 1.4 \pm 0.7 \times 10^{-35} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$

at 300 K. Oxygen atoms were produced initially in the $O(2^1D_2)$ state following the flash photolysis of CO_2 in the wavelength region 110-160 nm. It is concluded that both CO_2 and CO quench $O(2^1D_2)$ to the electronic ground state in these experiments.

The photolysis of CO₂ in the wavelength region $\lambda < 160$ nm produces oxygen atoms in the (¹D) state.¹ In the presence of a quenching gas such as argon, O(2¹D₂) may be deactivated to the ground state O(2³P_J). Alternatively, reaction with CO₂ or CO may occur:

$$O(2^{1}D_{2}) + Ar \rightarrow O(2^{3}P_{J}) + Ar, \qquad (1)$$

$$O(2^1D_2) + CO_2 \rightarrow \text{products},$$
 (2)

$$O(2^1D_2) + CO \rightarrow \text{products.}$$
 (3)

The fate of $O(2^1D_2)$ in reactions (2) and (3) has been the subject of some controversy. It has been proposed that reaction (2) produces CO_3 which is sufficiently stable to be lost by diffusion to the walls in many reaction systems.² This species has been isolated in solid matrices and identified by means of its infra-red absorption spectrum.³⁻⁵ While the results of Clerc and Reiffsteck ⁶ further suggest that, in the gas phase, the removal of $O(2^1D_2)$ by CO_2 does not yield $O(2^3P_J)$, the most recent evidence favours quenching of $O(2^1D_2)$ by this molecule to the ground state. Clerc and co-workers ^{6, 9, 10} have reported that CO removes $O(2^1D_2)$ by reaction to form CO_2 with a rate constant of 10^{-11} cm³ molecule⁻¹ s⁻¹ at room temperature. Such rapid collisional stabilization of a highly excited triatomic complex is improbable under their experimental conditions and indeed other evidence suggests that reaction (2) leads to quenching of $O(2^1D_2)$.^{8, 11} The conflicting evidence on both these questions has been discussed.^{1, 8, 11-15} Thus, further direct observations of oxygen atoms are required to resolve both points unambiguously. In this paper, we present further evidence obtained by directly monitoring the $O(2^{3}P_{J})$ atom by kinetic absorption spectroscopy in the vacuum ultra-violet which strongly supports quenching as the mechanism of reactions (2) and (3).

We have also studied the kinetics of the recombination of $O(2^3P_J)$ with carbon monoxide. Previous studies of this reaction have proved difficult and results have

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been generally inconsistent. The data for this reaction have been reviewed by Baulch *et al.*¹⁶ and more recently the reaction has been studied by direct observation of $O(2^3P_J)$ using a resonance fluorescence technique.¹¹ An upper limit has been placed on the rate of this reaction by the authors.¹⁷

EXPERIMENTAL

The basic apparatus for photoelectric monitoring of $O(2^3P_J)$ by absorption of the 130 nm resonance line $(3^3S_1^{\circ} \leftarrow 2^3P_J)$ following flash photolytic generation has been described previously.¹⁷ For the present studies, a reaction vessel similar to that described by Donovan ¹⁸ was employed coaxial with the vacuum ultra-violet flash photolysis lamp. This Pyrex vessel was of square cross-section with eight 22 mm diam. lithium fluoride windows cemented over porthole apertures cut in opposite faces to permit photolysis of CO_2 in the Schumann region. In the experiment described here, a single 5 μ F capacitor was discharged across a pair of lamp electrodes at a potential of 14 kV, yielding a photolysis energy of 490 J. Triggering was achieved by means of a series spark gap. Further modifications to the apparatus ¹⁷ included the use of a lithium fluoride lens on the atomic resonance lamp to improve the collection of light at 130 nm by the monochromator. The mains ripple previously present on the output of this lamp was eliminated in most of the present experiments by modifying the magnetron circuitry of the microwave generator. Rate data are quoted for 300 K.

British Oxygen Company Grade High Purity X gases were used in all reaction mixtures, and in a number of experiments, further attempts to remove trace impurities were made.

RESULTS AND DISCUSSION

FATE OF $O(2^1D_2)$ IN THE PRESENCE OF CO_2 AND CO

The decay of $O(2^{3}P_{J})$ following the flash photolysis of CO_{2} with wavelengths greater than 110 nm was monitored in absorption by means of the resonance line at 130 nm for periods up to 0.2 s following the photoflash. The value of γ in the absorption law

$$I_{\rm tr} = I_0 \exp\left[-\varepsilon (lc)^{\gamma}\right] \tag{i}$$

was taken to be 0.5 as found in previous experiments,¹⁷ and this value was used without further verification. The degree of dissociation of CO_2 was very small ($\approx 0.4 \%$) and thus the reaction scheme in the presence of an inert diluent gas M may be considered as follows:

$$CO_2 \rightarrow CO + O(2^1 D_2)$$

$$O(2^1 D_2) + M \rightarrow O(2^3 P_J) + M$$
(1)

$$O(2^{1}D_{2}) + CO_{2} \rightarrow \text{products excluding } O(2^{3}P_{J}) (CO_{3}?)$$
(2a)
$$O(2^{1}D_{2}) + CO_{2} \rightarrow O(2^{3}D_{2}) + CO_{2}$$
(21)

$$\mathcal{O}(2^1 D_2) + \mathcal{O}_2 \to \mathcal{O}(2^3 P_J) + \mathcal{O}_2. \tag{2b}$$

Under the experimental conditions employed, these reactions may be regarded as instantaneous, removal of $O(2^1D_2)$ being essentially complete within a few microseconds of the end of the photoflash.¹⁹ The above sequence of reactions will thus be followed by the relatively slow removal of $O(2^3P_J)$ and any CO_3 formed, by gasphase reaction and at the walls of the vessel. The concentration of $O(2^3P_J)$ immediately after the completion of the photoflash is therefore given by the expression

$$[O]_{t=0} = \alpha [CO_2] \frac{k_1 [M] + k_{2b} [CO_2]}{k_1 [M] + k_{2b} [CO_2] + k_{2a} [CO_2]},$$
(ii)

where α is the degree of dissociation of CO₂.

Fig. 1*a* shows the variation in the observed relative values of $[O]_{t=0}/[CO_2]$ measured as a function of CO_2 pressure and normalized about their mean value. Argon was added to maintain a total pressure of 39.9 kN m⁻². Small corrections have been applied to these values for the variation in α at the centre of the vessel due to absorption of light by CO_2 using a mean value for the absorption coefficient of CO_2 over the wavelength region of photolysis.²⁰ The form of the variation expected in $[O]_{t=0}/[CO_2]$ for complete quenching of $O(2^1D_2)$ by CO_2 ($k_{2a}/k_{2b} = 0$), 50 % quenching ($k_{2a}/k_{2b} = 1$) and complete reaction ($k_{2a}/k_{2b} = \infty$) are indicated.



FIG. 1.—The variation in $[O(2^3P_J)]_{t=0}$ resulting from the photolysis of CO_2 ($\lambda > 110$ nm) at different pressures. (E = 490 J). (a) \bigcirc , p (total with Ar) = 39.9 kN m⁻²; (b) \bigcirc , p (total with Ar) = 19.95 kN m⁻².

The curves have been calculated from (ii) on the basis of the relative rates of reaction of $O(2^1D_2)$ with CO_2 and argon (91 : 1, ref. (21)). Fig. 1b shows the corresponding results obtained at a total pressure of 19.95 kN m⁻². Although there is some scatter in the experimental results, they are consistent with quenching as the dominant mode of interaction of $O(2^1D_2)$ with CO_2 . The high rate of interaction of $O(2^1D_2)$ with CO_2^{21} has been generally confirmed ^{19, 22, 23} and recent work by the authors ²⁴ also supports this. However, Noxon ¹ has reported a slower rate for this process. Thus, whilst we conclude that CO_2 quenches $O(2^1D_2)$ to the ground state, there is the possibility of reaction to other products if the slow removal rate by CO_2^{-1} proves to be correct. Whichever of these alternatives is correct, the present results are in direct conflict with those of Clerc and Reiffsteck ⁶ who, under similar experimental conditions, report the complete reaction of $O(2^1D_2)$ to form CO_3 .

The effect of CO on the initial concentration of $O(2^3P_J)$ was investigated by flash photolyzing a fixed pressure of CO₂ (266 N m⁻²) with various pressures of CO in the presence of excess argon (total pressure = 39.9 kN m⁻²). No significant variation in $[O]_{t=0}$ was observed up to $P_{CO} = 5 \text{ kN m}^{-2}$. One may expect from the data of Cvetanovic and co-workers ^{8, 21} that, at this pressure of CO, 86 % of the $O(2^1D_2)$ will be removed by CO rather than by argon or CO₂. Similar results using helium in the place of argon as the diluent gas also showed no significant decrease in $[O]_{t=0}$

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with CO pressure. Thus, we may conclude that quenching of $O(2^1D_2)$ takes place on collision with CO rather than chemical reaction.

DECAY OF $O(2^{3}P_{J})$ IN THE PRESENCE OF CO_{2} AND INERT GASES

The kinetics of $O(2^{3}P_{J})$ following the flash photolysis of CO_{2} +inert gas mixtures was studied. The analysis was carried out by treating the observed decay as psuedo-first order,

$$-d [O(2^{3}P_{J})]/dt = k'[O(2^{3}P_{J})],$$
(iii)

and thus a plot of $\ln [O(2^3P_J)]$ against time should yield a straight line of slope -k'. From eqn (i), a plot of $\ln (\ln(I_0/I_{tr}))$ at 130 nm against time yields a straight line of slope $-\gamma k'$ ($\gamma = 0.5$), and this procedure was adopted by means of a least-squares



FIG. 2.—The variation of the first-order coefficient k' for the decay of $O(2^3P_J)$ produced from the photolysis of CO_2 with total pressure (Ar). $p_{CO_2} = 266 \text{ Nm}^{-2}$; E = 490 J; Full curve = experimental results, Dotted curve = extrapolation of experimental data from low to high pressure using the form k' = A/p (total).

computerized analysis. Fig. 2 shows the variation in k' observed following the flash photolysis of a fixed pressure of CO₂ at varying total pressures, using argon as the diluent gas. The broken curve represents a variation in k' of the form,

$$k' = A/p, \tag{iv}$$

which has been fitted to the experimental data at low total pressures, indicating removal of $O(2^3P_J)$ by diffusion to the walls of the vessel. The deviation from this curve at high pressures is attributed to gas-phase third-order reaction. The "long time" solution of the diffusion equation ²⁵ using a simplified geometrical model of the reaction vessel as a cuboid yielded the diffusion coefficient of $O(2^3P_J)$ in argon of $D_{O-Ar} = 0.64 \text{ cm}^2 \text{ atm s}^{-1}$ at 300 K. The corresponding experiment with helium as the diluent gas gave the result $D_{O-He} = 1.6 \text{ cm}^2 \text{ atm s}^{-1}$. These values are higher than those obtained by Yolles and Wise ²⁶ ($D_{O-Ar} = 0.39 \text{ cm}^2 \text{ atm s}^{-1}$, $D_{O-He} = 0.73 \text{ cm}^2 \text{ atm s}^{-1}$ (298 K)); however, we believe that these differences are adequately accounted for by the approximations employed in the present estimation and by the effect of concentration gradients along the length of the reaction vessel which must lead to the observed values being somewhat higher than the true values.

The contribution to the overall removal of $O(2^{3}P_{J})$ (k') due to third-order reaction,

viz., the difference in the ordinate between the solid and broken curves in fig. 2, was studied as a function of CO₂ pressure at two different total pressures of argon $(p_{\rm Ar} = 19.95 \text{ and } 39.9 \text{ kN m}^{-2})$. Computerized studies based on the reaction scheme

$$O + O + M \rightarrow O_2 + M \tag{3}$$

$$O + O_2 + M \to O_3 + M \tag{4}$$

$$O + O_3 \rightarrow 2O_2 \tag{5}$$

using the rate constants ^{17, 27} $k_3 = 1.65 \times 10^{-33}$ and $k_4 = 5 \times 10^{-34}$ cm⁶ molecule⁻² s⁻¹, and $k_5 = 1.5 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, indicated a degree of photodissociation of CO₂ of ~0.4 % (justifying the use of eqn (ii)). The removal of O(2³P_J) by diffusion at low pressures of CO₂ clearly contributes the dominant correction to the study of the overall decay in the presence of added CO.

DECAY OF $O(2^{3}P_{J})$ IN THE PRESENCE OF ADDED CO

By measuring the effect of added CO on k' we now investigate the reaction

$$O(2^{3}P_{J}) + CO + M \rightarrow CO_{2} + M.$$
(6)

Typical psuedo-first order plots for the decay of $O(2^3P_J)$ in the presence of added CO following the photolysis of a fixed pressure of CO_2 (266 N m⁻²) in the presence of argon at a given total pressure are shown in fig. 3. Fig. 4 shows the variation of k' with CO pressure, indicating pseudo-first order kinetics with respect to this molecule. The effect of total pressure on the rate of reaction (6) was also investigated by



FIG. 3.—Typical pseudo-first order plots for the decay of O(2³P_J) in the presence of carbon monoxide. $p_{CO_2} = 266 \text{ N m}^{-2}$, p (total with Ar) = 39.9 kN m⁻², E = 490 J. \bullet , $p_{CO} = 0$; \triangle , $p_{CO} = 0.676$; \Box , $p_{CO} = 1.305$; \bigcirc , $p_{CO} = 2.065$; \blacksquare , $p_{CO} = 3.99 \text{ kN m}^{-2}$.

flash photolyzing a fixed pressure of CO_2 (266 N m⁻²) and CO (1.33 kN m⁻²) at various total pressures. The contribution from reaction (6) towards k' was obtained by subtracting the diffusion rate calculated from fig. 2. The resulting first-order rate coefficient k" was attributed to reaction (6) and thus a plot of k" against total pressure should yield a straight line passing through the origin. The large body of data obtained in this way is shown in fig. 5. The scatter in this plot is considerably

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greater than would be expected from purely random error, and we must attribute this to the catalytic effect of trace impurities on the very slow reaction rate. The only trace impurity that was positively identified which might have affected the results was iron carbonyl which was present in some samples of bulb CO. The results presented here were all obtained with samples of CO which were shown to be free from iron carbonyl, or which were purified by slow passage through a spiral trap at 77 K. Purification of other gases used by cooling to 77 K before use also failed to improve the scatter, which appeared to be a function of the history of the reaction vessel, the slowest rates being found immediately following cleaning and



FIG. 4.—The variation of the first order coefficient k' for the decay of $O(2^3P_J)$ from the photolysis of CO₂, with the pressure of added CO. $p_{CO_2} = 266 \text{ N m}^{-2}$; p (total with Ar) = 39.9 kN m⁻²; E = 490 J.

thorough degassing of the vessel. Black and Slanger 11 in their study of this system, also enountered problems due to impurities and suggested the formation of C_3O_2 polymer on the walls of the vessel. Surface reactions in the present system are controlled by slow diffusion to the walls of the vessel. From the lowest consistent set of results, i.e., those least likely to be affected by impurity, we obtain the result : $k_{6(Ar)} = 1.4 \pm 0.7 \times 10^{-35} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (300 K). The full lines in fig. 4 and 5 describe this set of data. The corresponding result employing helium as the diluent gas yielded the result: $k_{6(\text{He})} = 1.4 \pm 0.7 \times 10^{-35} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (300 K). The results confirm the low rates for reaction (6) favoured by the work of Wong, Potter and Belles ²⁸ and of Black and Slanger,¹¹ and by the early results of Harteck and Dondes.²⁹ (The value obtained by Harteck and Dondes ²⁹ was 5×10^{-36} cm⁶ molecules⁻² s^{-1} , and those of Black and Slanger were 7×10^{-36} cm⁶ molecule⁻² s^{-1} (M = Ar) and 6×10^{-36} cm⁶ molecule⁻² s⁻¹, M = He)). Wong et al.²⁸ have obtained an upper limit of 10^{-34} cm⁶ molecule⁻² s⁻¹ for k_6 at 500 K, which extrapolates to a value of 2×10^{-35} cm⁶ molecule⁻² s⁻¹ at 300 K employing the activation energy of 10.5 kJ/mol suggested by Baulch et al.¹⁶ However, the uncertainty over the overall reaction order ¹⁶ suggests this temperature dependence of the reaction might be considerably more complicated. The value obtained by Kondratiev *et al.*³⁰ $(k_{6(Ar)} = 1.8 \pm 0.24 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$ following e.s.r. studies on $O(2^3P_J)$ appears to be high both in relation to the present data and other recent studies.



FIG. 5.—The variation of the diffusion-corrected first order coefficient k'' for the decay of O(2³P_J) in the presence of CO as a function of total pressure with added argon. $p_{CO_2} = 266 \text{ N m}^{-2}$; $p_{CO_2} = 1.33 \text{ kN m}^{-2}$; E = 490 J.

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