THE COLLISIONAL QUENCHING OF $O(2^1D_2)$ BY $COCl_2$, COFCl AND COF_2 USING ATOMIC ABSORPTION SPECTROSCOPY IN THE VACUUM ULTRAVIOLET

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Summary

Phosgene derivatives have hitherto been established as major products in the photo-oxidation of chlorinated fluorocarbons by ozone, a matter pertinent to stratospheric pollution. We report here absolute quenching rates for the overall removal of electronically excited oxygen atoms $O(2^1D_2)$ by the molecules $COCl_2$, COFCl and COF_2. $O(2^1D_2)$ generated by the repetitive pulsed irradiation of ozone was monitored photoelectrically by resonance line absorption in the vacuum ultraviolet ($\lambda = 115.2$ nm, $O(3^1D_2^0) \leftarrow O(2^1D_2)$). The following second order rate constants (k_Q in cm^3 molecule^{-1} s^{-1} at 300 K) are obtained: $k(COCl_2) = 7.1 \pm 0.9 \times 10^{-10}$, $k(COFCl) = 3.7 \pm 0.4 \times 10^{-10}$ and $k(COF_2) = 4.6 \pm 0.4 \times 10^{-10}$. These data are compared with previous relative rate measurements.

1. Introduction

Pollution of the stratosphere by chlorinated fluorocarbons, particularly CF_2Cl_2 and $CFCl_3$, and partial depletion of the ozone layer resulting from an ensuing complex photochemistry brought about by solar radiation is a subject of considerable current interest [1 - 3]. An important aspect of this is the reaction of electronically excited oxygen atoms $O(2^1D_2)$, 1.967 eV above the $O(2^3P_2)$ ground state [4], with various halocarbons and the products of their photo-oxidation. A number of relative rate measurements for the removal of $O(2^1D_2)$ by halogenated hydrocarbons using photostationary techniques have been reported. Pitts and coworkers [5, 6] describe relative rate data for chemical reactions of $O(2^1D_2)$ derived from the photolysis of N_2O at $\lambda = 228.8$ nm and similar experiments have been reported by Green and Wayne [7] using photolysis at the same wavelength. Jayanty *et al.* [8] report relative rate data for the total quenching of $O(2^1D_2)$ following the photolysis of O_3-N_2O- halogenated paraffin mixtures. More recently, we have obtained absolute rate data for the quenching of $O(2^1D_2)$

by a range of fluorinated and chlorinated hydrocarbons [9, 10], together with Cl_2 itself [11], using direct monitoring of the optically metastable oxygen atoms [12] by absorption spectroscopy in the vacuum ultraviolet (VUV).

Jayanty *et al.* [8] observed phosgene derivatives as major products in the photo-oxidation of chlorofluoromethanes, and recently these workers [13] have reported relative rate data for the quenching of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2. Similar observations have been made by Atkinson *et al.* [14] who report relative quenching rate data for $O(2^1D_2)$ with $COFCl$ and COF_2. It is therefore appropriate that direct absolute quenching rates for $O(2^1D_2)$ with the phosgene derivatives be measured. This is reported in this paper using resonance line absorption in the VUV.

2. Experimental

The experimental arrangement for monitoring $O(2^1D_2)$ by atomic absorption spectroscopy in the VUV has been described previously [9 - 11] and the essence of the system will only be summarized here. $O(2^1D_2)$ was generated by the repetitive (0.2 Hz) pulsed irradiation of ozone in the Hartley band continuum in the presence of excess helium buffer gas ($p(He):p(O_3) \approx 50\ 000:1$) to ensure that there was no significant temperature rise above ambient conditions. The electronically excited atoms were then monitored photoelectrically by resonance absorption at $\lambda = 115.2$ nm ($O(3^1D_2^0) \leftarrow O(2^1D_2)$) derived from a microwave-powered atomic flow lamp described in earlier publications [15, 16]. Detection of the attenuated signals at this wavelength was by means of a "solar blind" photomultiplier (E.M.R. 541G-08-18) mounted on the exit slit of a 1 m concave grating VUV monochromator (Hilger and Watts). After passage through a current-to-voltage converter employing a fast-settling operational amplifier [17] and through rapid response precision logarithmic circuitry [18, 19], the photo-electric pulses were then digitized and stored in a 200-point signal recovery system (Datalab, model 102A). The data were then transferred onto paper tape (Datadynamics 1133) for subsequent analysis in the University of Cambridge IBM 370 computer.

The attenuated signals were related to concentrations of $O(2^1D_2)$ by the modified Beer–Lambert law [20]:

$$I_{tr} = I_0 \exp \{-\epsilon(cl)^\gamma\} \tag{1}$$

The use of this expression for the particular resonance line employed here has been the object of recent detailed discussion arising from (a) a comparison of the kinetic data resulting from the present technique [15, 16, 21, 22] with those derived from time-resolved studies of the forbidden emission at $\lambda = 630$ nm ($O(2^1D_2) \rightarrow O(2^3P_J)$) [23] and (b) calculations of "curves of growth" for various line profiles associated with the $\lambda = 115.2$ nm transition in the spectroscopic source and the attenuating medium [24]. Details of this

discussion can be found in earlier papers [10, 22]. The early measurement of $\gamma = 0.41 \pm 0.03$ [15] was reconfirmed in later work [10, 22]. Of course, relative rate data obtained by the present method are independent of the magnitude of γ provided that this quantity remains sensibly constant over the observed kinetic decays of the excited atom.

2.1. Materials

Helium, krypton (for the photoflash lamp) and ozone were prepared as described previously [15]. $COCl_2$ from a cylinder (Air Products Ltd., 99%) was trapped at liquid nitrogen temperature (-196 °C) and degassed by a number of freeze–pump–thaw (FPT) cycles. It was then fractionally distilled from a $CHCl_3$ slush (-63 °C) to -196 °C. COF_2 and $COFCl$ were prepared by the action of SO_3 (in oleum) on CF_2Br_2 and $CFCl_3$ respectively according to ref. 25. The products of both of these reactions were purified by subjecting them to several FPT cycles at -196 °C and fractional distillation from a CH_2Cl_2 slush (-98 °C) to -196 °C. (We are indebted to the Mond Division of ICI for helpful discussion on the preparation of these two materials following ref. 25 and for a sample of CF_2Br_2.)

3. Results and discussion

An example of the computerized raw data in the form of the digitized signal of $\ln (I_0/I_{tr})$ at $\lambda = 115.2$ nm representing the decay of resonance absorption of $O(2^1D_2)$ in the presence of $COCl_2$ is given in Fig. 1. A series of first order kinetic plots, following eqn. (1), for the decay of $O(2^1D_2)$ in the presence of different pressures of $COCl_2$ is shown in Fig. 2. The slopes of such plots (Fig. 2) are given by $-\gamma k'$ where k' is the overall first order decay coefficient. This is then expressed in the standard form

$$k' = K + k_Q [Q] \tag{2}$$

where K is a constant in a series of kinetic experiments in which the quenching gas Q, in this case $COCl_2$, is varied. It includes first order rate contributions from diffusion, weak spontaneous emission [12] and, principally, quenching by undissociated ozone. k_Q is the absolute second order rate constant for removal of $O(2^1D_2)$ by the collisional partner Q.

The neglect of the extent of decomposition of the reactants in these low pulse energy experiments and the use of eqn. (2) based on initial conditions is seen to be a satisfactory approximation. The early experiments using the present attenuation technique on $O(2^1D_2)$ showed the extent of photolysis of the ozone–helium mixtures to be less than 1% [15] for similar experimental conditions to those described here. An approximate calculation based on treating the light emission from the flashlamp as a black body radiator of temperature $T = 6500$ K, following actinometric measurements on such sources by Christie and Porter [26], shows the extent of photolysis of the phosgene compounds to be negligible. Considering initially the ozone
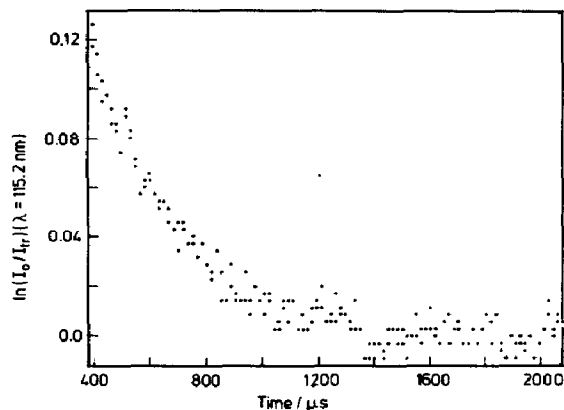
Fig. 1. Digitized time variation of ln (I_0/I_{tr}) at λ = 115.2 nm $(O(3^1D_2^0) \rightarrow O(2^1D_2))$ indicating the decay of resonance absorption by $O(2^1D_2)$ in the presence of $COCl_2$. $p(O_3)$ = 0.025 N m^{-2}; $p(COCl_2)$ = 0.014 N m^{-2}; p(total with He) $\approx$ 2.0 kN m^{-2}; E = 64 J; repetition rate, 0.2 Hz; average of 16 experiments; sweep rate, 10 μs per channel; delay, 100 μs.
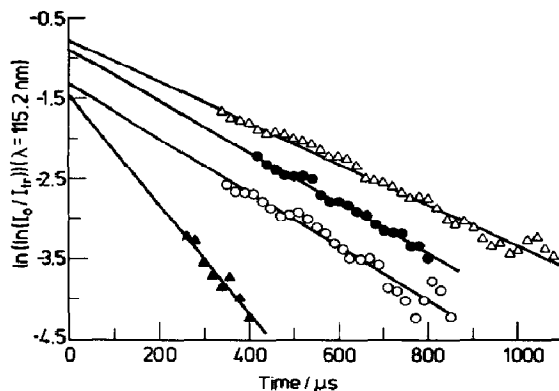
Fig. 2. Typical pseudo first order plots for the decay of $O(2^1D_2)$ obtained by monitoring the absorption of light at λ = 115.2 nm $(O(3^1D_2^0) \leftarrow O(2^1D_2))$ in the presence of $COCl_2$. $p(O_3)$ = 0.025 N m^{-2}; p(total with He) $\approx$ 2.0 kN m^{-2}; E = 64 kJ. $p(COCl_2)$ (N m^{-2}): $\triangle$, 0.0; $\bullet$, 0.014; $\bigcirc$, 0.21; $\blacktriangle$, 0.46.

itself, it is readily seen that this molecule is the principal light-absorbing species present, the broad Hartley band system showing a maximum at λ = 254 nm ($\epsilon(O_3)$ (254 nm) = 133 atm^{-1} cm^{-1} [27, 28]). In the UV $COCl_2$ exhibits a broad band centred at λ = 240 nm ($\epsilon(COCl_2)$ (240 nm) = 4.8 atm^{-1} cm^{-1} [29]) and a further band in the far UV still rising at λ = 200 nm ($\epsilon(COCl_2)$ (200 nm) = 8.1 atm^{-1} cm^{-1} [29]). COFCl gives rise to a broad band with a maximum lying at λ = 203 nm ($\epsilon(COFCl)$ (203 nm) = 1.5 atm^{-1} cm^{-1}) extending out to λ = 253 nm [30]. Further, for T = 6500 K, $W_\lambda/W_{\lambda(max, \lambda = 450nm)}$ (where W_λ has its usual significance for a black body radiator) at λ = 254, 253, 240, 203 and 200 nm takes the respective values 0.386, 0.381, 0.312, 0.143 and 0.139. Hence, this simple consideration of extinction coefficients and emission intensities shows that kinetic equations employing conditions of initial concentration are appropriate relative to the magnitudes of the errors inherent in the observed kinetic decays. The principal far UV electronic spectrum of COF_2 comprises about five bands lying between λ = 181.2 and 206.2 nm [31, 32], absorption associated with which is neglected in view of the quartz "cut-off" for the photolysis initiation involved in these experiments (λ $\approx$ 200 nm). Also, chain reactions initiated by Cl + O_3 from the photolysis of $COCl_2$ and COFCl would require chain lengths of the order of 17 - 90 simply to double the low extent of the ozone decomposition.

Figure 3 shows the rate data for the three phosgene derivatives investigated here, $COCl_2$, COFCl and COF_2, in the form of eqn. (2) ($\gamma k'$ versus p_Q). The slopes of these plots, with the above value of γ (0.41), yield
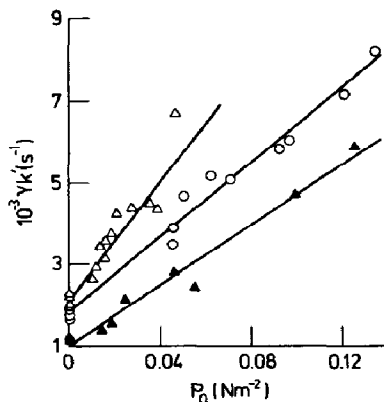
Fig. 3. Plots of pseudo first order rate coefficients $\gamma k'$ for the decay of $O(2^1D_2)$ in the presence of $COCl_2$, $COFCl$ and COF_2. p (total with He) $\approx$ 2.0 kN m^{-2} ($\gamma k'$ = 500 s^{-1} for $COFCl$): $\triangle$, $COCl_2$; $\blacktriangle$, $COFCl$; $\circ$, COF_2.

TABLE 1

Absolute second order rate constants k_Q at 300 K for the collisional removal of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2

Q	$10^{10}k_Q$ (γ = 0.41) (cm^3 molecule^{-1} s^{-1})	$10^{10}k_Q$ (γ = 1) (cm^3 molecule^{-1} s^{-1})
$COCl_2$	7.1 ± 0.9	2.9 ± 0.3
$COFCl$	3.7 ± 0.4	1.5 ± 0.1
COF_2	4.6 ± 0.4	1.9 ± 0.1
CO_2	1.7 ± 0.2 [22]	0.7 ± 0.06 [22]

TABLE 2

Relative rate data for the collisional removal of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2 (relative to N_2O)[a]

Q	This work	Atkinson et al. [14]	Jayanty et al. [13][b]
$COCl_2$	3.2 ± 0.4		1.57
$COFCl$	1.7 ± 0.2	2.8 ± 0.4	0.96
COF_2	2.1 ± 0.2	0.29 ± 0.04	0.41

[a] Relative to $k(N_2O)$ = 2.2 ± 0.2 × 10^{-10} cm^3 molecule^{-1} s^{-1} (300 K, γ = 0.41) [21].
[b] Quoted error about 10%.

the absolute second order collisional quenching constants for the removal of $O(2^1D_2)$ by these molecules together with the values derived from a γ value of unity for comparison. These are given in Table 1. Table 2 gives the data in relative form with the previously measured value of $k(N_2O)$ [21] as a standard determined by this method employing a γ value of 0.41. This standard was used in the previous relative rate determinations for the removal of $O(2^1D_2)$ by these molecules [13, 14].

There are no absolute data with which to compare directly the results of the present investigation (Table 1) because previous measurements were concerned with determining relative rates for $O(2^1D_2)$ as indicated in the introduction. We include for comparison in Table 1 the absolute quenching rate of $O(2^1D_2)$ by CO_2, determined by the present method [22]. The removal by CO_2 is dominated by physical quenching [33, 34] even though chemical reaction to yield either $O_2(a^1\Delta_g)$ or $O_2(b^1\Sigma_g^+)$ would in both cases arise from symmetry-allowed exothermic routes when initial and final states are correlated on the basis of the weak spin–orbit coupling approximation and assuming C_s symmetry in the collision complex [16]. The inclusion of halogen atoms in the quenching molecules, especially chlorine atoms, clearly enhances the removal efficiency. This was found with the study of $O(2^1D_2)$ quenching by fluorinated hydrocarbons where, for a given type of molecule, substitution by Cl atoms enhanced the rates, apparently leading to Cl atom abstraction [10]. On such a basis the result for COF_2 relative to that for COFCl (Table 1) appears high though the plot from which $k(COF_2)$ is derived (Fig. 3) is characterized by an error similar to those for the other two quenching gases. It would be reasonable to suppose that the physical quenching of $O(2^1D_2)$ by COF_2 would be faster than that by CO_2 (Table 1) purely in terms of molecular complexity, but not necessarily of the magnitude that was found here. Furthermore, the result for COFCl can be regarded confidently since its purity could be readily monitored by means of a standard spectrophotometer via its UV absorption spectrum (see earlier).

As regards the value of the quenching rates relative to that by N_2O (Table 2), the errors from this investigation should be small since the error in γ cancels in the determination of the ratio of the rates. The ratio of the relative rates determined by Atkinson *et al.* [14] to those obtained here (Table 2) yields the fraction of the total removal rate of $O(2^1D_2)$ arising from chemical processes. On this basis removal of $O(2^1D_2)$ by COFCl is clearly dominated by chemical reaction. Similarly, chemical reaction with COF_2 appears to account for more than 15% of the overall removal rate of the excited atom (Table 2), though we would not wish to speculate on the nature of the products. Notwithstanding our discussion of $k(COF_2)$ the relative rate data of Jayanty *et al.* [13] for the total removal of $O(2^1D_2)$ are clearly low.

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