IS CO_2 A GOOD QUENCHER OF $O_2(^1\Delta_g)$? A KINETIC REAPPRAISAL

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Summary

The rate at which $O_2(^1\Delta_g)$ is quenched by CO_2 is of great importance in interpreting air-glow studies of the atmospheres of both Mars and Venus. There has been a long-standing controversy in the literature about the rate coefficient for the quenching process. In this paper, further kinetic experiments using a flow system with direct detection of the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ emission system are described. The upper limit obtained for the rate coefficient was 3.6×10^{-19} cm^3 $molecule^{-1}$ s^{-1}. An explanation is advanced for the earlier discrepancies; this explanation is concerned with the use of energy-sensitive, but not specific, detection methods for the excited species.

1. Introduction

In recent years there have been several kinetic studies of the quenching of metastable $O_2(a\ ^1\Delta_g)$ by atmospheric gases [1 - 8]. The agreement between published rate constants has generally been good, with the exception of the value for quenching by CO_2. A decade ago, atmospheric interest was concerned mainly with air-glow phenomena on Earth [9, 10], so that the discrepancy in the CO_2 results was of minor importance in view of the low CO_2 abundance in the terrestrial atmosphere. However, the IR atmospheric band at $\lambda = 1.27$ μm, due to the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ transition, has been observed in the atmospheres of both Venus and Mars in probe [11, 12] and telescopic [13] experiments. Since the atmospheres of these planets consist predominantly of CO_2, a reliable rate constant $k_q(CO_2)$ for the quenching of $O_2(^1\Delta_g)$ by CO_2 is needed to evaluate possible production mechanisms [14].

Evidence of quenching was lacking in most of the laboratory investigations, so that upper limits for $k_q(CO_2)$ have been quoted that are dependent on experimental sensitivity. In general, these results have suggested $k_q(CO_2) \leqslant$

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8×10^{-20} cm^3 molecule^{-1} s^{-1}. However, Clark and Wayne [1] obtained a value of 4.0×10^{-18} cm^3 molecule^{-1} s^{-1}, while Yaron et al. [6] obtained 2.6×10^{-18} cm^3 molecule^{-1} s^{-1}: that is, apparent loss of $O_2(^1\Delta_g)$ was observed.

There are differences in the experimental methods used by the workers who observed quenching and by those who did not that might account for the conflicting results. First, both Clark and Wayne [1] and Yaron et al. [6] used a flow technique to obtain time resolution, while most of the other experimenters employed real-time decay measurements. Secondly, the two groups who observed quenching used indirect energy-sensitive methods of measuring the $O_2(^1\Delta_g)$ concentration: Clark and Wayne [1] used photoionization by the argon resonance lines (which cannot ionize ground state O_2), and Yaron et al. [6] used a calorimetric method. Those who did not observe quenching [4, 5, 8] generally employed optical emission to estimate $[O_2(^1\Delta_g)]$ either directly from the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ transition or indirectly (dimol emission or emission from $O_2(^1\Sigma_g^+)$ formed by energy pooling [15]).

The present experiments were performed to establish whether either of the experimental factors was responsible for the conflicting results. We retained the flow system, in an adaptation of the technique of Clark and Wayne, but used optical emission at $\lambda = 1.27$ μm to characterize the excited species. An improved germanium detector [16] gave sufficient sensitivity for these experiments, even when a monochromator was used to obtain wavelength specificity.

2. Experimental procedure

The $^1\Delta_g$ state of O_2 is conveniently produced in flow studies by passing a microwave discharge through molecular oxygen [15]. Unfortunately, atomic oxygen is also formed and can indirectly lead to loss of $O_2(^1\Delta_g)$ via the steps

$$O + O_2 \xrightarrow{M} O_3 \tag{1}$$

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

Although the oxygen atoms can be removed by a film of HgO placed immediately downstream of the discharge [15], we believe that this procedure is best avoided because of the possible interference of mercury in the system. Yaron et al. [6] have shown that an AgO surface similarly removes oxygen atoms but not $O_2(^1\Delta_g)$; AgO is unlikely to be a contaminant, but appreciable O_3 concentrations might still persist. The alternative method [1] is to so dilute the discharge products that the gas phase and wall deactivation processes

$$O_2(^1\Delta_g) + M \rightarrow O_2 + M \qquad k_q(M) \tag{3}$$

$$O_2(^1\Delta_g) \xrightarrow{\text{wall}} O_2 \qquad k_w \tag{4}$$

completely dominate over reaction (2). Since, in any case, the discharge products must be mixed with the quenching gas (if M is not O_2 itself), we used this technique. In order to provide variable contact times with a fixed-position detector, it is necessary to alter the point of injection of discharge products into the main (carrier) flow. To this end, we employed a sliding "trombone" injector. A movable U-shaped section of Pyrex tube was mounted rigidly together with the microwave discharge cavity on a platform that slid on rails. One end of the tube passed through a double O-ring seal into the main flow tube, while the other, similarly sealed, projected into a parallel dummy tube from which O_2 was supplied. All other aspects of the flow system were conventional. Figure 1 shows the essential features of the trombone
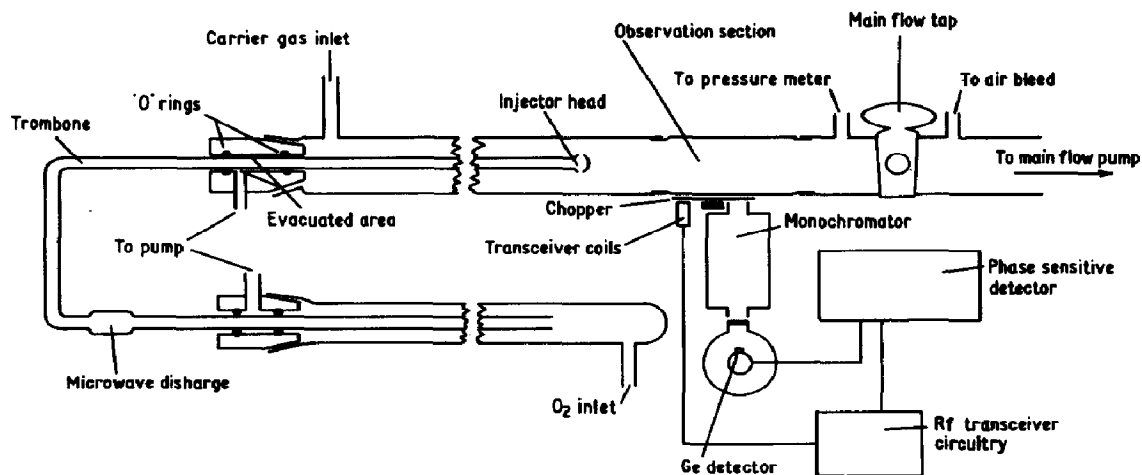

Fig. 1. A schematic outline of the sliding-injector flow apparatus.

configuration. The main flow tube was made of Pyrex (inside diameter, 36 mm); its length was 1 m and the sliding injector had a linear free movement of about 70 cm within it. Flow rates were measured with capillary flowmeters calibrated for the specific gases in use, and flow tube pressures were measured using either a capacitance manometer (MKS Baratron model 145 AH-10) or an electronic meter based on the National Semiconductors LX1702A device (itself calibrated against the Baratron). Linear flow velocities were typically about 0.4 m s^{-1}.

Relative concentrations of $O_2(^1\Delta_g)$ were determined from optical emission of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition at $\lambda = 1.27$ μm. The detection train consisted of a chopper (20 Hz), a monochromator (Bausch and Lomb model 33-86-25-03; bandwidth, approximately 10 nm full width at half-maximum) and a germanium cell. This cell is a photoconductive device, operated at liquid nitrogen temperature, and offers peak response close to the $O_2(^1\Delta_g)$ emission band. It was fabricated by us from high purity germanium, and further details of its construction and evaluation appear elsewhere [16]. Output signals were a.c. amplified and synchronously demodulated (Brookdeal model 9501D).

The gases used were CO_2 (BDH–Air Products; 99.98% CO_2), N_2 (BOC, "white spot") and O_2 (BOC). They were passed through molecular sieve traps on the high pressure side of the flow supply needle valves and then through appropriate refrigerant traps (liquid N_2 or solid CO_2–C_2Cl_3H slush) on the low pressure side immediately before entering the flow system.

In our experiments, the main flow was made up of a mixture of quenching gas (CO_2 or O_2) and inert N_2 buffer (known to have a quenching coefficient of less than 10^{-19} cm^3 molecule^{-1} s^{-1} for $O_2(^1\Delta_g)$ [1 - 8]). The total pressure in the flow tube was kept constant at about 10 Torr in any one series of experiments. Although the discharge dilution conditions needed to avoid interference by reaction (2) are well known [1], we established the specific conditions for our system by reducing the ratio of discharge flow (flow rate F_{O_2}) to carrier (flow rate F_M) until the total observed quenching reduced asymptotically to its limiting value [17]. In general, the asymptote was reached for $F_{O_2}/F_M <$ 0.04. It is, of course, this necessary dilution that places relatively high demands on detection sensitivity in our technique.

3. Results

Quenching experiments were carried out with M $\equiv$ O_2 as well as with M $\equiv$ CO_2. The concentrations of $O_2(^1\Delta_g)$ exhibited first-order decay for both gases. Figure 2 shows the variation in emission intensity as a function of dis-
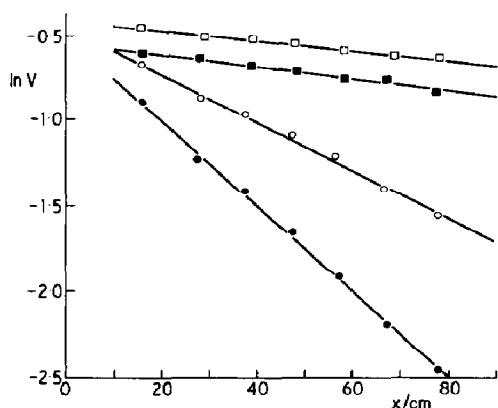

Fig. 2. Logarithm of intensity (signal voltage V) as a function of distance x between injector and observation port (flow velocity, approximately 40 cm s^{-1}): $\square$, $[CO_2]$ = 0.8 $\times$ 10^{17} molecule cm^{-3}; $\blacksquare$, $[CO_2]$ = 2.4 $\times$ 10^{17} molecule cm^{-3}; $\bigcirc$, $[O_2]$ = 1.4 $\times$ 10^{17} molecule cm^{-3}; $\bullet$, $[O_2]$ = 2.9 $\times$ 10^{17} molecule cm^{-3}.

tance between injector and detection point for two concentrations of each gas. It is immediately apparent that the slopes of the two logarithmic plots for M $\equiv$ CO_2 are nearly identical, suggesting that homogeneous quenching is weak. Using the measured flow velocities, pseudo-first-order loss rate constants $k' = k_w + k_q(M)[M]$ were evaluated and then plotted against [M]. Figure 3 shows the results.

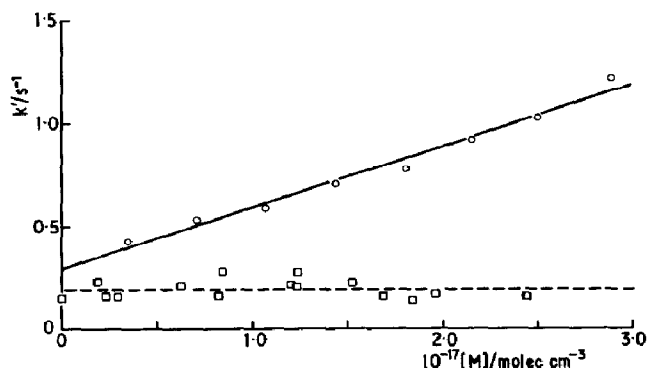Fig. 3. Pseudo-first-order decay rate constant k' as a function of [M]: $\circ$, $M \equiv O_2$; $\square$, $M \equiv CO_2$.

4. Discussion

The slopes of the two lines in Fig. 3 give the rate constants (95% confidence limits)

$$k_q(O_2) = (3.0 \pm 0.4) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_q(CO_2) = (-0.2 \pm 3.8) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

We take the positive 95% confidence bound as providing an upper limit for $k_q(CO_2)$ of 3.6×10^{-19} cm^3 molecule^{-1} s^{-1}. The corresponding upper limit for $k_q(CO_2)/k_q(O_2)$ is approximately 0.11. The series of runs using O_2 as the quenching gas was carried out in order to provide a rough check on the satisfactory operation of the system. The value obtained, $(3.0 \pm 0.4) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, is in agreement (within experimental error) with several previous determinations [1 - 8]. Nevertheless it must be added that recent measurements by Borrell *et al.* [7] and by Leiss *et al.* [8] have suggested a rate constant $k_q(O_2)$ of about half this value. If these latter results reflect calibration errors in our flow measurements or systematic errors from some other source, then, since our *ratio* of $k_q(CO_2)/k_q(O_2)$ will be unaffected, an even smaller upper limit for $k_q(CO_2)$ (approximately 1.8×10^{-19} cm^3 molecule^{-1} s^{-1}) would result.

It is clear that the upper limit of $k_q(CO_2)$ obtained in the present work is compatible neither with the results of Clark and Wayne [1] nor with those of Yaron *et al.* [6] but is consistent with the upper limits quoted by other workers (*e.g.* refs. 4, 5, 7, 8). There are two conclusions to be drawn from the new result. Firstly, it appears certain what limiting rate constant $k_q(CO_2)$ must be used for calculations relating to the atmospheres of Venus and Mars and, secondly, the discrepancies found in previous results are due to the detection system employed rather than to the method of time resolution (*i.e.* the flow technique as opposed to real-time measurement) involved.

We must now consider a possible way in which the energy-sensitive detection methods used by Clark and Wayne [1] and by Yaron *et al.* [6]

could introduce errors apparently only when CO_2 is used as quenching gas. The technique used by Clark and Wayne was photoionization by argon resonance radiation. The ionization potential of $O_2(^1\Delta_g)$ is 11.11 eV, that of $O_2(^3\Sigma_g^-, v'' < 2)$ is 11.69 eV, and the energy of argon resonance radiation used was predominantly 11.54 eV with less than 30% at 11.72 eV. Thus, in theory, $O_2(^1\Delta_g)$ may be ionized by the radiation whereas $O_2(^3\Sigma_g^-)$ may not. It was recognized that species of lower ionization potential present in the discharge could lead to spurious ion currents, and so tests were carried out in N_2 and O_2 carriers with Lyman α (10.10 eV) and krypton resonance (10.02 and 10.64 eV) lamps in order to show that no interfering ionizable species were present [1, 18]. However, it is possible that, in the CO_2 system, some excited state of oxygen, O_2^*, may have been present as well as $O_2(^1\Delta_g)$. We intend to show that the kinetic data of Clark and Wayne [1] are not inconsistent with this hypothesis.

At the time of Clark's experiment [18] there was no reason to suppose that CO_2 would behave differently from N_2 or O_2 as the carrier in a system containing the microwave discharge products of O_2. However, it has now emerged that the recombination of ground state (^3P) oxygen atoms leads to a population of metastable molecular oxygen states which is dependent on the presence or absence of CO_2. In particular, the c $^1\Sigma_u^-$ state [19] is greatly enhanced by the presence of CO_2 [20 - 23], whether at the atom recombination stage or later on. Observations of the atmospheres of Venus or Mars, in which CO_2 is predominant, also show the relative intensities of the Herzberg II (c $^1\Sigma_u^- \rightarrow$ X $^3\Sigma_g^-$) and IR atmospheric (a $^1\Delta_g \rightarrow$ X $^3\Sigma_g^-$) bands [11, 12] to be much larger than on Earth.

It seems to us possible, therefore, that the photoionization detection method of Clark and Wayne was responding to one or more of these more highly excited O_2^* states, in addition to $O_2(^1\Delta_g)$. Even relatively small concentrations of O_2^* might well make a significant contribution to the ionization current: the photoionization cross sections would be expected to be considerably higher than that of $O_2(^1\Delta_g)$, since the photon energy exceeds the ionization potential of the c state by more than 3 eV, whereas it is only 0.43 and 0.61 eV beyond the threshold for $O_2(^1\Delta_g)$ [19]. For $O_2(^1\Delta_g)$ itself there is an increase in photoionization cross section $\sigma_{1\Delta_g}$ of a factor of about 2 when the photon energy is increased a mere 0.3 eV beyond the argon resonance energy [24]. At λ = 106.7 nm (the stronger line in the argon resonance doublet when transmission of the LiF window is considered), $\sigma_{1\Delta_g} \approx 3 \times 10^{-18}$ cm^2; a photoionization cross section for O_2^* which is larger by a factor of 5 would not be unreasonable. Thus, if 10% of the ionizable gas in the flow system were O_2^*, it could contribute 50% of the observed ionization current. In the following treatment we assume that such a fraction of ionization current is the maximum that can reasonably be attributed to species other than $O_2(^1\Delta_g)$. It is probable that the metastable states of O_2 enhanced in the presence of CO_2 will be only weakly quenched by CO_2 itself; for example, Slanger [22] has suggested that $k_q(CO_2)$ for the $O_2(c\ ^1\Sigma_u^-)$ state will be less than 10^{-17} cm^3 molecule^{-1} s^{-1}. In examining the

results of Clark and Wayne in the light of our hypothesis, we may therefore assume that the decay of the O_2^* species is independent of $[CO_2]$ to a first approximation, even though the initial fraction of O_2^* may be heavily dependent on $[CO_2]$. Furthermore, since a constant pressure of carrier (dried air) was employed, we can represent all losses of O_2^* (collisional quenching, radiative or heterogeneous) by a single lumped pseudo-first-order rate constant.

Representing the fractional contribution of O_2^* to the ionization current I as α and the lumped first-order rate constant for loss of O_2^* as β, we may write the total ion current at time t as the sum of terms due to $O_2(^1\Delta_g)$ and O_2^*:

$$\frac{I_t}{I_{t=0}} = (1 - \alpha) \exp\{-(k_w + k_q(CO_2)[CO_2])t\} + \alpha \exp(-\beta t) \tag{5}$$

The results discussed earlier suggest that $k_q(CO_2)[CO_2]$ should be written as zero; Clark and Wayne found that $k_w = 0.16 \text{ s}^{-1}$ in their system, so that

$$\frac{I_t}{I_{t=0}} = (1 - \alpha) \exp(-0.16t) + \alpha \exp(-\beta t) \tag{6}$$

This equation can be used to calculate the fraction α needed for a particular value of β. First, β is arbitrarily assigned a value, which for the purposes of illustration is here chosen to be 1.0 s^{-1}. Then α is obtained by a least-squares analysis programme to give the best fit to the kinetic data of Clark and Wayne [1] for the five individual pressures used by these workers. The fit is constrained to pass through the origin, and intervals of 0.5 s were used over the time range employed (0 - 2.5 s) in the photoionization experiments. Although there are obvious departures from linearity in the ln(signal) *versus* time plot, the deviations are compatible with the scatter on the individual experimental points, using CO_2 as the quenching gas. The values of α obtained by this method require that not more than 40% of the photoionization signal results from O_2^*. The results are shown in Fig. 4, in which individual points represent the values calculated using eqn. (6) with $\beta = 1 \text{ s}^{-1}$; the lines are those derived from the photoionization experiments assuming simple quenching of $O_2(^1\Delta_g)$ alone. Although larger values of β allow smaller values of α (*i.e.* less O_2^* present), the dependence of α on β is minimal for $\beta > 1.0 \text{ s}^{-1}$ and the departure of the calculated points from ideal logarithmic behaviour is more serious.

Some speculation concerning the nature of O_2^* is now in order. Of the possible states of molecular oxygen that correlate with $O(^3P)$, the $O_2(c\ ^1\Sigma_u^-)$ state shows the most marked enhancement in the presence of CO_2 [20, 21] and certainly seems a plausible candidate for interference in the photoionization experiments. The excitation energy of $O_2(c\ ^1\Sigma_u^-)$ is approximately 4 eV, so that its ionization potential could be as low as 8.1 eV, some 3.4 eV less than the available photon energy. However, the species could not have been formed directly in the process
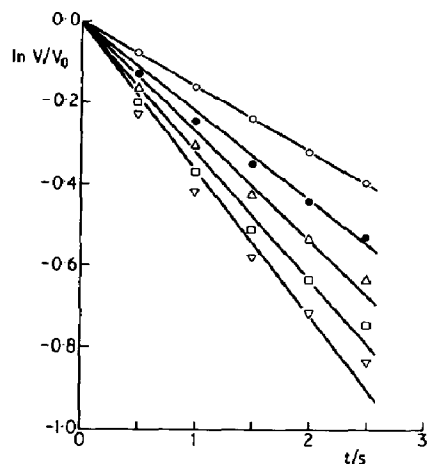
$$O + O + CO_2 \rightarrow O_2(c\ ^1\Sigma_u^-) + CO_2 \tag{7}$$

Fig. 4. Plots of $\ln(V/V_0)$ against contact time t: ———, curve derived from the data of Clark and Wayne [1] for the five $[CO_2]$ values used by these workers; $\circ$, $\bullet$, $\triangle$, $\square$, ∇, values calculated from eqn. (6) with $\beta = 1.0$ s^{-1}; $\circ$, $\alpha = 0.000$, $[CO_2] = 0.0 \times 10^{16}$ molecule cm^{-3}; $\bullet$, $\alpha = 0.145$, $[CO_2] = 1.6 \times 10^{16}$ molecule cm^{-3}; $\triangle$, $\alpha = 0.240$, $[CO_2] = 2.7 \times 10^{16}$ molecule cm^{-3}; $\square$, $\alpha = 0.335$, $[CO_2] = 4.0 \times 10^{16}$ molecule cm^{-3}; ∇, $\alpha = 0.405$, $[CO_2] = 5.0 \times 10^{16}$ molecule cm^{-3}. (See text for definition of α and β.)

since the discharge products were deliberately injected into the CO_2 only after [O] had decayed to a low value. Thus there must be an indirect source of $O_2(c\ ^1\Sigma_u^-)$, regardless of whether or not the state is excited in reaction (7). The possible existence of such an indirect excitation path has already been adduced (see, for example, refs. 23 and 25 for discussions).

The preceding suggested explanation for the results of Clark and Wayne [1] applies also to those of Yaron et al. [6], who used a calorimetric, and thus energy-sensitive, method. We are not, however, in a position to make a detailed analysis of the raw data of the calorimetric experiments.

5. Conclusions

In this paper we have produced further evidence that the efficiency of quenching of $O_2(^1\Delta_g)$ by CO_2 is low. A plausible explanation of previously measured relatively high quenching rates has been presented.

Adoption of a low value of $k_q(CO_2)$ for $O_2(^1\Delta_g)$ imposes fewer constraints on the efficiency of production of $O_2(^1\Delta_g)$ in the atmospheres of Mars and Venus. Nevertheless problems remain, particularly for Venus where it is not clear that the chlorine-containing species, postulated by Noxon [26] to excite $O_2(^1\Delta_g)$, do in fact play a part. We are currently investigating the possible excitation mechanisms.

Acknowledgments

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