

Short Communication

Revised quenching rate constants for metastable oxygen molecules $O_2(a^1\Delta_g)$

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Metastable $O_2(a^1\Delta_g)$ molecules are important constituents of the earth's atmosphere between 30 and 90 km altitude, where they are produced by the photolysis of ozone. During the daytime the concentration reaches a maximum of more than 3×10^{10} molecules cm^{-3} at 50 km [1]. Metastable oxygen molecules thus constitute a substantial atmospheric energy reservoir which has to be taken into account in models of the higher atmosphere. For this reason, precise rate constants have to be known for the quenching of $O_2(a^1\Delta_g)$ by atmospheric gases, particularly by ground state molecular oxygen which is several orders of magnitude more efficient than molecular nitrogen. Most of the published rate constants for oxygen as a quencher fall into the range $(2 - 2.4) \times 10^{-18}$ cm^3 molecule $^{-1}$ s $^{-1}$ [2 - 6]*. However, measurements in this laboratory which were published in 1971 [8] yielded a significantly lower value of $(1.7 \pm 0.1) \times 10^{-18}$ cm^3 molecule $^{-1}$ s $^{-1}$. The rate constant was deduced from first order decay measurements of $O_2(a^1\Delta_g)$ in a static reactor of volume 220 m 3 at total pressures below 500 mTorr. The decay of the metastables was monitored by means of the infrared atmospheric band $O_2(a^1\Delta_g \rightarrow b^3\Sigma_g^-)$ at 1.27 μ m. However, very high $O_2(a^1\Delta_g)$ concentrations had to be used to cope with the rather low sensitivity of the PbS detector available to us at that time. The direct measurements of the infrared atmospheric band were supplemented by decay measurements of the atmospheric band $O_2(c^1\Sigma_g^+ \rightarrow b^3\Sigma_g^-)$ at 7620 Å, for which a red-sensitive photomultiplier could be used. It was shown that this emission decayed with exactly twice the first order rate constant of $O_2(a^1\Delta_g)$ decay under the experimental conditions, owing to the energy pooling process $2O_2(a^1\Delta_g) \rightarrow O_2(c^1\Sigma_g^+) + O_2(b^3\Sigma_g^-)$ which establishes a dynamic equilibrium between both

* After completion of this work a recent publication by Borrell *et al.* [7] has come to our knowledge. These authors give a rate constant of $(1.57 \pm 0.05) \times 10^{-18}$ for the quenching of $O_2(a^1\Delta_g)$ by oxygen, in excellent agreement with our present result.

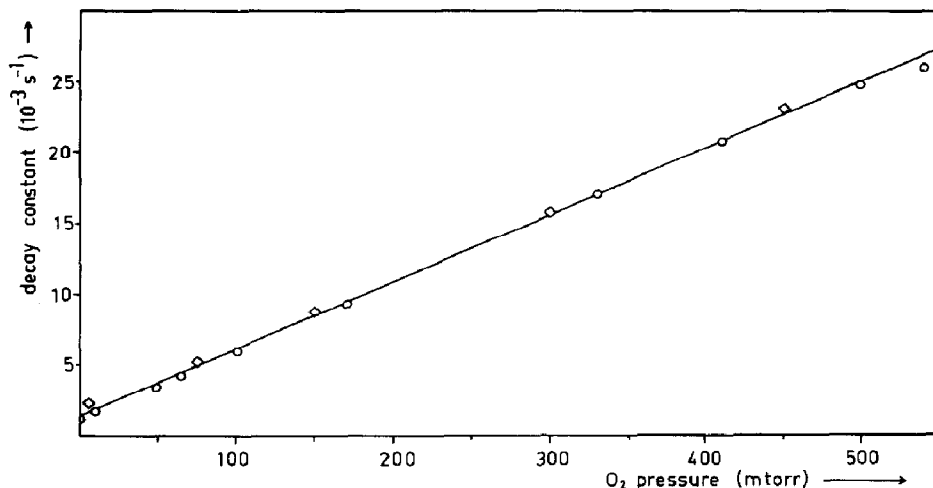


Fig. 1. Decay constants for $O_2(^1\Delta_g)$ as a function of oxygen pressure: \square , measurements in the presence of 0.5 mTorr NO_2 .

metastable molecules. Both methods yielded similar results within experimental accuracy. Consideration of possible systematic errors inherent in this technique, *e.g.* inclusion of second order reactions of $O_2(^1\Delta_g)$ at the high $O_2(^1\Delta_g)$ concentrations used [9], lead us to conclude that the rate constant of $(1.7 \pm 0.1) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was more probably an upper limit and could thus not be reconciled with the higher rate constants reported in the literature.

Still less satisfactory was the situation with regard to the quenching of $O_2(^1\Delta_g)$ by CO_2 for which our older measurements yielded an upper limit of $8 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8], to be compared with values of $(4 \pm 0.7) \times 10^{-18}$ reported by Clark and Wayne [5], less than 1.5×10^{-20} by Findlay and Snelling [3], and $(2.56 \pm 0.12) \times 10^{-18}$ from a recent publication of Yaron *et al.* [10]; all these results are derived from flow tube work. This rate constant is of minor importance in the earth's atmosphere, because of the low concentration of 320 ppm CO_2 in clean air, but it can be of considerable consequence for modelling of the atmosphere of Mars where the infrared atmospheric band has been observed [11], and where CO_2 is the predominant collision partner.

To clarify this controversial situation, we have repeated some of our rate constant measurements in the 220 m³ reactor with improved technical equipment. A germanium detector was substituted for the PbS detector used previously to measure the infrared atmospheric band. This increased the sensitivity by at least three orders of magnitude and allowed the infrared atmospheric band to be isolated with a monochromator instead of an interference filter. $O_2(^1\Delta_g)$ was generated in a microwave discharge using oxygen saturated with mercury vapour. The outflow of the discharge was passed into the 220 m³ reactor through a plug of silver wool to remove traces of oxygen atoms. At low pressure the metastable oxygen molecules decayed essentially by wall deactivation as soon as the discharge was turned

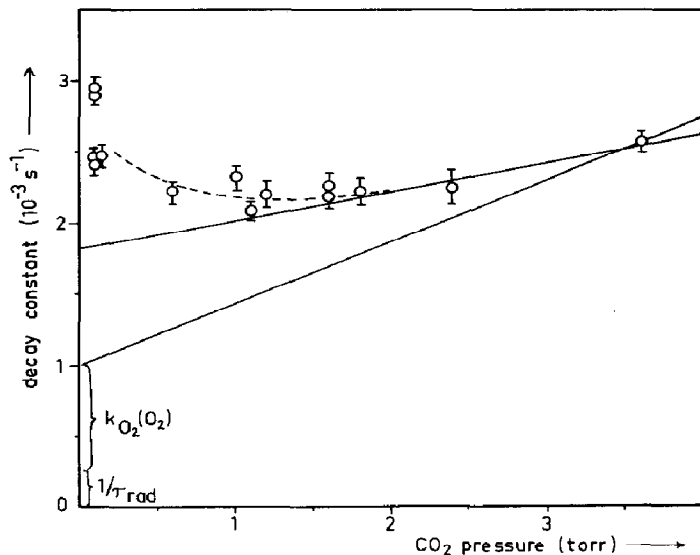


Fig. 2. Decay constants for $O_2(^1\Delta_g)$ as a function of CO_2 pressure at a constant oxygen pressure of 15 mTorr. The minimum intercept is given by $(1/\tau)_{\min} = (k_{O_2} [O_2] + 1/\tau_{\text{rad}})$, where τ_{rad} is the radiative lifetime of $O_2(^1\Delta_g)$ of 3900 s [13].

off. The time constant for wall loss was typically $3 \times 10^{-3} \text{ s}^{-1}$, corresponding to a wall coefficient of $\gamma = 4.3 \times 10^{-5}$. Quenching rate constants could be derived from plots of $1/\tau$ versus the pressure of an added gas at constant oxygen pressure. Figure 1 summarizes the data for molecular oxygen as the quencher. It can be seen that 0.5 mTorr NO_2 (to remove oxygen atoms, if present) had no systematic effect. The rate constant derived from the slope of the straight line is $k_{O_2} = (1.47 \pm 0.05) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in fair agreement with our earlier result [8]. The error limits given correspond to three standard deviations. This is also in good agreement with our rate constant of $(3.4 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for dry synthetic air [12].

Figure 2 represents some of our measurements with CO_2 as quenching gas. At pressures up to 1 Torr CO_2 the decay constant of $O_2(^1\Delta_g)$ was consistently found to decrease instead of to increase. A similar effect had been observed for N_2 , Ar and He which are also very poor quenchers of $O_2(^1\Delta_g)$. It is attributed to wall effects and to a slowing down of diffusion. Upper and lower limits of $1.3 \times 10^{-20} > k_{CO_2} > 6.0 \times 10^{-21}$ are deduced from the straight lines in Fig. 2. The upper limit is based on the assumption that wall quenching is completely suppressed at high CO_2 pressures, using a minimum intercept of $1/\tau_{\text{rad}} + k_{O_2} [O_2]$. The more probable lower limit is derived from the asymptote to the data points at the highest CO_2 pressures.

The rate constants for CO_2 and for O_2 are listed in Table 1, together with data for some quenchers whose rate constants had been given large error limits in our first publication. The reason for these large error limits was the very efficient quenching of $O_2(^1\Sigma_g^+)$ by these gases which prohibited decay measurements at 7620 Å at higher pressures. We feel that the decay

TABLE 1

Rate constants for quenching of $O_2(^1\Delta_g)$ by various gases

Quencher	Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	
	This work	Previous results from this laboratory [8]
O_2	$(1.47 \pm 0.05) \times 10^{-18}$	$(1.7 \pm 0.1) \times 10^{-18}$
CO_2	$1.3 \times 10^{-20} > k > 6 \times 10^{-21}$	$k \leq 8 \times 10^{-20}$
NH_3	$(4.41 \pm 0.46) \times 10^{-18}$	$(7 \pm 2) \times 10^{-18}$
H_2	$(4.15 \pm 0.39) \times 10^{-18}$	$(3.7 \pm 0.3) \times 10^{-18}$

measurements at $1.27 \mu\text{m}$ of our stopped-flow technique are more direct and are thus more reliable than flow tube measurements with other less specific methods of detection for $O_2(^1\Delta_g)$. The absolute error of our pressure measurements (made with an MKS Baratron) is estimated to be less than $\pm 5\%$. Wall and diffusion effects could increase this systematic error somewhat, but certainly not so much as to bring our k_{O_2} up to $2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, or to increase our k_{CO_2} by two orders of magnitude, to fit some of the literature data.

Acknowledgments

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