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Arnold M. Falick and Bruce H. Mahan

June 1967

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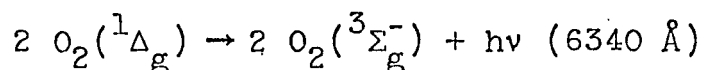
June, 1967

The Collisional-Radiative Reaction of $O_2(^1\Delta_g)$

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The reaction



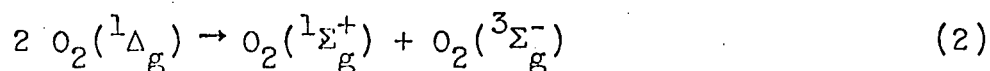
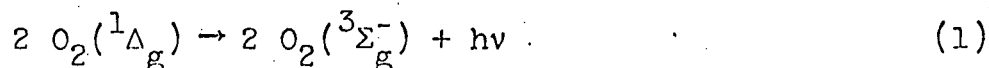
has been studied using EPR detection of $O_2(^1\Delta_g)$. The light intensity depends on the square of the concentration of $O_2(^1\Delta_g)$ and is unaffected by total pressure variations and the addition of inert gas. The rate constant for light emission was found to be $5 \pm 1 \times 10^{-23} \text{ cm}^3/\text{particle-sec}$. This appears to be consistent with the integrated absorption coefficient of ground state oxygen.

* Alfred P. Sloan Foundation Fellow.

It has been known for some time¹⁻³ that metastable electronically excited oxygen molecules are produced when gaseous oxygen is passed through an electrical discharge. Only recently, however, has there been any substantial progress⁴⁻¹⁰ in identifying these molecules, measuring their concentrations, and studying their reactions. The ${}^1\Delta_g$ state of O_2 has been identified by its ionization potential,¹ optical emission spectrum,⁴ and most recently by its EPR absorption spectrum.⁸ It is the excited state in highest concentration in the effluent gas, and may comprise as much as 10% of the total pressure.⁸ The ${}^1\Sigma_g^+$ state of O_2 is also metastable, but is present only to the extent of a few tenths of a percent.

The prevalence of $O_2({}^1\Delta_g)$ can in part be attributed to the fact that the electric dipole transition to the ground state violates the $g \rightarrow u$, $\Delta S = 0$, $\Delta \Lambda = 0, \pm 1$ selection rules. The state can decay by a magnetic dipole transition which is weakly forbidden by the orbital angular momentum selection rule, and as a result $O_2({}^1\Delta_g)$ has a radiative lifetime¹¹ of 45 minutes. The radiative lifetime¹² of $O_2({}^1\Sigma_g^+)$ is approximately 8 sec. This state is also much more susceptible to collisional quenching, and can be eliminated by the addition of water vapor to the discharge.

Although $O_2({}^1\Delta_g)$ reacts readily with unsaturated hydrocarbons and dissociates ozone to oxygen atoms, it is otherwise quite inert chemically. In pure oxygen two of its important homogeneous reactions are



The principal evidence for the first of these processes is the observation⁴ of emission bands at 6340 Å and 7030 Å. The combined energies of two $\text{O}_2(^1\Delta_g)$ molecules can give a 6340 Å photon if all molecules are in their ground vibrational states, or a 7030 Å photon if one of the product molecules is left in its first vibrational level. Support for this interpretation was provided by Bader and Ogryzlo,⁵ who used an isothermal calorimetric detector to show that the intensity of the 6340 Å emission was proportional to the square of the concentration of $\text{O}_2(^1\Delta_g)$. On the other hand, March, Furnival, and Schiff⁷ monitored the concentration of $\text{O}_2(^1\Delta_g)$ by its emission at 12,700 Å, and found that the emitted intensity at 6340 Å was proportional to the first power of the $\text{O}_2(^1\Delta_g)$ concentration. Detection of $\text{O}_2(^1\Delta_g)$ by its emission at 12,700 Å is made difficult by low sensitivity of photomultipliers in this spectral region. While the isothermal calorimetric technique has the required sensitivity, it could be complicated by lack of specificity and by an unknown thermal efficiency. The detection of $\text{O}_2(^1\Delta_g)$ by its EPR spectrum has the advantages of specificity and sensitivity, and provides a method for measuring absolute concentrations. We report here our determination of the order and rate constant of reaction (1) obtained by using the EPR technique.

EXPERIMENTAL

In this work we used a single tank of Matheson "Extra Dry" grade oxygen (99.6% purity), or oxygen prepared by thermal decomposition of potassium permanganate. There were no differences in the results obtained with gas from the two sources. General Dynamics helium (Grade A, 99.995% purity) and argon (99.99% purity), and Matheson nitrogen dioxide (99.5% purity) were also used.

During an experiment, oxygen was delivered from one or both of two 35 l stainless steel tanks to a conventional glass flow system at flow rates ranging from 0.03 to 0.58 cm³/sec at 1 atm. The gas first passed over a small amount of water contained in a trap at -10°C. The water vapor introduced removed O₂(¹Σ_g) from the discharge products and appeared to increase the concentration of O₂(¹Δ_g) by 20 to 30%. The gas then passed a small sidearm which contained mercury at 25°C, and entered a quartz air condenser which was the discharge tube. The discharge was excited inductively by a 200w radio frequency (13.56 MHz) diathermy unit. After the discharge the gas flowed over a film of mercuric oxide, past a titration inlet, through two light traps, and entered a reflectionless light cell of 125 cc volume. The mercuric oxide film removed oxygen atoms from the discharged gas. From the light cell the gas passed through a light trap and then through 55 cm of 15 mm i.d. tubing to the EPR cavity. Pressure measurements were made with a McLeod gauge, and were corrected for the pressure drop caused by the flowing gas.

The window of the light cell was covered by an annular mask and an interference filter ($\lambda_{\text{max}} = 6200 \text{ \AA}$, 400 \AA FWHM). A 2" dia Lucite light pipe 24" long transmitted the radiation to a liquid nitrogen cooled RCA 7265 photomultiplier. The light pipe was used to separate the photomultiplier from the EPR magnet. To eliminate the effects of any residual stray magnetic field on the photomultiplier sensitivity, all light measurements were made with the magnet set at the field corresponding to the $\text{O}_2(^1\Delta_g) M_J = 0 \rightarrow 1$ transition. The sensitivity of the photomultiplier was checked against a constant intensity light source, and daily variations we found to be rarely greater than 4%.

The absolute efficiency of the light detection system was determined by measuring the emission from the nitric oxide-oxygen atom reaction, using the spectral distribution and absolute intensities measured by Fontijn, Meyer, and Schiff.¹³ In these experiments, the oxygen atom concentration entering the light cell was determined by titration with NO_2 . After the titration, the flow of NO_2 was decreased to a small value, and the concentrations of NO and O calculated from the NO_2 flow rate and the initial oxygen atom concentration. The fraction of the total intensity of the 6340 \AA band passed by our interference filter was calculated from the emission spectrum published by Bader and Ogryzlo.⁵

The EPR spectrometer was a conventional X-band reflection type with 100 kHz magnetic field modulation and phase detection. A Varian V-4533 cylindrical cavity operating in the TE_{011} mode

was employed. This cavity was completely filled by a quartz cell of approximately 45 cc volume. The flowing gas passed through this cell to a ballast volume, trap and pump.

The concentration N of absorbing species is related to the integrated intensity I of an EPR absorption line for the transition $i \rightarrow j$ by

$$N = [I g_{\text{eff}} \beta kT Z] / [h \omega_0 |\mu_{ij}|^2 \exp(-E_i/kT)]$$

where g_{eff} is the effective gyromagnetic ratio, β is the Bohr magneton, Z is the molecular partition function, ω_0 is the absorption frequency, μ_{ij} is the transition matrix element, and the other symbols have their usual meaning. To measure the concentration of $O_2(^1\Delta_g)$, the $J = 2, M_J = 0 \rightarrow 1$ transition was used, for which $|\mu_{ij}|^2 = (4/3)\beta^2 f^+$. Here f^+ is a filling factor which depends on the microwave magnetic field in the cavity and the sample geometry. In order to calibrate the spectrometer sensitivity, the $K = 3, J = 4, M = 3 \rightarrow 4$ transition of $O_2(^3\Sigma_g^-)$ was used. The necessary parameters for this transition have been given by Tinkham and Strandberg.¹⁴ To calibrate the spectrometer for detection of atomic oxygen, the $K = 1, J = 1, M = -1 \rightarrow 0$ transition of molecular oxygen was used. Since the filling factors for the calibration and detection signals were the same, it was unnecessary to evaluate them. In the majority of the determinations of the $O_2(^1\Delta_g)$ concentration, only the peak height was measured. This was related to the integrated intensity by an experimentally determined pressure dependent calibration factor.

In a typical experiment, steady flow conditions were established, the discharge started, and the photomultiplier output recorded as the EPR spectrometer swept back and forth across the $M_J = 0 \rightarrow 1$ transition of $O_2(^1\Delta_g)$. The magnetic field sweep was so small it did not affect the photomultiplier sensitivity. After 5 to 10 sweeps had been made, the discharge power level was changed, and the procedure repeated.

RESULTS AND DISCUSSION

A large number of experiments were performed in order to determine the order of reaction (1). Figure 1 shows some typical data which demonstrate that the light intensity at 6340 Å is proportional to the square of the concentration of $O_2(^1\Delta_g)$. All other experiments made with total pressures between 0.1 and 1.0 Torr and various mixtures of oxygen with up to 75% helium or argon were consistent with a second order rate law for light emission.

The rate constants for reaction (1) measured in this work are given in Table 1 and are shown graphically in Fig. 2. These are calculated directly from the measured light and EPR signals, and are not corrected for the pressure drop and loss of $O_2(^1\Delta_g)$ between the light cell and the EPR cavity. The rate constant in pure oxygen appears to be independent of the total pressure in the range from 0.1 to 0.7 Torr. Some experiments were performed at higher pressures, but these showed increased scatter and rate constants that were 10 to 30% smaller than those obtained at the lower pressures. We found

that we could attribute these effects to small pressure changes due to the more rapid depletion of the oxygen in the reservoir, and feel the results at the higher pressures were not reliable.

Table II and Fig. (3) show that the apparent rate constant is unaffected when as much as 80% of the oxygen is replaced by argon. Similar results were obtained with oxygen-helium mixtures. This lack of effect of total pressure variation and inert gas addition on the second order rate constant for reaction (1) is consistent with the results of other workers.^{5,6,10}

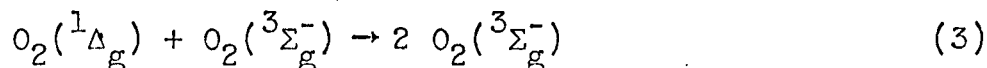
The experimental results are complicated by the fact that the light intensity and the concentration of $O_2(^1\Delta_g)$ were measured in cells separated by 55 cm of 1.5 cm i.d. tubing. Three factors may cause the concentration in the two cells to differ: homogeneous reactions such as (1) and (2), heterogeneous deactivation of $O_2(^1\Delta_g)$, and the pressure drop between the points of observation.

Because of the very long radiative lifetime of $O_2(^1\Delta_g)$, losses by radiation of isolated molecules are completely negligible. Similarly, losses through the collisional-radiative reaction (1) are negligible if the rate constants found in this work and by others⁶ are correct to within an order of magnitude.

Young and Black¹⁵ have reported a rate constant of approximately 3×10^{-14} cc/molecule-sec for reaction (2), which if correct would make this a source of substantial loss of $O_2(^1\Delta_g)$. Winer and Bayes⁹ and Arnold¹⁰ have found this value of k_2 to be several orders of magnitude too large to be consistent with

their measurements of the decay rate of $O_2(^1\Delta_g)$. We have reached the same conclusion, for the value of k_2 given by Young and Black requires that the concentrations of $O_2(^1\Delta_g)$ in our EPR cavity should have been 100 times smaller than we observed. Arnold¹⁰ found a value of 2.2×10^{-18} for k_2 . Since the concentrations of $O_2(^1\Delta_g)$ in our experiments were of the order of 10^{14} molecules/cc, and the elapsed time between cells was approximately 1 second, losses due to reaction (2) were negligible.

The reaction



can also deplete the $O_2(^1\Delta_g)$ concentration. Estimates of the upper limit for k_3 have been made^{9,10} which allow us to calculate that the loss of $O_2(^1\Delta_g)$ due to this process does not exceed 1%. In addition, if reaction (3) were important, we would expect the apparent rate constant to vary when oxygen was replaced with argon or helium. This was not observed, so we feel that collisional quenching of $O_2(^1\Delta_g)$ was not important.

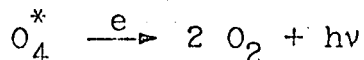
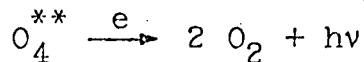
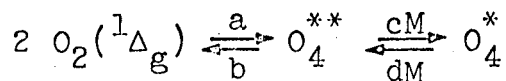
Two values for the number of collisions necessary to deactivate $O_2(^1\Delta_g)$ at a Pyrex surface have been made.^{9,10} If the value of 10^5 collisions found by Arnold¹⁰ applied to our system, we would expect the concentration of $O_2(^1\Delta_g)$ to decrease between the two cells by 20% for experiments at 0.2 Torr, and 10% for experiments at 0.6 Torr. This suggests that the uncorrected rate constants measured near the lower pressure should be 20% greater than those determined at 0.6 Torr. No such

trend is evident in the data of Fig. (2). If the average number of wall collisions necessary for deactivation were 2×10^5 , the increase in the apparent rate constant with decreasing pressure would be within the scatter of our experimental results. We conclude that heterogeneous loss of $O_2(^1\Delta_g)$ may cause our rate constant to be too large, but only by an amount which is of the order of the experimental scatter.

An estimate made using the Poiseuille equation indicated that the pressure drop between the light and EPR cells was approximately 15%. This was checked experimentally in the following manner. Since the widths of the EPR absorption lines were proportional to pressure, the pressure drop between the McLeod gauge and the EPR cavity could be determined by measuring the line width as a function of pressure in both static and flowing gas. The McLeod gauge was located between the light and EPR cells, and the pressure drop between the two cells could be reliably calculated from the known conductance of the tubing and the measured pressure drop between the gauge and EPR cell. The result was that the pressure in the light cell was $15 \pm 2\%$ higher than the pressure in the EPR cavity over the pressure range employed in the experiments. If we assume the fractional concentration of $O_2(^1\Delta_g)$ was the same in both cells, the pressure drop makes the apparent rate constant too large by 33%. Reduction of the average of the apparent rate constants by this factor gives $k_1 = 5.0 \pm 1 \times 10^{-23}$ cc/molecule-sec.

The value of k_1 found in this research is approximately a factor of five smaller than the result reported by Arnold, Browne, and Ogryzlo.⁶ Considering the difference in techniques used to measure the $O_2(^1\Delta_g)$ concentration, the order of magnitude agreement between the two results provides some satisfaction. The reason for the discrepancy between the values of k_1 is not clear. The major difficulty in the present work arises from the necessity of making the light emission and EPR absorption measurements at different points in the flow system. The errors associated with this should, however, tend to make our rate constant too large. The most obvious source of error in the calorimetric determination of $O_2(^1\Delta_g)$ is the possibility that the deactivated molecules are left with vibrational excitation, and thus that not all the electronic excitation energy is delivered to the wire. If this were to occur, a high value of k_1 would result.

The finding that k_1 is independent of total pressure and the nature of added inert gas suggests that the O_4 intermediate which radiates is either not bound, or, if bound, is in equilibrium with free $O_2(^1\Delta_g)$. The very small temperature coefficient of the reaction¹⁰ and the coincidence⁴ between the energy of the 6340 Å radiation and twice the energy of $O_2(^1\Delta_g)$ suggest that the intermediate has little if any binding energy in excess of the van der Waals attraction. Thus we have the reaction scheme



where O_4^{**} and O_4^* are two $\text{O}_2(^1\Delta_g)$ molecules unbound and bound respectively by the van der Waals potential. We have assumed that the emission probability is the same for the two intermediates.

An equilibrium constant K for the formation of bound and unbound dimeric molecules which are separated by distances less than a few times the Lennard-Jones parameter σ can be estimated by the method of Bunker and Davidson.¹⁶ They give the approximate expression

$$K = -2B + \frac{4\pi}{3} \sqrt{2} \sigma^3$$

where B is the second virial coefficient. Evaluation of this expression using the parameters for ground state molecular oxygen gives $K = 3 \times 10^{-22}$ cc/molecule. If we assume that the intensities of light emitted at 6340 Å and 7030 Å are equal, then we can calculate the total rate constant for step e as

$$e = \frac{2k_1}{K} = 0.33 \text{ sec}^{-1}$$

The corresponding radiative lifetime for the collision complex is 3 seconds. It is interesting to note that one can also calculate this radiative lifetime from the f value for the corresponding absorption in compressed oxygen. Robinson¹⁷ calculated

that $f = 3.5 \times 10^{-9}$ from the data of Salow and Steiner,¹⁸ which corresponds to a radiative lifetime of 1.5 seconds. The agreement between the values estimated from the rate constant and from the integrated absorption coefficient is encouraging, but of course depends on the somewhat arbitrary evaluation of the equilibrium constant.

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Table I. Rate constant Measurements in pure O₂.

Run No.	Pressure (Torr)	$k_1 \times 10^{23}$	O ₂ Source
112H	0.78	6.95	tank
115B	0.19	7.75	tank
116A	0.19	5.24	KMnO ₄
116B	0.21	6.84	KMnO ₄
116C	0.24	7.40	KMnO ₄
116D	0.29	7.55	KMnO ₄
116E	0.34	7.07	KMnO ₄
116F	0.38	7.40	KMnO ₄
116G	0.45	7.11	KMnO ₄
117D	0.65	8.04	tank
118B	0.54	9.43	tank
118C	0.74	7.48	tank
119A	0.10	6.67	KMnO ₄
119B	0.14	7.15	KMnO ₄
119C	0.16	7.07	KMnO ₄
119D	0.20	6.95	KMnO ₄
119F	0.39	8.11	KMnO ₄
119H	0.62	7.95	KMnO ₄
119I	0.75	6.35	KMnO ₄
123A	0.51	7.67	tank
124A	0.21	7.40	tank

Table II. Rate constant measurements in
 O_2 -Ar mixtures.

Run No.	Pressure (Torr)	$k_1 \times 10^{23}$	% O_2	O_2 Source
122A	0.50	8.04	68	KMnO ₄
122B	0.52	7.47	58	KMnO ₄
122C	0.50	7.51	45	KMnO ₄
122D	0.50	7.31	30	KMnO ₄
122E	0.50	7.35	22	KMnO ₄
123B	0.51	7.47	81	tank
123C	0.51	7.63	61	tank
123D	0.51	7.51	41	tank
124C	0.22	7.11	80	tank
124D	0.22	7.47	59	tank
124E	0.22	7.75	39	tank

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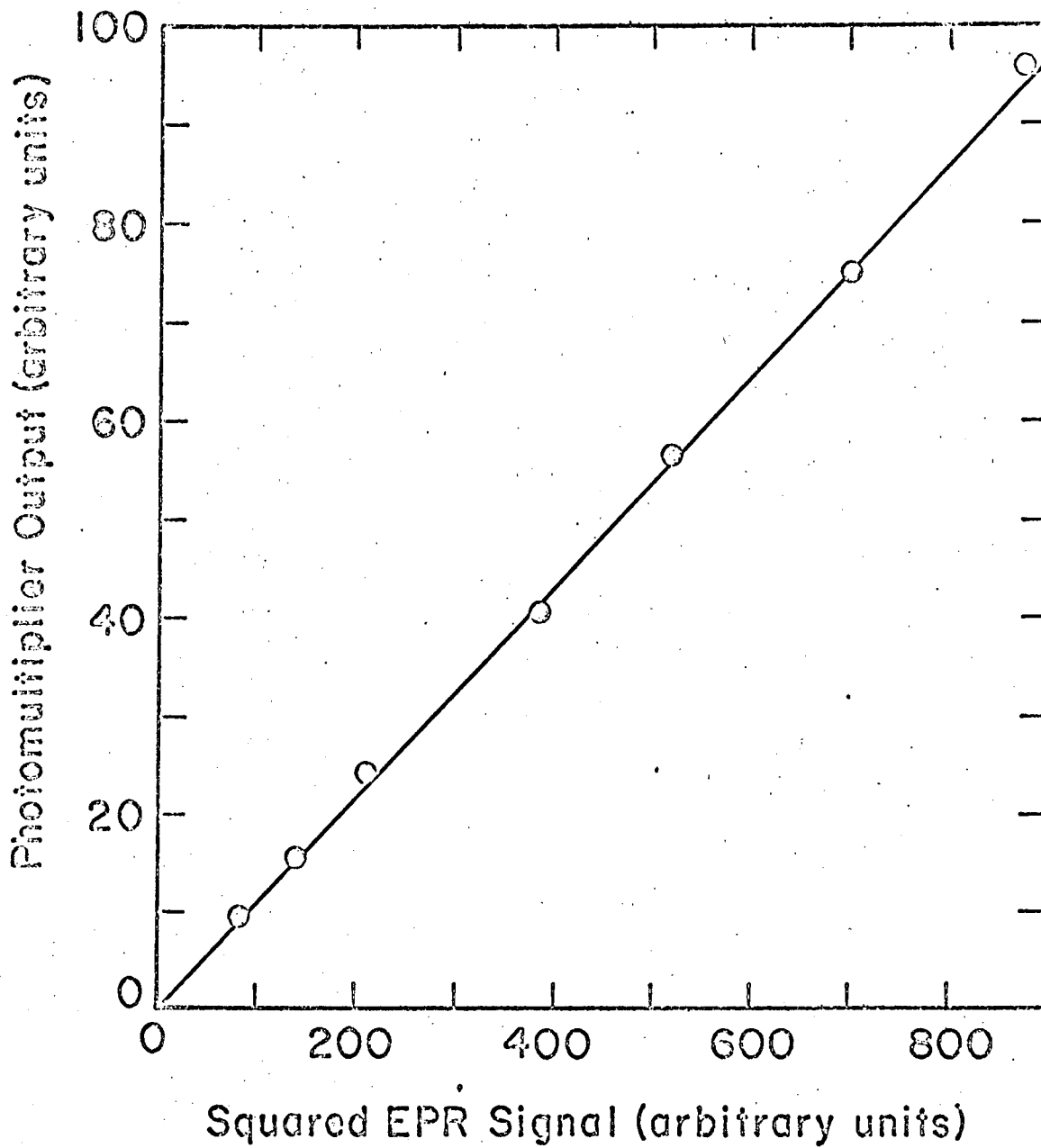


Figure 1. The dependence of the light intensity at 6340 Å as a function of the square of the $O_2(^1\Delta_g)$ concentration as measured by EPR.

Fig. 1

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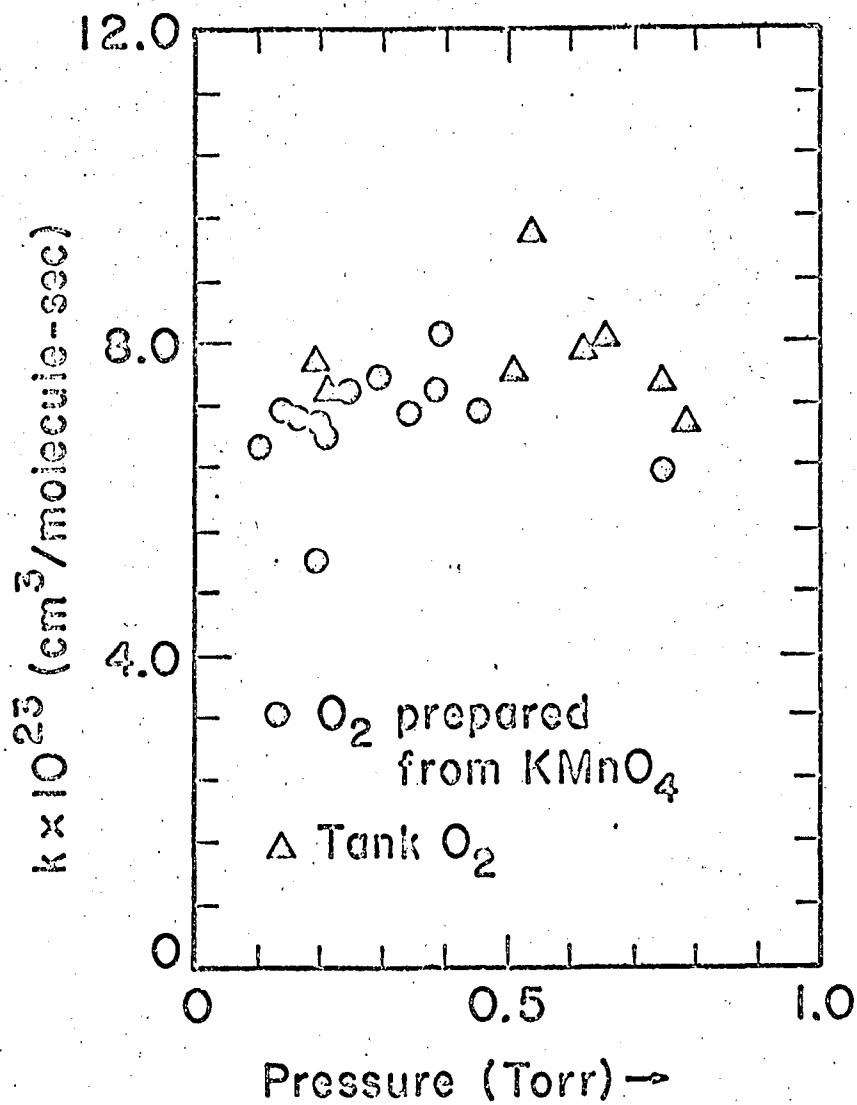


Figure 2. The dependence of the apparent rate constant for light emission on the total pressure of oxygen.

Fig 2

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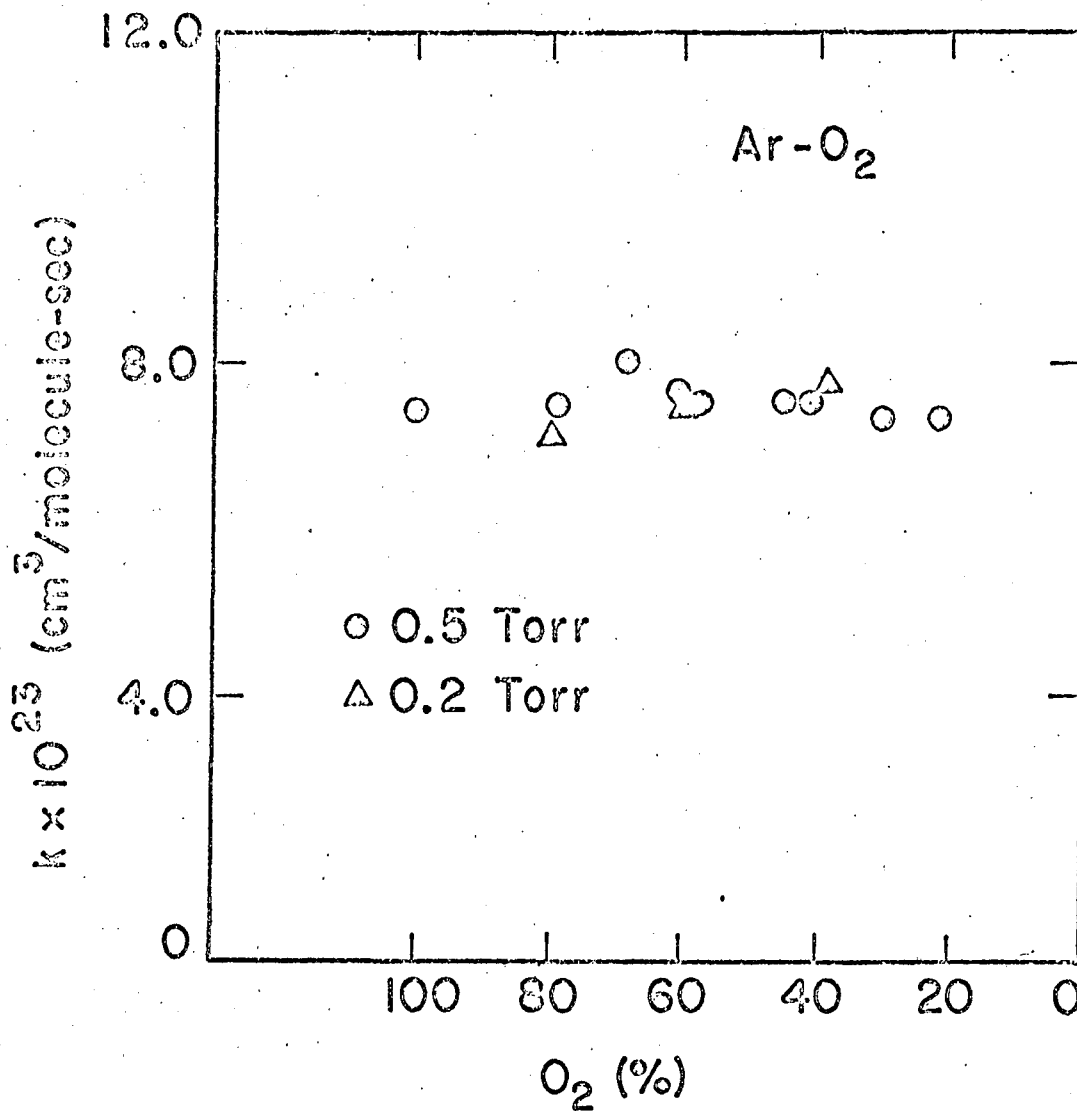


Figure 3. The dependence of the apparent rate constant for light emission on the mole percent oxygen in Ar-O₂ mixtures.

Fig 3

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