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ABSTRACT

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The vacuum ultraviolet photolysis of CO_2 has been investigated in the pressure region 150-760 mm Hg. At 1236 Å and around 1600 Å the quantum yields for carbon monoxide, oxygen and ozone are consistent with the direct photodissociation mechanism, while an increase in the quantum yields at 1470 Å indicates that at this wavelength, excited CO_2 molecules are also involved in the critical step. From the low rates of ozone formation observed in all cases, it is concluded that the photodissociation of CO_2 produces oxygen atoms in the metastable ^1D state. The quantitative evaluation of the data obtained with radiation at 1236 Å and around 1600 Å supports the following reaction mechanism:

$$CO_2 \xrightarrow{h\nu} CO + O \qquad k_1$$

$$O + O + M \rightarrow O_2 + M \qquad k_2$$

$$O + O_2 + M + O_3 + M \qquad k_3$$

$$O + O_3 \rightarrow 2\ O_2 \qquad k_4$$

and yields also $k_4/k_3(M) = 41$ and $k_3/\sqrt{k_2} = 4.35 \times 10^{-19}$. With the assumption that $k_2(^1D) = k_2(^3P) = 4.2 \times 10^{-33}$ $cc^2/molec^2$ sec, the absolute rate constants are estimated to be $k_3(^1D) = 2.8 \times 10^{-35}$ $cc^2/molec^2$ sec and $k_4(^1D) = 3 \times 10^{-14}$ cc/molec sec. Author

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REACTIONS OF ^1D OXYGEN ATOMS IN THE PHOTOLYSIS OF CARBON DIOXIDE

P. Warneck

1. INTRODUCTION

Photochemical processes occurring in planetary atmospheres under the influence of solar radiation depend greatly upon the relative abundance of atmospheric constituents. While oxygen is the major dissociable component in the Earth's atmosphere, this role is assumed by carbon dioxide in the atmospheres of Mars and Venus. The pertinent photochemical reactions for this case have been reviewed in a previous report,[1] as well as a number of problems discussed arising from inconsistencies concerning the interpretation of several experimental observations. Thus, the photolysis of the individual substances CO_2, CO, and O_2 were found to require additional experimental study.

The present report is concerned with the ultraviolet photolysis of carbon dioxide which has been reinvestigated at pressures between 150 and 760 mm Hg, utilizing krypton, xenon and hydrogen light sources. It could be confirmed that photodissociation

$$CO_2 \xrightarrow{h\nu} CO + O \qquad (1)$$

is the major primary process in the 1200-1700 Å wavelength region, but it has also been found that the oxygen atoms produced in this process are in the excited metastable ^1D state. Accordingly, the photolysis of CO_2 may provide a convenient framework for a study of the role of ^1D oxygen atoms in the reactions

$$2O + M \rightarrow O_2 + M \quad (2)$$

$$O + O_2(+M) \rightarrow O_3(+M) \quad (3)$$

$$O + O_3 \rightarrow 2O_2 \quad (4)$$

which in combination with (1) constitute the main CO_2 photodecomposition mechanism. There is little doubt that oxygen atoms are indeed produced in the primary process of carbon dioxide photodecomposition, since the CO_2 absorption spectrum in the 1200-1700 Å wavelength region exhibits two dissociation continua which are shown in Figure 1. Both continua have been associated[2] with a process of type (1). The participation of ^1D oxygen atoms in the CO_2 photodecomposition mechanism was first suggested by Mahan[3] who photolyzed CO_2 in the presence of small amounts of NO but failed to observe the chemiluminescence characteristic for ^3P oxygen atoms. In the present study of carbon dioxide photolysis, further evidence was derived from the rate of ozone formation, which was measured in addition to CO and O_2 quantum yields. Also, the ratio of the rate constants associated with Reactions (3) and (4) was determined and compared with the known ratio for ^3P oxygen atoms. Once this ratio is known, the measured rates of ozone formation will yield information concerning the absolute rate constants provided the rate of Reaction (2) is not too different from that for oxygen atoms in the ^3P ground state.

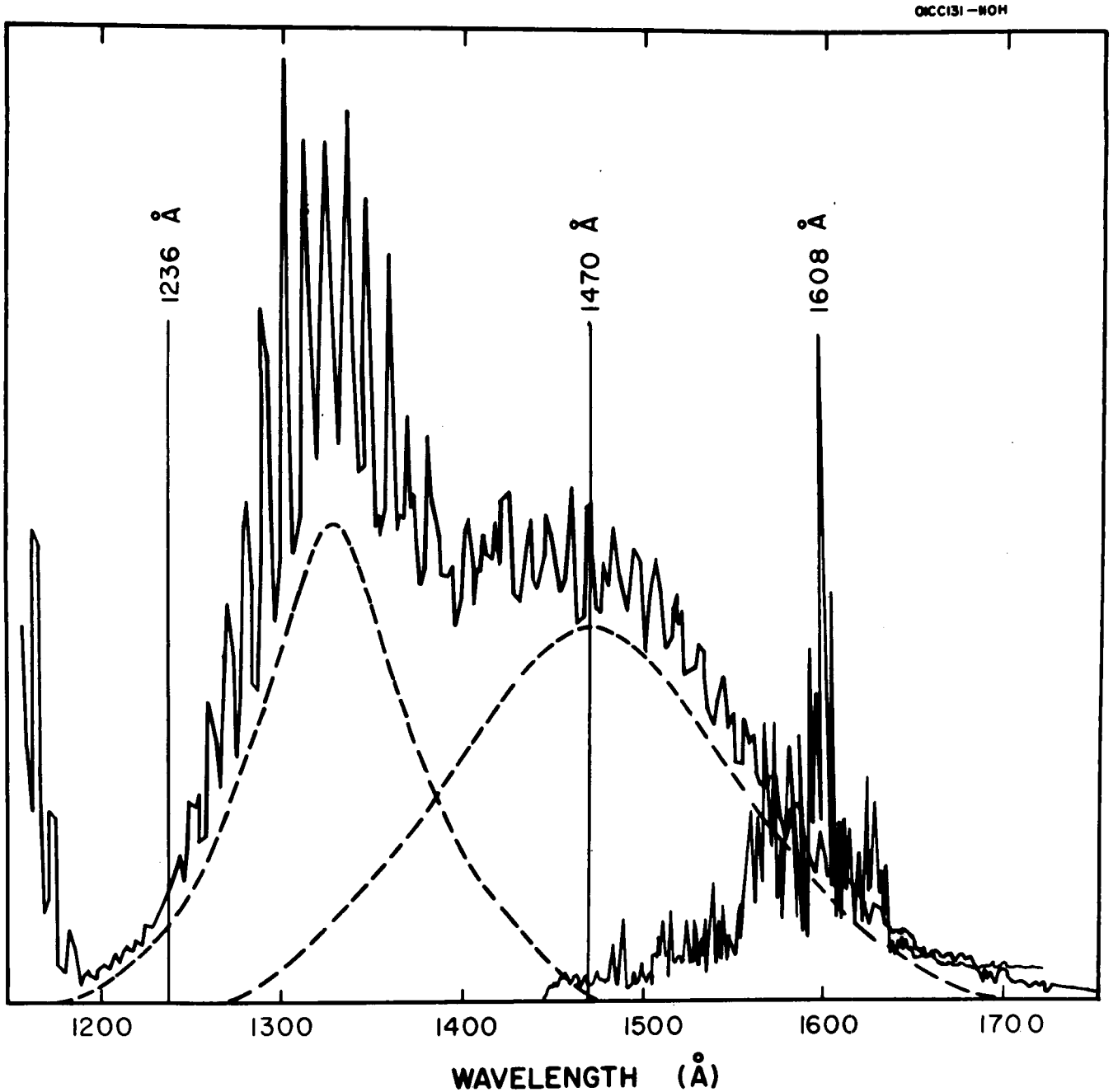

Figure 1. Vacuum ultraviolet absorption spectrum and continua (dashed) of carbon dioxide, superimposed by the emission lines: Kr 1236Å, Xe 1470Å, and the many lined hydrogen spectrum around 1600Å.

2. EXPERIMENTAL

2.1 Light Source and Actinometry

Experiments were performed with a cylindrical flow reactor consisting of two concentric Pyrex tubings, of which the outer one served as the gas inlet. The reactor was attached to a microwave-powered discharge lamp of similar design as a previously described hydrogen light source.[4] Separate discharge tubes, made of Pyrex or quartz, were employed for krypton, xenon and hydrogen in order to prevent contamination of the desired spectrum with foreign lines. The reactor and light source were separated by a window of suitable material. Lithium fluoride windows were employed in conjunction with krypton discharges, while for the other gases barium fluoride plates were inserted. Since BaF_2 does not appreciably transmit at wavelengths below 1400 Å, it provides a suitable cutoff filter eliminating, among other lines, Lyman-alpha at 1216 Å and the xenon line at 1295 Å. Accordingly, the vacuum ultra-violet emission spectra associated with the three light sources consisted mainly of the lines (a) Kr 1236 Å, (b) Xe 1470 Å, and (c) of the hydrogen many-lined spectrum centered near 1600 Å. The position of these emission lines relative to the CO_2 absorption continua is shown in Figure 1.

Integrated light source intensities ranged from 2×10^{15} to 2×10^{16} quanta/sec for krypton and xenon discharges, and up to 1×10^{16} quanta/sec for the hydrogen lamp. They were determined actinometrically from the rate of ozone formation in a flow of oxygen.[3,4] A quantum yield of

two[5,6] was assumed in accordance with the view that at atmospheric pressure almost all the oxygen atoms resulting from O_2 dissociation are converted into ozone. Only the 1165 Å krypton line is probably ineffective in dissociating O_2, since it falls into a region between bands where the O_2 absorption strength is low ($k \approx 0.5\ cm^{-1}$).[2] However, since the CO quantum yields obtained in CO_2 photolyses with the krypton lamp were close to unity, it is concluded that the 1165 Å line cannot contribute more than 10% of the intensity contained in the 1236 Å krypton line.

2.2 Quantum Yields

Ozone concentrations were determined from the absorption of the 2537 Å mercury line which lies near the maximum of ozone absorption in this spectral region. A measured flow of CO_2 was passed through the reactor, where ozone was formed as a photolytic product, and subsequently through a 40.5 cm long absorption tube fitted with quartz windows at both ends. A Pen-Ray mercury lamp and a rubidium telluride (solar blind) photomultiplier in conjunction with a high voltage power supply and a microammeter served to measure the extent of light absorption. Owing to the particular spectral characteristics of the mercury lamp and the photomultiplier combined, no additional filters were required for an adequate isolation of the 2537 Å mercury line. The ozone quantum yield is calculated from $Q(O_3) = [O_3]v/I$, where $[O_3]$ is the steady-state ozone concentration in the absorption tube, v is the bulk flow rate in cm^3/sec, and I in quanta/sec is the effective integrated intensity of the light source.

The amounts of carbon monoxide and oxygen produced during the photodecomposition of CO_2 were investigated in a closed system in which the gas was circulated by means of a magnetically-driven rotating stirrer. Prior to the introduction of CO_2 in the desired quantity, the system was prefilled with approximately 3 mm Hg of argon which served as a reference in the subsequent mass spectrometric analysis. Each sample drawn after completion of a photolysis run was subjected to liquid nitrogen temperature while being admitted to the mass spectrometer in order to minimize the contribution to the mass 28 peak originating from carbon dioxide.

With the exception of carbon dioxide, research-grade gases were employed without further purification. CO_2 was found to contain about 0.05% oxygen as well as 0.25% nitrogen and/or carbon monoxide. These gases were removed by subjecting a lecture bottle of CO_2 to liquid nitrogen temperature and pumping off the volatile components. Repeated application of this procedure was required before the desired degree of purification was achieved (less than 20 p.p.m. contamination as determined mass spectrometrically).

3. RESULTS

3.1 CO Quantum Yields

The data obtained by mass spectrometric analysis of samples drawn from the closed system are summarized in Figure 2. CO quantum yields of unity were found throughout the investigated pressure region when CO_2 was irradiated with light from krypton or hydrogen discharges, but the xenon light source resulted in an increase of the CO quantum yield from unity at lower pressures to an average of Q(CO)=1.17 at 740 mm Hg. Similarly, a comparatively higher oxygen quantum yield was observed in the latter case. This indicates a difference in the photolytic mechanism which must be active at the wavelengths of the lines emitted from a xenon discharge on one hand, and a krypton or hydrogen discharge on the other. The results obtained with the krypton lamp can be combined with the data reported by Mahan[3] to demonstrate that at 1236 Å the CO quantum yield is insensitive to pressure variations in the region 10-760 mm Hg; thus giving additional support to the conclusion that carbon monoxide is formed directly in the primary process. The observed oxygen quantum yields ($Q(O_2)$ = 0.3 for krypton and hydrogen, $Q(O_2)$ = 0.4 for xenon) were higher than those reported by Mahan, but still below the limit of $Q(O_2)$ = 0.5 to be expected if all oxygen atoms produced in the primary process recombined to yield molecular oxygen. However, the missing oxygen has been shown to exists in the form of ozone.

The time dependence of carbon monoxide and oxygen formation is plotted in Figure 3 for experiments in which a xenon discharge and pressures close to an atmosphere were employed. The observed linearity

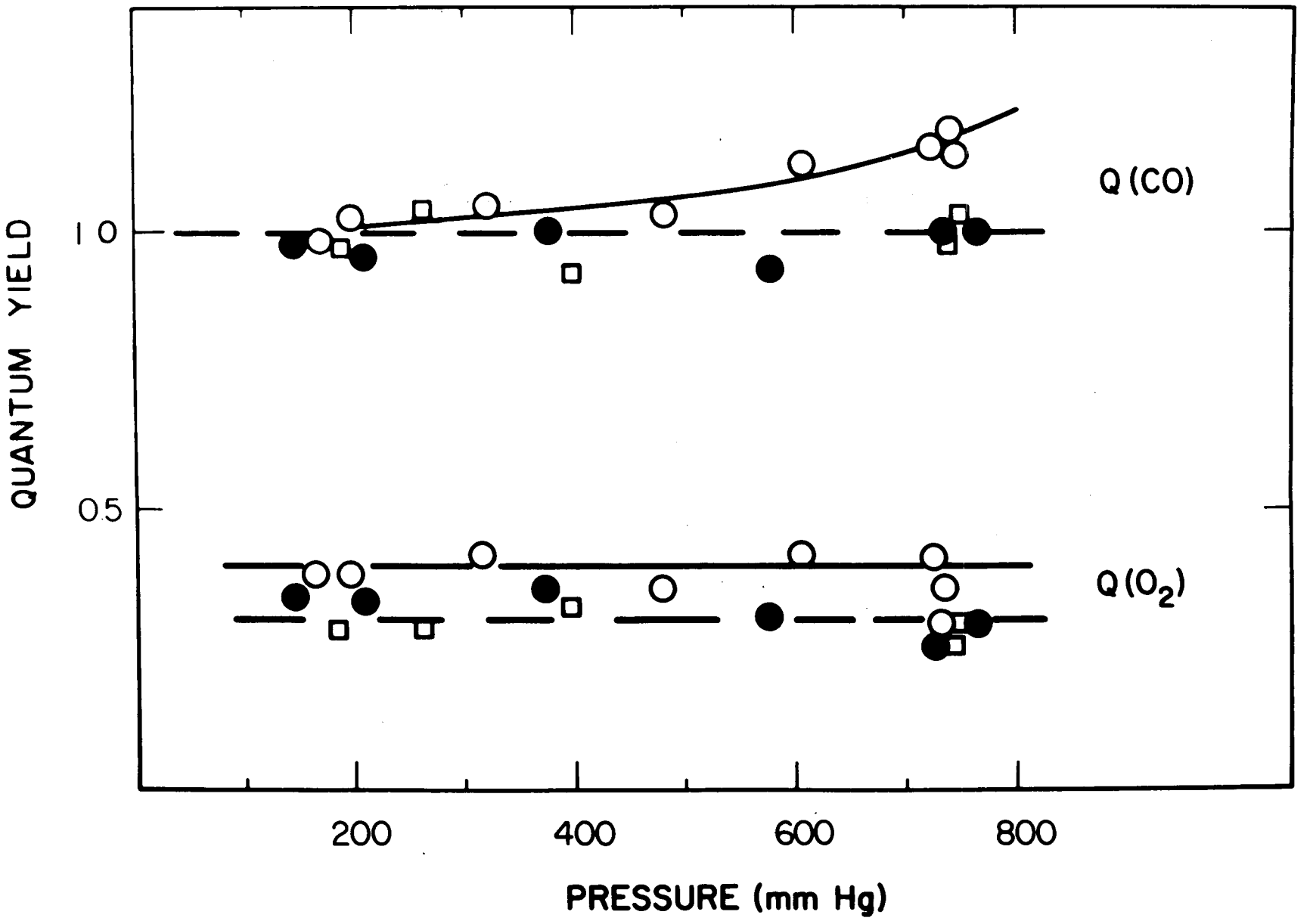

Figure 2. Quantum yields of carbon monoxide and oxygen; 10-min irradiation with intensities of about 10×10^{15} quanta/sec. Filled circles: at 1236Å; open circles: at 1470Å; squares: at about 1600Å.

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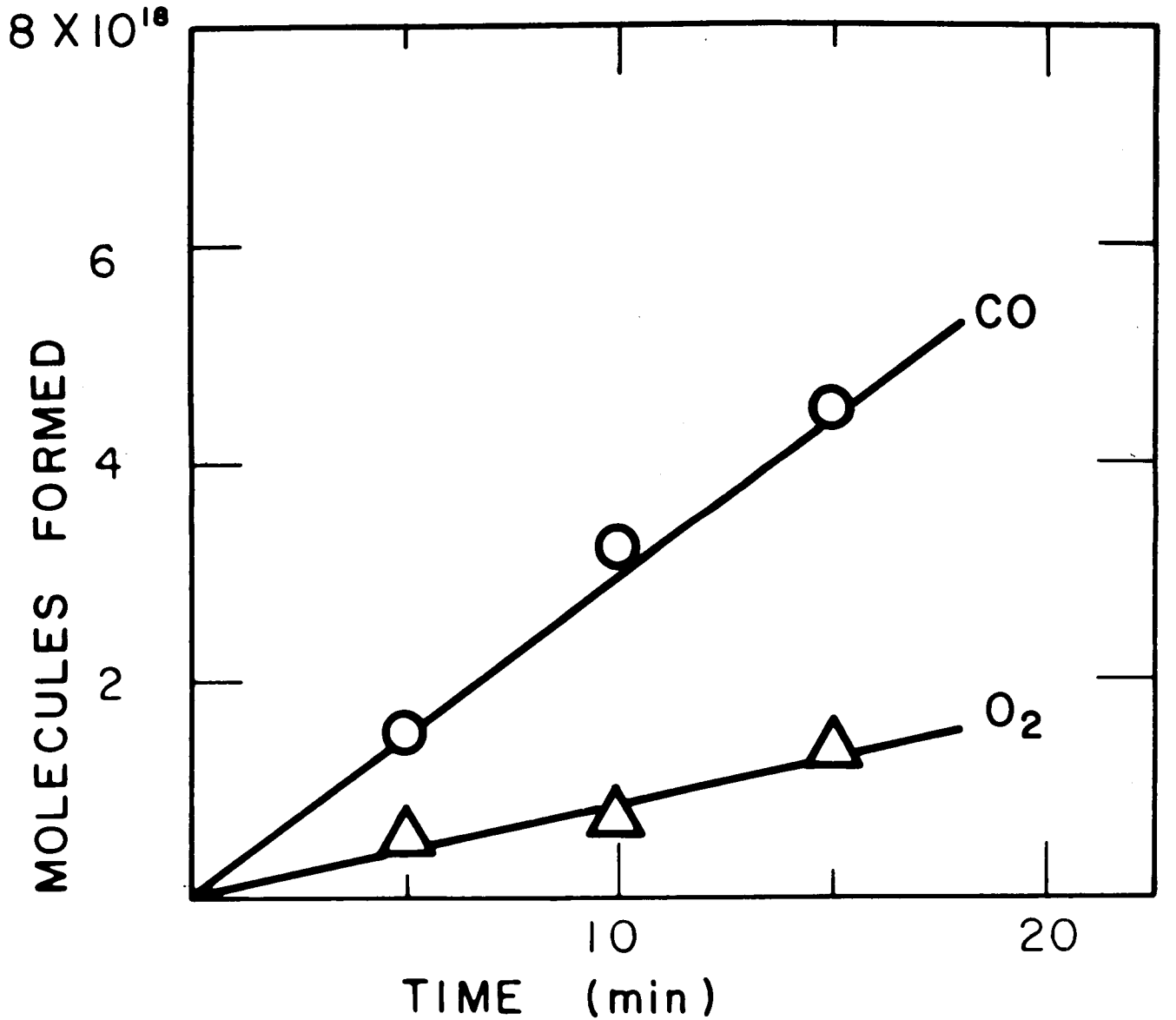

Figure 3. Time dependence of carbon monoxide and oxygen formation at 1470Å; irradiation intensity 5×10^{15} quanta/sec.

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substantiates the results presented in Figure 2, indicating that for the irradiation intervals and intensities applied the quantum yields are time independent. Further, since the straight lines obtained meet at the origin of the co-ordinates, the absence of perceptible amounts of impurities in the employed CO_2 is evidenced.

3.2 Ozone Quantum Yields

Most of the experiments designed to measure the amount of ozone formation were carried out at atmospheric pressure. As one could expect on account of the stoichiometry of the reactions involved, the observed ozone quantum yields depended strongly on the concentration of oxygen contained in the carbon dioxide, and also upon the applied flow rates and irradiation intensities. No ozone could be detected when a flow of extensively purified CO_2 was irradiated with the krypton or the hydrogen discharge, even if high light intensities and low flow rates were employed. As a consequence, in these cases, only an upper limit quantum yield of $Q(O_3) \leq 0.01$ can be given. The ozone quantum yields observed with the xenon light source irradiating pure CO_2 were in the range of $Q(O_3) = 0.015$, but this was still insufficient for an accurate determination of the intensity dependence.

Larger concentrations of ozone were found when the employed carbon dioxide contained a trace of oxygen (0.057%) making it worthwhile to study the corresponding ozone quantum yields as a function of radiation intensity under otherwise similar conditions. Figure 4 shows that the

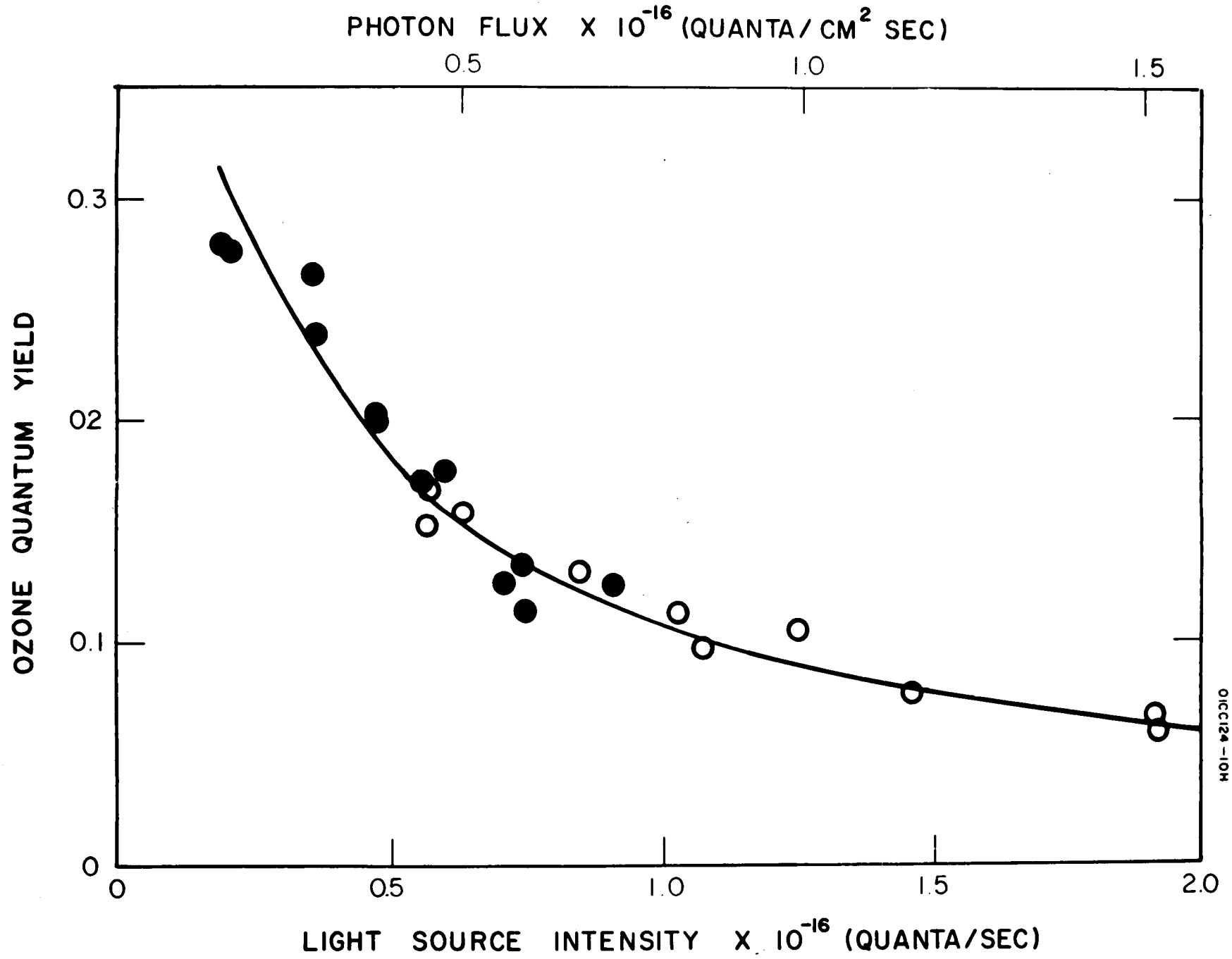

Figure 4. Ozone quantum yields for CO_2 containing 0.057% oxygen; average flow rate 1.9 cm^3/sec. Open circles: at 1236Å; filled circles: around 1600Å.

the data obtained separately with krypton and hydrogen discharges overlap quite closely, implying that the mechanism of ozone formation is the same in both cases. The increase in the ozone quantum yield with decreasing intensity is in accord with the kinetic mechanism. As the concentration of oxygen atoms is reduced, their attachment to molecular oxygen by reaction (3) is favoured in comparison to the second-order direct recombination (2). Similarly, reaction (4) is more effective at higher intensities owing to the larger absolute amounts of ozone involved.

No systematic study was performed with the xenon discharge under these conditions. However, as was the case with purified CO_2, the rate of ozone formed as a result of the 1470 Å irradiation was again greater than that observed at the other wavelengths. For example, with a xenon light intensity of 7.5×10^{15} quanta/sec an ozone quantum yield of $Q(O_3) = 0.225$ was determined, while according to Figure 4, the other discharges produce an average $Q(O_3) = 0.125$.

The pressure dependence of the ozone quantum yield was briefly explored employing carbon dioxide containing 0.057% oxygen and irradiating it with a constant intensity of light produced in the xenon discharge. According to the linear variation of oxygen concentration with pressure the production of ozone is expected to decrease as the pressure is reduced, provided the assumed photolytic mechanism is correct. Indeed, Figure 5 shows that the amount of ozone formation when expressed in % of that observed at 760 mm Hg exhibits an almost linear pressure dependence. Since with decreasing pressure reaction (4) becomes less effective

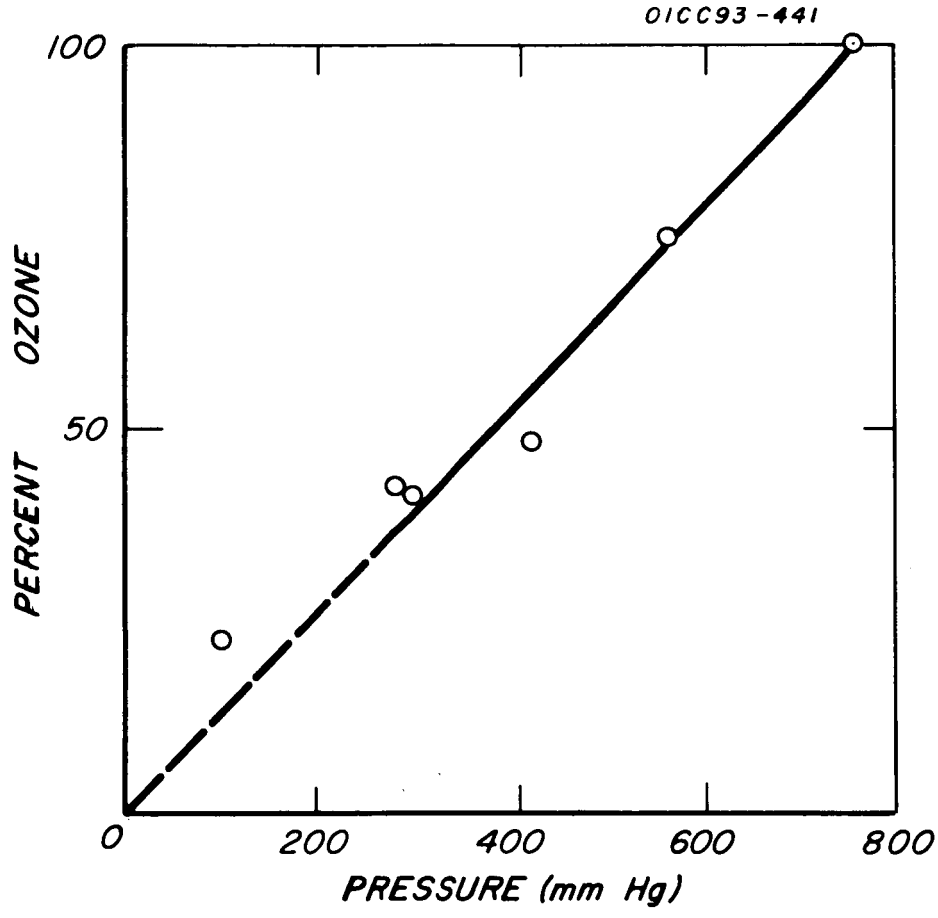

Figure 5. Pressure dependence of % ozone formation at 1470Å.

due to the smaller concentrations of ozone involved, the pressure dependence of the ozone quantum yield seems to indicate that reactions (2) and (3) have similar third-body requirements.

Although all of the above reported results concerning krypton and hydrogen radiation are qualitatively consistent with the invoked mechanism, the observed ozone quantum yields are considerably smaller than could be expected if the involved oxygen atoms were in the ^3P ground state. With the use of currently accepted values for the rate constants of ground-state oxygen atoms[7] one estimates, for example, ozone quantum yields in the range $Q(O_3) = 0.1$ for a 1 cm^3/sec flow of pure carbon dioxide, whereas the observed quantum yields are smaller by at least an order of magnitude. However, this result would not be unreasonable if the oxygen atoms generated in the CO_2 photolysis were in the metastable ^1D state rather than in the ^3P ground state, because in this case the formation of ozone by reaction (3) is spin forbidden so that the corresponding rate constant would be comparatively smaller. Although the formation of ^1S oxygen atoms is energetically feasible at 1236 Å, it can be precluded since the energy available at the onset of the involved continuum is insufficient (see Figure 1). Thus, it appears that the photodissociation of carbon dioxide produces ^1D oxygen atoms. To provide a more quantitative test, the ratio of the rate constants of reactions (3) and (4) was measured and compared with the known value associated with ^3P oxygen atoms. A carbon dioxide + oxygen mixture containing 2.66% oxygen was prepared and irradiated with light from the

krypton discharge. The ratio of the absorption cross-sections for carbon dioxide and oxygen at 1236 Å is quite favourable so that only one-tenth of the available radiation intensity is absorbed by the oxygen contained in the mixture. However, the high oxygen concentration promotes reactions (3) and (4) relative to reaction (2) rendering the latter unimportant. Table 1 demonstrates that the resulting ozone quantum yields are in the vicinity of unity, but a considerable variation with the applied intensities and flow rates is also noticeable.

Table 1. O_3 QUANTUM YIELDS AND VALUES FOR $\gamma = k_4/k_3[M]$ IN THE 1236 Å PHOTOLYSIS OF CO_2 CONTAINING 2.66% O_2

Run No.	v cm^3/sec	1×10^{-16} $\frac{quanta}{sec}$	$Q(O_3)$	γ	γ_1^a corrected	γ_2^b
79/80	1.84	1.135	0.722	24.4	31.0	34.8
81/82	2.04	0.726	0.81	24.2	34.9	39.1
83/84	2.06	0.71	0.782	30.5	41.5	46.5
85/86(A)	4.6	1.68	0.81	23.6	34.1	38.2
85/86(B)	4.6	1.76	0.774	28.5	39.3	43.8
87/88(A)	4.5	1.59	0.763	33.2	44.5	50.1
87/88(B)	4.5	1.45	0.838	21.8	33.2	41.8
89/90	4.7	1.14	0.865	23.0	38.1	42.2
91/92	4.7	0.592	0.935	19.0	45.3	50.8
93/94	3.2	0.373	0.938	19.5	48.2	53.6
95/96	3.15	0.302	0.988	42.3	37.8	41.2
97/98	3.15	0.204	1.032	----	31.0	35.0
99/100	3.1	1.07	0.785	29.5	46.2	51.8
101/102	3.2	1.54	0.755	25.5	34.0	38.2

[a] corrected assuming $O_2 + h\nu \rightarrow 2O(^1D)$.

[b] corrected assuming $O_2 + h\nu \rightarrow O(^1D) + O(^3P)$.

average $\gamma_1 = 38.5 \pm 4.8$, $\gamma_2 = 43.4 \pm 5.3$.

4. DISCUSSION

The low ozone quantum yields could not have been obtained if ^1D oxygen atoms were rapidly deactivated by collisions with carbon dioxide. The conclusion that collisional deactivation is relatively unimportant is corroborated by a study of Katakis and Taube[8] who found that ^1D oxygen atoms produced in the 2537 Å photolysis of ozone undergo an exchange reaction with CO_2 rather than deactivation.

Figure 1 shows that at the wavelengths of the xenon and hydrogen radiation the absorption is predominantly due to the first continuum appearing at longer wavelengths, while there is negligible contribution of the second continuum towards shorter wavelengths. Conversely, the line at 1236 Å is almost solely absorbed by the second continuum with negligible contribution from the first. Since the results obtained separately with the krypton and the hydrogen light source are essentially identical, it can be inferred that the transitions represented by the two absorption coninua lead to identical dissociation products, namely carbon monoxide and ^1D oxygen atoms. The effect of the xenon 1470 Å line can now be considered. In view of the preceding conclusion it is apparent that the increase in the quantum yields observed at this wavelength must be caused by the partial absorption in the overlying band system, which at this wavelength accounts for approximately 30% of the total absorption strength. Accordingly, the results are explained in terms of reactions involving excited CO_2 molecules

$$CO_2 \xrightarrow{h\nu} CO_2^* \qquad (5)$$

$$CO_2^* + CO_2 \longrightarrow 2CO + O_2, \qquad (6)$$

which must occur in addition to the photodissociation mechanism (1) through (4). These reactions can account for the increase of the quantum yields observed for all the products. At pressures below 150 mm Hg, where the CO quantum yield is unity, the CO_2^* molecule presumably predissociates or re-emits the photon which subsequently is re-absorbed, preferentially in the continuum. The only finding not entirely consistent with this supposition is the lack of pressure dependence concerning the O_2 quantum yields obtained with the xenon discharge.

For a quantitative interpretation of the measurements the physical conditions of the experiments must be described by a suitable theoretical model. Since the reactions induced by CO_2 photolysis at atmospheric pressures are confined to a narrow region in the vicinity of the window, which is characterized by a certain degree of turbulence owing to the reversal flow in this region, it appears appropriate to perform calculations on the basis of stirred reactor theory. In the photolysis of CO_2 containing 2.66% oxygen the O_2 concentration is so large that it remains approximately constant even if all the oxygen atoms are consumed in the formation of ozone. Also, reaction (2) can be considered negligible. The stirred reactor equations then read:

$$(v/R)[O_3] = [O](k_3[O_2][M] - k_4[O_3]),$$

$$(v/R)[O] = (I/R) - [O](k_3[O_2][M] + k_4[O_3]),$$

where the concentrations refer to the outgoing (steady-state) concentrations, v is the flow rate, R the reaction volume, and I the integrated

irradiation intensity. If the oxygen atoms are largely consumed within the boundary of the reaction volume, $(v/R)[O] \ll I/R$, and the equations can be combined to express the ratio of the rate constants in terms of the previously defined O_2 quantum yield:

$$\gamma = \frac{k_4}{k_3[M]} = \frac{[O_2]v}{IQ(O_3)} \times \frac{1 - Q(O_3)}{1 + Q(O_3)} \quad . \qquad \text{(A)}$$

Note that the reaction volume R has cancelled.

When this equation is employed in conjunction with the data shown in Table 1, one obtains the γ values entered in column 5. These are about five times greater than the highest value available for ^3P oxygen atoms, $\gamma(^3P) = 5$, which can be derived using the rate constants $k_4(^3P) = 2.5 \times 10^{14}$ cm^3/molecules sec[9] and $k_3(^3P) = 2 \times 10^{-34}$ cm^6/molecules^2 sec[7]. However, equation (A) does not yet take into account the simultaneous photodissociation of oxygen in the mixture so that a correction is required making the discrepancy even greater. Because of the existing uncertainty regarding the dissociation products of oxygen at 1236 Å, two cases were considered: one in which it was assumed that the dissociation products are two ^1D oxygen atoms, and a second case involving a ^1D and a ^3P oxygen atom of which the latter was supposed to undergo immediate ozone formation. The correspondingly corrected γ values are shown, respectively, in columns 6 and 7 of Table 1. The averaged values are seen to be approximately the same in both cases, suggesting $\gamma \approx 41$. Despite a considerable variation in the intensities and flow rates the average deviation from the mean is about 12%, supporting the

employed reaction mechanism. The high values obtained for γ are considered sufficient evidence that the CO_2 photodissociation products are carbon monoxide and ^1D oxygen atoms.

The data shown in Figure 4 may now be analyzed by a similar precedure, assuming that the stirred reactor theory is again applicable. Reactions (2) through (4) have to be included in this case, leading to the equations:

$$\frac{v}{R}[O_3] = [O]\left(k_3(O_2)(M) - k_4(O_3)\right)$$

$$\frac{v}{R}[O] = \frac{I}{R} - 2k_2[O]^2[M] - [O]\left(k_3(O_2)(MO + k_4(O_3)\right)$$

If it is again assumed that $\frac{v}{R}[O] << \frac{I}{R}$, these equations can be combined to give

$$\beta^2 = \frac{k_3^2}{k_2} = \frac{2v^2}{R[M]I}\,\frac{Q(O_3)^2}{F\left(F - GQ(O_3)\right)} \quad . \qquad \text{(B)}$$

with $F = \left(\frac{(O_2)v}{I} - \gamma Q(O_3)\right)$ and $G = \left(\frac{(O_2)v}{I} + \gamma Q(O_3)\right)$.

The steady-state concentration of oxygen in this case differs from $[O_2]_o$, but it can be conveniently determined from the mass balance equation

$$[O] + 2\left([O_2] - [O_2]_o\right) + 3[O_3] = \frac{I}{v}$$

under the provision that the O-atom concentration is negligible in comparison with both the ozone concentration and the concentration of the oxygen produced. It is interesting to note that the expression for β contains the reaction volume R. This is a consequence of the square dependence of oxygen atom concentration which is involved in the rate for Reaction (2)

Unfortunately, with the experimental conditions applied, R is not clearly defined so that it must be estimated. It is evident that the outside diameter of the cylindrical reaction volume is given by that of the inner reactor tube, but the effective length of the cylinder is uncertain. For the present purpose an estimate of R has been obtained by two independent methods: (a) from the depth where 90 percent of the incoming radiation is absorbed, and (b) from geometrical considerations concerning the size of the flow pocket where turbulence presumably prevails. Both estimates yield $R \approx 1\ cm^3$ and this value has been used in conjunction with Equation (B). It should be noted that the first method of estimating R involves the CO_2 absorption cross section, which as a function of wavelength depends on the type of radiation applied. Accordingly, it appears that different reaction volumes have to be employed in Equation (B) for the two sets of data obtained separately with the krypton and the hydrogen lamp. However, as it can be gleaned from Figure 1 that the absorption cross sections at 1236 Å and around 1600 Å are comparable in magnitude, the derived values for R differ only slightly. The resulting error is certainly negligible in comparison with the unknown error of estimation.

In Tables 2 and 3 are shown the values for β which were derived on the basis of Equation (B) using $R = 1\ cm^3$ and $\gamma = 41$. Table 2 utilizes the data obtained with light from the krypton lamp while Table 3 shows the results for hydrogen radiation. Both sets of results are mutually and internally consistent, indicating once again that the invoked reaction mechanism is applicable. On averaging the results for β employing

TABLE 2. O_3 quantum yields and values for $\beta = k_3/\sqrt{k_2}$ in the 1236Å photolysis of CO_2 containing 0.057% O_2.

Run No.	v cm^3/sec	I x 10^{-16} quanta/sec	$Q(O_3)$	β x 10^{19}
35/36	1.85	1.25	0.103	2.3
37/38	2.0	0.573	0.170	3.2
41/42	1.72	1.92	0.057	2.64
43/44	1.91	1.91	0.065	2.89
45/46	1.87	1.46	0.0705	4.43
47/48	1.82	0.603	0.158	3.89
49/50	1.75	0.57	0.152	4.38
51/52	2.2	1.03	0.112	4.26
51/53	1.95	1.08	0.096	3.9
		Average $\beta = 3.55 \pm 0.71 \times 10^{-19}$		

TABLE 3. O_3 quantum yields and values for $\beta = k_3/\sqrt{k_2}$ in the 1600Å photolysis of CO_2 containing 0.057% O_2.

Run No.	v cm^3/sec	$I \times 10^{-16}$ quanta/sec	$Q(O_3)$	$\beta \times 10^{-19}$
56/57	1.79	0.722	0.126	4.14
58/60	1.98	0.740	0.133	4.61
59/60	1.92	0.740	0.116	6.99
61/62	1.8	0.580	0.178	3.34
64/65	2.06	0.570	0.170	6.33
67/74	1.87	0.474	0.198	4.42
68/74	1.86	0.474	0.201	4.16
69/75	2.02	0.36	0.266	5.36
70/75	2.01	0.36	0.237	7.17
71/78	1.98	0.20	0.278	root imag. $Q(O_3)$ too small.
72/78	1.97	0.20	0.280	
		Average $\beta = 5.15 \pm 1.24 \times 10^{-19}$		

both sets of data, one obtains $\beta = 4.3 \pm 1.0 \times 10^{-19}$ cc/molec $sec^{\frac{1}{2}}$. This value will now be employed in estimating the absolute values of the rate constants k_3 and k_4. For this purpose, it is assumed that the rate constant k_2 involved in the recombination of ^1D oxygen atoms is similar in magnitude to the one governing the recombination of ^3P oxygen atoms. The latter rate constant and the associated third-body efficiencies have recently been determined,[10,11] establishing $k_2 = 4.2 \times 10^{-33}$ $cc^2/molec^2$ sec for CO_2 as the acting third body. Accordingly, it is set

$$k_3(^1D) = \beta\sqrt{k_2(^3P)}$$

whence

$$k_3(^1D) = 2.8 \times 10^{-35}\ cc^2/molec^2\ sec\ .$$

Thus, the rate constant for ozone formation involving ^1D oxygen atoms is by about an order of magnitude smaller than that involving ^3P oxygen atoms,[6] a finding which can be attributed to the difference in spin. It should be noted that owing to the root relationship between the two rate constants, any uncertainty concerning k_2 would result in an uncertainty of $k_3(^1D)$ of only half the size. Unless k_2 is grossly in error, therefore, $k_3(^1D)$ appears to be reasonably well established. Accepting this value for k_3, finally, we obtain with $\gamma = 41$ the rate constant $k_4 = 3 \times 10^{-14}$, which is of the same size if not faster than the equivalent rate constant for ^3P oxygen atoms.

Summing up, it has been established that the photolysis of carbon dioxide in the 1200-1750 Å wavelength region generates ^1D oxygen atoms,

which predominantly react with themselves to form molecular oxygen and ozone. The measurement of O_3 quantum yields has been found a convenient tool for determining the ratios of the rate constants for the involved reactions. Estimates for absolute rate constants have been obtained on the basis of the assumption that the homogeneous recombination of ^1D oxygen atoms has a rate similar to that of ^3P oxygen atom recombination.

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