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Photolysis of Carbon Dioxide

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The vacuum ultraviolet photolysis of carbon dioxide has been investigated. Kinetic data and quantum yield measurements indicate that electronically excited (^{1}D) oxygen atoms are produced in the primary process at 1470 A and 1236 A. Such a primary process is consistent with the tentative spectral assignments which have been made for carbon dioxide.

REVIOUS investigations^{1,2} of the photolysis of **I** carbon dioxide have left the mechanism of the reaction in doubt. Groth¹ found the quantum yield of carbon monoxide at 1470 A to be near unity and suggested that oxygen atoms are formed in the primary process. Groth used a flow system and a gold-plated reaction vessel to prevent ozone formation, and thus his work cannot provide any indication of the detailed fate of the oxygen atom presumably produced in the primary process. Jucker and Rideal² state that the quantum yield of carbon monoxide is close to two, and conclude that no oxygen atoms are involved in the photolysis. They propose a mechanism which involves the reaction of a photoexcited carbon dioxide molecule with a normal molecule to give oxygen and carbon monoxide in one step. If this mechanism were to be correct, it would require a revision of the proposals that have been made for the fate of carbon dioxide molecules in the upper atmosphere.³ We have re-examined the photolysis of carbon dioxide at 1470 A in an effort to make a choice between the two mechanisms, and also have extended the investigation to shorter wavelengths in order to test the effect of excitation energy on the primary photochemical process.

EXPERIMENTAL

The light source used in the early part of this research was a 60-cycle electrical discharge through xenon. A calcium fluoride window was placed in such a way that the reaction cell viewed the discharge axially. With a power dissipation of 1000 w this lamp delivered 1014 quanta of 1470 A radiation per sec through a window 25 mm in diam. The maximum intensity was obtained with a voltage drop of 500 v and a xenon pressure of 50 μ . This lamp was abandoned because the commercial neon sign electrodes gradually deteriorated.

The greater part of the work was done with microwave discharge lamps. A QK-61 magnetron (10-cm continuous wave) tuned to a cylindrical cavity was operated at a power input of 100 w. The discharge took place in a quartz tube of 25 mm diam located axially in the cavity. By adjusting the pressure in the tube to a few microns and by tuning the cavity the discharge could be brought to within a few millimeters of the window mounted on the end of the tube. The relatively short light path through unexcited gas minimized reabsorption of resonance radiation. A lithium fluoride window was used in conjunction with a pure krypton filling to obtain the 1236 A resonance line of krypton. A krypton discharge combined with a synthetic sapphire window had no photochemical effect on carbon dioxide, which indicates that the effective radiation from the krypton discharge was indeed confined to wavelengths less than 1450 A. A discharge through xenon together with a sapphire window provided essentially monochromatic radiation of 1470 A wavelength. Although a two-millimeter thickness of sapphire absorbs approximately one-half of the incident radiation at 1470 A, sapphire was used as a window in

¹ W. Groth, Z. physik. Chem. (Leipzig) **B37**, 307 (1937). ² H. Jucker and E. K. Rideal, J. Chem. Soc. **1957**, 1058. ³ D. R. Bates, *The Earth as a Planet*, edited by G. P. Kuiper (University of Chicago Press, Chicago, Illinois).

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FIG. 1. The yield of carbon monoxide as a function of photolysis time at 1470 A. The pressure of carbon dioxide was 10 millimeters.

preference to calcium fluoride because of its superior mechanical properties.

The maximum output of the krypton lamp was 10¹⁵ quanta per sec through a window 25 mm in diam, and that of the xenon lamp was a factor of four lower. The lamps were often operated at less than maximum intensity in order to improve their stability. Various mixtures of helium with the heavier rare gases were tried as lamp fillings, but none improved the performance.

A cylindrical reaction vessel 25 mm in diam and 10 cm in length was fastened directly to the window of the lamp. The cell was serviced by a mercury free gas storage manifold. All pressures were measured with a thermocouple gauge or an electrically indicating spoon gauge. A conventional gas micro-analytical system which had provision for combustion of carbon monoxide and absorption of carbon dioxide completed the apparatus.

Mass spectrometric analyses were conducted with an instrument employing the Consolidated 21-620 analyzer tube.

All gases were purest available commercial grades, further purified by bulb to bulb distillation. Mass spectrometric analyses showed satisfactory purity in

TABLE I. The photolysis of carbon dioxide at 1470 A.

Run	Time (sec)	CO ₂ pressure (mm)	CO (micromoles)	O ₂ (micromoles)
1	1200	35	0.22	0.0055
2	600	35	0.091	0.0046
3	900	35	0.15	0.0056
4	300	35	0.041	0.0040
5	150	35	0.041	0.0036
ба	600	10	0.42	0.0050
7	900	10	0.56	0.0049
8	300	10	0.15	0.0035
9	150	10	0.052	0.0022
10	450	10	0.27	0.0045
11	300	10	0.24	0.0042

^a Runs at 10-mm pressure were made with a higher light intensity than those at 35 mm.

all cases except nitric oxide, which contained small amounts of nitrogen. This impurity was of no chemical consequence, and could easily be corrected for in the mass spectrometric analyses for carbon monoxide.

RESULTS AND DISCUSSION

I. Experiments with 1470 A Light

A preliminary set of experiments showed that the total yield of noncondensable material was independent of the pressure when essentially all the light was absorbed by carbon dioxide. Most of the data were then obtained at carbon dioxide pressures of 10 mm and 35 mm. Figure 1 and the data in Table I show that at both pressures the yield of carbon monoxide is a linear function of the illumination time. The extent of the decomposition of carbon dioxide ranged from 0.3% to 3% at the lower pressure, and from 0.1% to



FIG. 2. The yield of oxygen as a function of photolysis time at 1470 A. The pressure of carbon dioxide was 10 mm.

0.4% at the higher pressure. These figures are somewhat misleading, since at 10 mm pressure one-half of the light is absorbed in the first three centimeters of the reaction cell, and at 35-mm pressure the corresponding distance is 0.83 centimeters. The effective percentage decompositions thus may be as much as a factor of 3 to 10 higher than those quoted above, but are still less than 10%.

The amount of oxygen produced and its time variation are shown in Fig. 2 and in Table I. The oxygen found both by mass spectral and chemical analysis is considerably less than one-half the amount of carbon monoxide produced. Furthermore, the data indicate that the amount of oxygen produced approaches a value which is time independent. This finding seems to correspond to the observations of Jucker and Rideal, who state that the photochemical yield as measured by pressure change decreased rapidly with time of illumination. Since it seemed likely that the missing oxygen should be present as ozone, an irradiated sample was collected in a quartz absorption cell without being allowed to come into contact with stopcock grease. The ultraviolet spectrum showed the broad absorption band of ozone. Because of the breadth of this band and the small amount of products involved, no quantitative determinations of ozone were made.

It is convenient to discuss these results in terms of a mechanism involving oxygen atoms

$$\mathrm{CO}_2 + h\nu \rightarrow \mathrm{CO}_2^* \qquad I_{\mathrm{abs}}$$

$$CO_2^* \rightarrow CO + O$$
 (1)

$$20 + M \rightarrow O_2 + M \tag{2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{3}$$

and the excited molecule reaction proposed by Jucker and Rideal augmented by a step in which ozone is produced.

$$CO_2 + h\nu \rightarrow CO_2^*$$
 I_{abs}

$$CO_2^* + CO_2 \rightarrow 2CO + O_2$$
 (4)

$$\mathrm{CO}_2^* + \mathrm{O}_2 \longrightarrow \mathrm{CO} + \mathrm{O}_3. \tag{5}$$

In addition to the indicated possibilities, ozone might be produced by the photolysis of molecular oxygen. However, since the experiments involve almost total absorption of the light by carbon dioxide, any absorption by the product molecules must decrease the yield of carbon monoxide. The fact that the carbon monoxide yield is a linear function of time suggests that absorption by the products is not important. To confirm this supposition, we may calculate the fraction of light absorbed by the molecular oxygen using the absorption coefficients⁴ listed in Table II. In the runs done at 35 millimeters pressure, the amount of light absorbed by the molecular oxygen present at the end of the reaction would be 0.2% of the total incident radiation, if the products were to be uniformly distributed over the whole reaction vessel. Since most of the products are concentrated in the first two centimeters of the cell, a more reasonable estimate of the fractional light absorption of oxygen would be 1%. The concentration of ozone is expected to be slightly less than one third the concentration of carbon monoxide, with the consequence that ozone can absorb no more than 2 or 3%of the light incident on the reaction cell. Similar calculations show that the absorption of light by the products

TABLE	II.	Absorption	a coefficients.*
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	1470 A	1236 A
CO ₂	18	3.4
O_2	355	14
\mathbf{O}_{λ}	100	300
NO	10	56
CO	0.7	0.8

⁸ Absorption coefficients are in units of cm^{-1} for gases at one atmosphere pressure and 25°C. The data refer to natural logarithms.

⁴ K. Watanabe, M. Zelikoff, and E. Inn, "Absorption Coefficients of Several Atmospheric Gases," Air Force Cambridge Research Center Technical Report No. 52–23.

TABLE III. The effect of added oxygen.

Run	Time (sec)	CO ₂ pressure (mm)	O ₂ pressure (mm)	R ^a
12	600	35.0	0.17	0.96
13	600	35.0	0.16	0.95
14	600	35.0	0.20	1.00

^a R is defined as the ratio of the amount of CO obtained by photolysis of the mixture to the amount obtained from the photolysis of pure carbon dioxide.

is also negligible in the runs done at 10 millimeters pressure. We can conclude that formation of ozone does not occur through photolysis of oxygen, and that no inner filter is to be expected either from oxygen or ozone.

It is a consequence of the excited molecule mechanism that any variation in the rate of production of oxygen must result in a variation of the rate of formation of carbon monoxide. From a steady-state treatment of the excited molecule mechanism we obtain

$$d(\text{CO})/dt = \frac{I_{\text{abs}}[2k_4(\text{CO}_2) + k_5(\text{O}_2)]}{k_4(\text{CO}_2) + k_5(\text{O}_2)}$$

for the rate of production of carbon monoxide and

$$d(O_2)/dl = \frac{I_{abs}[k_4(CO_2) - k_5(O_2)]}{k_4(CO_2) + k_5(O_2)}$$

for the rate of oxygen formation. These expressions show that when the oxygen concentration is essentially zero the initial rate of carbon monoxide formation is

$$[d(CO)/dt]_{initial} = 2I_{abs}$$

After the oxygen concentration has reached its steady value the rate of carbon monoxide production has fallen to

$$[d(CO)/dt]_{final} = 1.5I_{abs}.$$

At the shortest irradiation times the oxygen produced corresponds to approximately one-half of the steadystate concentration. Therefore, the expected change in the rate of production of carbon monoxide over the range of decompositions investigated should amount to approximately 20% of the initial rate. Such a change should be detectable as a curvature in Fig. 1. Neither the data obtained at 10-mm pressure nor those obtained at 35 mm show any decreasing trend in the rate of formation of carbon monoxide.

To eliminate the possibility that any variation in the rate of production of carbon monoxide had gone undetected, oxygen was deliberately added to the reaction mixture and the yield of carbon monoxide compared with that occurring in the photolysis of pure carbon dioxide. The ratio of k_4 to k_5 was estimated from the value of the steady-state concentration of oxygen in the photolysis of pure carbon dioxide, and sufficient oxygen was added to the mixtures to insure that 99% of the excited carbon dioxide molecules would form

TABLE IV. The effect of added nitric oxide	TABLE]	IV. The	effect (of ac	lded 1	nitric	oxide.	
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Run	Time (sec)	CO ₂ pressure (mm)	NO pressure (mm)	O ₂ /CO	Ra
15	600	13	0.005	0.17	1.0
16	600	14	0.016	0.19	1.1
17	600	26	0.080	0.40	1.0
18	600	40	0.080	0.35	1.1

* R is defined as in Table III.

ozone. At the same time, no more than one-tenth of the light incident on the mixtures was absorbed by oxygen. If the excited molecule mechanism is correct, the yield of carbon monoxide from the mixtures should be at least 30% lower than from the photolysis of pure carbon monoxide. As demonstrated by the data in Table III, the presence of considerable amounts of added oxygen does not affect the yield of carbon monoxide beyond that expected on the basis of the inner filter effect. Thus the experiments with added oxygen as well as the time dependence of the carbon monoxide yield are inconsistent with the excited molecule mechanism.

There is a further objection to the excited molecule mechanism. At the maximum concentrations of oxygen existing in the photolysis of pure carbon dioxide an electronically excited carbon dioxide molecule would encounter an oxygen molecule approximately every 10^{-4} second. Since the calculated radiative lifetime of carbon dioxide is 10^{-6} sec, formation of ozone by step 5 would seem very unlikely.

Runs 15–18 (Table IV) demonstrate that the addition of small amounts of nitric oxide definitely increases the oxygen to carbon monoxide ratio, presumably at the expense of the ozone yield. Furthermore, the absolute yield of carbon monoxide is unaffected by the addition of nitric oxide. These runs reinforce the conclusion that the mechanism by which carbon monoxide is produced is independent of the processes which produce oxygen or ozone. The atomic mechanism is consistent with such a conclusion.

The effect of nitric oxide on the oxygen yield may be explained by adding the steps

$$O + NO + M \rightarrow NO_2 + M$$
 (6)

$$O + NO_2 \rightarrow O_2 + NO$$
 (7)

to the atomic mechanism. If the oxygen atoms involved are in the ${}^{3}P$ state, reactions (6) and (7) are extremely fast. Since it appears that the atoms involved in the photolysis of carbon dioxide are not in the ${}^{3}P$ state (*vide infra*) and since reactions (6) and (7) may not be fast for electronically excited atoms, the possibility that the reaction sequence

$$O + O_2 + M \rightarrow O_3 + M \tag{3}$$

$$O_3 + NO \rightarrow NO_2 + O_2$$
 (8)

is responsible for the increased oxygen yield must not

be ignored. However, if nitrogen dioxide is formed in this way, the oxygen yield should be no greater than the original amount of nitric oxide in the mixture or no greater than 33% of the carbon monoxide yield, whichever is smaller. In runs 17 and 18 the oxygen yield is greater than 33% of the carbon monoxide yield, and in runs 15 and 16 the oxygen yield did exceed the original amount of nitric oxide in the mixture. The reactions of oxygen atoms therefore provide a more satisfactory explanation of the effect of nitric oxide addition.

Since the photolysis of carbon dioxide is a convenient reaction for estimating the intensities of vacuum ultraviolet light sources it is desirable to know the absolute quantum yield of the reaction. To determine the output of the lamp we photolyzed mixtures of carbon monoxide and oxygen and determined the amount of carbon dioxide produced. The primary photochemical process in oxygen at these wavelengths is without question the formation of a ${}^{3}P$ and a ${}^{1}D$ oxygen atom. Even though the rate of reaction of an oxygen atom with an oxygen molecule is approximately 40 times greater⁵ than with a carbon monoxide molecule, exclusive formation of carbon dioxide will occur if the concentration of carbon monoxide is much greater than the concentration of oxygen. A difficulty in the design of the experiment arises because carbon monoxide absorbs 1470 A light. The carbon monoxide spectrum in this region consists of sharp bands, and possibly a weak underlying continuum. Watanabe and coworkers⁴ state that this continuum may be due to an oxygen impurity in the carbon monoxide used in the spectral measurements. This is reasonable since the energy of a light quantum of 1470 A wavelength is insufficient to dissociate the carbon monoxide molecule, and a continuum is not to be expected. In any case, only a maximum possible value of the absorption coefficient is known. In our experiments the pressure of carbon monoxide was 22 mm and that of oxygen was in the range 0.040 to 0.060 mm. To determine whether absorption of light by carbon monoxide was a complicating factor at these concentrations, pure carbon monoxide was photolyzed and the amount of carbon dioxide determined. These experiments showed that in the experiments with oxygen-carbon monoxide mixtures, the contribution of reactions caused by photoexcited carbon monoxide to the carbon dioxide yield was negligible. By the comparison of four separate photolyses of the oxygen-carbon monoxide mixtures with four photolyses of pure carbon dioxide the quantum yield of carbon monoxide was found to be 1.1 ± 0.1 . This result is consistent with the findings of Groth. It should be emphasized that due to the possibility of ozone formation in the actinometer this value is an upper limit. Finally, it should be realized that a quantum yield near unity is consistent with the atomic

⁵ W. Groth, Z. physik. Chem. (Leipzig) B37, 315 (1937).

mechanism, but not with the excited molecule mechanism, which would predict a value greater than 1.5.

As a further test of the atomic mechanism, an attempt was made to detect the chemiluminescence of the reaction

$$O + NO \rightarrow NO_2 + h\nu, \qquad (9)$$

which might occur during the photolysis of NO-CO₂ mixtures. For these experiments the ordinary reaction cell was replaced by a fluorescence cell consisting of two perpendicular Raman tubes. A photomultiplier and filter system permitted the detection of light emitted at right angles to the radiation from the lamp. Although the green chemiluminescence from reaction (9) could easily be detected in the photolysis of mixtures of O₂ and NO, N₂O and NO, and from the photolysis of pure NO, there was no indication of any emission from NO-CO₂ mixtures. These facts strongly

TABLE V. The photolysis of carbon dioxide at 1236 A.

Run	Time (sec)	CO ₂ pressure (mm)	CO (micromoles)	O ₂ (micromoles)
19	60	44	0.315	0.028
20	600	44	2.00	0.028
21	1200	44	3.25	0.018
22	300	44	1.14	0.055
23	900	44	2.57	0.020
24	20	44	0.125	0.013
25	600	10	1.89	0.005
26	300	10	0.87	0.0057
27	60	10	0.19	0.0071
28	20	10	0.059	0.0034
29	900	10	2.58	0.0045
30	300	10	0.90	0.0037
31	180	.10	0.53	0.0070
32	60	10	0.125	0.0066

suggest that ${}^{3}P$ oxygen atoms are in no way involved in the photolysis of carbon dioxide. Such a conclusion is consistent with the calculations which showed that molecular oxygen produced in the reaction did not undergo subsequent photolysis. The conclusion that ${}^{3}P$ oxygen atoms are not produced in the primary process is supported by the spectral assignments of Walsh⁶ and Mulliken⁷ who identify the 1470 A absorption band in CO₂ as a transition to a ${}^{1}\Delta_{u} - {}^{1}B_{2}$ state. Such an electronic state would correlate with the ${}^1\!\Sigma$ state of CO and the ^{1}D state of the oxygen atom. The dissociation to the excited oxygen atom is energetically allowed at these wavelengths since only 7.4 electron volts are required, while the energy of a 1470 A quantum corresponds to 8.3 electron volts. A mechanism involving ^{1}D oxygen atoms would thus appear to be consistent with available spectroscopic information, as well as the kinetic data presented here.

II. Experiments with 1236 A Light

The data obtained by using 1236 A radiation are



FIG. 3. The yield of carbon monoxide as a function of photolysis time at 1236 A. The pressure of carbon dioxide was 44 mm.

displayed in Table V and Figs. 3 and 4. Although the results are similar to those obtained with 1470 A light, the dependence of carbon monoxide yield on irradiation time shows significant deviation from linearity. The fact that the oxygen yield reaches an approximately constant value is now more clearly demonstrated because the greater intensity of the krypton lamp permitted higher percentage decomposition within a reasonable time. Ozone was also detected as a reaction product at this shorter wavelength.

The nonlinear relation between carbon monoxide yield and time must either result from an inner filter effect or from a reaction between electronically excited carbon dioxide and oxygen molecules to form ozone. From the absorption coefficients in Table II and the oxygen yields one can calculate the fractional light absorption by the maximum amount of O_2 which is produced is 0.2% when the carbon dioxide pressure is 10 mm and 0.7% in those runs made at 44 millimeters pressure. It therefore is very unlikely that photolysis of oxygen is responsible for ozone formation or the nonlinear relationship between carbon monoxide and time. Ozone is more likely to cause an inner filter effect. At decompositions where the oxygen yield has reached its maximum, the amount of ozone is somewhere



FIG. 4. The yield of oxygen as a function of photolysis time at 1236 A. The pressure of carbon dioxide was 44 mm.

⁶ A. D. Walsh, J. Chem. Soc. 1953, 2260.

⁷ R. S. Mulliken, Can. J. Chem. 36, 10 (1958).

Run	Time (sec)	CO₂ pressure (mm)	NO pressure (mm)	O ₂ /CO	$R^{\mathbf{a}}$
33	600	10	0.080	0.43	1.15
34	900	44	0.080	0.38	1.3
35	150	44	0.080	0.40	1.0

TABLE VI. Effect of added nitric oxide at 1236 A.

^a R is defined as in Table III.

between 0.1 and 1 micromole. The corresponding fractional light absorption by ozone in the runs made at 44 millimeters pressure is between 4% and 40%. This much absorption can easily account for the time dependent rate of production of carbon monoxide.

To test this proposal, nitric oxide was introduced into the reaction mixture in an attempt to prevent ozone formation. The data in Table VI show that the ratio of oxygen to carbon monoxide increases upon addition of nitric oxide, which indicates that ozone formation is suppressed. Furthermore, it is clear that the addition of nitric oxide increases the carbon monoxide yield in experiments in which the irradiation time is relatively long, but does not affect the yield in experiments with short irradiation times. It would appear that the only way in which the yield of carbon monoxide may be increased by addition of nitric oxide is through elimination of ozone as an inner filter. Thus, both the effect of added nitric oxide and the calculations of the fractional light absorption of ozone present a consistent explanation of the decrease of the rate of carbon monoxide production with time.

The importance of the inner filter effect precludes a choice between the two mechanisms based only on the data obtained from the photolysis of pure carbon dioxide. The fact that when nitric oxide is added the carbon monoxide yield increases even though the oxygen concentration goes up is, however, some indication that reaction (5) is not important. Moreover, the calculated radiative lifetime of the electronic state of carbon dioxide excited by 1236 A light is slightly



FIG. 5. The photoionization current at 1236 A as a function of nitric oxide pressure. The curvature is due to ion-electron recombination at the higher pressures.

shorter than 10^{-6} sec, and collisions between excited carbon dioxide and oxygen molecules occur at most every 5×10^{-5} sec. On this basis the excited molecule mechanism does seem to offer a less satisfactory explanation of the facts than does the atomic mechanism.

In order to facilitate a choice between the two mechanisms, the quantum yield of carbon monoxide was determined. The photochemical reaction between oxygen and carbon monoxide can not be used as an actinometer at 1236 A. Most of the light incident on a mixture containing enough excess carbon monoxide to react with all oxygen atoms would be absorbed by the carbon monoxide itself. The fate of an electronically excited carbon monoxide molecule in such a mixture is not at all clear, and thus the amount of photolytically produced carbon dioxide cannot be used to measure light intensity. However, the photoionization current



FIG. 6. The photoionization current in nitric oxide as a function of applied voltage. The nitric oxide pressure is 0.50 mm.

generated in the photolysis of nitric oxide can be used to estimate the light intensity, since the photoionization cross section of nitric oxide is known. Electrodes were inserted in the reaction cell, an appropriate potential was applied and the photocurrent measured with a galvanometer having a sensitivity of 5.0×10^{-9} amp/mm. Three different electrode geometries were used. In the first experiments a tungsten wire was located axially in the reaction cell and was surrounded by a cylindrical grid located at the wall. This arrangement had the advantage that the tungsten wire exposed a very small surface to the incident light, and therefore only very small photoelectric currents were produced even when the wire was biased at -100 v. However, because of the extremely high field at the central electrode sporadic electrical breakdown of the gas took place whenever more than 100 v were applied to the electrodes. The second and third electrode geometries consisted of two copper gauze electrodes located at opposite walls of the cell. In one case the electrodes extended the full length of the reaction cell, and in the other arrangement the electrodes were 2.0

cm long. The apparent efficiencies for electron-ion collection of the three systems varied slightly due to the fact that the light entering the reaction vessel was not collimated. To minimize errors due to this situation, the electrodes which were 2.0 cm long were used for the actinometry.

Figure 5 shows the photoelectric current as a function of nitric oxide pressure at a fixed electrode potential of 100 v. The curvature of the plot is more pronounced than would be expected from the equation

$$i \propto I_{abs} = I_0 [1 - \exp(-klP)]$$

when the value of the absorption coefficient k reported by Watanabe⁸ is used. Here i is the photocurrent, lis the length of the electrodes, and P is the pressure of nitric oxide in atmospheres. The exaggerated curvature indicates that a noticeable amount of ion-electron recombination occurs at pressures as low as 0.5 millimeter. This interpretation is substantiated by the fact that the photocurrent actually started to decrease when the pressure of nitric oxide was increased beyond 0.5 millimeter.

The variation of photocurrent with applied voltage at a pressure of 0.5 mm of nitric oxide is shown in Fig. 6. As is to be expected at this pressure, a saturation current is approached only at the highest applied voltage. At pressures of 0.01 mm saturation currents were obtained at approximately 45 v.

In the experiments in which the quantum yield was to be measured the lamp was deliberately run at reduced intensity in order to avoid high concentrations of ions and electrons which would favor recombination. A comparison of four runs in which carbon dioxide was photolyzed with four separate measurements of the photoionization current of nitric oxide resulted in a value of 1.2 ± 0.1 for the quantum yield of carbon monoxide. The most obvious systematic error in this determination would be failure to collect all ion pairs generated photolytically, which would result in a quantum yield which would be too large. The value of

⁸ K. Watanabe, J. Chem. Phys. 22, 1564 (1954).

quantum yield is directly proportional to the photoionization cross section of nitric oxide and thus is subject to an additional uncertainty of $\pm 10\%$. Since the photolyses of carbon dioxide were carried out at pressures at which 80% of the incident light was absorbed, any small errors in the absorption coefficient of carbon dioxide are not important sources of error in the quantum yield determination. A value of the quantum yield of carbon monoxide which is near unity is consistent with the atomic mechanism, but not with the excited molecule mechanism.

As had been the case at 1470 A, it proved impossible to detect ${}^{3}P$ oxygen atoms in the photolysis of carbon dioxide at 1236 A by means of their chemiluminescent reaction with nitric oxide. Since the chemiluminescence could easily be observed in the photolysis of oxygen, nitrous oxide, and nitric oxide we are again forced to conclude that any oxygen atoms involved in the photolysis of carbon dioxide must be electronically excited. From an energetic point of view the atoms produced may be ${}^{1}S$ or ${}^{1}D$. No definite identification of the excited electronic state of carbon dioxide which is involved here has been made, but Mulliken⁷ has suggested that it may be related to a ${}^{1}\Delta g$ state of the linear molecule, which would imply dissociation to a ^{1}D atom is most probable. The similarities in the photolytic behavior at both wavelengths makes this conclusion seem reasonable.

In summary, it would appear that an atomic mechanism presents a consistent explanation of the quantum yield measurements and kinetic data obtained in this work. Since a photoexcited carbon dioxide molecule need not collide with another molecule in order to form carbon monoxide, the proposal of Bates³ for the photolytic dissociation of carbon dioxide in the upper atmosphere seems reasonable.

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