Mercury Photosensitized Decomposition of Carbon Dioxide by 1849 Å ($Hg^*6^1P_1$)

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(Received January 24, 1961)

Few studies[1,2] have been made of reactions induced by the 1849 Å mercury resonance line, because of the difficulty of eliminating the effect of the other resonance line of mercury at 2537 Å.

In the case of carbon dioxide most of the above difficulties may be reduced. The possibility of direct photolysis by 2537 Å is eliminated since carbon dioxide is transparent above 1850 Å. The excitation energy of 6^3P_1 of mercury, 112.2 kcal., is insufficient to bring about the reaction

$$CO_2+Hg^*(6^3P_1) \rightarrow CO+O+Hg(^1S_0)$$

and the reaction

$$CO_2+Hg^*(^3P_1) \rightarrow CO+HgO$$

is slow and has no important effect[3] on the photosensitized decomposition by 6^1P_1 of mercury. The excitation energy of 6^1P_1 of mercury, 153.9 kcal., is sufficient to bring about the decomposition of carbon dioxide.

Therefore, it is possible to investigate the photosensitized decomposition and the direct photolysis of carbon dioxide induced by the resonance line at 1849 Å without any important interference caused by the resonance line at 2537 Å.

Experimental

Photosensitized Decomposition.—Carbon dioxide obtained from sodium bicarbonate was dried by passing it over calsium chloride and magnesium perchlorate. Then the gas was stored after purification by bulb to bulb distillation, using dry ice and liquid nitrogen. Before each run, gases noncondensable in ilquid nitrogen were remonved by pumping in liquid nitrogen.

The reaction was carried out in a cylindrical fused quartz cell (5 cm. in diameter 10 cm. long) illuminated by the radiation from a low pressure mercury lamp operated at a constant current 90 ma. from a 2000 V. leakage transformer. The gas saturated with mercury vapor by passing it over a mercury surface in a heated U tube, was introduced into the reaction cell. To keep the gas saturated with mercury vapor throughout a run, liquid mercury was intoduced into the reaction cell. When no liquid mercury was introduced in the cell, the reduction of the rate of the reaction was observed by the depletion of mercury due to the formation of the oxide of mercury. The temperature of the reaction cell was kept at room temperature.

The gaseous products, noncondensable in liquid nitrogen, were analysed in a conventional analysis system. The amount of noncondensable gas was measured by compressing it into a constant volume burette using a small mercury diffusion pump backed by a Töepler pump. The volume of carbon monoxide in the noncondensable products was determined by means of copper oxide heated at around 300°C.

Direct Photolysis.—In the investigation of the direct photolysis, the carbon dioxide used was prepared in a system completely free from mercury vapor in order to eliminate the mercury photosensitization. The pressure of carbon dioxide in the reaction cell was measured by means of a Bourdon gauge. After the photolysis, the gaseous products noncondensable in liquid nitrogen, were analysed by connecting the reaction cell to an analysis system by means of a ground joint.

Since the absorption coefficient of carbon dioxide at 1849 Å is very small[4], the investigation was carried out in a higher pressure region than in the case of photosensitization. The reaction was carried out at room temperature.

Results

Photosensitization.—Carbon monoxide was the only product which was noncondensable in liquid nitrogen, and no oxygen was detected. This means that the rate of formation of oxygen is at most a few percent of that of carbon monoxide. A colored substance, assumed to be an oxide of mercury, was found on the surface of the front window of the reaction cell. This was soluble in dilute sulfuric acid and was removed by flaming in vacuum.

The average rate of production of carbon monoxide, (amount of carbon monoxide produced)/(irrandiation time), depends on the time of irradiation and the pressure of carbon

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[1] C. C. McDonald, A, Kahn and H. E. Gunning, *J. Chem. Phys.*, **22**, 908 (1954).

[2] J. D. McGilvery and C. A. Winkler, *Can. J. Chem.*, **30**, 194 (1952).

[3] In fact, the formation of an oxide of mercury and carbon monoxide was observed in the experiment using a filter which cuts off the light below 2300 Å. But the rate of this reaction was very slow and showed that its effect would be negligible.

[4] E. C. Y. Inn, K, Watanabe and M. Zelikoff, *J. Chem. Phys.*, **21**, 1648 (1953).

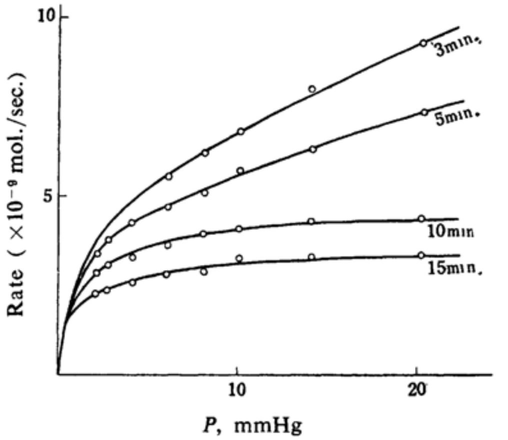

Fig. 1. The average rate of production of carbon monoxide in photosensitized decomposition of carbon dioxide.

TABLE I. THE AVERAGE RATE OF PRODUCTION OF CARBON MONOXIDE IN PHOTOSENSITIZED DECOMPOSITION OF CARBON DIOXIDE

Pressure	Rate ($\times 10^{-9}$ mol./sec.)				$r_0(t=0)$
mmHg	3 min.	5 min.	10 min.	15 min.	
2.0		3.39	2.78	2.23	4.06
2.6		3.79	3.00	2.30	5.27
4.0		4.22	3.23	2.59	5.56
6.0	5.56	4.66	3.58	2.80	7.41
8.0	6.18	5.10	3.89	2.86	8.44
10.0	6.78	5.70	4.00	3.21	8.83
14.0	7.97	6.26	4.28	3.25	11.52
20.0	9.30	6.98	4.30	3.30	14.11
40.0	13.62	11.56	8.57		17.64

dioxide as shown in Table I and in the plots in Fig. 1.

The gradual decrease of transparency of the front window of the reaction cell by the formation of the oxide of mercury, decreases the rate of production of carbon monoxide (i. e., the rate of decomposition of carbon dioxide) with the increase of irradiation time t. Therefore, the initial rate r_0 was obtained by extrapolation to $t=0$ assuming the formula

$$r=r_0+at+bt^2$$

where the constants a and b depend on the pressure of carbon dioxide.

The initial rates for various pressures are given in Table I (last column) and the plots in Fig. 2.

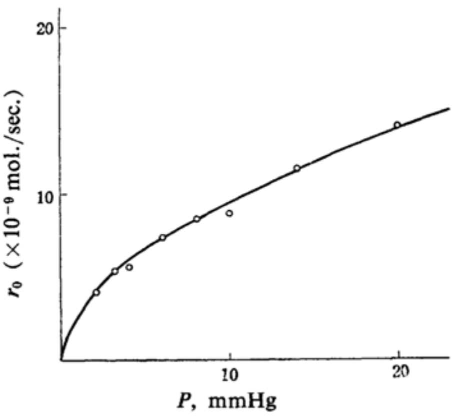

Fig. 2. The initial rate of carbon monoxide in photosensitisation.

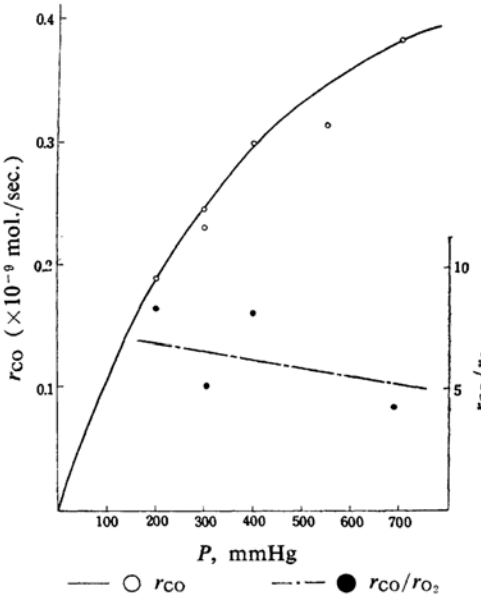

Fig. 3. The results of direct photolysis of carbon dioxide by 1849 Å.

TABLE II. THE RESULTS OF DIRECT PHOTOLYSIS OF CARBON DIOXIDE BY 1849 Å

Pressure	Rate ($\times 10^{-9}$mol./sec.)		
mmHg	r_{CO}	r_{O_2}	r_{CO}/r_{O_2}
200	0.189	0.027	7.0
300	0.229	0.044	5.2
	0.245	0.013	18.8*
400	0.299	0.042	7.1
550	0.312	0.009	34.6*
700	0.383	0.090	4.3

* The reaction cell was flamed and pumped before introduction of carbon dioxide.

Direct Photolysis. — The products, non-condensable in liquid nitrogen, were oxygen and carbon monoxide in a ratio around 1 : 5, which is far from the stoichiometric ratio of 1 : 2. No solid deposit was found on the front window of the reaction cell. The results are shown in Table II and in Fig. 3. It will be seen from the data in Table II that the rate of oxygen formation was markedly reduced when the reaction cell was flamed in pumping before a run.

Discussion

In the case of direct photolysis, the deficiency of oxygen produced is greatly affected by the flaming in pumping. Therefore this deficiency of oxygen could be explained by assuming the wall reaction

$$\mathrm{O}+\mathrm{O}+\mathrm{Wall} \rightarrow \mathrm{O_2}\ (\mathrm{Wall})$$

In the investigation of photodecomposition of carbon dioxide by the resonance radiation from the xenon lamp, Wijnen⁵⁾ and Tanaka⁶⁾ observed that oxygen and carbon monoxide were obtained in the ratio 1 : 9 at room temperature and 1 : 3 at 300°C. This increase of oxygen production at a higher temperature can be explained by the decrease of oxygen adsorbed (or absorbed) on the wall of the reaction cell.

Some of the deficiency of oxygen may be the result of the formation of ozone by the reaction

$$\mathrm{O_2}+\mathrm{O}+\mathrm{M} \rightarrow \mathrm{O_3}+\mathrm{M}$$

Mahan⁷⁾ observed that ozone was formed in his experiment of the photodecomposition of carbon dioxide by the xenon lamp. Since ozone absorbs the resonance line at 2537 Å and is then decomposed, the deficiency of oxygen can not be explained entirely by the formation of ozone.

In the photosensitized decomposition, no oxygen was detected and the oxide of mercury was deposited on the window of the cell. Therefore, the possible reactions which will form the oxide of mercury may be as follows:

a) $\mathrm{CO_2}+\mathrm{Hg}^*(6^1P_1) \rightarrow \mathrm{CO}+\mathrm{HgO}$

or

b)
$$\begin{array}{ll} \mathrm{CO_2}+\mathrm{Hg}^*(6^1P_1) & \rightarrow \mathrm{CO_2}^*+\mathrm{Hg}(^1S_0) \\ \mathrm{CO_2}^* & \rightarrow \mathrm{CO_2}+h\nu \\ \mathrm{CO_2}^* & \rightarrow \mathrm{CO}+\mathrm{O} \\ \mathrm{O}+\mathrm{Hg}+\mathrm{M} & \rightarrow \mathrm{HgO}+\mathrm{M} \\ \mathrm{O}+\mathrm{O}+\mathrm{Wall} & \rightarrow \mathrm{O_2}\ (\mathrm{Wall}) \end{array}$$

Callear, Patrick and Robb⁸⁾ suggested that the oxide of mercury was formed in the mercury photosensitized reaction of oxygen by the following

$$\mathrm{O_3}+\mathrm{Hg}^* \rightarrow \mathrm{O_2}+\mathrm{HgO}$$

In the present investigation, however, it is unlikely that the oxide of mercury was formed by the above reaction, since the concentration of oxygen in the reaction cell was very low.

The approximate value of the quenching cross section (σ^2) of carbon dioxide for excited mercury atoms $\mathrm{Hg}^*(6^1P_1)$ may be obtained by assuming that the rate of production of the carbon monoxide is equal to the rate of decomposition and to the rate of the quenching reaction of excited mercury atoms by carbon dioxide. From this view point, the mechanism is assumed to be the following:

$$\begin{array}{lll} \mathrm{Hg}+h\nu & \rightarrow \mathrm{Hg}^*(6^1P_1) & I_{\mathrm{abs}} \\ \mathrm{Hg}^*(6^1P_1) & \rightarrow \mathrm{Hg}+h\nu & k_1 \\ \mathrm{Hg}^*(6^1P_1)+\mathrm{CO_2} & \rightarrow \mathrm{CO}+\mathrm{HgO} & \\ \quad\text{or} & \rightarrow \mathrm{Hg}+\mathrm{CO}+\mathrm{O} & k_2 \end{array}$$

Thus the relation between the initial rate of production of carbon monoxide and the pressure of carbon dioxide will be written as

$$1/r_0=1/I_{\mathrm{abs}}+k_1/I_{\mathrm{abs}}k_2P \qquad (1)$$

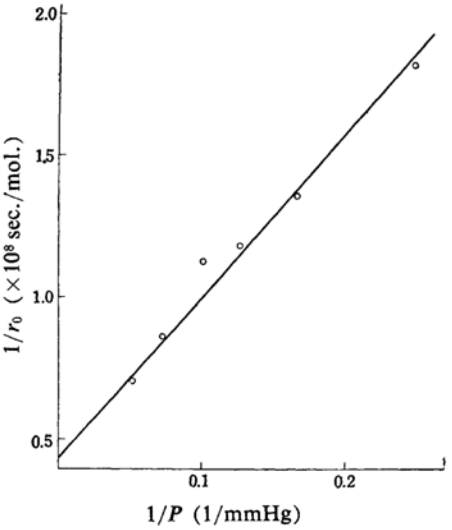

Fig. 4. The plots of $1/r_0$ against $1/P$.

where r_0 is the initial rate of production of carbon monoxide and P is pressure of carbon dioxide. The plots of $1/r_0$ against $1/P$ is linear as shown in Fig. 4. Therefore, utilizing Eq. 1 and from the result shown in Fig. 4, it was found that $\sigma^2=320$ or 64 Å^2 according to whether the life time of excited mercury atom, $\mathrm{Hg}^*(6^1P_1)$, is 0.3×10^{-9} or 1.6×10^{-9} sec.⁹⁾

It will be difficult to determine the correct value of the quenching cross section even if the exact life time of the excited mercury atom is given. The value of the apparent quenching cross section calculated by Eq. 1 will be smaller than the correct one when other quenching reactions which do not form carbon monoxide are not negligible. Another

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5) M. H. J. Wijnen, ibid., **24**, 851 (1956).

6) Unpublished data.

7) B. H. Mahan, *J. Chem. Phys.*, **33**, 959 (1960).

8) A. B. Callear, C. R. Patrick and J. C. Robb, *Trans. Faraday Soc.*, **55**, 280 (1959).

9) A. C. G. Mitchel and M. W. Zemansky, "Resonance Radiation and Excited Atoms", The McMillan Co., New York (1934).

difficulty will be in the uncertainty in the effective life time of excited mercury atom due to reabsorption of the resonance radiation of 1849 Å. The resonance radiation emitted by an excited mercury atom will be absorbed by another mercury atom in the ground state, with some probability. This leads to an increase of the effective life time of the excited mercury atom and to an increase in the apparent quenching cross section.

However, it is possible to think that the quenching cross section of carbon dioxide for $Hg^*(6^1P_1)$ is larger than 2.48 Å^2 for $Hg^*(6^3P_1)$[10].

This is supported by the consideration that the attractive interaction between the excited mercury atom $Hg^*(6^1P_1)$ and carbon dioxide is stronger than that between $Hg^*(^3P_1)$ and carbon dioxide. The lower excited singlet states of carbon dioxide have higher energies than $Hg^*(6^1P_1)$[11]. The lowering of the energies of the excited states of mercury atom due to the induced dipole-dipole interaction at large intermolecular distance is written

$$\Delta E_k = \sum_j W(\mu_k \cdot \mu_j)/E_k - E_j$$

where E_k is the energy of the excited state k of the mercury atom, E_j is the energy of the excited state j of carbon dioxide and $W(\mu_k \cdot \mu_j)$ is the interaction energy between transition moment of the mercury atom μ_k and that of carbon dioxide μ_j. Therefore, this induced dipole-dipole interaction has a much stronger effect for $Hg^*(6^1P_1)$ than for $Hg^*(6^3P_1)$ because of their energies and transition moments. In a similar consideration the charge transfer interaction is more effective in $Hg^*(6^1P_1)$ since the energy difference between $Hg^*(6^1P_1)$ and the charge transfer state is smaller than in the case of $Hg^*(6^3P_1)$.

Summary

The photosensitized decomposition of carbon dioxide by $Hg^*(6^1P_1)$ and the direct photolysis by 1849 Å was investigated by the static method.

The product in photosensitization was carbon monoxide and no oxygen was detected. The deficiency of oxygen in the product may be due to the formation of an oxide of mercury which was deposited on the front window of the reaction cell.

In photolysis of carbon dioxide, carbon monoxide and oxygen were produced in the ratio around 5 : 1. The deficiency of oxygen may be due to the wall effect and partly due to the formation of ozone.

The apparent quenching cross section was obtained by assuming a simple mechanism. The large value of the apparent quanching cross section of $Hg^*(6^1P_1)$ is discussed from the point of view of intermolecular interaction between the excited mercury atom and carbon dioxide in the ground state.

The author is greatly indebted to Professor Ikuzo Tanaka for his continuous encouragement and discussions.

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[10] M. W. Zemansky, *Phys. Rev.*, 36, 919 (1930).

[11] R. S. Mulliken, *Can. J. Chem.*, 36, 10 (1958).