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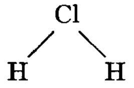
transition state. A bent configuration, on the other hand, would have a much higher transmission coefficient. It is quite obvious that if the bond angle in a bent



transition state is decreased, the hydrogen atoms approach each other, producing an increased interaction. The bending frequency will consequently increase to give a value of α greater than unity. This, together with a smaller I_{H_2Cl}/I_{HClH} ratio, will then largely balance the value of K_3/K_5, i.e., the resulting transmission coefficients K_3 and K_5 will be of the same order of magnitude.

The above considerations show that only a linear H–Cl–H transition state gives an unusually low transmission coefficient and that a more realistic bent configuration can account for the observed rate ratios by the absolute reaction rate theory, without the assumption of a low transmission coefficient for the H+ClH exchange reaction.

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Reactions of ${}^1D$ Oxygen Atoms in the Photolysis of Carbon Dioxide. II.*

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(Received 30 July 1964)

The vacuum-uv photolysis of CO_2 containing initially no oxygen was investigated in a closed system and the quantum yields of ozone and oxygen determined. The quantum yield for ozone production was found to be below $Q(O_3) \leq 0.03$, which is insufficient to explain the oxygen deficiency observed in the O_2 quantum yields. The $[O_2]/[CO]$ ratio was found to depend on the light intensity, on the time interval after which an irradiated sample was subjected to analysis, and on the ratio of carbon dioxide to admixed rare gas concentration. The results concerning the $[O_2]/[CO]$ ratio can be explained by the formation of CO_3 due to the attachment of ${}^1D$ oxygen atoms to CO_2. This reaction is in competition with the third-body recombination of ${}^1D$ oxygen atoms.

INTRODUCTION

CARBON monoxide and oxygen are well-established products arising from the photodecomposition of CO_2 in the 1200–1700-Å wavelength region.[1–3] Carbon monoxide formation is known to proceed with a quantum yield of unity[4]—in accordance with the view that photodissociation constitutes the major primary process[5]—but the O_2 quantum yield appears to be a variable depending on the imposed experimental conditions. If the O_2 quantum yield is expressed in terms of the ratio $R = [O_2]/[CO]$, the data obtained by Mahan[2] and before him by Wijnen[3] show this ratio to be in the vicinity of $R = 0.1$, while Schiff[6] and the present author[1] found $R = 0.3$. It is significant that the reported $[O_2]/[CO]$ ratios are much smaller than the theoretical value $R = 0.5$ which should be expected if oxygen and carbon monoxide were the sole products. The existing lack of material balance obviously points to the evolution of one or more additional products and two suggestions have been made in this respect: (a) that ozone is a product, and (b) that the formation of CO_3 should be considered. Evidence for formation of ozone was obtained by Mahan, but no quantitative data were taken. The flow experiments described in I showed ozone production to be negligible when pure CO_2 was employed, although appreciable quantities of ozone were observed when oxygen was present in small amounts. The suggestion of CO_3 formation, on the other hand, was advanced by Dainton[7] on account of photolysis experiments undertaken in comparison with the radiolysis of CO_2. While the radiolysis experiments gave a material balance with ozone and oxygen as products, an oxygen deficiency was observed in the photolysis of CO_2 with ozone being conspicuously absent. The difference in behavior in the two types of experiments is

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* This work supported by National Aeronautics and Space Administration under Contract NASw–840.

[1] P. Warneck, Discussions Faraday Soc. (to be published) (subsequently denoted as I).

[2] B. H. Mahan, J. Chem. Phys. **33,** 959 (1960).

[3] M. H. J. Wijnen, J. Chem. Phys. **24,** 851 (1956).

[4] The slight deviation at higher pressures observed with 1470-Å radiation is disregarded in this paper.

[5] W. Groth, Z. Physik. Chem. **B37,** 307 (1937).

[6] H. I. Schiff (private communication).

[7] F. S. Dainton, Discussions Faraday Soc. (to be published).

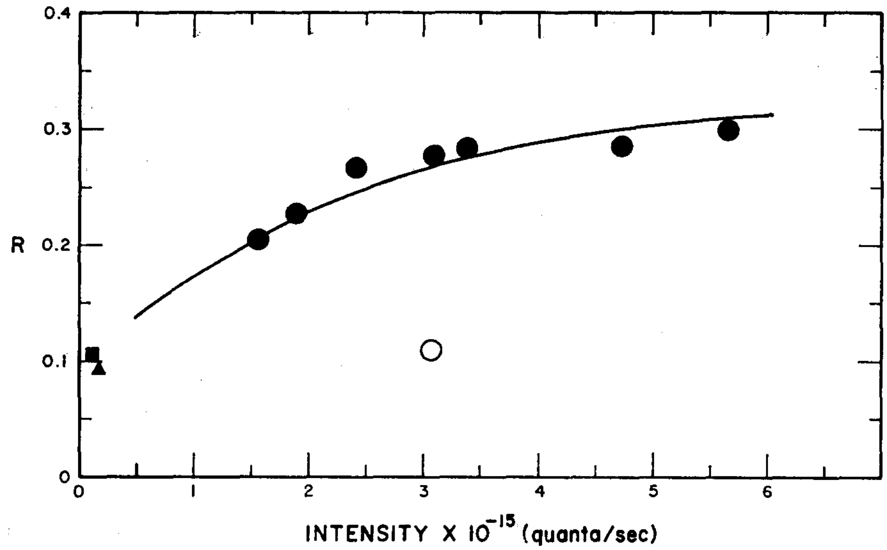

FIG. 1. Variation of $R=[O_2]/[CO]$ with light intensity at atmospheric pressure, ●— present data (H_2 lamp); ■—Wijnen (1470 Å); ▲—Mahan (1470 Å); ○—Mahan (1236 Å).

explained on the basis that the oxygen atoms produced in the radiation chemical case are in the ^3P ground state, whereas the photolysis of CO_2 produces oxygen atoms in the metastable ^1D state.

In view of this situation, then, there arose the need to reinvestigate the extent of ozone formation in the vacuum-uv photolysis of CO_2 and to study the $[O_2]/[CO]$ ratio as a function of various experimental parameters. In the present work the amount of ozone formation was found insufficient to account for the oxygen deficiency reflected in the O_2 quantum yields. The $[O_2]/[CO]$ ratio was determined to depend on the light intensity, on the time interval after which an irradiated sample was subjected to analysis, and on the ratio of carbon dioxide to admixed rare-gas concentration. The results are shown to be consistent with the assumption that an unstable addition compound, namely CO_3, is formed by attachment of ^1D oxygen atoms to carbon dioxide.

EXPERIMENTAL RESULTS

The experimental arrangement has been described in I. The present experiments were carried out employing the closed system in conjunction with the hydrogen light source, the radiation being passed through a BaF_2 window. The amount of CO formation was utilized as an internal actinometer. As before, the gas was circulated by means of a rotating stirrer in order to avoid product accumulation in the vicinity of the window. Samples were analyzed mass spectrometrically using the procedure previously outlined. The purification of CO_2 has also been described.

A. Ozone Formation

Ozone appeared to be one of the conceivable products. In order to determine the extent of ozone formation in the experiments employing the closed system, a number of runs were performed after which the irradiated gas was swept into a 2% potassium iodide solution using helium as a carrier gas. Typically in these experiments the gas was irradiated with an intensity of about 3×10^{15} quanta/sec over a period of 15 min. No indication for iodine formation could be obtained under these conditions even using starch as an indicator. An upper limit to the ozone quantum yield can be placed at $Q(O_3)\leq0.03$ on the basis of comparison experiments in which a flow of oxygen was irradiated with known light intensity. This agrees with the results obtained earlier in the flow system and also with the findings reported by Dainton.[7] It is also evident that ozone formation cannot account for the observed oxygen deficiency, so that the formation of CO_3 appears to provide the most promising alternative explanation. Although in the present work it has not been possible to detect CO_3 analytically, it will be shown subsequently that the behavior of the $[O_2]/[CO]$ ratio is consistent with the hypothesis of CO_3 formation.

B. Variation of *R* with Light Intensity

The discrepancy among the $[O_2]/[CO]$ ratios found in several independent investigations led to the belief that R is a function of the light intensity, and this has been substantiated in experiments carried out at atmospheric pressure. Figure 1 shows the results for a series of runs in which the irradiation period was ten minutes. Also entered in this figure are values derived from the data by Mahan[2] and by Wijnen.[3] Their results for 1470-Å radiation can be seen to fit into an extrapolation of the present data, but the value derived for 1236-Å krypton radiation appears to be too low. The reason for this discrepancy is not apparent. The general behavior exhibited by R in Fig. 1 is characteristic of photochemical systems in which a radical recombination reaction occurs in competition with another reaction, its rate involving the radical concentration in a linear fashion. Accordingly, since oxygen atoms are the known intermediates in the photolysis of CO_2, the observed intensity dependence of R can be taken as evidence that a significant portion of the evolved O_2 is formed by way of atom recombination.

C. Time Dependence of *R*

In the course of the present experiments it was noticed that the $[O_2]/[CO]$ ratio increased whenever the irradiation of a sample was not immediately followed up by analysis. This led to an investigation of the time dependence of R which is shown in Fig. 2. As usual, CO_2 was photolyzed for 10 min, but the irradiated gas was kept in the reactor for additional periods of time after the light source had been switched off. As Fig. 2 demonstrates, the $[O_2]/[CO]$ ratio steadily increases with time until a value of $R=0.42$ is reached after 60 min. This is already close to the theoretical value of $R=0.5$, indicating that an unstable product (presumably CO_3) is formed releasing oxygen in the process of decomposition. In an attempt to isolate this product a sample of irradiated CO_2 was subjected to dry-ice temperature. No conspicuous deposit occurred. After pumping off the volatile components, the dry-ice–acetone bath was removed and sufficient time allowed for the decomposition of any remaining unstable material. No oxygen and only negligible amounts of CO_2 could be detected in a subsequent mass spectrometric analysis.

D. Effect of Added Rare Gas

Support for the occurrence of a reaction between oxygen atoms (in the ^1D state) and CO_2 has come from a series of irradiation experiments in which helium was added as an inert constituent. Helium, the lightest of the rare gases, was used in preference to others in order to avoid a large-scale deactivation of the metastable excited oxygen atoms. The only activity that helium can enter is to aid oxygen-atom recombination as a third body, while the reaction of oxygen atoms with CO_2 remains uninfluenced. With both reactions in competition, a large excess of helium is expected to promote the recombination reaction relative to that of carbon dioxide. Correspondingly, the $[O_2]/[CO]$ ratio is expected to increase. In the present experiments the CO_2 partial pressure was kept at 22 mm Hg so that the amount of light deposition within a certain volume of the reactor was not subject to variation. Owing to the low-absorption cross section of CO_2 at the applied wavelengths, the penetration of radiation under these conditions is appreciable, a depth of 14 cm being reached at the point where 90% of the incident radiation is absorbed. After addition of various amounts of helium, the mixtures were irradiated for 15 or 20 min with approximately constant light intensity. The measured $[O_2]/[CO]$ ratios are shown in Fig. 3 in a plot versus $[He]/[CO_2]$. The data reveal indeed an increase of R with increasing helium concentration, thus strengthening the arguments advocating CO_3 formation. It is interesting to note that previously no pressure effect was observed in experiments employing pure CO_2. This is again in accord with the suggested mechanism of two competing reactions, since in this case CO_2 is also functioning as the acting third body in the recombination reaction. Accordingly, it appears that the assumption of CO_3 being a product besides O_2 and CO can account for all the facts associated with CO_2 photolysis, and this is reflected also in the analytical treatment of the results in the next section.

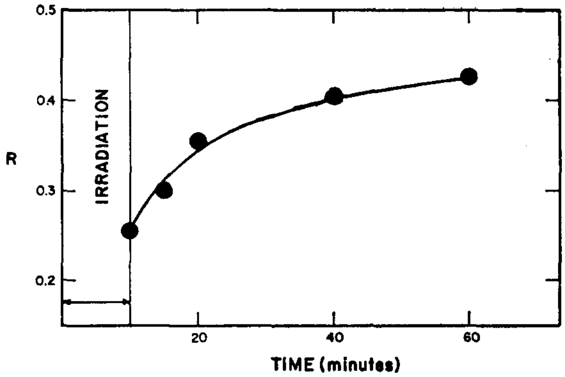

FIG. 2. Time dependence of $R=[O_2]/[CO]$ after irradiation; atmospheric pressure of CO_2; light intensity about 3×10^{15} quanta/sec.

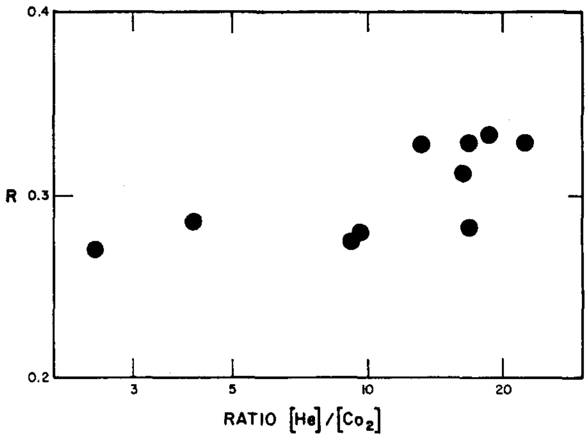

FIG. 3. Dependence of $R=[O_2]/[CO]$ on the ratio of admixed helium to carbon dioxide concentration. Carbon dioxide pressure 22 mm Hg. Effective light intensity about 1×10^{15} quanta/sec.

DISCUSSION

In discussing the results it should be kept in mind that the oxygen atoms produced by photodissociation of carbon dioxide are in the excited metastable ^1D state and that, in the present system, collisional deactivation is relatively unimportant. Katakis and Taube[8] have shown that ^1D oxygen atoms undergo an exchange reaction with CO_2 while oxygen atoms in the ^3P ground state do not. This difference in chemical behavior can account for the formation of CO_3 in the case that ^1D oxygen atoms are involved. In fact, Katakis and Taube postulated CO_3 as an intermediate in the observed isotope exchange.

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[8] D. Katakis and H. Taube, J. Chem. Phys. **36**, 416 (1962).

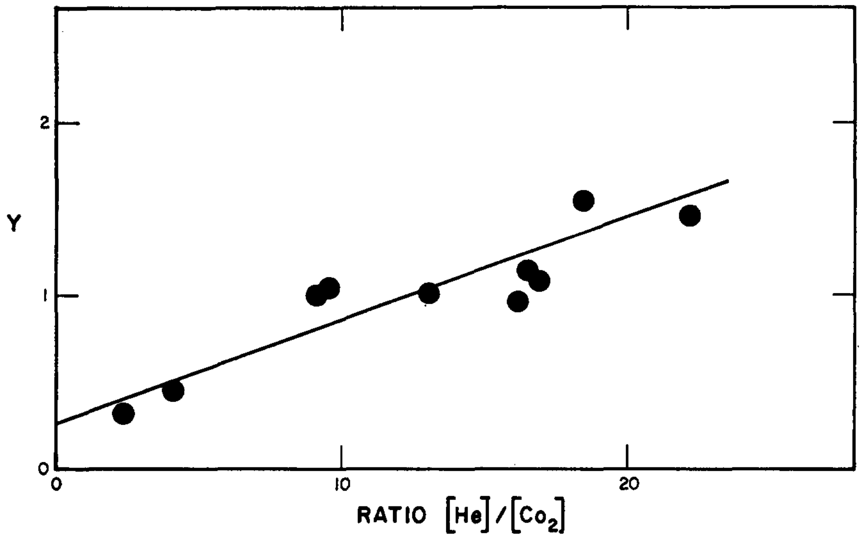

FIG. 4. Plot of Y (see text) versus $[He]/[CO_2]$ making use of the data shown in Fig. 3.

Accordingly, the present results can be interpreted in terms of the following simple mechanism involving oxygen in the metastable ^1D state

$$CO_2 \xrightarrow{h\nu} CO+O,$$

$$2O+CO_2 \xrightarrow{k_1} O_2+CO_2,$$

$$2O+He \xrightarrow{\epsilon k_1} O_2+He,$$

$$O+CO_2 \xrightarrow{k_2} CO_3,$$

$$CO_3 \xrightarrow{k_3} CO_2+\tfrac{1}{2}O_2.$$

The thermal decomposition of CO_3 is here assumed to follow first-order kinetics. From the data shown in Fig. 2, the room-temperature rate constant can be estimated to be $k=5\times10^{-4}\ \mathrm{sec}^{-1}$, which is sufficiently small to make this reaction negligible for irradiation times below about 10 min. For irradiation periods up to 20 min, as they were used in the experiments with helium admixture, the effect of the decomposition reaction can be taken into account by corrective terms. The assumption that steady-state conditions are applicable for oxygen atoms leads to the following set of equations:

$$[CO_3]=(k_2/k_3)[O][CO_2][1-\exp(-k_3t)],$$

$$\frac{[O_2]}{[CO_3]}=\frac{k_1[O][CO_2](1+\epsilon[He]/[CO_2])+0.5k_3[CO_3]}{(k_2[O][CO_2]-k_3[CO_3])},$$

$$I/V=2k_1[O]^2[CO_2](1+\epsilon[He]/[CO_2])+k_2[O][CO_2].$$

Here, I is the applied radiation intensity deposited within the volume V and ϵ is the efficiency of helium as a third body compared with CO_2. Also, by virtue of the mass balance relation and $R=[O_2]/[CO]$:

$$[O_2]/[CO_3]=[R/(1-2R)].$$

The use of these four equations makes it possible to express R as a function of the light intensity, and of the helium and carbon dioxide ratio, in the following way

$$Y=\left(\frac{1-R}{1-2R}\right)e^{-k_3t}\left(2\frac{1-R}{1-2R}e^{-k_3t}-1\right)$$

$$=\frac{k_1I}{k_2^2V[CO_2]}\left(1+\frac{\epsilon[He]}{[CO_2]}\right).$$

A treatment of the data obtained in the experiments with helium admixture in terms of this last equation is shown in Fig. 4. Correcting for the slight variations of the light intensity, the points can be seen to fall on a straight line when Y is plotted versus the $[He]/[CO_2]$ ratio. From the slope of the line and the intercept with the ordinate one obtains $\epsilon=0.24$, i.e., the third-body efficiency of carbon dioxide for oxygen-atom recombination is found to be about four times that of helium.

The data shown in Fig. 4 can also be evaluated with respect to k_1/k_2^2 if the reaction volume V is approximately known. In the series of experiments having helium admixed, the reaction volume was estimated from the depth at which 90% of the radiation had been absorbed and from the known diameter of the reactor (2 cm). The resulting volume $V=43$ cc leads to value of $k_1/k_2^2=7.8\times10^3$ sec. Furthermore, an estimate of k_2 can be obtained if it is assumed that the rate constant associated with the recombination of ^1D oxygen atoms is similar in magnitude to the one governing the recombination of ^3P ground-state oxygen atoms. This latter rate constant and the associated third-body efficiencies have been determined by Reeves *et al.*,[9] and by Morgan and Schiff,[10] establishing $k_1(^3P)=4.2\times10^{-33}\ \mathrm{cc^2/molecule^2\cdot sec}$ for CO_2 as the acting third body. Accordingly, if one can set $k_1(^1D)\approx k_1(^3P)$, the rate constant for CO_3 formation is estimated to be $k_2\approx7\times$

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[9] R. R. Reeves, G. Manella, and P. Harteck, J. Chem. Phys. **32**, 632 (1960).

[10] J. E. Morgan and H. I. Schiff, J. Chem. Phys. **38**, 1495 (1963).

10^{-19} cc/molecule·sec. It should be noted that due to the square relationship between the two rate constants the uncertainty concerning $k_1(^1D)$ results in an uncertainty of k_2 of only half that value.

The results obtained for the intensity variation of R (Fig. 1) can be subjected to a similar treatment. An approximately linear relationship is obtained for Y as a function of intensity, with a slope of 2.6×10^{-16}. From the reactor geometry in the vicinity of the window, the effective reaction volume is estimated to be $V=1$ cc, resulting in $k_1/k_2^2=6.5\times10^3$. This is in good agreement with the above derived value, indicating that the employed mechanism can correctly describe the available data.

In view of the over-all results presented in this paper, it can now be concluded that the oxygen deficiency observed in the photolysis of CO_2 can indeed be explained by the formation of CO_3—owing to the attachment of ^1D oxygen atoms to CO_2—but not by the assumption of ozone formation. However, specific proof for the existence of CO_3 by means of its detection is presently still lacking. Since it had been found by Katakis and Taube that ground-state oxygen atoms are unreactive with respect to carbon dioxide, the present results can again serve to demonstrate that the oxygen atoms resulting from CO_2 photodissociation are in the metastable ^1D state, and that in this chemical system they persist long enough to react.

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Intermolecular Forces: The Triangle Well and Some Comparisons with the Square Well and Lennard-Jones*†

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(Received 15 June 1964)

Extending the methods of Kihara and of Alder and Pople for B_3 and using a machine procedure for B_4, we have calculated the virial coefficients for a potential with a hard core and a linear, finite attractive well. A comparison of these results with the SW and LJ potentials reveals distinctions which become more marked as one goes to higher coefficients. For B_3 the TW is systematically closer to the LJ and this result is interpreted by analysis of the contributions made to B_3 by collision situations ranging from three particles in the attractive well to three in the repulsive field. A nonzero force is seen to be necessary if the detailed behavior of B_3 is expected. For B_4 larger differences were noted and the so-called "area rule" was not obeyed even approximately, in contrast to B_3. The critical constants were computed by truncating the series at B_4, and the results compared to those for a SW and a LJ.

1. INTRODUCTION

THE first few virial coefficients have been calculated for a wide variety of potential models. Commonly, it is asserted that the second virial coefficient B_2 is not especially sensitive to the detailed shape of the potential, and to support this view attention is drawn to the reasonable correspondence with experiment which can be achieved without undue labor for such simple models as the Sutherland, square-well, and bireciprocal potentials.[1]

More elaborate models have also been employed especially for B_2, and these include the exponential-six,[2] Morse,[3] Rydberg,[4] and spherical-shell[5] potentials. Recently, however, Munn,[6] elaborating the earlier efforts of Guggenheim and McGlashan,[7] has shown that a detailed analysis of the fields for the noble gases reveals that the "best" two-body potential has no simple analytical representation.

In the face of this it might be reasonable to inquire into the reasons for studying still another model potential, especially one of somewhat simplified form. The principal reason lies in the expectation that a simple analytical form permits more elaborate exact calcula-

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† A portion of the work reported here was performed at the University of Michigan and was taken in part from a thesis submitted by M. J. Feinberg in July 1963 in partial fulfillment of the requirements for the degree of Doctor of Philosophy at that institution.

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