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Reaction Rate Measurements of $O({}^{3}P)$ Atoms by Resonance Fluorescence.* II $O({}^{3}P) + CO + M \rightarrow CO_{2} + M$; M = He, Ar, N₂

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Absolute rate constants for the reaction $O({}^{3}P)+CO+M\rightarrow CO_{2}+M$ have been determined at 300°K for M = He, Ar, and N₂, using oxygen resonance radiation as a probe to monitor the relative atom concentration during decay time measurements. The rate constants are, in units of cm⁶ molecules⁻²·second⁻¹, $k_{He} = 6 \pm 1.5 \times 10^{-36}$, $k_{Ar} = 7 \pm 3.5 \times 10^{-36}$, and $k_{N2} = 1.4 \pm 0.4 \times 10^{-35}$. The O(³P) is produced by O₂ photodisociation at 1470 Å, at which wavelength O(¹D) is also formed. The observations indicate that the O(¹D) – CO interaction results in O(¹D) deactivation to O(³P), not CO₂ formation.

INTRODUCTION

The three-body reaction $O(^{3}P) + CO + M \rightarrow CO_{2} + M$ has been the subject of considerable controversy for many years. Uncertainties about its temperature dependence and orders-of-magnitude discrepancies between various investigations of its reaction rate are still prevalent,¹ and it is not clear whether the data are more reliable now than 10 or 20 years ago. Obviously, the reaction can be of great importance in combustion processes, and a new and critical need for accurate data has arisen recently when it was ascertained that the atmospheres of Mars and Venus consist principally of CO_2 . There is no reason to expect CO_2 to be stable to solar uv radiation; its dissociation has been extensively studied in the laboratory, and it is expected to produce CO and O atoms in the planetary atmospheres. Since measurements of these two species by planetary probes and ground-based spectrometry indicate their concentrations to be very low, there appears to be an efficient recombination mechanism for O and CO, and a reliable rate for the three-body reaction is needed to determine its possible importance.

Measurements of the three-body rate at room temperature are sparse. Kaufman² and Clyne and Thrush³ set upper limits, which are, respectively, 1.4×10^{-33} and 8×10^{-35} cm⁶ molecules⁻² · sec⁻¹. Early work by Groth⁴ indicated that the rate is 1/40 as fast as the rate of $O+O_2+M\rightarrow O_3+M$, but present knowledge of the complexities that can arise in the system he used would make this value questionable, although it turns out to be in excellent agreement with the authors' results. Recent work by Kondratiev⁵ gives a value of $10^{-35.5\pm0.3} \times$ $\exp(2980\pm 660)/RT$ cm⁶ molecules⁻² · sec⁻¹ for M = CO₂, in contrast to the positive activation energy suggested in the review by Baulch.¹ An even more recent presentation by Kondratiev⁶ suggests a value of $10^{-34.69\pm0.60} \times$ $\exp(2610\pm 860)/RT \text{ cm}^{6} \text{ molecules}^{-2} \cdot \sec^{-1} \text{ for } M = O_{2}$ a rate more than twice as fast as that of $O+2O_2 \rightarrow$ $O_3 + O_2$.

It may be seen that there is an urgent need for a new approach to the problem. A resonance fluorescence technique for monitoring $O({}^{3}P)$ atoms has been developed by the authors (see Part I of this paper)⁷ and it

has been shown to give accurate results for the rate of the well-studied reaction $O+O_2+M\rightarrow O_3+M$. In the present work, the measurements have been extended to the O+CO+M reaction, for M=He, Ar, and N_2 .

EXPERIMENTAL

The general experimental technique has been discussed in the preceding paper but in essence the apparatus consists of a reaction cell, a pulsed 1470-Å lamp that photodissociates O_2 , an oxygen resonance lamp, the light from which is scattered by $O({}^{3}P)$ atoms into a solar blind photomultiplier, and a signal integration unit that adds the $O({}^{3}P)$ decay curves after each pulse.

The handling of CO presents some particular problems, as it has been determined previously that measurements of $O({}^{3}P)$ become quite difficult in the presence of CO. When NO₂ chemiluminescence was used as a monitor of $O({}^{3}P)$, addition of CO caused an irreversible loss of intensity of the NO₂ afterglow, i.e., when the CO was turned off the light did not come back.⁸ Extensive treatment of the cell walls with an air or O₂ discharge brought some recovery, but it was often necessary to wash the cell with soap and water. The most likely explanation is that a sequence of steps such as the following results in C₃O₂ polymer formation on the walls,⁹ which greatly increases the efficiency of atom removal, γ , at the walls:

$$h\nu$$

$$CO \rightarrow CO^{*}(d \ ^{3}\Delta, e \ ^{3}\Sigma^{+}, a' \ ^{3}\Sigma^{+}),$$

$$CO^{*} \rightarrow CO(a \ ^{3}\Pi) + h\nu,$$

$$CO(a \ ^{3}\Pi) + CO \rightarrow C_{2}O + O,$$

$$C_{2}O + CO + M \rightarrow C_{3}O_{2},$$
walls
$$C_{3}O_{2} \longrightarrow polymer.$$

Initially, the same sort of behavior was observed in the present system. The possibility that it might be related to an impurity in the CO was considered, but trapping by liquid N_2 did not alleviate the problem. A typical analysis of the Matheson C.P.-grade CO(>99.5%) is

shown in Table I; the dimethyl ether and iron carbonyl are expected to be completely removed by liquid nitrogen. It was eventually discovered that by working at high buffer gas pressure (>25 torr) and by permitting a certain increase in the γ of the walls to occur, a stable condition was reached under which O(³P) decay rates could be measured. For a "clean" system, O(³P) lifetimes in the cell of 0.6 sec were obtained, whereas the stable level after CO treatment was 0.2 sec (after severe CO contamination values of 40 msec were found, requiring air discharge cleaning of the walls).

The necessary data for the evaluation of the rate constants are measurements of $O({}^{3}P)$ decay rates as a function of CO. Unfortunately, the reaction is so slow that it was necessary to measure quite small differences in the $O(^{3}P)$ lifetimes, and this was difficult to do because the cell walls still exhibited some instability. It was undesirable to use excessive CO pressures, for fear of the effect on the walls, and total pressures greater than 200 torr were not used because of the pumping characteristics of the system. To measure the small $O(^{3}P)$ decay rate changes, it was felt that it was better to measure the decay rate repetitively at extreme CO pressures, typically 0 CO and 1.0 torr CO, and make the assumption that the points in between defined a straight line. A single complete plot (Fig. 1) was made to show that a typical line is straight, and subsequently only measurements at CO extremes were made and averaged.

The CO used was a 10% mixture of CO in He. The addition of 1 torr CO necessitated the addition of 10 torr of the mixture, so for 0 CO measurements the pressure was always balanced by addition of 10 torr He. The effect of this addition was subsequently subtracted when evaluating the reaction rate constants. For all experiments, an O₂ pressure of 0.1 torr was used.

In the presence of CO, the integrated photomultiplier signal, a summation of 300–1000 pulses from the Xe lamp, consisted of two parts, an instantaneous decay and a generally much less intense slow decay. The rapid decay is due to contamination of the Xe lamp with CO, in spite of gettering, which results in emission and resultant scattering in the cell of the CO fourth positive system.^{9,10} This was of no consequence, as the fast decay was simply ignored, its decay time being

TABLE I.	Typical	Matheson	C.Pgrade	CO analysis.
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Impurity	Concentration (ppm)
N_2	900
Dimethyl ether	200
CO_2	80
Ar	18
O_2	15
Fe(CO)5	10
H2, He, NO	not detected (<4)



FIG. 1. τ^{-1} vs [CO]. [He] = 80 torr, [O₂] = 0.1 torr.

equal to the lamp turnoff time of 100 μ sec. Subsequently used pulsed lamps will have a filter chamber that will permit filtering of the CO radiation by flowing CO.

RESULTS AND DISCUSSION

As stated in the previous section, it was found desirable to measure the O(³P) decay rate, τ^{-1} , repetitively at 0 CO and a fixed CO concentration (1.0–1.6 torr), to determine a value for the decay rate per unit CO concentration. In Fig. 1 is shown a complete plot of τ^{-1} vs [CO] at 75 torr He, to demonstrate that the data do fall on a straight line, which is naturally an implicit assumption if the above method is to be used. In Table II the raw data for $M = N_2$ are presented, which are representative of those obtained for M = He and Ar. $\Delta \tau^{-1}$ is the difference between successive measured values of τ^{-1} . An arithmetic average of all the values at each pressure is taken as the most probable value of $\Delta \tau^{-1}$, and the error bars correspond to the standard deviation.

The average values of $\Delta \tau^{-1}/\Delta$ [CO] are plotted in Figs. 2 and 3, with a value of 0.06 and 0.07 sec⁻¹ torr⁻¹ subtracted from the Ar and N₂ data, respectively, to correct for the fact that measurements were made in the presence of 9 and 10 torr He (the CO diluent). The number of measurements taken for each data point is shown on the figures. The reason for the lack of precision in the Ar data compared to He and N₂ is uncertain; the fact that higher Ar pressures could not be used was definitely a hinderance. However, as indicated below, the line drawn through the average Ar points gives a rate constant quite consistent with those for He and N₂.

The $O({}^{3}P)$ decay rate is a measure of all $O({}^{3}P)$ losses in the system and may be expressed as

$$\tau^{-1} = k_1 [CO] [M] + k_2 [CO] + k_3 [L] + L', \qquad (1)$$

where k_1 is the three-body rate, k_2 is a possible two-body rate for the reaction

$$O(^{3}P) + CO \rightarrow CO_{2}$$
(2a)

$$\Box \rightarrow \mathrm{CO}_2^* \rightarrow \mathrm{CO}_2 + h\nu,$$
 (2b)

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FIG. 2. $\Delta \tau^{-1} / \Delta [CO]$ vs [He], $[O_2] = 0.1$ torr, number of measurements for each data point given in parenthesis.

 k_3 is an O(³P) two-body equivalent loss rate with any impurity, and L' includes diffusional losses and the system pumpout time. Measurement of $\Delta \tau^{-1}/\Delta$ [CO] then gives a value for k_1 [M]+ k_2 , and plots of $\Delta \tau^{-1}/\Delta$ [CO] vs [M], as in Figs. 2 and 3, gives lines with slopes of k_1 and intercepts of k_2 . A term proportional to k_3 may also be included in the intercept if one supposes that an O(³P)-consuming impurity is brought in with the CO; the term would have the value ck_3 , where c=[L]/[CO]. As is to be expected, the lines have roughly the same intercept, 0.25–0.4 sec⁻¹ · torr⁻¹. Values of k_1 obtained from the slopes are presented in



FIG. 3. $\Delta \tau^{-1} / \Delta$ [CO] vs [M], [O₂]=0.1 torr, number of measurements for each data point given in parenthesis.

TABLE II. $O({}^{3}P)$ decay rate measurements for $O({}^{3}P) + CO + N_{2} \rightarrow CO_{2} + N_{2}.$

Pressure	-1-+0.00	-1	$\Delta \tau^{-1}$
(torr)	τ at 0 CO	τ ¹ at 1.1 torr CO	(sec +)
29	6. 53 sec ⁻¹		
29		7.35 sec ⁻¹	0.82
29	6.53 sec ⁻¹		0.82
29		7.63 sec ⁻¹	1.10
29	6.53 sec ⁻¹		1.10
47		8.77 sec ⁻¹	
47	8.00 sec^{-1}		0.77
47		9.80 sec ⁻¹	1.80
47	8.07 sec ⁻¹		1.73
47		8.80 sec ⁻¹	0.73
47	7.81 sec ⁻¹		0.99
47		9.34 sec ⁻¹	1.53
47	8.20 sec ⁻¹		1.14
47		9.66 sec ⁻¹	1.46
78		14.93 sec ⁻¹	
78	13.70 sec ⁻¹		1.23
78		15.86 sec ⁻¹	2.16
78	13.88 sec ⁻¹		1.98
78		15.63 sec ^{-1}	1.75
78	14.08 sec ⁻¹		1.55

Table III, with reasonable error limits. If the intercept values correspond to a two-body $O({}^{3}P)$ loss rate involving CO, then it is a very slow reaction, having a maximum rate of 10^{-17} cm³ molecules⁻¹·sec⁻¹. This is three orders of magnitude faster than the known radiative recombination rate (2b),¹ but considerably slower than the supposed two-body rate measured by others (2a).¹

The values obtained for k_1 are the lowest yet observed for this reaction rate constant and as such are the least likely to be influenced by impurities or catalytic effects. The big remaining problem is to satisfactorily determine the activation energy for the reaction, because for combustion processes the rate at higher temperatures is of greater interest, while for the planetary atmospheres, the rate at temperatures of $\sim 200^{\circ}$ K is more important. As stated in the Introduction, it is still not yet clear whether the activation energy is negative or positive. If it is negative, as is the case for other three-body

TABLE III. Reaction rate constants for

	k_1 O(³ P)+CO+M \rightarrow CO ₂ +M		
at 300°K.	<u> </u>		
	М	$k_1 \text{ (cm}^6 \text{ molecules}^{-2} \cdot \text{sec}^{-1})$	
	He	$6 \pm 1.5 \times 10^{-36}$	
	Ar	$7\pm3.5\times10^{-36}$	
	N_2	$1.4{\pm}0.4{ imes}10^{-35}$	

reactions involving $O(^{3}P)$ atoms and triatomic products, such as $O+O_2+M$ and O+NO+M, and is of the magnitude of 2.8 kcal suggested by Kondratiev,^{5,6} it may play a role in CO₂ recombination in the Mars and Venus atmospheres.

A value for the rate constant for $O + CO + CO_2 \rightarrow 2CO_2$ can be deduced from the relative efficiencies of He, Ar, and N_2 as third bodies, which are in the ratio of 1:1.2: 2.3. A comparison with the $O+NO+M \rightarrow NO_2+M$ reaction,¹¹ which might be expected to have similar mechanics, shows ratios of 1:1.2:1.9. For the latter reaction, the ratio $k_{\rm CO_2}/k_{\rm N_2}$ is 1.4, and application of this ratio to the O+CO+M reaction gives a rate constant for M is CO₂ of $2.0\pm0.4\times10^{-35}$ cm⁶ molecules⁻²·sec⁻¹. For the Mars atmosphere suggested by McElroy,¹² the temperature in the 0-80-km altitude range is on the order of 150-200°K. For a 2.8-kcal negative activation energy the three-body rate constant in this temperature range would then be about 10⁻³³ cm^6 molecules⁻²·sec⁻¹ for M is CO₂, and the reaction would be more important in the stabilization of the CO₂ atmosphere than has previously been assumed.^{13,14}

A point of considerable interest is that these experiments have demonstrated the effect of the interaction of $O(^{1}D)$ and CO. In an earlier paper⁷ we indicated that it seemed likely that the interaction was reactive, forming CO_2 in a fast two-body recombination, rather than one involving energy transfer, i.e., $O(^{1}D) + CO \rightarrow$ $O(^{3}P) + CO$. This conclusion was in agreement with experiments of Clerc and Reiffsteck.15 However, CO was for a number of reasons difficult to handle, and our conclusions were necessarily tentative, particularly in view of the fact that recombination seemed an unlikely

TABLE IV. 1304-Å fluorescence intensity (arbitrary units) 47 torr He, 0.1 torr O₂.

0 CO	1.6 torr CO	
 79	71	
86	83	
91	81	
92	82	
Av 87	Av 79	

process. Recently, Paraskevapoulos and Cvetanović¹⁶ have published a paper indicating that the interaction is fast (a comparison of their relative rates with known absolute ones indicates a constant of 1×10^{-10} cm³ molecules⁻¹ · sec⁻¹) and does not lead to CO₂ formation. We are now in a position to agree with them. The Xe lamp used in our experiments photodissociates O₂ to $O(^{1}D) + O(^{3}P)$. The rate constant for $O(^{1}D)$ deactivation by O_2 is almost the same as for CO. Thus, in the experiments done at low He pressure [He is a very ineffective deactivant for $O(^{1}D)$],¹⁶ CO was present in a 16-fold excess over O_2 , and if CO formed CO_2 with $O(^{1}D)$, then the resonance fluorescence intensity with CO present should be only one-half that found with no CO. Table IV shows the observed fluorescence intensities for the data taken at 47 torr He, with corrections made for the increased $O(^{3}P)$ decay rate in the presence of CO. It is seen that CO has only a slight effect on the $O(^{3}P)$ signal, which is entirely accounted for by its weak absorption of the oxygen resonance radiation, and therefore its interaction with $O(^{1}D)$ leads only to $O(^{3}P)$ formation. Measurements of the CO absorption coefficients for the three oxygen lines will be discussed in a subsequent paper.

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