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LABORATORY CO₂ PHOTOLYSIS STUDIES RELATED TO PLANETARY ATMOSPHERES

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ABSTRACT

Three tasks were accomplished on Contract NSR 05-019-252 during 1971:

- The $\text{CO}(a^3\Pi)$ state, the upper state of the Cameron bands, was characterized with respect to its average radiative lifetime and its quenching coefficients for a series of simple molecules. This information is vital for an understanding of the observed emission-versus-altitude profiles of the Cameron bands in the Mars and Venus atmospheres.
- The CO_2 recombination reaction $[\text{O}(^3\text{P}) + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M}]$ was studied as a function of temperature. For $\text{M} = \text{CO}$, the rate constant can be expressed as $k = 6.5 \times 10^{-33} \exp(-4340 \pm 550/RT) \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$, whereas the rate for $\text{M} = \text{CO}_2$, the pertinent species in the planetary atmospheres, is 1.6 times greater. It is difficult to see how this homogeneous recombination can be significant at any altitude in the Martian atmosphere.
- The quantum yield for CO_2 photodissociation was measured in the 1200-1500 Å region, using atomic line sources. The yield throughout this spectral region was much lower than that measured at 1470 Å, the lowest value obtained being 8% at 1304 Å. This work was preliminary, and further studies are required to determine to what extent the CO_2 photodissociation rates that have been assumed for the planetary atmospheres will need reevaluation. At present it appears that a reduction by at least a factor of three will be necessary.

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INTRODUCTION

All the studies carried out on this project were for the purpose of explaining and interpreting information on the Mars and Venus atmospheres. As the data from the Mariner probes increases our knowledge of these atmospheres, new questions are simultaneously raised to which answers can often be found in the laboratory.

One of the major unanswered questions concerns the apparent lack of dissociation of the CO_2 atmospheres of these planets under solar irradiation, when laboratory studies would indicate that an atmosphere consisting primarily of CO and O_2 would be more stable. The answer lies in one of two areas: Either current ideas about CO_2 photodissociation are in error, or else there are rapid processes that permit CO and oxygen atoms, formed by photodissociation, to recombine. Clark and Noxon¹ and Felder, et al.² have looked at the former area and have concluded that at $1470 \text{ \AA}$ and longer wavelengths complete photodissociation takes place, i.e., that the quantum yield for CO production is 1.0. Our own measurements at $1470 \text{ \AA}$ have shown a quantum yield of unity for $\text{O}(^3\text{P})$ production but Inn and Heimerl³ measured a CO quantum yield of 0.75 at $1470 \text{ \AA}$ (and 0.5 at longer wavelengths), so some basis for controversy exists. From the appearance of the CO_2 absorption spectrum, there are reasons to believe that a value of 0.75 is realistic, although the corollary to this conclusion is that at low pressures CO_2 irradiated at $1470 \text{ \AA}$ should fluoresce. This has not been observed.

With respect to the recombination processes, our previous work⁴ had shown that homogeneous $\text{O} + \text{CO} + \text{M}$ recombination is quite slow and could not be effective at high altitudes. A number of people have made calculations, based on our recombination rate, of the required eddy diffusion coefficient for bringing $\text{O}(^3\text{P})$ and CO down to low altitudes. These

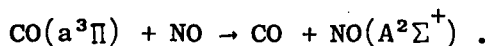
calculations have been based on the assumption of a negligible temperature coefficient for the recombination reaction, which is typical for a three-body reaction. However, the scattered and unreliable temperature data that existed suggested that the reaction might have a significant positive activation energy, which would make the recombination rate even lower in the cold atmospheres of the planets. For this reason we measured the activation energy for the recombination.

The Mariner spectra have shown that one of the principal spectral features of the Martian UV airglow is the CO Cameron bands ($a^3\Pi \rightarrow X^1\Sigma^+$). To interpret the variation of emission intensity with altitude, it is necessary to have values for the radiative lifetime and to know the CO_2 quenching rate for the $\text{CO}(a^3\Pi)$ molecule. The range of calculated and experimental values for the lifetime was 3 to 4 orders of magnitude, and no quenching measurements had ever been performed. We carried out the measurements and found good agreement with the data of other investigators that became available during the past year.

RESULTS

CO Cameron Bands

Our work on the CO Cameron bands was published in 1971.⁵ The source of CO($a^3\Pi$) involved a newly developed technique for pumping the CO($d^3\Delta$)_{v=5} level from the ground state, followed by a cascading transition to the CO($a^3\Pi$) levels. Direct detection of the $a^3\Pi \rightarrow X^1\Sigma^+$ emission was possible, and an enhanced signal could be produced by using the energy transfer reaction



Quenching rates for CO₂, CO, N₂, H₂, O₂, and NO were measured; they were generally found to be very rapid. An average radiative lifetime was measured from observation of the fraction of cascading photons that subsequently gave Cameron band emission, and a knowledge of the CO self-quenching rate. A value of 4.4 msec was obtained, within a factor of two of recent calculations.⁶

O(³P) + CO + M Recombination

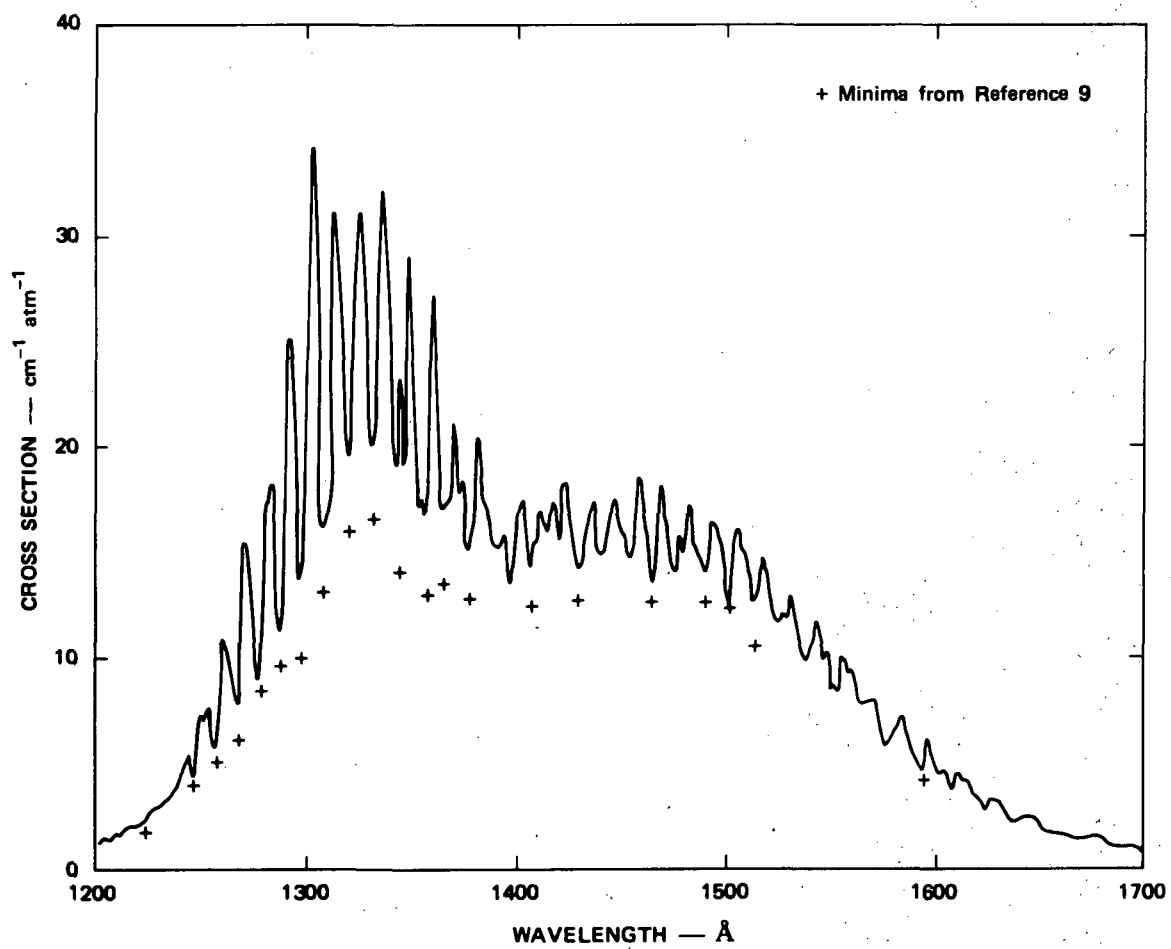
Our work has been submitted to the Journal of Chemical Physics and is included as the Appendix. Our earlier room-temperature work⁴ had suffered from problems with CO purity, which were solved in this investigation. Stuhl and Niki⁷ recently presented room temperature data showing rate coefficients a factor of six lower than we had reported earlier. Our recent measurements agree with theirs, and the new temperature data show a positive activation energy of 4.3 ± 0.5 kcal/mole. Using emission from the CO flame bands, it was found possible to make measurements as a function of CO₂ pressure, so that the rate for $\text{O}(^3\text{P}) + \text{CO} + \text{CO}_2 \rightarrow 2 \text{CO}_2$ could be obtained.

For a temperature of 200° K, representative of the Martian lower atmosphere, a rate coefficient of $2 \times 10^{-37} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$ is deduced, a factor of 100 lower than has been used for the eddy diffusion calculations. This figure makes the problem much worse and means that homogeneous recombination will not be pertinent at any altitude, so catalysis and surface recombination appear to be the most tenable explanation for the apparent recombination rate (but see below).

CO₂ Photodissociation

Very recent and preliminary measurements show quite clearly that assumptions of a unit quantum yield for CO₂ photodissociation throughout the vacuum uv region (1200-1700 Å) are erroneous. There are two distinct absorption regions, 1200-1400 Å and 1400-1700 Å, and it appears that in the lower region photon absorption leads to small photodissociation quantum yield, while in the higher region there is a greater degree of dissociation. Figure 1 shows the CO₂ absorption spectrum in the region of interest, from the measurements of Watanabe et al.⁸ The resolution obtained in this study was 1 Å. Later work of Nakata et al.,⁹ carried out at 0.2 Å resolution, is shown on Figure 1 as giving minima significantly lower than those of the earlier work.

Researchers dealing with the planetary atmosphere have tended to ignore the implications of the structure observed in the CO₂ absorption spectrum. The strong peaks in the 1250-1400 Å region are obviously related to vibrational levels in a bound CO₂ state, so absorption to these levels will not lead to dissociation in the initial step. Subsequent radiation to a dissociating state may result in O + CO production, but no spectral evidence indicates that there is such an emission, nor has fluorescence been observed



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FIGURE 1 CO₂ ABSORPTION SPECTRUM—REFERENCE 8

in the vacuum uv region. Thus, it appears that, for lack of observation of light emission from CO₂, total dissociation has been assumed by default.

We carried out measurements of CO production at five wavelengths. Experiments were done in a static system, and the buildup of CO was monitored by emission from the CO 4+ bands, which are excited by light from a CO discharge lamp. The relative intensities of the dissociating lamps were determined by measurements with a solar blind phototube and appropriate gas filters.

The initial measurements show that, as expected, the quantum yield for CO production depends on the degree of structure in the absorbing wavelength region. The results, shown in Table 1, are given relative to the quantum yield at 1470 Å. At 1302-1306 Å there is an absorption peak, and the quantum yield is only 8%. At 1236 Å, which is barely out of the structured region, the value is 16%; at 1216 Å, where there is negligible structure, the value is 35%. At 1492 Å, which is in the long wavelength continuum, as is 1470 Å, the yield is only 41%.

Table 1
CO QUANTUM YIELDS

Wavelength Å	Quantum Yield (relative to that at 1470 Å)
1216	0.35 ± 0.15
1236	0.16 ± 0.04
1302-1306	0.08 ± 0.02
1470	1.00
1492	0.41 ± 0.10

DISCUSSION

The implications, for the planetary atmospheres, of the low CO_2 photodissociation quantum yields are very significant. Since the work of Inn and Heimerl³ indicates that the CO quantum yield is 0.5 to 0.75 in the 1470-1650 Å region, while the solar radiation flux in the two absorption regions (1200-1400 Å and 1400-1700 Å) is approximately in the ratio of 1:2, it appears that the total CO_2 photodissociation in these regions may be only one-third of that previously assumed.

If CO_2 does not dissociate, then what becomes of the energy? The only possibility is that it results in fluorescence. The experiments carried out by Clark and Noxon¹ indicated that in the 1500-1700 Å region no more than 1% of the energy put into CO_2 can cause fluorescence. This is clearly inconsistent with the results of Inn and Heimerl³ and Sach¹⁰, who find that in this wavelength region only 50% of photon absorption leads to dissociation of CO_2 .

There are two plausible reasons why Clark and Noxon may not have detected fluorescence. Although one may calculate a CO_2^* lifetime of 10^{-7} sec from the absorption strength, there are numerous examples of triatomic molecules in which the radiative lifetimes are 5 to 100 times longer than indicated by the integrated absorption coefficients.¹¹ This phenomenon is caused by perturbing effects of nearby excited states; if it occurs with CO_2 , it is not surprising that no fluorescence is observed, for quenching could then be important at the pressures used. This leads to the second point: quenching cross sections may be very large for CO_2^* , at least five times larger than the value Clark and Noxon used in their paper. Combining these two effects, one may readily conceive that their upper limit of 1% fluorescence could become 25% and thus be quite consistent with the CO quantum yield measurements.

Another important point may be made with reference to the Mariner spectra, where there is no indication of CO_2 fluorescence. In the short-wavelength region ($1200\text{--}1400\text{ \AA}$) investigated in our study, where the CO quantum yields are quite low, 90% of the solar radiation is in the L_α line. In the Martian atmosphere, this line is absorbed mainly below 90 km; at 100 km the optical depth is 0.003/km. As the spectra taken by Mariners 6 and 7 were limited to altitudes greater than 100 km, and the reproduced spectra¹² were for 140 to 180-km altitudes, it is not surprising that no CO_2 fluorescence was observed.

It is of considerable importance to determine the spectral region in which fluorescence would occur. If it took place at wavelengths close to that of the exciting light, it could be reabsorbed by CO_2 and would ultimately result in dissociation. Thus, even if the quantum yield were not unity for a single absorption, most of the absorbable light could still lead to dissociation, and a radiative transfer problem would have to be solved to determine how the energy was deposited. If fluorescence occurred in a two-step process, there being an intermediate CO_2 electronic state¹³ at 46000 cm^{-1} , then radiation would probably occur above $4000\text{ \AA}$ for both stages, which would be an additional reason for lack of fluorescence observations from Mariners 6 and 7.

Discrepancies exist between our current measurements and early measurements¹⁴ at $1236\text{ \AA}$ that indicated a CO quantum yield of unity. However, since most recent work has been done at $1470\text{ \AA}$, and there have already been many revisions of conclusions based on the early studies, this particular disagreement does not seem to be a serious one.

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APPENDIX

KINETICS OF $O(^3P) + CO + M$ RECOMBINATION

by

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ABSTRACT

Rate coefficients have been measured over the temperature range 250-370° K for the three-body recombination of $O(^3P)$ with CO. Earlier results at 300° K have been reevaluated and were found to have been influenced by unknown impurities in the CO, which have now been removed by more elaborate purification methods. For CO as the third body, the rate constant is given by $k = 6.5 \times 10^{-33} \exp(-4340 \pm 550/RT) \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$. For N_2 and CO_2 , the 296° K rate constants are 2.3 and $6.2 \times 10^{-36} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$, respectively.

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INTRODUCTION

In a previous publication,¹ new rate constants for the reaction $O(^3P) + CO + M \rightarrow CO_2 + M$ were reported, lower than any previously measured. Within a short time these new rates were confirmed,^{2,3} and it appeared that the large discrepancies that had previously existed⁴ had been laid to rest. Subsequently, we decided to measure temperature coefficients for the reaction, since these were also a matter of considerable controversy. New methods for CO purification were employed, since it was felt that the scatter in the data in the previous work was related to contaminants in the CO. The result of this new investigation has been a decrease in the previously measured rate by a factor of ~ 6 , giving values close to the recent measurements of Stuhl and Niki.⁵ The difference between the new data and the old is entirely attributable to the composition of the CO; the three-body rate is so low that trace impurities are important, and certain unidentified impurities, which are now eliminated, previously had a controlling effect on the wall recombination coefficient and presumably also on the homogeneous rates. The nature and reproducibility of our present measurements make us confident that our values of the reaction rate are reliable.

Experimental

The basic instrumental design has been described in an earlier publication.⁶ As before, oxygen atom resonance fluorescence at 1302-1306 Å was used to monitor the reaction rate, except for $M = \text{CO}_2$. A PAR waveform eductor was used to enhance the signal/noise ratio in the observed atom decay curves. Curves of $\log I$ versus time were displayed directly by means of a log amplifier. These atom decay curves were logarithmic over at least one decade. Additional light intensity was obtained by driving the Xe and Kr resonance lamps by microwave rather than rf excitation. Figure 1 shows both I and $\log I$ curves versus time for a typical experiment.

The most significant change is in the method of purification of CO. In earlier studies it was found that CO had a disastrous effect on $\text{O}(^3\text{P})$ atom concentrations in a reaction cell. The addition of CO during an experiment in which O atoms were being measured by NO_2 chemiluminescence caused the light intensity to decrease drastically, with little recovery when the CO was turned off. Washing the cell was often the only way to regenerate it. It was immaterial whether the CO was used directly out of the cylinder (Matheson C.P. grade) or from a liquid CO reservoir at 77° K. In the earlier work it appeared that no more than 1 torr CO could be used before the $\text{O}(^3\text{P})$ atom loss rates began to change, and even in the 0-1 torr range the resultant data had a high degree of scatter.

In our first experiments with CO in the current study, C.P. grade CO at reduced pressure was passed through a glass bead trap cooled with liquid N_2 . The observed rate constants were then found to be a factor of two lower ($6 \times 10^{-36} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$ instead of 1.4×10^{-35}) than previously reported for $M = \text{N}_2$, and CO no longer had an irreversible effect on the cell $\text{O}(^3\text{P})$ atom loss rate. However, the rate coefficients obtained depended to some extent on the particular CO cylinder used, so there was still an undesirable component entering the system with the CO.

Ultimately we employed the purification scheme devised by Millikan and White⁷ for their work on CO vibrational fluorescence. The CO passed through two copper coils, the first cooled with dry ice-acetone packed with alumina, the second cooled with liquid O₂ and packed with copper wool. A liquid O₂-cooled glass bead trap was situated between the copper wool trap and the reaction cell. With this method, the lowest reaction rates were obtained and they no longer depended on the CO batch. Millikan and White felt that removal of an undetermined organic impurity made their experiment successful. Possibly in the present case the problem was with iron carbonyl, although it is surprising that the measures previously used would not remove this readily condensable material. Nevertheless, the contaminant was certainly a material unique to CO stored in steel cylinders, since no other investigated gas has ever affected the O(³P) wall loss rates in such a manner. With this method of purification, it is possible to raise the pressure of CO in the cell to at least 100 torr CO without any observable effect on the wall recombination coefficient. It should be noted that Stuhl and Niki⁵ obtained their results using only 77° K condensation of CO for purification.

Temperature variation of the cell was obtained by flowing preheated air or prechilled N₂ through a chamber that enclosed the cell. The incoming gas to the cell was preheated or cooled, in a glass heat-exchanger. Thermocouples on the cell wall and immersed in the gas within the cell were used to measure the temperature. In general the wall and gas temperatures agreed within 5° C. During the course of an experiment, the temperature of the cell was kept constant by means of a controller which automatically adjusted the heat input to the heat transfer fluid.

Most of the measurements were made with the O(³P) resonance fluorescence technique previously used.⁶ However, for the measurements with M = CO₂, it was necessary to use another method to monitor O(³P), since

CO₂ is opaque to 1304 Å radiation. Therefore the chemiluminescence of CO₂ was employed, where dissociation of CO₂ generates O(³P) atoms, which then react with CO [O(³P) + CO → CO₂ + hν]. The light was observed by means of an EMI 9558A phototube equipped with a Wratten 18 A filter. This method gave results agreeing with the resonance fluorescence data for the M = CO reaction, and therefore was used with confidence for the M = CO₂ experiment.

Results

Owing to the very slow reaction rates, it was found more convenient to make measurements for M = CO than for M = N₂. For example, for a mixture of 100 torr N₂ and 10 torr CO, the O(³P) loss rate due to the recombination reaction is only 3.0 sec⁻¹ at 300° K. Addition of a greater fraction of CO requires that the effects of M = CO and M = N₂ be separated, which means that the rate for M = CO must be measured in any case. On the other hand, for M = CO, the O(³P) recombination loss rate for 50 torr CO is 13 sec⁻¹, and the experiment can be carried out in a pure CO system [with a trace of O₂ to generate the O(³P) atoms]. Therefore, some measurements were made for M = N₂, but the bulk of the room temperature work and the studies at other temperatures were made for M = CO.

Since the rate of the reaction O(³P) + O₂ + CO → O₃ + CO is 100 times faster than the CO₂ recombination reaction, it is necessary to correct the rate data for the contribution from this reaction. In most of our experiments, O₂ was added to a pressure of 20 mtorr to serve as an O(³P) source. The data points in the figures have had the appropriate correction subtracted from them; it is particularly important at the low temperatures.

The total O(³P) loss rate is given by

$$L = \tau^{-1} = k_{\text{CO}}^{\text{M}} [\text{CO}][\text{M}] + k_{\text{CO}}^{\text{CO}} [\text{CO}]^2 + k_{\text{O}_2}^{\text{M}} [\text{O}_2][\text{M}] + k_{\text{O}_2}^{\text{CO}} [\text{O}_2][\text{CO}] + k_{\text{w}} + k_{\text{p}} \\ + a (k_1 [\text{CO}] + k_2 [\text{CO}][\text{M}]) + b (k_3 [\text{M}] + k_4 [\text{M}]^2) \quad , \quad (1)$$

where τ^{-1} is the measured time constant, k_{CO} and k_{O_2} are the respective CO_2 and O_3 recombination rate coefficients, k_w is a wall loss coefficient, k_p is the cell pump-out rate, a and b are mole fractions of $O(^3P)$ -destroying impurities coming in with the CO and M gas, respectively, k_1 and k_3 are two-body rate coefficients for a and b , and k_2 and k_4 are three-body rate coefficients for a and b . For an experiment in which $M = CO$, Eq. (1) reduces to

$$\tau^{-1} = k_{CO}[CO]^2 + k_{O_2}[CO][O_2] + k_w + k_p + ak_1[CO] + ak_2[CO]^2 \quad (2)$$

For a total pressure of 20 mtorr O_2 the $O(^3P)$ loss rate is in the 3-4 sec^{-1} range. When we subtract from this the cell pump-out rate, the maximum rate of loss on the walls is $\sim 1 \text{ sec}^{-1}$. Hence substitution of $\tau_D \sim 1 \text{ sec}$ in the diffusion expression $\tau_D = \frac{R^2 p}{15D} + \frac{4R}{3\bar{v}\gamma}$ (where R is a characteristic dimension, p is pressure, D is a diffusion coefficient, $\bar{v}$ is the molecular velocity, and γ is the wall recombination coefficient) requires that $\gamma \leq 10^{-4}$ and that the rate of loss by diffusion is not substantially changed by changing the CO pressure for the CO pressures used in the experiment ($\leq 70 \text{ torr}$). Therefore the pressure dependence of k_w can be neglected. When $k_{O_2}[CO][O_2]$ is subtracted out of Eq. (2), a plot of τ^{-1} versus $[CO]^2$ will be linear if ak_1 is negligible and will have a slope of $k_{CO} + ak_2$. In Figure 2 is shown the data for $M = CO$ at 296° K. The plot is indeed linear and has an intercept of $\sim 2.8 \text{ sec}^{-1}$. Figures 3 and 4 show the data for other temperatures; these plots are also linear in $[CO]^2$.

The data for $M = N_2$ are shown in Figure 5, in which the slopes of τ^{-1} versus $[CO]$ plots are plotted against the N_2 pressure at which they were taken. Subtracting out $k_{O_2}^{CO}[O_2][CO]$ and $k_{CO}^{CO}[CO]^2$, the slopes are given by $(k_{CO} + ak_2) \cdot [N_2] + ak_1$, and the plot in Figure 5 should then have a slope of $k_{CO} + ak_2$.

Figure 6 shows data for τ^{-1} versus $[\text{CO}]$ for $M = \text{CO}_2$, with corrections applied to each point for the contribution of $\text{O} + \text{CO} + \text{CO} \rightarrow \text{CO}_2 + \text{CO}$. These data were taken with a Kr lamp as the dissociation source, because 1236 Å radiation has a smaller cross section for CO_2 , by a factor of four, than 1470 Å radiation. The reason this was felt to be important is that unity optical depth for 50 torr CO_2 at 1236 Å corresponds to an absorption length of 4.5 cm, whereas at 1470 Å it is only 1 cm. A nonuniform spatial distribution of the $\text{O}(^3\text{P})$ atoms in the cell can be expected to give false decay curves, having an initial lag in the decay as the atoms diffuse across the cell from their point of formation near the lamp window to the region where they are optically detected. Such lags were present in the decay curves obtained with an Xe lamp. Switching to a Kr lamp alleviated the problem. In Figure 7, the slopes of Figure 6 are plotted against $[\text{CO}_2]$, the resultant line having a slope, as previously discussed, of $k_{\text{CO}} + ak_2$.

The 296° K rate constants are presented in Table 1 for $M = \text{CO}$, N_2 , and CO_2 , and compared to other recent work, on the assumption that ak_2 is zero, a point to be discussed in the next section.

Table 1

RECOMBINATION RATE COEFFICIENTS

$$k(\text{O} + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M}) \times 10^{36} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1} (296^\circ \text{K})$$

References	He	Ar	N ₂	CO	CO ₂	N ₂ O
1	6	7	14	--	--	--
2	14	14	--	--	--	--
3	--	--	--	--	--	18
5 ^a	1.5	--	2.0	2.9	--	--
Present work	--	--	2.3 ± 0.4	3.9 ± 0.7 ^b	6.2 ± 0.9	--

a. Rate coefficients expressed at 296° K instead of 300° K, using 4.3 kcal/mole activation energy.

b. From line in Figure 8.

In order to convince ourselves of the accuracy of the temperature measurements, the activation energy for the reaction $O(^3P) + O_2 + N_2 \rightarrow O_3 + N_2$ was measured. A value of 1.56 kcal/mole was obtained, compared to the value of 1.8 kcal/mole reported by Clyne et al.⁸ Thus, if there is any systematic error in our temperature measurements, it is in the direction of the low temperatures being higher than measured, and the high temperatures being lower.

Discussion

Not only have the rates for the CO_2 recombination reaction been in question, but it has not even been clear whether the reaction has a positive or negative temperature coefficient. In a review publication, Baulch et al.⁴ conclude that the reaction has a positive activation energy, but recent measurements of Kondratiev^{9a,b} indicate the opposite, as do shock tube measurements of Lin and Bauer.¹⁰ A negative temperature coefficient would of course be consistent with most known three-body reactions.

Assuming that the slopes in Figures 2-4 are a measure of the CO_2 recombination coefficient, a plot is presented in Figure 8 of k_{CO} versus $1/T$ for $M = CO$. The line corresponds to the expression $k = 6.5 \times 10^{-33} \exp(-4340 \pm 550/RT) \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$. The error bars on the points represent the standard deviation of the random errors, and most probably the largest systematic error is due to temperature measurements. The average deviation of the points from the line in Figure 7 corresponds to 6°C , which is a reasonable experimental error limit. It was substantiated that the interior cell temperature and the wall temperature were maintained within 5°C of each other, independent of cell pressure. On the basis of the direction of our temperature measurements for the $O + O_2 + N_2$ reaction, it is likely that the value of 4.3 kcal/mole is a maximum rather than a minimum.

Also shown on Figure 8 is a point obtained for the rate coefficient from CO_2^* chemiluminescence decay rather than $\text{O}(^3\text{P})$ decay. The reasonable agreement shows the validity of the method; the point agrees well with the measurements of Stuhl and Niki,⁵ who used the same technique.

With regard to the possible contribution of the term ak_2 to the slopes in Figures 2-6, the only way to discount the effect of a contaminant entering with the CO and participating in a three-body reaction is to take note of the positive activation energy. Virtually all known three-body reactions have small negative temperature coefficients, and there is no curvature in the plot of Figure 8 to suggest multiple reactions. The previous measurements^{1,2} demonstrated third-order behavior, and it would have been interesting to ascertain whether in those experiments the temperature coefficients were negative, since they must have been related to reactions other than the one under study.

In the work of Simonaitis and Heicklen³ an activation energy of 4.1 kcal/mole was measured for the low-pressure region; change in reaction order was observed in the pressure domain of several hundred torr N_2O . The good agreement in activation energy is encouraging, although their value for $M = \text{N}_2\text{O}$ is three times larger than ours for $M = \text{CO}_2$. It is conceivable that there is a unique chemical effect involving N_2O which makes it a particularly efficient third body. However, on the basis of our experience with CO contamination, we would tend to look in that direction first as an explanation for the difference. It is unfortunate that N_2O was the only third body used in this study.

Several years ago the $\text{O} + \text{CO} \rightarrow \text{CO}_2 + h\nu$ reaction was studied by Clyne and Thrush.¹¹ They ascertained that the reaction was third order, since the light intensity was independent of pressure, but dependent on the nature of the buffer gas. They observed a positive activation energy of 3.7 kcal/mole and concluded that spin change was not the rate-limiting

step in CO_2 formation. They postulated an energy barrier in the $^3\text{B}_2$ CO_2 potential energy curve [the $^3\text{B}_2$ state correlates with $\text{CO}(X^1\Sigma^+) + \text{O}(^3\text{P})$] and concluded that the positioning of the $^3\text{B}_2$ and $^1\text{B}_2$ states was such that crossing to the $^1\text{B}_2$ state, from which emission occurs, was expected to be rapid compared to the rate of barrier crossing. They felt that the total recombination process and the light emission process would involve the same energy barrier, although they were unable to measure the rate of the overall reaction.

Lin and Bauer¹⁰ have made shock tube measurements of the total recombination rate and have developed a quite different picture. They obtain a rate expression of $k_{\text{CO}} = 7.8 \times 10^{-36} \exp(+23800/RT) \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$. They claim that the rate-determining step involves a radiationless transition between the $^3\text{B}_2$ state and the $^1\Sigma_g^+$ ground state. The crossing is calculated to be 7.5 kcal/mole below the $^3\text{B}_2$ dissociation limit, thus leading to a negative activation energy. They argue that the principal recombination process is different from the minor channel involved in light emission, which they think involves a $^3\text{B}_2 - ^1\text{B}_2$ crossing, but of a different form than that described by Clyne and Thrush.¹¹

Furthermore, they conclude that in the light emission process, the positive activation energy is due not to an energy barrier but to the height of the crossing above the dissociation limit; i.e., spin change should determine the reaction rate.

On the basis of our measurements we would find ourselves in agreement with Clyne and Thrush's interpretation, for two reasons. In the first place, we find for the overall rate a pre-exponential factor of $3.7 \times 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$, for $\text{M} = \text{N}_2$, compared to a value for a typical spin-allowed process¹² such as $\text{O}(^3\text{P}) + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$, of 2.9×10^{-33} . Thus, the observed difference of five orders of magnitude in the rates for NO_2 and CO_2 recombination is not due to the time required for spin change. Secondly, our activation energy for the overall reaction is positive

and overlaps that of Clyne and Thrush, within the error limits. Therefore, we conclude that at the high temperatures (1500-3000° K) used by Lin and Bauer, there is a different mechanism taking place than that obtaining in the lower temperature experiments. (This conclusion assumes, of course, that the shock tube experiment does not suffer from the same CO impurity problems that have plagued most previous investigations of this reaction).

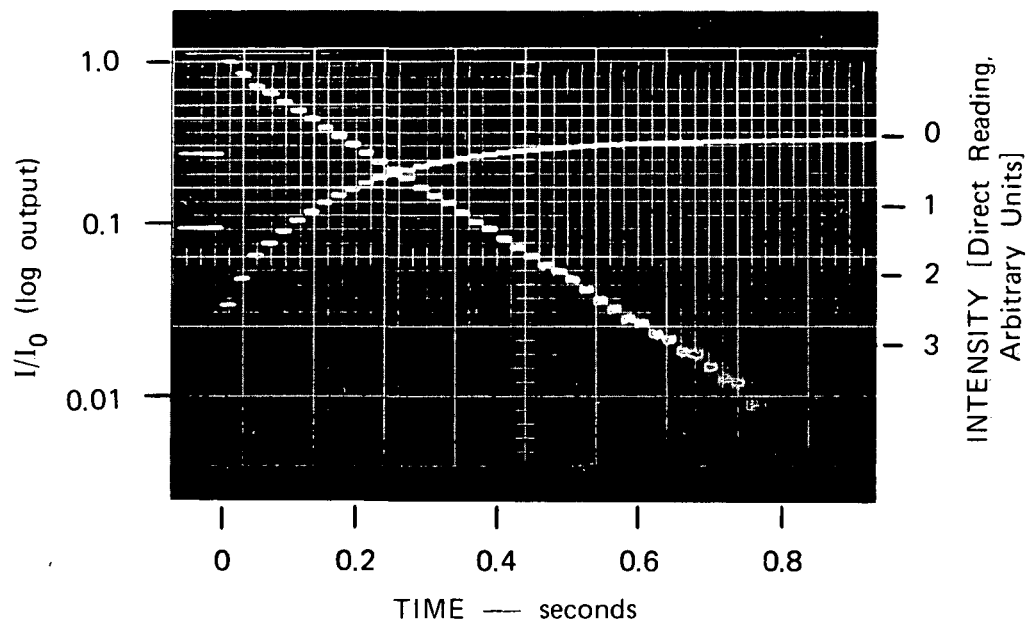
Our interest in measuring the rate for $M = \text{CO}_2$ is due to the fact that in the Venusian and Martian atmospheres, the most obvious mechanism for the recombination of the $\text{O}(^3\text{P})$ and CO produced by photodissociation of CO_2 is by the reaction $\text{O}(^3\text{P}) + \text{CO} + \text{CO}_2 \rightarrow 2\text{CO}_2$. At a Martian surface temperature of 200° K, the rate coefficient for $M = \text{CO}_2$ is $2 \times 10^{-37} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$. For a surface pressure of 6 torr CO_2 , and a CO/CO_2 mixing ratio of 0.01, the lifetime of an oxygen atom against homogeneous CO_2 recombination is four hours. This is the minimum lifetime; at higher altitudes the lifetime will be many orders of magnitude longer. One may easily calculate how important CO_2 recombination would be at the relatively low altitude of 25 km, assuming that the $\text{O}(^3\text{P})$ concentration will be principally determined by the $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$ reaction. For a CO/CO_2 mixing ratio of 0.01, and a dissociation rate¹³ of $5 \times 10^5 \text{ cm}^{-3} \text{ sec}^{-1}$, the CO_2 recombination rate is sufficient to recombine only 3% of the CO produced. This figure suggests that even the high eddy diffusion rates that have been discussed as a means of getting CO and O down to low enough altitudes for recombination to take place will not in themselves be adequate to prevent buildup of CO and O_2 in the atmosphere; either the recombination process must involve catalyzed or heterogeneous reactions, or else assumptions about the CO_2 photodissociation rate are in error. This latter point is to be discussed in a subsequent paper.

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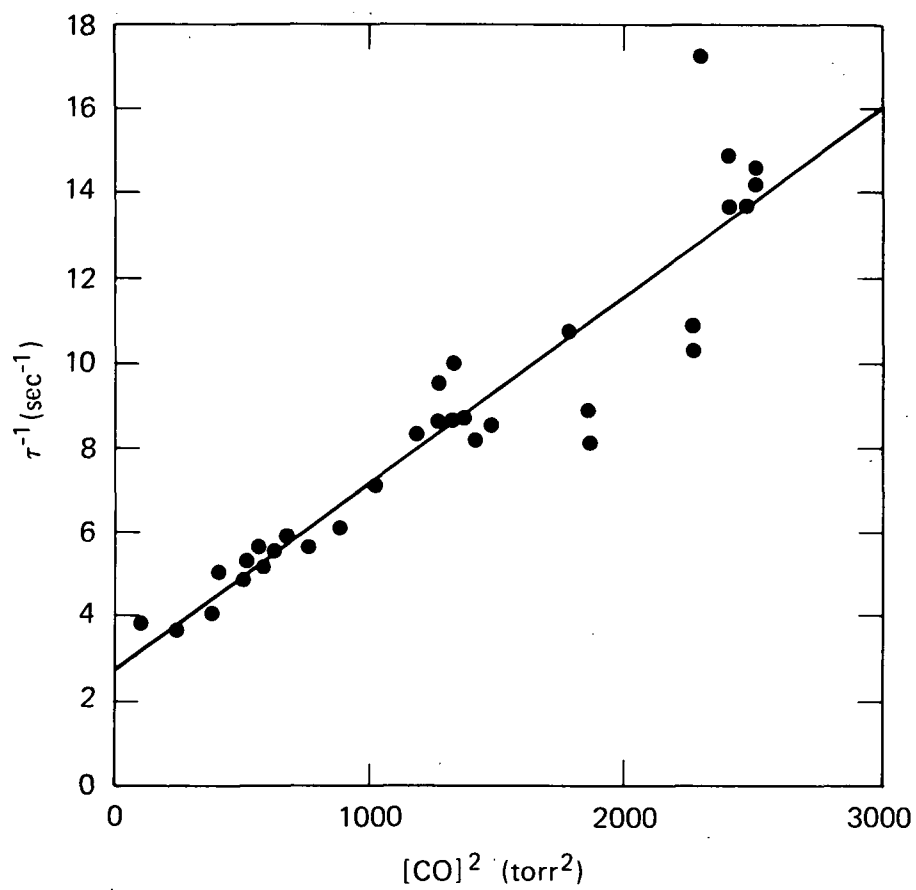
FIGURES

1. Oscilloscope decay trace. $[\text{CO}] = 24$ torr, $[\text{O}_2] = 20$ mtorr, $T = 296^\circ \text{K}$.
Left index refers to the log output (straight line), right index to the relative intensity (curve, decaying from bottom to top).
2. $\text{O}(^3\text{P})$ decay rate versus $[\text{CO}]^2$, $[\text{O}_2] = 20$ mtorr, $T = 296^\circ \text{K}$.
3. $\text{O}(^3\text{P})$ decay rate versus $[\text{CO}]^2$, $[\text{O}_2] = 20$ mtorr.
 Δ 274°K
 $\circ$ 254°K
4. $\text{O}(^3\text{P})$ decay rate versus $[\text{CO}]^2$, $[\text{O}_2] = 20$ mtorr.
 $\circ$ 372°K
 Δ 335°K
5. $\text{O}(^3\text{P})$ decay rate per torr CO versus $[\text{N}_2]$, $T = 296^\circ \text{K}$.
6. $\text{O}(^3\text{P})$ decay rate versus $[\text{CO}]$, $T = 296^\circ \text{K}$.
 $\times$ 78 torr CO_2
 Δ 40 torr CO_2
 $\circ$ 20.5 torr CO_2
7. $\text{O}(^3\text{P})$ decay rate per torr CO versus $[\text{CO}_2]$, $T = 296^\circ \text{K}$.
8. Rate constant for $\text{O}(^3\text{P}) + \text{CO} + \text{CO} \rightarrow \text{CO}_2 + \text{CO}$ versus $1/T$.
 $\circ$ $\text{O}(^3\text{P})$ resonance fluorescence detection
 Δ CO_2^* chemiluminescence detection



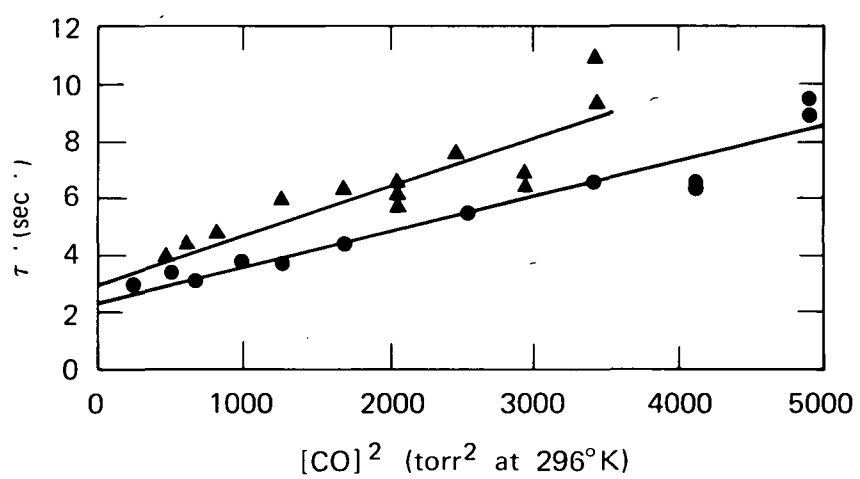
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FIGURE 1



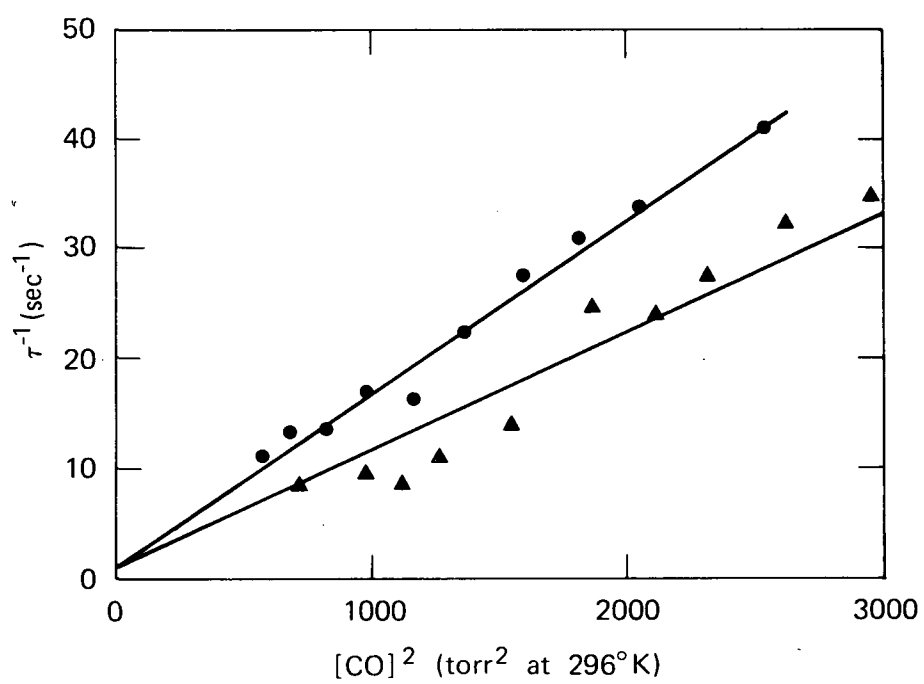
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FIGURE 2



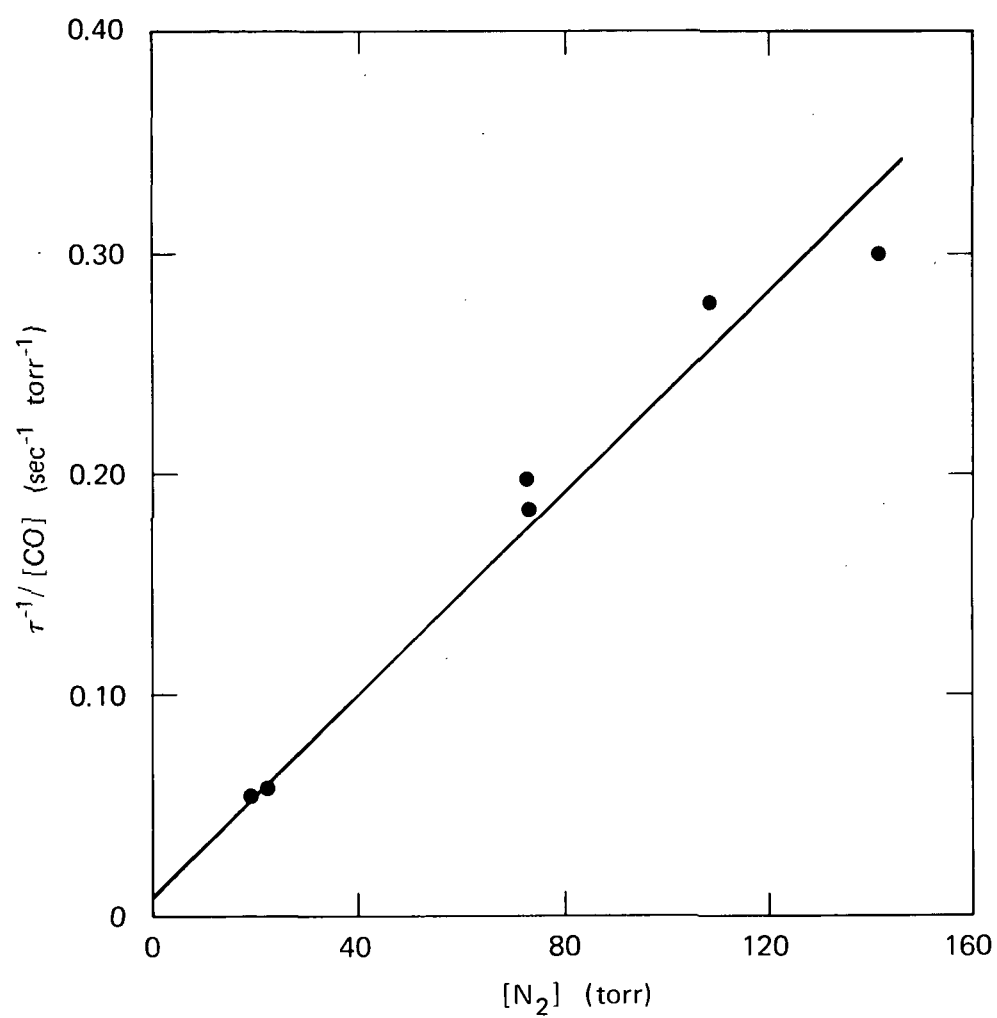
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FIGURE 3



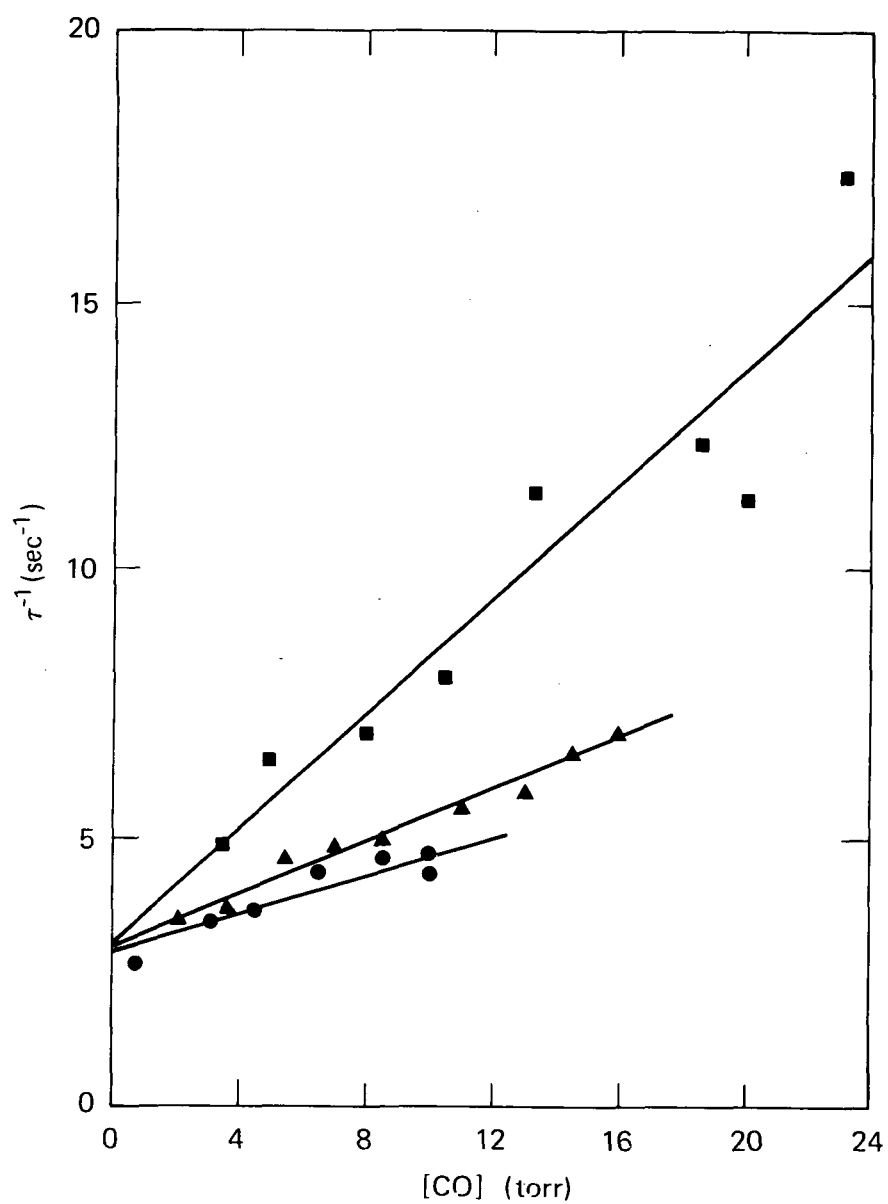
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FIGURE 4



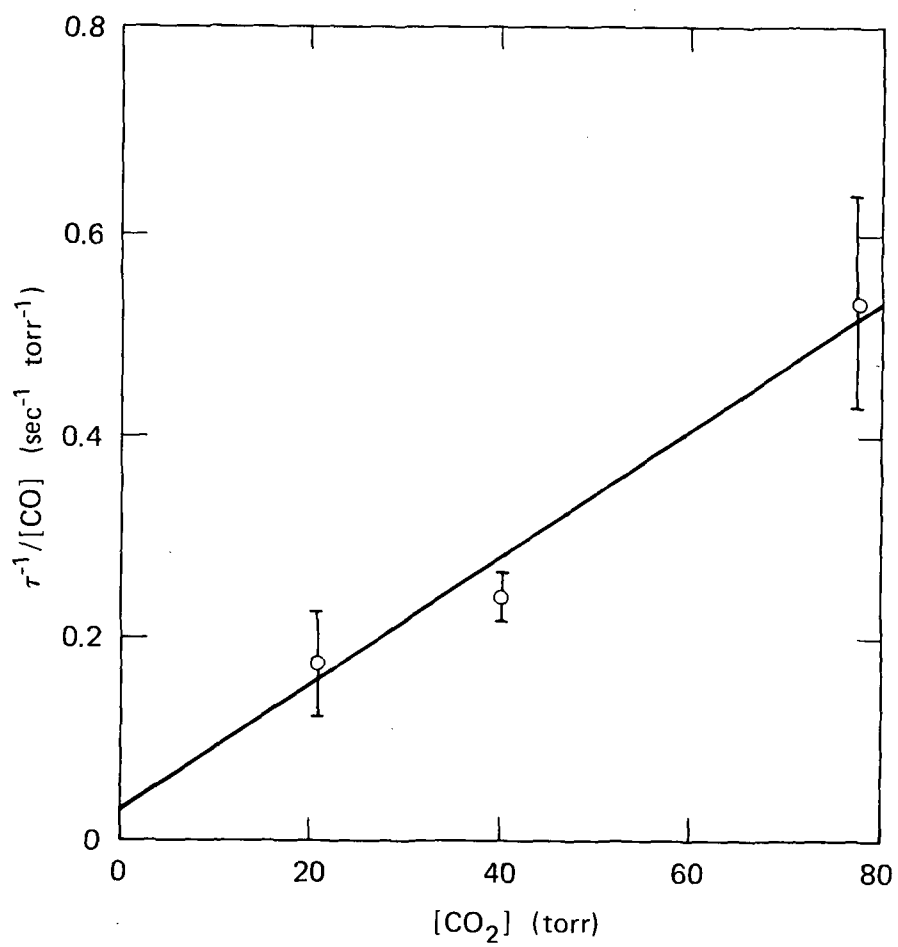
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FIGURE 5



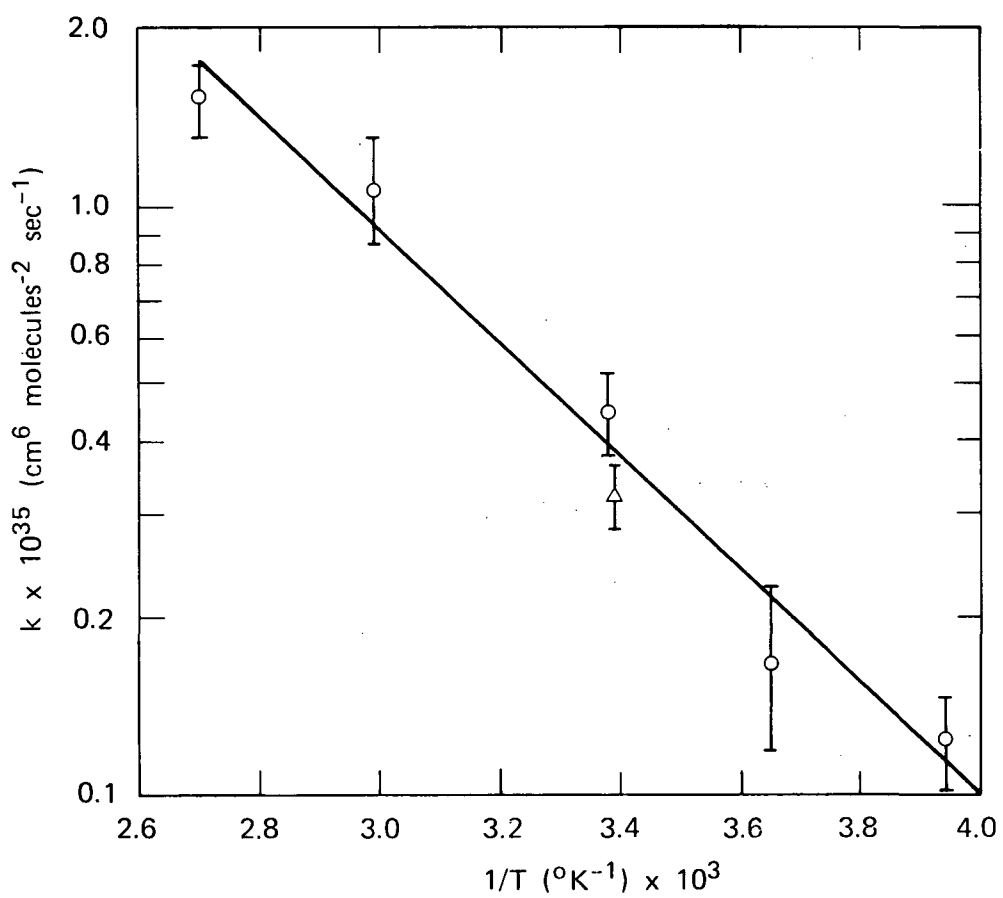
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FIGURE 6



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FIGURE 7



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FIGURE 8