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A SHOCK TUBE STUDY OF THE RECOMBINATION OF CARBON MONOXIDE AND --ETC(U)

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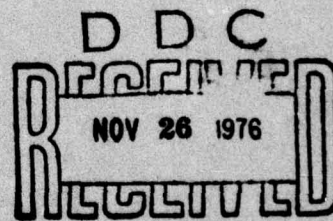
### A SHOCK TUBE STUDY OF THE RECOMBINATION OF CARBON MONOXIDE AND OXYGEN ATOMS

BY

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PROJECT SQUID HEADQUARTERS  
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## PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH  
AS RELATED TO JET PROPULSION  
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

CONTRACT N00014-75-C-1143, NR-098-038

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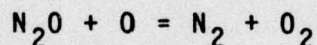
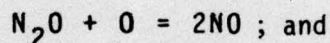
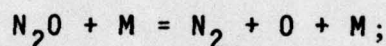
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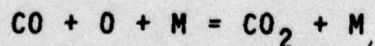
# ABSTRACT

Time resolved emissions from  $\text{CO}_2$  and the radiative recombination of CO and O (flame-band emission) have been monitored in a variety of  $\text{N}_2\text{O}/\text{CO}/\text{Ar}$  mixtures. These mixtures were studied behind reflected shock waves at temperatures between 2100-3200 K and total concentrations between  $2.5\text{--}7.7 \times 10^{18}$  molec/cm<sup>3</sup>. The flame-band detector was calibrated so that absolute concentrations of atomic oxygen could be determined. This data was shown to be consistent with the following mechanism:



with  $k_1 = 4.5 \times 10^{-10} \exp(-226\text{kJ}/\text{RT}) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and  $k_2 = k_3 = 7.7 \times 10^{-11} \exp(-117\text{kJ}/\text{RT})$ . This combination was also shown to be consistent with earlier data from this laboratory.

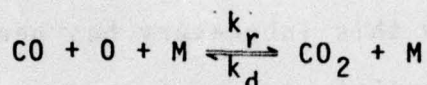
$\text{CO}_2$  was observed to increase linearly with time in these experiments and an apparent recombination rate constant defined as  $k_{\text{app}} \equiv d\text{CO}_2/dt/([\text{CO}][\text{O}][\text{M}])$  was measured and found to be a function of pressure. This behavior was attributed to the presence of very small concentrations of hydrogenous impurities. Data at higher pressures were used to estimate the rate constant for the recombination:



since the effect of impurities was minimized here. It was found that  $k_v = (1.6 \pm 0.3) \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$  between 2100-3200 K. This value is shown to be consistent with recent studies of  $\text{CO}_2$  dissociation which report "normal" activation energies.

# INTRODUCTION

Although room temperature measurements of the recombination reaction



generally show good agreement [1], there is no such consensus at higher temperatures. Direct high temperature measurements have been attempted by several groups. Brabbs and Belles [2] reported  $6 \times 10^{-35} \leq k_r \leq 3 \times 10^{-34} \text{ cm}^6 \cdot \text{molec}^{-2} \cdot \text{s}^{-1}$  for  $2800 \leq T \leq 3600 \text{ K}$ . The results were not considered sufficiently precise to determine the effect of temperature. Lin and Bauer [3] reported  $k_r = 7.8 \times 10^{-36} \exp(+99.5 \text{ kJ/RT})$  for  $1500 \leq T \leq 3000 \text{ K}$ . Hardy, et al., [4] investigated the recombination between 1200 and 2400 K and determined an upper limit of  $6 \times 10^{-34}$  at 1500 K. A comparison of these values shows that the Lin-Bauer results are highest and that the reported negative activation energy of 99.5 kJ appears to be too large. For example, the Lin-Bauer value at 1500 K is forty times larger than the upper limit of Hardy, et al. Much of this discrepancy can be attributed to the choice of rate constants used in the numerical integrations of Lin and Bauer.

This uncertainty as to the magnitude and temperature dependence of  $k_r$  is particularly unfortunate since there exists a corresponding uncertainty with regard to  $k_d$ . Here activation energies have ranged from 309 to 460 kJ/mole. It has been shown [5] that small concentrations of organic impurities can drastically effect the interpretations of the dissociation experiments and thus assignment of an activation energy to the dissociation reaction is particularly diffi-

cult. A reliable value of  $k_r$  at high temperatures could then serve as a useful guide in assigning an activation energy to  $k_d$ .

→ For some time now this laboratory has been utilizing nitrous oxide as a high temperature source of oxygen atoms [6]. Recently, an independent technique has been used to calibrate the detector system for oxygen atoms. With this calibration factor known, more refined experiments have been performed in which the absolute oxygen atom concentration can be monitored as a function of time. It was found that only slight modifications of earlier rate constant assignments were required to quantitatively explain these new results.

In this light it is now felt that the dissociation kinetics of  $N_2O$  are reasonably well understood. Thus the  $CO_2$  production rate in  $N_2O$  <sup>sub r</sup>  $CO$  mixtures has been measured in an attempt to determine  $k_r$ . It is shown that small amounts of impurities can drastically affect the  $CO_2$  production rate. Analysis of this impurity effect has yielded estimates of the actual recombination rate constant between 2100 and 3200 K. The value of  $k_r$  <sup>sub r</sup> determined in this way is shown to be consistent with the recent measurements of  $k_d$  <sup>sub d</sup> reported by Wagner [4,7], and Kiefer [8], which yielded 'normal' activation energies for  $CO_2$  dissociation.

↑

## EXPERIMENTAL

The 7.6 cm shock tube and gas handling system have been described previously [9,10]. For these experiments infrared emission was collimated by two slits 1.5 mm wide and 5 mm high placed 50 mm apart. The CO<sub>2</sub> emission was isolated with a 4.27  $\mu$ m interference filter (FWHM = 0.18  $\mu$ m); it was then focussed by a spherical mirror onto the sensitive element of a liquid-nitrogen-cooled indium antimonide detector. Visible emissions were monitored by an RCA 1P28A/V1 photomultiplier mounted behind a 450 nm interference filter (FWHM = 6.5 nm) and two 1 mm wide X 2 mm high collimating slits 38 mm apart. These collimating slits are smaller than those used previously to further reduce the amount of scattered light reaching the detector. The visible slits used here resulted in a fiftyfold reduction in signal relative to that obtained with the 1.5 mm wide X 19 mm high slits used earlier [10]. Preliminary experiments with the larger slits showed peculiarities along portions of the signal-time profile that disappeared when the smaller slits were used. In like manner, the somewhat shorter IR slits used here gave better-shaped profiles in CO<sub>2</sub> calibration experiments.

The IR detector-preamp had a nominal response time of 1  $\mu$ sec and the response time of the visible system was measured to be less than 2  $\mu$ sec. The signals from these detectors were recorded on either a Biomation Model 805 transient recorder or an oscilloscope-camera combination.

Mixtures were made with N<sub>2</sub>O supplied by either Liquid Carbonic (99.9% stated minimum purity) or AIRCO (99.995%), CO supplied by Matheson (99.99%) and AIRCO argon (99.9998%). The CO was slowly

passed through a coil of copper tubing at 77° K prior to introduction to the vacuum line. The shock tube was typically pumped to 2.5 mPa with an observed leak-outgassing rate of 2.5 mPa/min..

Shocks were usually initiated within one minute of pump isolation so that the nominal background pressure was 5 mPa. Helium was used as the driver gas in all experiments, and shocks were initiated by both spontaneous and manual rupture of Mylar diaphragms.

## RESULTS

A variety of  $N_2O/CO/Ar$  mixtures initially at pressures of 1.2-4.0 kPa were heated behind reflected shock waves to 2015-3440 K. Measured incident shock velocities were used to compute the no-reaction conditions behind the reflected shock. As in the earlier work [6,10], there was little difference in conditions calculated using a constant velocity assumption and those where the measured velocities were extrapolated to the observation window. Invariably, these two methods yielded temperatures within 40 K. The conditions listed in Table I were obtained with the constant velocity assumption.

A pressure transducer in the plane of the observation windows allowed for direct measurement of the post-shock pressure as well as to serve as an indicator of the arrival of the reflected shock. These arrival times were consistent with those calculated from the incident shock velocity data. The agreement between the measured and calculated post-shock pressures was most satisfactory. For most mixtures the observed pressure was within a few percent (i.e., the measurement error) of that calculated. In the worst cases the difference was only 6%. This pressure profile was observed to be constant over the interval where time resolved emission data were obtained. This observation was taken to mean that the ideal shock assumptions were applicable.

The signal at  $4.27 \mu m$  was observed to increase abruptly upon shock front passage and then decline to a non-zero plateau before beginning to increase linearly on a time scale of hundreds of micro-

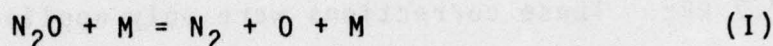
seconds. The initial rise and decay is due to  $N_2O$  emission and the non-zero plateau results from CO emission. The linear rise at later times is attributed to  $CO_2$  production. The measured rate of signal change in this linear region was converted to a  $CO_2$  production rate using calibration factors obtained in a series of  $CO_2/Ar$  experiments. It was shown that the observed signal was directly proportional to the  $CO_2$  concentration for the conditions of these experiments. Values observed for this constant rate of  $CO_2$  production are listed in Table I. Data reported for Mixtures A & B were obtained from measurement of scope traces, whereas all other data were collected with the transient recorder.

Systems containing oxygen atoms and carbon monoxide are known to emit radiation whose intensity is proportional to the product of the concentrations of these species [11]. Here, this emission was monitored at 450 nm. Schott's partial equilibrium technique [11] was used to calibrate this signal for oxygen atoms by shocking a mixture of  $H_2/O_2/CO/CO_2/Ar$  to 2000-2700 K. Quasistable concentrations of oxygen atoms and carbon monoxide are rapidly attained and remain for some time prior to the onset of recombination. These concentrations are easily calculated with an appropriate set of equilibrium constants. Background emissions were estimated from separate experiments with an  $H_2/O_2/Ar$  mixture and subtracted from the observed signals. Use of the corrected (constant) signal in conjunction with the calculated "partial-equilibrium" concentrations of CO and O was sufficient to calibrate the system. The observed temperature dependence of this calibration factor was consistent

with that reported by Schott, et al [11]. Use of this factor in the  $\text{N}_2\text{O}/\text{CO}/\text{Ar}$  experiments was straightforward. The observed signal was first corrected for background emissions obtained in a series of experiments with a 1%  $\text{N}_2\text{O}/\text{Ar}$  mixture at an initial pressure of 2.7 kPa. These corrections were only applied to those  $\text{N}_2\text{O}/\text{CO}/\text{Ar}$  mixtures with 1%  $\text{N}_2\text{O}$  and initial pressures of 2.7 kPa. The observed  $\text{CO}_2$  concentration was sufficiently small to justify the assumption that the CO concentration remained at its initial value. Use of this initial value and the calibration factor then allowed the corrected signal to be converted into a corresponding oxygen atom concentration. It was observed that this concentration rapidly approached a constant value which was maintained for hundreds of microseconds. In some cases the signal was observed to fall slightly below the plateau value at longer times. The plateau values are listed in Table I as  $[\text{O}]_{\text{rxn}}$ . Although values are not reported for mixtures other than those when the background emissions were available, the magnitude of the uncorrected signals in those cases were consistent with those reported. Values of  $[\text{O}]_{\text{rxn}}$  for Mixtures A & B were obtained from the transient recorder, and those for Mixtures C & D were taken from oscilloscope traces. It is felt that the data obtained from the oscilloscope traces are less accurate. Here it was more difficult to apply background corrections, and the voltages could not be measured as accurately. It is estimated that the  $[\text{O}]_{\text{rxn}}$  data in Mixtures A & B are good to about 5%, whereas that in C and D are only good to 10%.

# DISCUSSION

N<sub>2</sub>O Dissociation Kinetics. It is generally accepted that the dissociation of nitrous oxide occurs via the following mechanism with  $k_{II} \cong k_{III}$ :



Recent work in this laboratory [6,10] has suggested that the ratio  $k_I/(k_{II} + k_{III})$  is much higher than previously thought [12]. The concentration of atomic oxygen produced in N<sub>2</sub>O dissociation is clearly very sensitive to the value of this ratio; hence the observation of oxygen atom concentrations reported in this work allows for a more definite assignment of rate constants in this system. Since CO must be added to monitor the oxygen atoms, the possibility of two competing reactions must be considered:



There is experimental evidence to suggest that neither of these reactions appreciably perturbs the oxygen atoms produced via Reactions (I)-(III). Note in Fig. 1 that, within the scatter, the oxygen atom concentration is not decreased as CO is doubled. This observation is consistent with Lin and Bauer's [3] reported value of  $k_{IV}$ ; use of that value in calculations showed a negligible decrease in the oxygen atom concentration in a mixture of 1% N<sub>2</sub>O/4.35% CO/Ar. The observed constant value of the corrected 450 nm signal suggests that Reaction (V) is not a major sink for oxygen atoms. This is confirmed

by the observed low  $\text{CO}_2$  production rates. Thus the addition of CO should not affect the kinetics of Reactions (I)-(III).

Numerical integrations of Reactions (I)-(III) were done with various combinations of  $k_I - k_{III}$  in an attempt to simultaneously match the observed concentrations of atomic oxygen reported in this work and the observed  $\text{N}_2\text{O}$  decay rate reported earlier [6]. For completeness, these calculations included Reaction V with  $k_V = 1.75 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ . The effect of V was checked by varying  $k_V$  from  $1.5\text{--}2 \times 10^{-34}$ . In all cases this change resulted in less than a 2% change in the O-atom profile. It was found that the combination  $k_I = 4.5 \times 10^{-10} \exp(-226 \text{ kJ/RT}) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  and  $k_{II} = k_{III} = 7.7 \times 10^{-11} \exp(-117 \text{ kJ/RT})$  gave a good fit to both these observables. Fig. 1 illustrates the agreement with respect to oxygen atom production. In like manner this set predicts  $\text{N}_2\text{O}$  decay rates well within the standard deviations of those observed [6] between 2000 and 3000 K.

This value of  $k_I$  compares favorably with that reported earlier [6], while  $k_{II}$  and  $k_{III}$  are about a factor of two higher than earlier suggestions. Use of these new values also gave good agreement for all of the other observations in our earlier work. These new assignments make possible quantitative agreement between calculations and observations regarding the  $\text{N}_2\text{O}$  decay rate [6], the production of atomic oxygen, the time scale for atomic oxygen production [10], and the effects of small amounts of added  $\text{H}_2$  [6].

This success in modeling a variety of types of data on the  $\text{N}_2\text{O}$  system suggests that the dissociation kinetics are now reasonably well understood. Further support for this contention is the recent work of Dove, et al. [13] who report a value for  $k_{II}$  and  $k_{III}$  in this temperature range in excellent agreement with that reported here.

The Recombination of O and CO. The observed linear rate of  $\text{CO}_2$  production when  $\text{N}_2\text{O}/\text{CO}/\text{Ar}$  mixtures were shocked could easily be rationalized in terms of Reactions (I)-(III) and (V). The constant flame-band signal is perfectly consistent with the linear rate of  $\text{CO}_2$  growth. Here the detector system is sufficiently sensitive that the "initial rate" can be observed on a time scale of hundred of microseconds. Even in the case of the highest observed rates of  $\sim 10^{19}$  molec  $\text{cm}^{-3} \text{ s}^{-1}$ , the amount of  $\text{CO}_2$  produced in 500  $\mu\text{sec}$  is only 10% of the O-atom concentration and 3% of the CO concentration. Since  $\text{CO}_2$  dissociation has been shown [7] to be second order in this region, the recombination reaction is expected to exhibit third-order kinetics. In this light, an apparent recombination rate constant,  $k_{\text{app}}$ , has been defined as

$$k_{\text{app}} \equiv \frac{d\text{CO}_2/dt}{[\text{CO}]_i [\text{O}]_{\text{rxn}} [\text{M}]}$$

For Mixtures A-D,  $[\text{O}]_{\text{rxn}}$  is taken as the observed value shown in Table I. For the other mixtures,  $[\text{O}]_{\text{rxn}}$  was calculated using values of  $k_{\text{I}} - k_{\text{III}}$  which gave the best fit to the  $\text{N}_2\text{O}$  dissociation kinetics. As was pointed out earlier, the observed flame-band signal was consistent with those calculated values of  $[\text{O}]_{\text{rxn}}$ , but lack of a background correction precluded direct use of the flame-band signal here. Values of  $k_{\text{app}}$  are listed in Table I and shown in Fig. 2.

A brief inspection of Fig. 2 is sufficient to suggest that  $k_{\text{app}}$  cannot be directly identified with  $k_{\text{V}}$ . Such an attempt would not be consistent with the expectation that  $k_{\text{V}}$  was measured at the low pressure limit in these experiments. Attempts to rationalize the data in terms of the recombination occurring in the fall-off region

would also lead one into serious difficulties. This would conflict with the observations of Wagner and Zabel [7], and would require that fall-off region to come at much lower pressures than expected for such a simple molecule. On the other hand, it is difficult to rationalize the high  $k_{app}$  values for the 1.2 kPa experiments as simple experimental error since additional experiments at even lower initial pressures yielded even higher values for  $k_{app}$ .

An alternative explanation for the observed pressure dependence of  $k_{app}$  is the possibility that an alternate channel for  $CO_2$  production is opened at lower pressures. In this system such a possibility appears quite likely. The recombination process, being third-order, drops off rapidly as the pressure is lowered and thus a second-order process, though negligible at higher pressures, could begin to make a significant contribution to the total rate. In this system the large concentration of oxygen atoms can rapidly react with any hydrogenous species present to produce OH radicals. These, in turn, can react with CO to produce  $CO_2$  via  $OH + CO \rightarrow CO_2 + H$ . This effect would not simply be a transitory perturbation at early times since the hydrogen atoms produced in conjunction with the  $CO_2$  can reform OH by reacting with  $O_2$ . A simplified mechanism where the impurities are assumed to be either  $H_2O$  or  $CH_4$  is listed in Table II. Qualitative evidence to support this idea of impurity effects was obtained from a series of experiments when the tube was only pumped a few minutes prior to a shock. Here the background pressure was an order of magnitude higher than normal. It was observed that higher

values of  $k_{app}$  were obtained at all initial pressures, but that the effect was much more dramatic at the lower pressures.

The influence of small amounts of impurities were estimated by numerically integrating the mechanism shown in Table II. The procedure used assigned an (initially) arbitrary value to  $k_V$ , assigned concentrations of  $CH_4$  and  $H_2O$ , and treated the computed  $CO_2$  profile in exactly the same way as the experimental profiles to obtain a value of  $k_{app}$ . Any value of  $k_{app}/k_V$  greater than unity demonstrated an enhancement in  $CO_2$  production that was caused by the impurities. Several calculations included the recombination reactions  $O + O + M \rightarrow O_2 + M$  and  $O + NO + M \rightarrow NO_2 + M$ , but the results were not changed by this addition. The calculations were also checked by several runs at zero impurity concentrations. Here, as expected,  $k_{app}/k_V \approx 1.0$ .

These calculations demonstrated that, under certain circumstances, the  $CO_2$  production rate was remarkably sensitive to very small impurity concentrations. Of particular interest was the observation that the  $CO_2$  profile exhibited the same deceptively simple linear growth even when an appreciable fraction of  $CO_2$  was being produced via Reaction VII. As expected, the increase in the value of  $k_{app}/k_V$  was significantly greater at lower initial pressures. This effect is further enhanced by the fact that the contribution of impurities from the shock tube via outgassing is more severe (on a relative basis) at the lower initial pressures.

The impurities that might be present in these experiments are likely to come from either those initially present in the gases used or those arising from outgassing of the shock tube. It was estimated

that the upper limit of impurities originally in the gases used could be represented by 10 ppm  $\text{CH}_4$  and the  $\text{H}_2\text{O}$  pressures arising from outgassing as 12 mPa; these estimates are well above those computed from the nominal purities of the gases and the measured leak/outgassing rate. Calculations using these estimates are summarized in Table III. The reasonable agreement between these results and the observed  $k_{\text{app}}$  values strongly suggests that the variation of  $k_{\text{app}}$  with pressure can be ascribed to the increasing importance of side reactions at the lower pressures. Attempts to quantitatively correct for these impurity effects are particularly difficult. Not only is it impossible to accurately determine the nature and concentration of the impurities, but the detailed mechanisms and associated rate constants are uncertain. The prudent approach is obviously to focus on those experiments at the higher pressures where the effects of impurities are minimized. Thus, the data at 2.7 and 4.0 kPa are considered to be of most importance in assignment of a recombination rate constant. Note in Figure 2 that these data are consistent with the concept that the impurity contribution is small here. The 4.0 kPa values are only slightly lower than those observed at 2.7 kPa. Also note that the 2.7 kPa data exhibit essentially no temperature dependence. This is significant since the calculations showed a marked increase in  $k_{\text{app}}$  at lower temperatures. This seems to suggest that the actual impurities in the 2.7 kPa mixture were even smaller than assumed. In any event, it is clear that the data unequivocally rules out assignment of a large negative temperature dependence to  $k_v$ . Figure 2 indicates that Mixture E (at 4 kPa) gives values of  $k_{\text{app}}$  ~10% larger than Mixture G. Such an observation is also consistent with the impurity hypothesis.

One would expect Reaction V to proceed ~3.7 times as rapidly in G with its increased concentrations of O and CO. Thus the possibility of CO<sub>2</sub> formation via VII is enhanced in Mixture E relative to G. Mixture G should represent the  $k_{app}$  data least affected by impurities. Table III suggests that here  $k_{app} \approx 1.15 k_V$ . However, the apparent overestimate of the impurity effect at 2.7 kPa suggests that a reasonable assessment is that  $k_{app}$  is less than 10% higher than  $k_V$ . Thus it would appear that  $k_V \approx 1.6 \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$  near 2800 K. The lack of a temperature dependence in the 2.7 kPa experiments suggests this value of  $k_V$  is a reasonable estimate over the entire range of these experiments.

The three most likely sources of systematic error in these experiments are the CO<sub>2</sub> calibration factor, the O-atom determination, and the calculation of reflected shock concentrations. The measured (temperature-dependent) calibration factors showed good reproducibility; it is estimated that the error introduced in the conversion of the observed signal to the reported CO<sub>2</sub> production rate is much less than 10%. The O-atom calibrations were done with several mixtures at low initial pressures to minimize the influence of recombination reactions. Although errors in assignment of post-shock concentrations are potentially serious since  $k_V$  is a third order rate constant, such errors are believed to be small since such good agreement was obtained between measured and observed pressures. Thus it is felt that the uncertainty due to these three factors is on the order of 10%. Standard deviations in measured values of  $k_{app}$  for each of the 2.7 kPa and 4.0 kPa mixtures were obtained as an estimate of the

measurement errors. The average of the quantity  $2 \sigma/k_{app}$  was 15%. Thus, the overall uncertainty in this work appears to be on the order of 20% and a reasonable estimate of  $k_V$  is  $(1.6 \pm 0.3) \times 10^{-34}$  between 2100 and 3200 K.

This value is consistent with that obtained by Brabbs and Belles [2] and the limit obtained by Hardy, et al. [4], but is clearly at odds with that reported by Lin and Bauer [3]. In a recent review [18], Troe combines the most recent studies of  $CO_2$  dissociation [4,7,8] with the well established recombination rate data at low temperatures to recommend an expression for the recombination rate between 300 and 3000 K. This expression gives  $k_V = 1.18 \times 10^{-34}$  at 2100 K and  $9.3 \times 10^{-35}$  at 3000 K. It is felt that the agreement between this expression and that observed in this work is sufficiently good, both in magnitude and temperature dependence, to suggest that the high temperature data on the  $CO_2$  system is now consistent. In particular, this work presents added evidence that the dissociation of  $CO_2$  exhibits a "normal" activation energy and that the lower values obtained in earlier work were probably due to complications introduced by impurities.

Table I. Summary of Experimental Observations

| Composition*               |                       | T(K) | (10 <sup>18</sup> molec.cm <sup>-3</sup> ) | (10 <sup>16</sup> molec.cm <sup>-3</sup> ) | [O] <sub>rxn</sub>                                          | dCO <sub>2</sub> /dt                                                       | k <sub>app</sub> |
|----------------------------|-----------------------|------|--------------------------------------------|--------------------------------------------|-------------------------------------------------------------|----------------------------------------------------------------------------|------------------|
| Mixture                    | %N <sub>2</sub> O %CO |      | (10 <sup>18</sup> molec.cm <sup>-3</sup> ) | (10 <sup>16</sup> molec.cm <sup>-3</sup> ) | (10 <sup>18</sup> molec.cm <sup>-3</sup> .s <sup>-1</sup> ) | (10 <sup>-34</sup> cm <sup>6</sup> .molec <sup>-2</sup> .s <sup>-1</sup> ) |                  |
| Initial Pressure ≈ 2.7 kPa |                       |      |                                            |                                            |                                                             |                                                                            |                  |
| A                          | 1.01 2.00             | 2255 | 4.64                                       | 2.28                                       | 2.37                                                        | 2.36                                                                       |                  |
|                            |                       | 2270 | 4.62                                       | 2.35                                       |                                                             |                                                                            |                  |
|                            |                       | 2410 | 4.75                                       | 2.55                                       | 3.34                                                        | 2.19                                                                       |                  |
|                            |                       | 2590 | 4.85                                       | 3.24                                       |                                                             |                                                                            |                  |
|                            |                       | 2670 | 4.92                                       | 3.35                                       |                                                             |                                                                            |                  |
| B                          | 1.00 2.09             | 2695 | 4.90                                       | 3.39                                       |                                                             |                                                                            |                  |
|                            |                       | 2015 | 4.41                                       | 1.40                                       |                                                             |                                                                            |                  |
|                            |                       | 2135 | 4.53                                       | 1.92                                       | 2.34                                                        | 2.84                                                                       |                  |
|                            |                       | 2245 | 4.61                                       | 2.28                                       | 2.54                                                        | 2.51                                                                       |                  |
|                            |                       | 2305 | 4.66                                       | 2.26                                       | 2.53                                                        | 2.47                                                                       |                  |
| C                          | 1.00 4.35             | 2525 | 4.82                                       | 3.24                                       |                                                             |                                                                            |                  |
|                            |                       | 2690 | 4.95                                       | 3.81                                       | 3.98                                                        | 2.04                                                                       |                  |
|                            |                       | 2925 | 5.08                                       | 3.94                                       | 5.07                                                        | 2.39                                                                       |                  |
|                            |                       | 3080 | 5.14                                       | 4.33                                       | 5.22                                                        | 2.18                                                                       |                  |
|                            |                       | 3250 | 5.28                                       | 4.29                                       |                                                             |                                                                            |                  |
| D                          | 1.00 4.27             | 3440 | 5.33                                       | 4.11                                       |                                                             |                                                                            |                  |
|                            |                       | 2150 | 4.66                                       | 1.69                                       | 3.27                                                        | 2.05                                                                       |                  |
|                            |                       | 2230 | 4.74                                       | 1.99                                       | 3.94                                                        | 2.03                                                                       |                  |
|                            |                       | 2390 | 4.87                                       | 2.76                                       | 5.98                                                        | 2.10                                                                       |                  |
|                            |                       | 2535 | 4.98                                       | 2.87                                       | 6.82                                                        | 2.20                                                                       |                  |
| E                          | 0.50 1.04             | 2600 | 5.00                                       | 2.86                                       | 5.97                                                        | 1.92                                                                       |                  |
|                            |                       | 2700 | 5.08                                       | 3.12                                       | 7.18                                                        | 2.05                                                                       |                  |
|                            |                       | 2835 | 5.17                                       | 3.51                                       | 8.70                                                        | 2.13                                                                       |                  |
|                            |                       | 2890 | 5.20                                       | 3.39                                       | 10.2                                                        | 2.56                                                                       |                  |
|                            |                       | 3065 | 5.30                                       | 3.43                                       | 9.14                                                        | 2.18                                                                       |                  |
|                            |                       | 3175 | 5.37                                       | 3.67                                       | 9.76                                                        | 2.12                                                                       |                  |
|                            |                       | 2540 | 5.00                                       | 3.05                                       | 7.06                                                        | 2.17                                                                       |                  |
|                            |                       | 2835 | 5.17                                       | 3.77                                       | 8.78                                                        | 2.04                                                                       |                  |
|                            |                       | 2875 | 5.16                                       | 3.92                                       | 8.09                                                        | 1.82                                                                       |                  |
|                            |                       | 2865 | 4.92                                       | -                                          | 1.19                                                        | 2.24                                                                       |                  |
|                            |                       | 2870 | 4.92                                       | -                                          | 0.97                                                        | 1.83                                                                       |                  |
|                            |                       | 3010 | 4.96                                       | -                                          | 1.11                                                        | 1.99                                                                       |                  |
|                            |                       | 3150 | 5.03                                       | -                                          | 1.09                                                        | 1.84                                                                       |                  |

Table I. Summary of Experimental Observations (continued)

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| Composition*                       |          | Tot. Conc. | $[O]_{rxn}$ |                                              | $dCO_2/dt$                                                     | $k_{app}$                                                         |
|------------------------------------|----------|------------|-------------|----------------------------------------------|----------------------------------------------------------------|-------------------------------------------------------------------|
| Mixture                            | $\%N_2O$ | $\%CO$     | $I(K)$      | $(10^{18} \text{ molec}\cdot\text{cm}^{-3})$ | $(10^{18} \text{ molec}\cdot\text{cm}^{-3}\cdot\text{s}^{-1})$ | $(10^{-34} \text{ cm}^6\cdot\text{molec}^{-2}\cdot\text{s}^{-1})$ |
| Initial Pressure $\approx 1.2$ kPa |          |            |             |                                              |                                                                |                                                                   |
| F                                  | 2.02     | 8.66       | 2625        | 2.48                                         | 4.92                                                           | 3.67                                                              |
|                                    |          |            | 2725        | 2.49                                         | 5.13                                                           | 3.44                                                              |
|                                    |          |            | 2745        | 2.53                                         | 5.49                                                           | 3.48                                                              |
|                                    |          |            | 2875        | 2.55                                         | 6.58                                                           | 3.74                                                              |
|                                    |          |            | 2990        | 2.58                                         | 5.78                                                           | 2.96                                                              |
| Initial Pressure $\approx 1.3$ kPa |          |            |             |                                              |                                                                |                                                                   |
| C                                  | 1.00     | 4.35       | 2505        | 2.47                                         | 1.41                                                           | 3.45                                                              |
|                                    |          |            | 2680        | 2.53                                         | 1.61                                                           | 3.29                                                              |
|                                    |          |            | 2745        | 2.55                                         | 1.45                                                           | 2.78                                                              |
|                                    |          |            | 2845        | 2.59                                         | 1.87                                                           | 3.28                                                              |
|                                    |          |            | 3000        | 2.63                                         | 2.24                                                           | 3.59                                                              |
|                                    |          |            | 3180        | 2.71                                         | 2.51                                                           | 3.51                                                              |
|                                    |          |            | 3190        | 2.65                                         | 2.10                                                           | 3.14                                                              |
| Initial Pressure $\approx 4.0$ kPa |          |            |             |                                              |                                                                |                                                                   |
| E                                  | 0.50     | 1.04       | 2855        | 7.32                                         | 3.29                                                           | 1.90                                                              |
|                                    |          |            | 2925        | 7.36                                         | 3.49                                                           | 1.96                                                              |
|                                    |          |            | 2945        | 7.42                                         | 3.31                                                           | 1.81                                                              |
| G                                  | 0.67     | 2.86       | 2740        | 7.45                                         | 10.9                                                           | 1.78                                                              |
|                                    |          |            | 2770        | 7.48                                         | 11.0                                                           | 1.76                                                              |
|                                    |          |            | 2905        | 7.64                                         | 11.1                                                           | 1.62                                                              |

\*Balance of all mixtures was Argon.

Table II. Possible Mechanism for CO<sub>2</sub> Production

|      | Reaction                                               | Rate Constant* |                | Reference |
|------|--------------------------------------------------------|----------------|----------------|-----------|
|      |                                                        | A              | E <sub>a</sub> |           |
| I    | N <sub>2</sub> O + M = N <sub>2</sub> + O + M          | 4.5 E - 10     | 226            | This work |
| II   | N <sub>2</sub> O + O = 2NO                             | 7.7 E - 11     | 117            | This work |
| III  | N <sub>2</sub> O + O = N <sub>2</sub> + O <sub>2</sub> | 7.7 E - 11     | 117            | This work |
| V    | CO + O + M = CO <sub>2</sub> + M                       | 1.7 E - 34     | 0              | See text  |
| VI   | O + H <sub>2</sub> O = 2OH                             | 6.3 E - 10     | 82             | 14        |
| VII  | OH + CO = CO <sub>2</sub> + H                          | 3.8 E - 12     | 24             | 15        |
| VIII | H + O <sub>2</sub> = OH + O                            | 1.6 E - 10     | 63             | 16        |
| IX   | O + CH <sub>4</sub> = CH <sub>3</sub> + OH             | 2.6 E - 10     | 33             | 17        |
| X    | O + CH <sub>3</sub> = CH <sub>2</sub> O + H            | 1.0 E - 10     | 0              | 17        |
| XI   | O + CH <sub>2</sub> O = H + CO + OH                    | 1.0 E - 10     | 0              | 17        |

\*Expressed in the Arrhenius form,  $k = A \exp(-E_a/RT)$ .  
A in cm-molecule-sec units; E<sub>a</sub> in kJ/mol.

Table III. Effect of Impurities on  $k_{app}$

| T (°K) | $k_{app}$ ( $10^{-34}$ cm <sup>6</sup> molec <sup>-2</sup> s <sup>-1</sup> )      |                                                                                       |                                                                                        |
|--------|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
|        | Mixture F<br>$P_i \approx 1.2$ kPa<br>(10ppm H <sub>2</sub> O & CH <sub>4</sub> ) | Mixture D<br>$P_i \approx 2.7$ kPa<br>(5ppm H <sub>2</sub> O, 10ppm CH <sub>4</sub> ) | Mixture G<br>$P_i \approx 4.0$ kPa<br>(3 ppm H <sub>2</sub> O, 10ppm CH <sub>4</sub> ) |
| 2200   | —                                                                                 | 2.93                                                                                  | —                                                                                      |
| 2600   | 3.65                                                                              | 2.40                                                                                  | 2.11                                                                                   |
| 3000   | 3.05                                                                              | 2.21                                                                                  | 1.96                                                                                   |

In all cases the rate constants in Table II were used.

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# LEGENDS

Fig. 1. Values of  $[O]_{\text{rxn}}/[N_2O]_i$  versus temperature at initial pressures of 2.7 kPa. (a) Mixtures containing ~2% CO: ● = Mixture A; ▲ = Mixture B. The solid line is calculated for Mixture B at an initial pressure of 2.7 kPa using the rate constants cited in the text. (b) Mixtures containing ~4.3% CO: ○ = Mixture C; △ = Mixture D. The solid line is calculated for Mixture C.

Fig. 2 Values of the apparent rate constant for recombination versus temperature. Initial pressures near 1.2 kPa: ○ = Mixture F; △ = Mixture C. Initial pressure near 2.7 kPa: ● = Mixture A; ▲ = Mixture B; ■ = Mixture C; ◆ = Mixture D; ▼ = Mixture E. Initial pressures near 4.0 kPa: □ = Mixture E; ◇ = Mixture G.

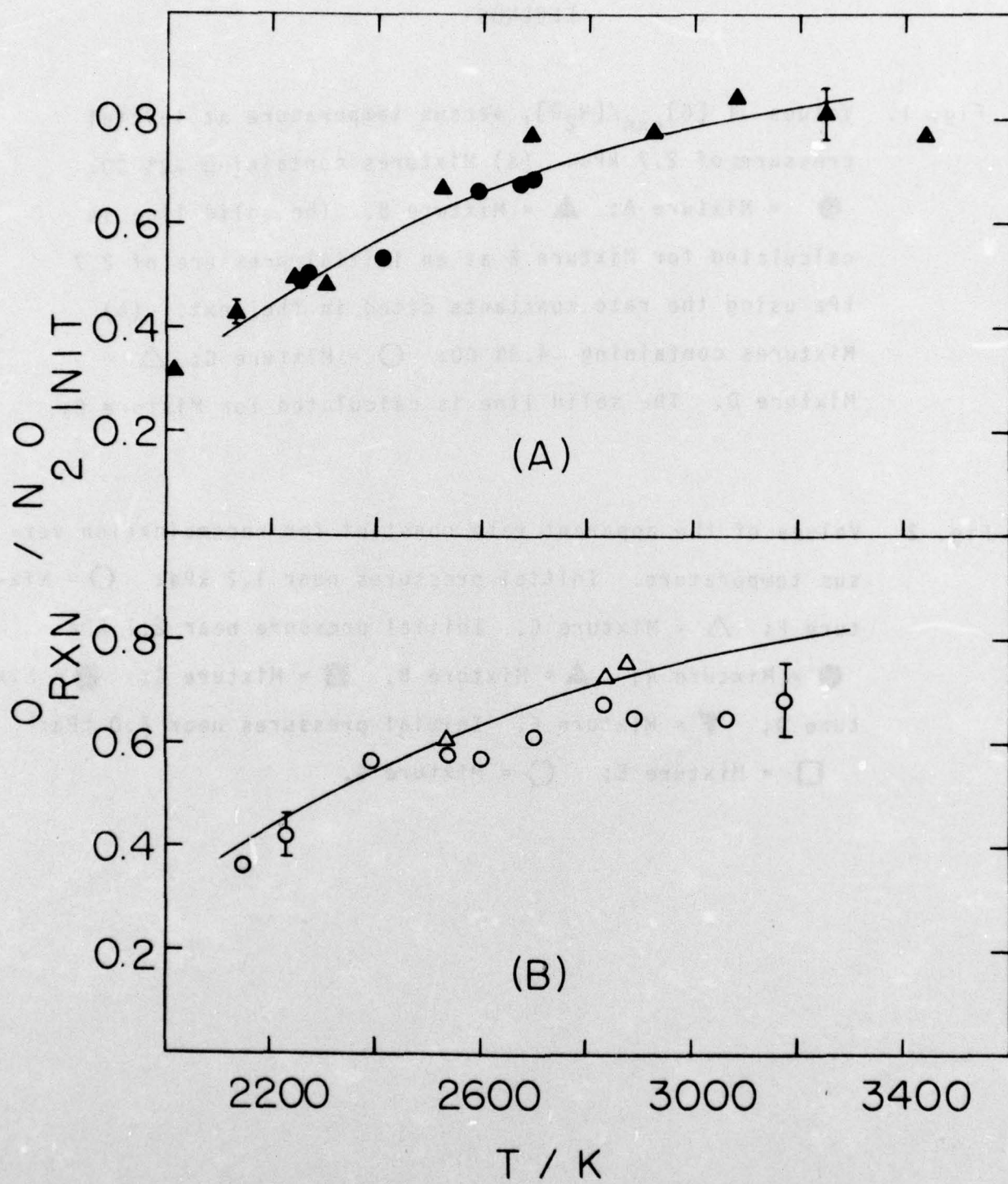


FIGURE 1

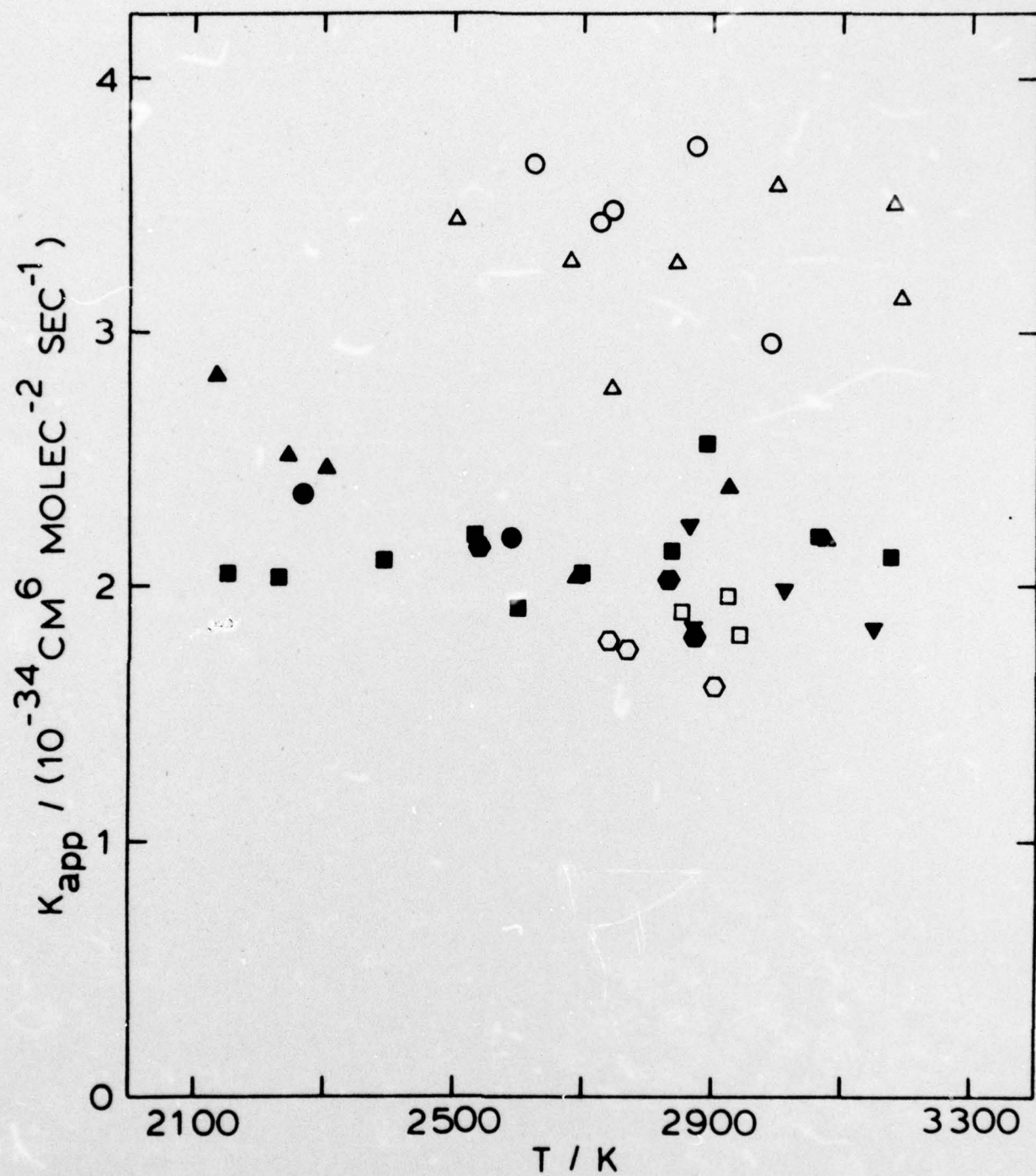


FIGURE 2

| REPORT DOCUMENTATION PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                       | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM                                       |
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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Shock Waves<br>Shock Tube Kinetics<br>Recombination Reaction<br>N <sub>2</sub> O Dissociation                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                       |                                                                                   |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Time resolved emissions from CO <sub>2</sub> and the radiative recombination of CO and O (flame-band emission) have been monitored in a variety of N <sub>2</sub> O/CO/Ar mixtures. These mixtures were studied behind reflected shock waves at temperatures between 2100-3200K and total concentrations between 2.5-7x10 <sup>18</sup> molec/cm <sup>3</sup> . The flame-band detector was calibrated so that absolute concentrations of atomic oxygen could be determined. This data was shown to be consistent with the following mechanism: N <sub>2</sub> O + M = N <sub>2</sub> + O + M; N <sub>2</sub> O + O = 2NO; and N <sub>2</sub> O + O = N <sub>2</sub> + O <sub>2</sub> with k <sub>1</sub> = 4.5x10 <sup>-10</sup> exp(-226kJ/RT) cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> and k <sub>2</sub> = k <sub>3</sub> = 7.7x10 <sup>-11</sup> . |                       |                                                                                   |

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$\exp(-117\text{kJ/RT})$ . This combination was also shown to be consistent with earlier data from this laboratory.

$\text{CO}_2$  was observed to increase linearly with time in these experiments and an apparent recombination rate constant defined as  $k_{\text{app}} \equiv d\text{CO}_2/dt/([\text{CO}][\text{O}][\text{M}])$  was measured and found to be a function of pressure. This behavior was attributed to the presence of very small concentrations of hydrogenous impurities. Data at higher pressures were used to estimate the rate constant for the recombination  $\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$ , since the effect of impurities was minimized here. It was found that  $k_y = (1.6 \pm 0.3) \times 10^{-34} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$  between 2100-3200 K. This value is shown to be consistent with recent studies of  $\text{CO}_2$  dissociation which report "normal" activation energies.

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