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Reaction of Carbon Dioxide with Atomic Oxygen and the Dissociation of Carbon Dioxide in Shock Waves

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The reaction of oxygen atoms with carbon dioxide has been investigated from 2800–3200°K using the decomposition of N_2O as a source of oxygen atoms: $O+CO_2\rightarrow CO+O_2$ (1). Over the temperature range, the value of k_1 was found to be $\log k_1=-10.59(\pm0.79)-(32\,500\pm10\,900)/4.58\ T$ cm^3/particle sec, which is much larger than the recent literature value. The addition of molecular oxygen decreased the observed rate of CO_2 removal in Reaction (1). The decomposition of CO_2 in the second-order pressure region in neon diluent was investigated over the temperature range 2900–4000°K, and it was shown that the contribution of Reaction (1) to the gross decomposition rate is significant, but does not account for the anomalously low activation energy of CO_2 decomposition. The corrected first-order rate constant for the reaction $CO_2+Ne\rightarrow CO+O+Ne$ (2) at a density of 1.35×10^{18} particle/cm^3, is $\log k_2=7.71(\pm0.36)-(74\,100\pm6300)/4.58T$ sec^{-1}. The rate constant for the reaction $O_3+NO\rightarrow N+O_2$ (3) is estimated as $k_3=1.5\times10^{-14}$ cm^3/particle·sec at 3000°K, and a suggested upper limit for the rate constant of the reaction $NO+CO_2\rightarrow NO_2+CO$ (6), is $k_6\leq5\times10^{-15}$ cm^3/particle·sec at the same temperature.

I. INTRODUCTION

For some time the only estimate of the rate coefficient for the reaction of carbon dioxide with oxygen atoms, Reaction (1), was obtained from the well-established equilibrium constant using the rate constant for the back Reaction (−1) determined indirectly in a study of the complex chain oxidation of carbon monoxide by Sulzmann *et al.*[1] (recently confirmed by Drummond[2]):

$$O+CO_2\rightarrow CO+O,\qquad \Delta H^\circ_{3000}=3.8\ \text{kcal/mole}. \tag{1}$$

Bartle and Myers[3] reported recently a direct determination of the rate of Reaction (1) in which the instantaneous decomposition of ozone provided O atoms in the presence of CO_2 over the temperature range 3500–5500°K. The value of k_1 obtained is consistent with that predicted using Sulzmann's rate coefficient for (−1) and the equilibrium constant.

Work in this laboratory concerned primarily with the rate of the exchange reaction $^{18}O+C^{16}O\rightarrow C^{18}O+^{16}O$ in $C^{16}O$ and $^{18}O_2$ mixtures[4] indicated that either k_{-1} was an order of magnitude greater than the published value by Sulzmann[1] and Drummond[2] or that chain branching resulting from H_2 impurities and producing oxygen atoms, after the manner suggested by Brokaw,[5] was occurring. Therefore, we have undertaken an independent study of the rate coefficient for Reaction (1).

The many investigations by shock-tube workers on the decomposition of carbon dioxide,

$$CO_2+M\rightarrow CO+O+M,\qquad \Delta H^\circ_{3000}=126.6\ \text{kcal/mole} \tag{2}$$

in the second-order pressure region from 3000–8000°K using pure and diluted CO_2 have been recently reviewed.[6] The results all indicate an Arrhenius activation energy smaller than the endothermicity of Reaction (2). Several authors[6,7] have pointed out that the apparent first-order decay rate can be affected by an uncertain contribution from Reaction (1), which is the secondary reaction in the decomposition process. Thus we have also undertaken an investigation of the rate of decomposition of carbon dioxide in order to evaluate the coupling of Reactions (1) and (2).

A subsidiary study of N_2O decomposition in the temperature range of interest was necessary to determine the O-atom concentration produced by this reaction, which could then be used for a study of Reaction (1) and to ensure that this O-atom concentration was not depleted over extended reaction times by recombination processes.

II. EXPERIMENTAL

The use of a time-of-flight mass spectrometer coupled to a shock tube for the study of chemical kinetics has been described.[4,8] The shock heated gas is sampled from the reflected shock zone through a conical copper nozzle on the end wall of the shock tube and is analyzed mass spectrometerically. In this work H_2 driver gas was used, and the shock wave was initiated by perforating aluminum-foil diaphragms with a spring-loaded knife. Real time analysis of the gas is practical because the spectrometer can produce a complete mass spectrum every 20 μsec. The only change in the operating conditions since previous work was a decrease of an order of magnitude in the sensitivity of the elctron

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[2] L. J. Drummond, Australian J. Chem. **21**, 2631 (1968).

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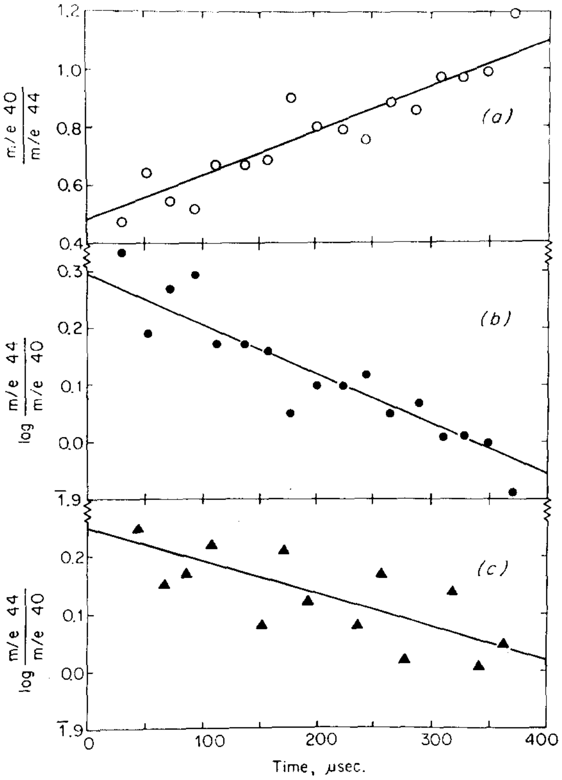

FIG. 1. Treatment of typical experimental data. (a) Reaction of CO_2 with an equal concentration of O atoms at 2921°K. Plot of reciprocal CO_2/Ar mass peak ratio with time (second-order treatment). (b) Reaction of CO_2 with an equal concentration of O atoms at 2921°K. Plot of log(CO_2/Ar mass-peak ratio) with time (pseudo-first-order treatment). Same experiment as in 1(a). (c) CO_2 unimolecular decomposition. Plot of log(CO_2/Ar mass-peak ratio) with time at 3691°K.

multiplier detector, resulting in an increased signal-to-noise ratio.

The properties of the unreacted gas mixture after passage of the shock wave were calculated from standard thermodynamic data[9] using an IBM 1620 computer, as has been described earlier.[10] A zero-order temperature correction to the no-reaction temperature was made for cooling due to the over-all endothermicity of the reactions involved, at half the observed extent of reaction. In these experiments the temperature range was 2700–4000°K, and the total density behind the reflected shock was close to 1.4×10^{18} particle/cm.[3]

A small amount of argon (typically 1%) was introduced into all gas mixtures as an internal standard. All measurements of mass peaks on a particular spectrum were related to the argon mass peak on that spectrum. Thermal ions were prevented from entering the mass spectrometer by a positively biased grid placed before the ionizing region. Ionization was achieved with 30-V electrons.

All least-squares Arrhenius lines were calculated by standard linear regression procedures using an IBM 1620 computer. Each point was weighted according to the relative uncertainty in it. The uncertainty was defined as half the difference between the maximum and minimum rates which could be reasonably deduced from graphs such as those in Fig. 1.

The gases used were taken from Matheson Co. cylinders and were CO_2 "bone-dry grade"; N_2O "98%-pure grade"; O_2, Ne, and Ar "research grade." The N_2O and the CO_2 were vacuum distilled before use.

III. RESULTS

A. N_2O Decomposition and the Formation of O Atoms

Under the experimental conditions of this study the concentration of N_2O fell to 5% of its original value within 70 μsec even at the lowest temperature used (2800°K). This is consistent with the rate of decomposition of N_2O determined in this laboratory at still lower temperatures.[4]

It was found that the oxygen-atom signal present after all N_2O was pyrolyzed remained constant for the 380 μsec duration of an experiment. By analysis of the mass peaks of molecular oxygen and nitric oxide, it was established that over the temperature range investigated (3200–2800°K) 3% N_2O decomposed into 0.4% NO, 0.4% O_2, 2.8% N_2, and 1.8% O atoms, within a 20% uncertainty. The percentages were deduced using experimentally determined ionization cross sections for NO and O_2 and assuming conservation of mass. Thus a value of 2% for O-atom concentration could be assumed with reasonable confidence.

It was observed that a small but measurable decrease in NO concentration and a corresponding increase in O_2 concentration gradually occurred. This can be explained in terms of the reaction scheme:

$$O+NO\rightarrow N+O_2, \qquad (3)$$

$$N+NO\rightarrow N_2+O, \qquad (4)$$

in which, according to published data,[11,12] $k_4 \gg k_3$ so that $-d(\ln[NO])/dt=2\,k_3[O]$. From our observations we deduce an approximate value of $k_3=1.5\times10^{-14}$ cm^3/particle·sec at 3000°K, which is consistent with the published value[11] ($k_3=2.3\times10^{-14}$ cm^3/particle·sec).

B. The Reaction of Carbon Dioxide with O Atoms

The data was obtained from a standard mixture containing 3% N_2O (~2% O atoms), 2% CO_2, 1% Ar, 94% Ne. The use of equal reactant concentrations simplifies the treatment of the second-order kinetic data. Since the disappearance of N_2O requires only a small fraction of the observation time, N_2O at $m/e=44$ does not interfere with the measurement of CO_2 at

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the same $m/e=44$. The disappearance of the parent CO_2 peak with time was measured at temperatures at which the direct CO_2 decomposition rate was unimportant. For equal concentrations of O and CO_2, it can be stated

$$-d[CO_2]/dt=k_1[CO_2][O]=k_1[CO_2]^2,$$

so that

$$\frac{d(1/[CO_2])}{dt}=k_1.$$

A plot of the data treated in this way is given in Fig. 1(a).

Figure 2 shows a least-squares Arrhenius plot of the values of k_1 obtained from plots such as that shown in Fig. 1(a) from 2800 to 3200°K. The expression obtained is

$$\log k_1=-10.59(\pm 0.79)$$

$$-(32\,500\pm 10\,900)/4.58T \text{ cm}^3/\text{particle}\cdot\text{sec}.$$

It was found useful to determine the pseudo-first-order decay coefficient for CO_2 in the standard mixture to facilitate comparison with the unimolecular rate of disappearance of CO_2 observed in the absence of O atoms. The true order of the reaction with respect to each of the reactants was also most readily determined from the pseudo-first-order treatment of the various mixtures.

The following approximate expression can be applied within our experimental uncertainty:

$$-d\ln[CO_2]/dt=k_1[O]_{\text{mean}}=k_1''$$

since the oxygen-atom concentration undergoes only a moderate change during the observation period. A plot of the data from one experiment treated in this way, $\log[CO_2]$ vs time, is given in Fig. 1(b). Figure 3 shows an Arrhenius plot of these pseudo-first-order rate constants.

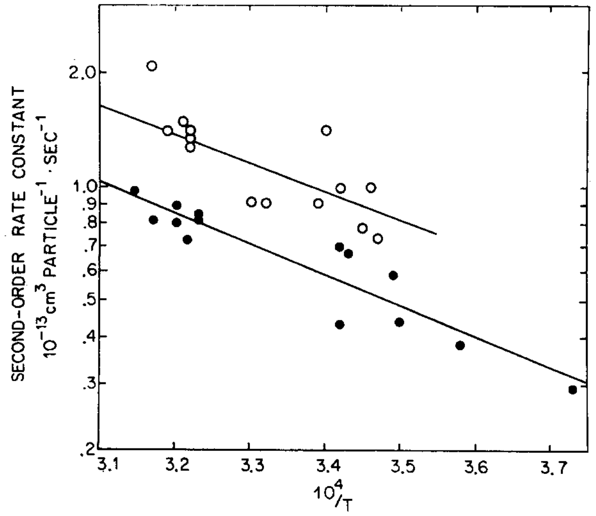

FIG. 2. ○, Arrhenius plot of k_1, the second-order rate constant for $O+CO_2$. ●, Arrhenius plot of k_1', the second-order rate constant for $O+CO_2$ with added molecular oxygen (see text).

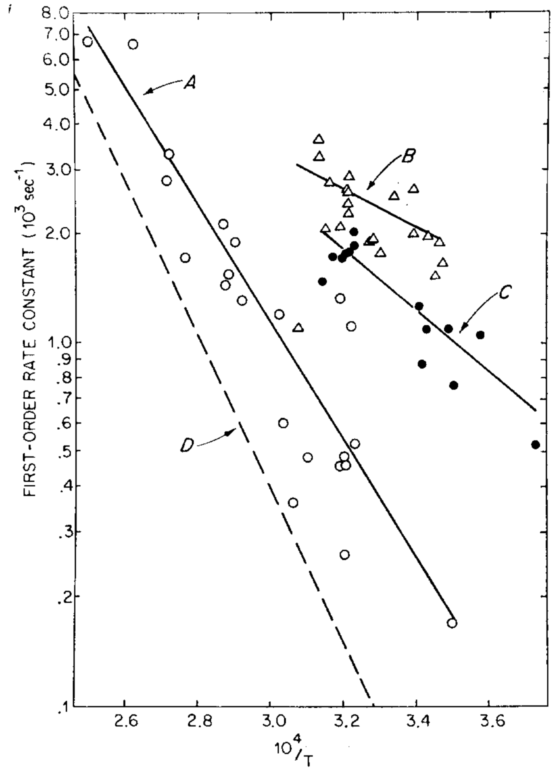

FIG. 3. *A*. Gross first-order rate constant for CO_2 decomposition in 1.35×10^{18} particle/cm^3 of Ne (○). *B*. Pseudo-first-order rate constant k_1'' for $O+CO_2$ (△). *C*. Pseudo-first-order rate constant k_1''' for $O+CO_2$ with added molecular oxygen (see text) (●). *D*. First-order rate constant deduced for 1.35×10^{18} particle/cm^3 of Ar from Ref. 12 (dashed line).

The pseudo-first-order rate constant for CO_2 disappearance, k_1'', was half that for the standard mixture when a mixture containing 1% O atoms, 2% CO_2 was used. For a mixture containing 2% O atoms, 1% CO_2 the value of k_1'' was the same as for the standard mixture. This confirms that the reaction is first order in CO_2 and in O atoms.

The nature of the reaction was further explored by measuring the rate of O_2 appearance. If the assumed mechanism is correct, this rate can be defined by

$$d[O_2]/dt=-d[CO_2]/dt=k_1[CO_2]_{\text{mean}}[O]_{\text{mean}}.$$

If the average values for $[CO_2]$ and $[O]$ are inserted, the rate constants k_1 thus obtained are in agreement with those determined from CO_2 disappearance, within the uncertainties involved.

The rate of removal of NO by reaction with O-atoms[4] was determined for the standard mixture, and the data was analyzed according to the scheme of the preceding section. The rate constant k_3, deduced for the rate of removal of NO by O atoms, was unaffected within experimental uncertainties by the presence of CO_2.

A mixture otherwise identical with the standard mixture, but with molecular oxygen added, 3% N_2O (~2% O atoms), 2% CO_2, 2% O_2, 1% Ar, 92% Ne was used. The data were analyzed exactly as above to give second-order rate constants, k_1', and the pseudo-first-order rate constants, k_1'''. The corresponding least-squares Arrhenius plots are displayed in Figs. 2 and 3, respectively.

The second-order rate constants were about 40% lower than those observed in the absence of molecular oxygen. The value obtained for the least-squares line is

$$\log k_1' = -10.46(\pm 0.37) - (37\,200 \pm 5300)/4.58T \text{ cm}^3/\text{particle}\cdot\text{sec}.$$

C. The Rate of Carbon Dioxide Decomposition

Mistures of CO_2, containing 1%, $1\frac{1}{2}$%, and 2% of CO_2, in Ne, were decomposed in reflected shock waves over the temperature range 2900–4000°K.

The measured CO_2/Ar mass-peak ratio decayed over 380 μsec according to first-order kinetics within experimental uncertainties with the extent of reaction ranging from 20%–70%. A typical plot of the $\log[CO_2]$ vs time is given in Fig. 1(c). The temperature dependence of the first-order rate constants obtained is presented in the form of a least-squares Arrhenius plot (A) in Fig. 3, which includes all data. Also shown in Fig. 3 is an Arrhenius line (D) based on the rate expression for CO_2 decomposition in Ar as diluent determined by Wagner *et al.*[13]

The least-squares Arrhenius line yields the following expression for k_2 at an average total density of $1.35 \times 10^{+18}$ particle/cm³:

$$\log k_2 = 7.91(\pm 0.37) - (74\,000 \pm 6300)/4.58T \text{ sec}^{-1}.$$

In this work we were able to follow the appearance of product CO as well as the disappearance of CO_2. The rate of CO appearance agreed with the rate of CO_2 decay. The O-atom mass peak, corrected for contributions due to the CO_2 cracking pattern, showed, qualitatively, a reproducible leveling to a constant value which suggests that Reaction (1) is making some contribution to the over-all decay rate. This is supported by a very small, but detectable, formation of O_2 after long reaction times.

A mixture of NO and CO_2 ($1\frac{1}{2}$% NO, 2% CO_2, 2% Ar, $95\frac{1}{2}$% Ne) was shocked, and the first-order rate of disappearance of CO_2 was evaluated. The rate for the five runs ($T \sim 3200$°K) was indistinguishable from the rate of CO_2 decomposition found above in the absence of NO. We conclude that an upper limit for the rate constant of

$$NO + CO_2 \rightarrow CO + NO_2 \qquad (5)$$

at this temperature is $k_5 \leq 5 \times 19^{-15}$ cm³/particle·sec.

Table I is a summary of the experimental runs.

IV. DISCUSSION

A. The Reaction $O + CO_2$

Inspection of the first-order data presented in Arrhenius form in Fig. 3 shows that the observed rate of CO_2 disappearance is more than a factor of four faster when 2% O atoms are added to CO_2 than when CO_2 is studied alone. Thus in the mixtures studied, the unimolecular rate of disappearance of CO_2 by Reaction (2) represents a negligible contribution to the measured rate of Reaction (1).

The removal of NO by reaction with O atoms in Reactions (3) and (4) (Results, Sec. A) means that some N atoms are present in the reaction mixture. However, the steady-state N-atom concentration is too low to affect the observed rate of CO_2 consumption by the reaction

$$N + CO_2 \rightarrow NO + CO \qquad (6)$$

even if the highest literature value for k_6 is assumed.[14] Furthermore, Reaction (6) regenerates NO, so that if this reaction were important, the rate of NO disappearance would be reduced in mixtures containing CO_2. No such reduction was observed.

The reaction of CO_2 with the small amount of NO present as a decomposition product of N_2O due to a reaction

$$NO + CO_2 \rightarrow CO + NO_2 \qquad (5)$$

might increase the apparent rate of CO_2 reaction with O atoms. However, the already mentioned determination of the magnitude of k_5 suggests an upper limit of 1/30 of the observed value of k_1.

Inspection of the Arrhenius plots of Fig. 2 reveals that the second-order rate constant for Reaction (1) is reduced by the addition of molecular oxygen. The rate constant of the back reaction (k_{-1}) is expected to be comparable in magnitude with k_1 since the equilibrium constant for

$$O + CO_2 \rightleftharpoons CO + O_2 \qquad (1)$$

fixes the ratio of the forward to back rate constants as close to 3 over the temperature range used. The addition of molecular oxygen is thus expected, from estimates of the concentrations of the various species, to produce a reduction of about 10% in the observed second-order rate coefficients under our conditions. The observed reduction in rates is larger than this, being about 40%. However, the uncertainties in the least-squares lines and in the estimates of the mean concentrations make the observed reduction not inconsistent with the predicted one. We can merely conclude that molecular oxygen does depress the rate.

Prior work with the TOF instrumentation[4] led to a rate constant for Reaction (−1) about 30-fold greater

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TABLE I. Summary of experimental data.

Temperature		Density	Rate		Fraction	Composition %	
No reaction	Corrected	10^{18} particles/cm^3	1st order (10^3 sec^{-1})	2nd order (10^{-13} cm^3/particle sec.)	of CO_2 consumed	O atom	CO
3275	3156	1.47	2.80±0.50	2.09±0.33	0.64	2.	2.
3255	3136	1.47	2.10±0.20	1.14±0.13	0.55	2.	2.
3225	3106	1.50	2.70±0.40	1.35±0.20	0.59	2.	2.
3225	3106	1.50	2.70±0.30	1.41±0.13	0.62	2.	2.
3235	3116	1.49	2.96±0.25	1.48±0.13	0.64	2.	2.
3225	3106	1.50	2.50±0.25	1.29±0.10	0.54	2.	2.
3145	3026	1.48	1.79±0.20	0.91±0.07	0.52	2.	2.
3000	2881	1.47	1.66±0.20	0.73±0.07	0.46	2.	2.
3075	2951	1.49	2.04±0.20	0.92±0.10	0.49	2.	2.
3020	2901	1.45	1.55±0.20	0.78±0.07	0.42	2.	2.
3040	2921	1.49	1.99±0.20	1.00±0.07	0.52	2.	2.
3125	3006	1.47	1.95±0.20	0.90±0.10	0.51	2.	2.
3065	2946	1.50	2.73±0.25	1.43±0.10	0.64	2.	2.
3010	2891	1.49	1.90±0.35	1.00±0.13	0.50	2.	2.
3170	3110	1.41	1.18±0.35	···	0.44	1.	2.
2790	2730	1.38	0.89±0.26	···	0.27	1.	2.
3265	3205	1.44	1.30±0.15	···	0.38	1.	2.
3305	3245	1.42	1.18±0.25	···	0.44	1.	2.
3375	3256	1.45	1.09±0.20	···	0.45	2.	1.
3305	3186	1.48	3.30±0.25	···	0.71	2.	1.
3305	3186	1.46	3.60±0.25	···	0.74	2.	1.
3295	3176	1.44	2.05±0.25	···	0.54	2.	1.
3235	3116	1.44	2.24±0.30	···	0.54	2.	1.
3160	3041	1.43	1.91±0.25	···	0.52	2.	1.
3110	2991	1.43	2.50±0.20	···	0.61	2.	1.
3565	3487	1.38	1.49±0.30	···	0.34	···	2.
3500	3422	1.36	1.33±0.30	···	0.34	···	2.
3750	3626	1.40	1.80±0.30	···	0.54	···	2.
3830	3684	1.42	3.08±0.30	···	0.57	···	2.
3600	3485	1.36	2.10±0.30	···	0.50	···	2.
3170	3129	1.33	0.48±0.15	···	0.18	···	2.
3350	3304	1.33	0.60±0.20	···	0.20	···	2.
2905	2859	1.30	0.17±0.30	···	0.20	···	2.
3160	3098	1.34	0.52±0.20	···	0.27	···	2.
3605	3474	1.22	1.40±0.50	···	0.57	···	2.
3170	3134	1.33	0.46±0.15	···	0.20	···	2.
3275	3224	1.33	0.48±0.15	···	0.22	···	2.
3170	3131	1.34	0.27±0.20	···	0.17	···	2.
3160	3121	1.34	0.46±0.30	···	0.17	···	2.
3955	3815	1.38	6.80±0.60	···	0.81	···	1.5

TABLE I (*Continued*)

Temperature		Density 10^{18} particles/cm^3	Rate		Fraction of CO_2 consumed	Composition %	
No reaction	Corrected		1st order (10^3 sec^{-1})	2nd order (10^{-13} cm^3/particle sec.)		O atom	CO_2
3380	3311	1.31	1.18±0.25	···	0.40	···	1.5
3315	3263	1.33	0.36±0.20	···	0.30	···	1.5
3185	3119	1.31	1.10±0.40	···	0.38	···	1.5
3170	3113	1.32	1.30±0.40	···	0.49	···	1.
4105	4005	1.39	6.90±0.60	···	0.87	···	1.
3770	3685	1.37	3.40±0.50	···	0.74	···	1.
3530	3447	1.33	1.90±0.40	···	0.72	···	1.
The following runs contain 2% O_2							
3245	3126	1.56	1.81±0.20	0.89±0.09	0.48	2.	2.
3225	3106	1.54	1.81±0.20	0.72±0.06	0.48	2.	2.
3215	3096	1.55	2.06±0.20	0.94±0.09	0.49	2.	2.
3300	3181	1.53	1.50±0.40	0.98±0.09	0.42	2.	2.
3275	3156	1.56	1.76±0.40	0.81±0.16	0.42	2.	2.
3245	3126	1.53	1.72±0.20	0.81±0.13	0.49	2.	2.
3215	3096	1.50	1.83±0.25	0.83±0.13	0.49	2.	2.
2940	2921	1.52	0.87±0.20	0.43±0.09	0.34	2.	2.
3045	2926	1.52	1.27±0.25	0.70±0.09	0.34	2.	2.
3035	2916	1.53	1.10±0.40	0.69±0.16	0.34	2.	2.
2975	2856	1.49	0.75±0.20	0.44±0.09	0.34	2.	2.
2800	2681	1.50	0.52±0.25	0.29±0.09	0.19	2.	2.
2985	2866	1.50	1.09±0.35	0.59±0.13	0.28	2.	2.
2910	2791	1.49	1.03±0.20	0.38±0.06	0.30	2.	2.

than the Sulzmann[1] and Drummond[2] value, if no chain branching due to hydrogenous impurities occurred. Other shock-tube work in this laboratory[15] in which the infrared emission of CO_2 in the incident shock zone was followed suggests a value of k_{-1} in agreement with the value found in the earlier TOF work. Combination of this earlier value[4] of k_{-1} with the presently determined value of k_1 gives a ratio which is consistent with the equilibrium constant,[11] within the experimental uncertainties. Thus at 3000°K the observed ratio k_1/k_{-1} is 3.8, while K is 2.9. It is noteworthy, however, that both these rate constants are at least an order of magnitude greater than the values of Sulzmann, Myers, and Bartle[1] and Bartle and Myers,[3] which also give the thermodynamically correct ratio. We are unable to explain this puzzling result.

B. The Effect of $O+CO_2$ Reaction on CO_2 Decomposition

Attempts were made to adjust the observed rate of CO_2 disappearance in the CO_2–neon mixtures to take into account the rapid scondary Reaction (1) of O atoms with CO_2. The technique for dealing with such coupled first- and second-order reactions is described in standard kinetic texts.[16] An iterative calculation of the average O-atom concentration, starting with the observed values of k_1 and k_2 and known extents of CO_2 decomposition, was carried out using this method. The value of k_2 was successively adjusted and rapidly converged to a value approximately $\frac{2}{3}$ of k_2 (observed) at both the highest and lowest temperatures used. Thus the activation energy given earlier

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remains unchanged at 74±6 kcal/mole, but the absolute rate is reduced.

An alternative experimental method for evaluating the unimolecular rate constant k_2 would be a study of the pressure dependence of the gross CO_2 decomposition. However, the instrumentation used is not well suited to pressure-dependence studies since there is a distorting effect on the spectra produced by the variable pressures in the mass spectrometer, and so no such study was pursued.

The rate of Reaction (2) was less than a factor of 2 higher than previous studies of this reaction which used Ar as diluent, and the activation energy deduced was within the range observed in prior studies.[6] We conclude that the contribution of Reaction (1) to the decomposition of CO_2 in our work cannot explain the low activation energy relative to the endothermicity for Reaction (2). We are unable to offer any new explanation for this phenonenon.

The absolute values of the rate constants cited in this paper could be in error by a factor of 2, and the observed activation energies are poorly established due to the small temperature range which could be used, but the order of magnitude disparity between the absolute rates determined here and those presented in the literature[13] far exceeds the error limits of our instrumentation.

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Electron Densities from Gas-Phase Electron Diffraction Intensities. I. Preliminary Considerations[*]

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The intensity of electrons and x rays scattered by a freely rotating molecule is determined, in the kinematic approximation, solely by the nuclear–nuclear, electron–nuclear, and electron–electron radial distribution functions of the molecule. Although these functions are one-dimensional, the latter two contain some information about the three-dimensional distribution of electrons in the molecule because the electrons are distributed relative to several nuclear reference positions and the spatial distribution of the nuclei is known. The purpose of this series of papers is to investigate the extent to which this information can be deciphered. Although published accounts have purported to show that the electron density $\rho(\mathbf{r})$ can be determined uniquely from the scattered intensity, we demonstrate that, in fact, the transformation is not unique. Nevertheless, if certain, not unreasonable, restrictions are imposed upon the form of $\rho(\mathbf{r})$, it becomes possible to make fairly detailed inferences about the three-dimensional character of the density. We propose a procedure which, although not guaranteeing a unique transformation, provides a means for deriving chemically significant knowledge about the molecular electron density from experimental gas-phase intensities.

INTRODUCTION

Although electron diffraction, x-ray diffraction, and rotational spectroscopy are the principal methods for determining molecular geometries, each measures quite different properties of molecules. Rotational spectra depend on the positions of nuclei through the moments of inertia, whereas x-ray diffraction intensities depend only on the planetary electrons. Electron diffraction offers the added advantages and complications stemming from its sensitivity to both the arrangement of nuclei and the distribution of planetary electrons. Recently, several papers have been devoted to the problem of determining electron charge distributions in addition to the more conventional determination of molecular structures by gas-phase x-ray and electron diffraction. Bartell and Gavin[1] showed that diffraction intensities are quite sensitive to effects of electron correlation in atoms as well as to one-electron densities. Tavard and co-workers[2] developed somewhat similar ideas for molecules. A few experimental measurements[3–5] have been made which indicate the feasibility of studying charge distributions with chemically useful accuracy. Particularly for molecules, the implications of

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