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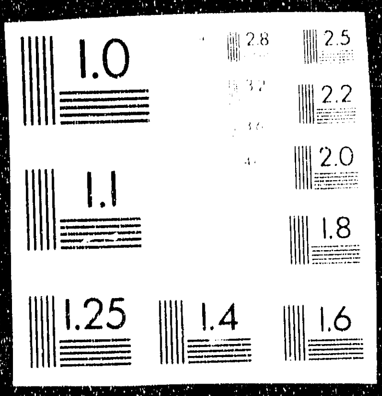

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Direct Studies of the Thermal Decomposition of N_2O and CO_2 and of the Reaction of CO with O_2

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Abstract

The thermal decomposition of N_2O and CO_2 was investigated by monitoring the kinetics of formation of $O(^3P)$ atoms in the reflected shock regime using atomic resonance absorption spectrophotometry (A.R.A.S.). The temperature range was 1805K to 2379K for N_2O and 2332K to 2869K for CO_2. Total densities were $3\text{-}4 \times 10^{18}$ molecules cm^{-3} and hence the reported rate constants are at or near the low pressure limit for unimolecular decomposition. The results were expressed by the following Arrhenius equations:

CO_2 $\quad k(T) = (1.63 \pm 1.96) \times 10^{-8} \exp(-122565 \pm 5183/RT)\ cm^3\ molecule^{-1}\ s^{-1}$

N_2O $\quad k(T) = (6.02 \pm 2.81) \times 10^{10} \exp(-53397 \pm 1865/RT)\ cm^3\ molecule^{-1}\ s^{-1}$

Uncertainties in the Arrhenius expressions are given at the one standard deviation level and the mean deviations of the experimental data from the respective expression are ±18.6% and ±30.7%. Corresponding values for the reverse reaction, $k_{rev}(CO_2)$ were computed from the expression $k_{for}/k_{rev} = K_c$. The value obtained for $k_{rev}(CO_2)$ was $(2.18 \pm 0.83) \times 10^{-34}\ cm^6\ molecule^{-2}\ s^{-1}$, independent of temperature from 2332K to 2869K.

Preliminary results are also reported for the direct determination of the rate constant for the reaction, $CO + O_2 \rightarrow CO_2 + O$, from measurements of the initial rate of formation of $O(^3P)$ atoms.

Introduction

The highly endothermic thermal decomposition reactions:

$$N_2O(^1\Sigma^+) \rightleftharpoons N_2(^1\Sigma g^+) + O(^3P) \tag{1}$$

$$CO_2(^1\Sigma^+) \rightleftharpoons CO(^1\Sigma^+) + O(^3P) \tag{2}$$

are both examples of non-adiabatic unimolecular dissociations in which the reactant and products are in different spin states thus violating the conservation of spin. The detailed mechanism of each reaction is not fully understood.[1,2] Current understanding is that the molecules are first excited adiabatically into higher rovibrational states of the singlet ground state, followed by a surface crossing into a repulsive triplet state. Such reactions are characterized in their high pressure limits by low frequency factors (10^{11}-10^{12} s^{-1}) and by activation energies that are expected to be between the bond dissociation energies to form $O(^1D)$ or $O(^3P)$.

Both reactions are important to developing a fuller understanding of unimolecular kinetics and its application to combustion chemistry. Both have been extensively investigated experimentally and theoretically and the kinetic information developed has been comprehensively reviewed.[1,3,4,5,6] Early shock tube studies of the CO_2 reaction reported surprisingly low activation energies ($70 \leq E_a \leq 100$ kcal mole^{-1}) for dissociation even allowing that they were carried out at or near the low pressure limit of the fall-off regime.[3] Further experiments showed that contamination from H and OH radicals, originating from trace amounts of H_2O, H_2, hydrocarbons and O_2, were likely responsible because of the following reactions.

$$H + CO_2 \rightarrow OH + CO$$

$$O + H_2 \rightarrow OH + H$$

$$H + O_2 \rightarrow OH + H.$$

Even in two more recent studies,[11,12] both of which employed the more direct and sensitive $O(^3P)$ atomic resonance spectrometry, widely different values for E_a, 85.3 and 104.4 kcal mole^{-1}, were obtained. Only one set of measurements for k_{diss} at or near the high pressure limit has been reported.[10] An activation energy of 130 kcal mole^{-1} was determined (compare $\Delta H^o(2)$ = 126.5 kcal mole^{-1} at 3000K) together with an appropriately low pre-exponential factor of 1.3×10^{11} s^{-1}.

The decomposition of N_2O and the removal of CO by O-atoms, being relatively slow, are both of limited but significant importance in the overall combustion process. The kinetics of the O + CO + M reaction has not been measured directly at high temperatures and the rate constant is not well established;[4,6] its temperature dependence is even more uncertain. The same can be said for the reaction,[3,4,6]

$$CO + O_2 \rightarrow CO_2 + O(^3P) \qquad (3)$$

for which only one direct rate constant measurement has been reported.[13] Because this reaction is so slow, it also is highly sensitive to trace impurities, particularly to OH formation and its reactions.

$$O + H_2O \rightarrow OH + OH$$

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 \rightarrow O + OH.$$

In the present study, we report new, direct measurements of the rate constants for reactions (1) and (2) at or near their low pressure limits. These were determined in the reflected shock regime from direct measurements of rates of $O(^3P)$ formation using atomic resonance to monitor changes in concentration. Calibration results for the $O(^3P)$ spectrophotometer are also described. In addition, preliminary results are reported for the rate constant of reaction (3).

Experimental

The original shock tube apparatus, its operation, and subsequent modifications have been described elsewhere.[14,15,16,17] The shock tube is operated in the flash photolysis (FP-ST) or thermal (Th-ST) mode and atomic resonance absorption spectrophotometry[18,19] (A.R.A.S.) is used to monitor changes in concentrations of $O(^3P)$ atoms.

The resonance lamp was operated at a pressure 7 torr with a mixture of 0.1% of O_2 in He and a microwave power level of ~100 Watts. An oxygen atom filter, which was simply a microwave discharge in a flowing mixture of 10% O_2 in He, was located between the lamp and the shock tube window. By measuring the voltage signal from the photomultiplier with and without the discharge, the fraction of resonance radiation emitted by the lamp was determined. For this study, this fraction was about 0.75. A vacuum U.V. CaF_2 window, placed in the optical path between the filter and the shock tube window, allowed transmission of the resonance triplet lines, centered at 130.4 nm, but effectively blocked the lower lying resonance line emissions from H and N atoms. The photomultiplier housing was purged by a steady flow of N_2. If f is the fraction of resonance radiation, I_o is the total incident intensity ($\equiv V_o$ volts) and I_t is the transmitted intensity at time t ($\equiv V_t$ volts), then, ABS, the absorbance at time t, (assuming the Beer-Lambert law holds) is given by the expressions.

$$ABS_t = \mathrm{Ln}\left(I_o f / I_o f - (I_o - I_t)\right) = -\mathrm{Ln}\left(1 - (Vo-Vt)/V_o f\right)$$

The baseline level $I_o = V_o$ is usually taken as the signal level in the reflected regime immediately following passage of the shock front past the observation window, except at very high temperatures, where it can sometimes be obscured by the fast formation of atoms. In these experiments, the baseline is determined from compression ratios measured with appropriate concentrations of reactant mixtures at lower temperatures where no atoms are formed.[17a,17b]

The O-atom spectrophotometer was calibrated by completely decomposing measured concentrations of N_2O to produce known concentrations of O-atoms.[19,20] Thirty five calibration runs were made over the temperature range, 1880K to 2379K with concentrations of N_2O that ranged from 9.94×10^{-7} to 1.69×10^{-6} mole fraction. The Beer-Lambert law was obeyed, and α the apparent absorption coefficient was evaluated from the expression,

$$ABS_{\infty} = \alpha \ell \, [N_2O]$$

where ABS_{∞} is the maximum absorbance measured and ℓ is the path length (6.02 cm). The mean value obtained for $\alpha \ell$ was $(7.5 \pm 2.4) \times 10^{-15}$ cm^2 $atom^{-1}$ where the error is expressed at the two standard deviation level.

The temperature (T_5), density (ρ_5) and pressure (P_5) in the reflected shock regime were calculated using ideal shock theory from the measured values of the incident shock velocity, the test gas composition, the initial temperature and the initial pressure[21,22,23]. Vibrational equilibrium was assumed to be complete and boundary layer effects could be neglected under the experimental conditions employed. Errors in determining the Mach numbers ranged from 0.5 to 1% leading to corresponding errors in T_5 and ρ_5 of 1 to 2%.

The helium and argon were of stated purity 99.9999% (M.G. Industries). The nitrous oxide (M.G. Industries 99.99%) was further purified by the freeze-thaw technique at 90K. The carbon dioxide (Matheson Research grade, 99.995%) was similarly purified. The CO (Scientific grade, 99.997%) was obtained from M.G. Industries and used without further purification. The 0.1%O_2/He, and 10% O_2/He, 0.1% H_2/He and 10% H_2/He mixtures were of stated purity 99.999% (M.G. Industries).

Results and Discussion

Reaction: $N_2O \rightarrow N_2 + O(^3P)$.

A typical O-atom transmission trace obtained when a N_2O/argon mixture is shock heated to 2145K is shown in Fig. 1. The corresponding absorbance values are plotted in the insert according to the equation relating the build-up of product concentration $O(^3P)$ for the first order decomposition of reaction (1).

$$- d[N_2O]/dt = d\,[O(^3P)]/dt = k_1^{uni}\,[N_2O]_t = k_1^{uni}\Big[[O(^3P)]_\infty - [O(^3P)]_t\Big]$$

Then, assuming the Beer-Lambert law holds,

$$\mathrm{Ln}\,(ABS_\infty - ABS_t) = \mathrm{Ln}\,(ABS_\infty) - k_1^{uni}t.$$

The unimolecular decomposition is assumed to be in the low pressure limit at these high temperatures and at the relatively small values of the experimental densities ($3\text{-}4\times10^{18}$ molecules cm^{-3}) of the reflected regime, and thus $k_1^{\circ}(T) = k_1^{uni}(T)/[M]$ cm^3 $molecule^{-1}$ s^{-1}.

Fig. 2 shows the absorbance data for the same run; the dotted line is the value of $ABS_\infty = 0.222$ and the solid line through the data points is the fit to the first-order build-up equation:

$$ABS_t = 0.222\,(1\text{-}\exp(-5754\pm43t)).$$

The rate constant data for 42 experimental runs that were made over the temperature range 1805K to 2379K are listed in Table 1 along with the relevant experimental conditions and are plotted in Fig. 3 according to the Arrhenius equation. Concentrations of N_2O ranged from 9.94×10^{-7} to 1.60×10^{-6} mole fraction. A linear least-squares fit to the data yielded the Arrhenius expression:

$$k_1^{\circ}(T) = (6.02\pm2.81)\times10^{-8}\,\exp(-53397\pm1165/RT)\ cm^3\ molecule^{-1}\ s^{-1}.$$

The uncertainties are given at the one standard deviation level and the mean deviation of the experimental data from the expression is ±18.6%. Kinetic modelling of the reacting system with all possible reactions and available rate constant data confirmed that there were no kinetic complications from secondary reactions. The present data are compared with previously measured data in Table II and Fig. 3. Although it is observed that the present values of $k_1^o(T)$ are slightly but consistently larger than the published data, the agreement among most of the data is very good, especially when one considers that different analytical techniques were used and that experiments were carried out behind incident and reflected shock waves. No deviations from the Arrhenius equation were observed over the limited temperature range investigated but in a recent evaluation, taken over a greater range in temperature, a decreasing slope, i.e. a decreasing apparent activation energy, has been observed. These results confirm that the apparent activation energy in the low pressure limit, is about 15 kcal^{-1} mole^{-1} larger than the minimum required for dissociation into $O(^3P)$ atoms ($\Delta H^o_0 = +$ 38.56 kcal mole^{-1}) and about 30 kcal smaller than for dissociation into $O(^1D)$ atoms ($\Delta H^o_0 = +$ 83.93 kcal mole^{-1}).

Reaction: $CO_2 + M \rightarrow CO + O(^3P)$

A typical transmission trace observed in experiments in which CO_2 is thermally decomposed in the reflected regime is shown in Fig. 4. Because dissociation occurs so rapidly and because CO_2 has a significant absorption cross section for the $O(^3P)$ resonance radiation, the baseline for the reflected regime was determined from measurements of compression ratios. These were determined at lower temperatures where no measurable dissociation occurs. Absorbance values were observed to increase linearly with time, as shown in Fig. 5 and initial rates of reaction, k_{obs} in units of ABS s^{-1}, were obtained from the slopes of linear least-squares fits. Only 0.008 to 0.03% of the CO_2 molecules was decomposed during each experiment. Pseudo-first-order kinetics therefore applies and the bimolecular rate constant, k_2^o, is given by the expression,

$$k_2^o = k_{obs}/[M]\,[CO_2]\,\alpha\ell$$

where [M] is the total density, $[CO_2]$ is the initial concentration of CO_2 and $\alpha\ell$ is the calibration constant for the O-atom spectrophotometer ($4.5\text{x}10^{-14}$ cm^3 atom). Varying the concentration of CO_2 by a factor of 4 had no effect on the derived values of $k_2^o(T)$ confirming that under the experimental conditions there were no kinetic complications from secondary reactions. Experimental measurements were made over the temperature range, 2332K to 2869K. The rate constant data are listed in Table III and are plotted according to the Arrhenius equation in Fig. 5. Also listed in Table III are the initial test gas pressures (P_1), the measured Mach number (M_s), the observed rate of $O(^3P)$ formation in units of ABS s^{-1}, the corresponding temperatures (T_5) and densities (ρ_5) in the reflected regime and the values of k_2^o (the bimolecular rate constant calculated assuming that the experiments were made in the low pressure limit). The data from the 32 individual experiments are well represented by the Arrhenius expression:

$$k_2^o(T) = 1.63\pm1.96\text{x}10^{-8}\exp(-122565\pm5183/RT)\ cm^3\ molecule^{-1}\ s^{-1}$$

The deviations are shown at the one standard deviation level and the mean deviation of the experimental data points from the fit is ± 30.7%. Shown also in Fig. 5 are the recent data obtained by Burmeister and Roth,[12] who also employed atomic resonance abosrption to monitor the rate of formation of O-atoms. The agreement is excellent especially when one notes that independent photometer calibrations were required and that experimental conditions, though similar, were not identical. On the other hand, the present results do not agree with those of the recent direct study by Fujii et al.[11] who reported the Arrhenius expression:

$$k_2^{o}(T) = 4.17\times10^{-11}\ \exp(-87000/RT)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

As can be seen from Fig. 5, they are in reasonable agreement with those reported for higher temperatures by Wagner and co-workers[9,10] and by Kiefer[8] who employed the laser schlieren technique. The observed activation energy, 123±5 kcal mol^{-1} is much larger than the values reported by these authors (105-110 kcal mol^{-1}) but is less than that deteremined in the high pressure limit (131 kcal mol^{-1}). Apparent activation energies for the low pressure limit are expected to be somewhat less on theoretical grounds at the much higher temperatures employed in these studies.

Reaction: $O(^3P) + CO + M \rightarrow CO_2 + M$.

Rate constants for the reaction, k_{-2}^{o}, were evaluated from the measured values of k_2^{o} and the equilibrium constant, K_c, from the relationship

$$k_{for}/k_{rev} = K_c = k_2^{o}/k_{-2}^{o}$$

K_c at each experimental temperature was evaluated from the data tabulated in the JANAF Thermochemical Tables.[26] These results are also tabulated in Table III. The rate constant, $k_{-2}^{o}(T)$, in the low pressure limit is observed to be independent of temperature within experimental error and is given by:

$$k_{-2}^{o}(T) = (2.18\pm0.63)\times10^{-34}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}}$$

for the temperature range from 2332K to 2869K.

These rate constant values are in reasonable agreement with previously determined values obtained indirectly in this temperature range.[6] More direct measurements of the rate constant at lower temperatures (e.g. 1000K) are needed so that the temperature dependence of this reaction can be determined more precisely. Attempts to measure the rate constant around 1000K directly by flash photolyzing mixtures of CO_2 and CO were unsuccessful.

Reaction: $O(^3P) + CO_2 \rightarrow CO + O_2$.

The rate constant for the reaction

$$O(^3P) + CO_2 \rightleftharpoons CO + O_2 \qquad (-3)$$

is very slow. Experiments were carried out using the FP-ST technique in an attempt to measure its valued directly at high temperatures. Mixtures of CO_2 in argon ($X_{CO2} = 0.01$) were flash photolyzed at temperatures around 2000K to produce concentrations of $O(^3P)$ atoms of ~5×10^{12} atoms cm^{-3}. Over the time frame allowed by the technique at these temperatures (several hundred microseconds) no reaction could be detected.

Although the reverse of reaction (-3),

$$CO + O_2 \rightarrow CO_2 + O \qquad (3)$$

is exothermic by about 5 kcal mol^{-1} (1500-2500K),[3] the rate constant, k_3, is reported to have an activation energy[3,13] of 50-65 kcal mol^{-1} that presumably represents a barrier to the bimolecular reaction. The most direct study, to date, on the kinetics of reaction (3) is that reported by Thielen and Roth.[13] In that study, which thoroughly documented the experimental system and corrections for O_2 dissociation, O-atom formation was monitored using atomic resonance absorption. Their rate constant expression derived from the O-atom absorption data is,

$$k_3 = 8.4 \times 10^{-11} \exp(-31800K/T)\ cm^3\ molecule^{-1}\ s^{-1},$$

which yields rate constant values that agree reasonably well with Dean and Kistakowsky[27] and Sulzmann et al.[28] At temperatures below about 2500K, however, this expression diverges (to give lower values of k_3) from that recommended by Baulch et al.[3] This discrepancy was discussed by Thielen and Roth[13] in terms of impurity effects (mainly due to trace amounts of H_2O).

In the present preliminary study, rate constant values for reaction (3) were derived from O-atom formation rates in experiments that were similar to those reported by Thielen and Roth;[13] and at $T \approx 2500K$ the results of the present work were in close agreement to those reported in that earlier study[13] ($k_3 \approx 3.0 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}). However, at lower temperatures, O-atom formation rates were increasingly too large compared to those predicted from their Arrhenius expression.[13] Also, the O-atom formation profile was observed to be initially non-linear, prior to becoming linear at later times, as is shown in Fig. 8 for a run at 2150K. This behavior was investigated by simulating the kinetics using the reaction mechanism given in Table IV and the ACUCHEM program.[29] The simulations confirmed the relatively minor effect of H_2O (at high temperatures, i.e. $T > 3000K$) that was observed experimentally by Thielen and Roth.[13] At lower temperatures ($T \approx 2000K$) the perturbing effects due to the impurities H_2O and H_2 remained relatively small. On the other hand, the kinetic consequences of the rapid formation of very small [H] (e.g. from a trace of hydrocarbon) were remarkable. This effect is demonstrated in Fig. 9 for a simulation performed at $T=2000K$ with an assumed level of $[H]_o$ (initial H-atom concentration presumed to be from hydrocarbon impurity) of only 0.2 ppm. The shape of the [O] profile is similar to the experimental one shown in Fig. 8 and the rate constant (k_3) derived from the linear build-up of [O] is about 2 times larger than the input value (calculated from the expression for $k_3(T)$ of Thielen and Roth[13]). Also, it is interesting to note that the [H] (in the simulation, Fig. 9) falls to a steady state value of only about 1×10^{10} atoms cm^{-3}, i.e. an essentially undetectable level. The magnitude of this effect escalates rapidly as the temperature is decreased. At 1700K, the effect of 0.2 ppm $[H]_o$ is to increase k_3^{app} (the apparent value of k_3 from the simulated [O] build-up rate) by more than an order of magnitude; and at 1500K the effect of 0.2 $[H]_o$ is to increase k_3^{app} by about a factor of 70. The magnitude of this catalytic effect of small concentrations of H-atoms has apparently not been commented on previously. Further work in this laboratory will pursue an investigation of this remarkably large impurity effect particularly with regard to its influence on measurements of k_3.

Conclusions

The present shock tube results for reaction (1) are in reasonable agreement with previous measurements, although the results from our derived expression for $k_1(T)$ are systematically slightly higher. In the case of reaction (2) measurement on the forward reaction are in excellent agreement with those of Burmeister and Roth[13] but strongly disagree with those of Fujii et al.[11] This may result from problems with their operating behind incident shock waves but, more likely, arises from the well-documented effects of trace impurities. We were unsuccessful in measuring $k_{-2}^{o}(T)$ by the FP-ST technique at temperatures around 1000K, but calculations from the expression $k_{-2}^{o}(T) = k_2^{o}(T)/K_c(T)$ gave results in agreement with previously published data for this temperature range. Preliminary experimental results and kinetic modelling studies showed a remarkable influence of trace hydrogen atom forming impurities that can efficiently catalyze the formation of O-atoms in the CO/O_2 system. Further work is necessary to describe this catalytic effect more quantitively and to determine its effect on rate constant measurements for the reaction of CO with O_2.

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Table I. Rate Constant Data for the Reaction $N_2O + M \rightarrow N_2 + O + M$.

P_1/Torr	M_s[a]	ρ_5[b]	T_5/K[c]	k[d]	k_{bi}[e]
		$X_{N_2O} = 1.585 \times 10^{-6}$			
15.04	2.972	3.214	2102	4.263	1.32
15.12	3.030	3.256	2194	11.03	3.39
15.06	3.141	3.316	2356	23.37	7.05
14.95	3.152	3.289	2379	18.27	5.56
		$X_{N_2O} = 1.599 \times 10^{-6}$			
15.10	2.937	3.144	2090	5.308	1.69
15.12	2.993	3.194	2165	11.42	3.44
14.64	2.993	3.093	2165	10.27	3.35
15.18	3.041	3.245	2231	15.67	4.83
15.02	3.056	3.222	2251	14.63	4.54
15.23	2.962	3.203	2117	8.92	2.78
15.06	2.731	2.965	1819	0.524	0.177
15.37	2.891	3.162	2029	2.767	0.875
15.34	2.813	3.087	1928	1.963	0.636
15.09	2.909	3.129	2046	3.062	0.978
14.62	2.844	2.978	1961	1.761	0.591
15.50	2.828	3.143	1941	1.394	0.444
14.81	3.044	3.179	2228	7.245	2.70
15.23	2.814	3.076	1924	1.545	0.502
14.78	2.847	3.013	1965	1.866	0.619
15.22	2.828	3.086	1941	1.504	0.487
15.10	2.785	3.033	1880	1.368	0.451
15.09	2.826	3.058	1938	2.373	0.776
14.87	2.940	3.110	2088	4.459	1.43
15.11	2.946	3.165	2095	5.624	1.78
14.96	2.983	3.163	2145	5.746	1.82
14.61	3.022	3.119	2197	8.096	2.60

Table I. Rate Constant Data for the Reaction $N_2O + M \rightarrow N_2 + O + M$. (cont.)

P_1/Torr	M_s[a]	ρ_5[b]	T_5/K[c]	k[d]	k_{bi}[e]
$X_{N_2O} = 1.693 \times 10^{-6}$					
15.10	2.756	2.997	1851	0.940	0.314
14.88	2.731	2.940	1813	0.512	0.174
15.21	2.752	3.015	1846	0.793	0.263
15.21	2.785	3.035	1893	1.049	0.346
15.25	2.715	2.977	1805	0.976	0.328
15.04	2.726	2.947	1819	0.756	0.256
14.90	2.933	3.100	2084	4.409	1.42
15.18	2.885	3.107	2028	3.941	1.27
15.10	2.892	3.097	2037	3.242	1.05
15.04	2.849	3.048	1982	2.369	0.78
14.97	2.957	3.124	2124	7.783	2.49
15.28	2.966	3.195	2135	7.001	2.19
15.09	2.968	3.157	2139	7.478	2.37
$X_{N_2O} = 9.94 \times 10^{-7}$					
14.99	3.046	3.218	2280	11.39	3.54
15.12	3.104	3.291	2312	12.45	3.78
14.73	3.946	3.085	2095	4.559	1.48

---

a - The error in measuring the Mach number is typically about ±0.7% at the one standard deviation level.

b - Units of density are 10^{18} molecules cm^{-3}.

c - The error in temperature is estimated to be no more than ±1.5%.

d - Units of k are 10^3 s^{-1}.

e - Units of k_{bi} are cm^3 $molecule^{-1}$ s^{-1}.

Table II. $N_2O \rightarrow N_2 + O(^3P)$ Comparison of Expression for $k_1^{\circ}(T)$, M = Ar.

A^a	n	θ	Temp K	References
8.32×10^{-10}	0	29190 27680-28183	1500-2500	Olschewski et al. (1966) Troe (1975) Comment
8.32×10^{-10}	0	29190	1500-2500	Baulch et al. (1973) Evaluation
4.47×10^{-10}	0	27180	2100-3200	Dean and Steiner (1977)
2.34×10^{-10}	0	25810	1810-3360	Monat et al. (1977)
2.4×10^{-9}	0	30800	1600-2500	Roth & Just (1977)
6.47×10^{-10}	0	28870	1700-2400	Endo et al. (1979)
6.17×10^{-10}	0	27660	1680-2560	Sulzman et al. (1980)
1.15	-2.5	32710	1500-3600	Hanson & Salimian (1984)
1.54×10^{-9} 7.80×10^{-10}	0 0	29927 29253	$1400\text{-}2200^b$ $1500\text{-}2140^c$	Frank & Just (1985)
1.66×10^{-9}	0	30191	1600-2500	Fujii et al. (1989)
6.02×10^{-10}	0	26873	1805-2379	This study (1991)

a - $k_1^{\circ}(T) = A\, T^n \exp(-\theta/T)$ cm^3 $molecule^{-1}$ s^{-1}.

b - Expression for Argon densities = $4.2\text{-}9.6 \times 10^{18}$ molecules cm^{-3}.

c - Expression for Argon densities = $1.8\text{-}3.6 \times 10^{-19}$ molecules cm^{-3}.

Table III. Rate Constant Data for the Reaction $CO_2 + M \rightarrow CO + O + M$.

P_1/Torr	M_s[a]	Rate[b]	ρ_5[c]	T_5/K[d]	k_1[e]	K_c[f]	k_{-1}[g]
$X_{CO_2} = 2.482 \times 10^{-3}$							
10.29	3.147	241	2.299	2334	4.08	2.66	1.53
10.51	3.198	94	2.319	2462	1.56	10.48	1.49
10.61	3.321	547	2.457	2584	8.11	34.08	2.38
10.37	3.319	549	2.345	2641	8.92	56.96	1.58
10.75	3.360	905	2.507	2642	12.9	57.47	2.24
10.65	3.381	1993	2.485	2682	28.9	81.32	3.56
10.44	3.377	1343	2.426	2686	20.5	84.15	2.43
10.30	3.399	1900	2.419	2700	29.0	94.75	3.07
10.32	3.397	1902	2.407	2715	29.3	107.5	2.74
10.27	3.422	3233	2.422	2735	49.3	126.8	3.89
10.02	3.423	1973	2.348	2755	32.1	149.3	2.15
10.25	3.422	3299	2.426	2765	50.3	161.9	3.09
10.26	3.464	3476	2.421	2819	53.1	247.8	2.15
10.19	3.440	3199	2.356	2828	51.2	265.7	1.94
10.14	3.497	4082	2.406	2869	63.2	362.4	1.75
14.83	3.134	58	3.282	2332	0.47	2.604	1.86
14.85	3.174	108	3.326	2380	0.841	4.432	1.96
14.84	3.175	143	3.313	2389	1.17	4.885	2.40
14.73	3217	183	3.341	2433	1.47	7.781	1.94
14.48	3.257	513	3.311	2490	4.19	13.88	3.01
14.99	3.268	828	3.367	2557	6.54	26.51	2.48
15.02	3.384	1102	3.530	2668	7.92	72.10	1.10
14.88	3.382	1069	3.485	2675	7.88	76.58	1.03
$X_{CO_2} = 4.80 \times 10^{-3}$							
10.63	3.318	684	2.470	2564	5.17	28.31	1.83
10.33	3.326	670	2.410	2576	5.33	31.65	1.69
10.19	3.370	3043	2.380	2658	24.9	66.11	3.76
15.18	3.157	248	3.409	2342	0.89	2.914	3.40
15.22	3.156	267	3.384	2364	1.08	3.721	2.92
15.15	3.208	363	3.428	2422	1.43	6.937	2.06
15.16	3.224	793	3.453	2436	3.08	8.027	3.74
15.14	3.280	614	3.476	2525	2.33	19.54	1.17
15.16	3.296	717	3.492	2549	2.72	24.58	1.11

Table III. Rate Constant Data for the Reaction $CO_2 + M \rightarrow CO + O + M$ (cont.)

P_1/Torr	M_s[a]	Rate[b]	ρ_5[c]	T_5/K[d]	k_1[e]	K_c[f]	k_{-1}[g]
			$X_{CO_2} = 9.974 \times 10^{-3}$				
10.26	3.368	4394	2.381	2676	17.3	77.24	2.24
10.34	3.474	8365	2.486	2790	30.2	197.6	1.53
15.01	3.214	410	3.458	2392	0.762	5.045	1.51
15.09	3.251	1172	3.503	2445	2.20	8.809	2.50
15.19	3.321	3122	3.494	2606	5.70	41.67	1.37

---

a - Error in measuring Mach number is typically ±0.7% at the one standard deviation level.

b - First-order rate of the reaction; units are ABS s^{-1}.

c - Units of density are 10^{18} molecule cm^{-3}.

d - The error in temperature is estimated to be no more than ±1.5%.

e - Units of k_1 are 10^{-19} cm^3 molecule $^{-1}$ s^{-1}.

f - Units of equilibrium constant, K_c, are 10^{14} molecule^{+1} cm^{-3}.

g - Units of k_{-1} are 10^{-34} cm^6 molecule^{-2} s^{-1}.

Table IV. Reaction Mechanism for the CO/O_2/Ar System, with Trace H_2 and H_2O.[a]

Reaction	A	n	θ	Ref. No.
$CO + O_2 \rightarrow CO_2 + O$	8.4(-11)	0	31800	13
$H + O_2 \rightarrow OH + O$	3.1°(-10)	0	8273	30
$O + H_2O \rightarrow OH + OH$	9.2(-11)	0	9612	31
$OH + OH \rightarrow O + H_2O$	8.9(-12)	0	1057	31
$H + H_2O \rightarrow H_2 + OH$	4.6(-10)	0	11560	32
$OH + H_2 \rightarrow H_2O + H$	3.6(-16)	1.51	1726	32
$O + OH \rightarrow O_2 + H$	2.05(-11)	0	0	30
$O + H_2 \rightarrow OH + O$	3.1(-10)	0	6855	33
$O + CO_2 \rightarrow CO + O_2$	2.8(-11)	0	26461	3
$H + OH \rightarrow O + H_2$	8.1(-21)	2.8	1953	6
$O_2 + Ar \rightarrow O + O + Ar$	2.0(-10)	0	54250	4
$H_2O + Ar \rightarrow H + OH + Ar$	2.1(-10)	0	50330	34
$H_2 + Ar \rightarrow H + H + Ar$	3.7(-10)	0	48354	3
$H + CO_2 \rightarrow OH + CO$	2.5(-10)	0	13231	3
$OH + CO \rightarrow CO_2 + H$	--	-	--	35[b]

---

a - Rate constants parameters for $k(T) = AT^n \exp(-\theta/T)$; units are cm^3 $molecule^{-1}$ s^{-1} for bimolecular reactions and cm^6 $molecule^{-2}$ s^{-1} for termolecular reactions.

b - $k(T) = 1.2 \times 10^{-13} \exp(+9.2 \times 10^{-4} \times T)$ cm^3 $molecule^{-1}$ s^{-1}.

Figure Captions

Figure 1. Typical Transmission signal observed for the thermal decompostion of N_2O in the reflected shock regime. P_1 = 14.96 torr, M_s = 3.022, T_5 = 2145K, ρ_5 = 3.12×10^{18} molecules cm^{-3}, X_{N2O} = 1.599×10^{-6}. Inset: First order plot of the corresponding absorbance data over the build-up time, k_{obs} = 5746 s^{-1}, ABS_{max} = 0.222.

Figure 2. Plot of the absorbance build-up corresponding to the transmission signal of figure 1. o - experimental data points, ——— Fit of the first-order equation, $ABS_t = ABS_{max}(1-\exp(-k_{obs}t)$. k_{obs} = 5746 s^{-1}, ABS_{max} = 0.222. $k_1^o = k_{obs}/M$ = 2.60×10^{-19} cm^3 $molecule^{-1}$ s^{-1}.

Figure 3 Arrhenius plot of k_1^o data listed in Table 1 for the reaction $N_2O \rightarrow N_2 + O(^3P)$. Solid line through the data is the linear least squares fit, $k_1^o(T) = 6.02 \times 10^{-10}$ exp(-53400/RT cm^3 $molecule^{-1}$ s^{-1}). Lower solid line is the recommended fit of Hanson and Salimian (1984), $k_1^o(T) = 1.15 \times T^{-2.15}$ exp(-65000/RT). Dashed line represents the experimental data of Frank and Just, (19) $k_1^o(T)$ = 1.54×10^{-9} exp(39460/RT). Dotted line represents the experimental data of Fujii et al. (1989), $k_1^o = 1.66 \times 10^{-9}$ exp(-58,990/RT).

Figure 4. Typical transmission signal observed for the thermal decomposition of CO_2 in the reflected regime. P_1 = 10.34 torr, M_s = 3.474, T_5 = 2790K, ρ_5 = 2.486×10^{18} molecules cm^{-3}, X_{CO2} = 9.974×10^{-3}. Baseline of reflected regime is at 0.0654 volts.

Figure 5. Plot of the corresponding absorbance data for Fig. 4. o - experimental data points, ——— Linear fit to data, k_{obs} = 8365 ABS s^{-1}, $k_2^o = k_{obs}/[M][CO_2]\alpha\ell$ = 2.82×10^{-19} cm^3 $molecule^{-1}$ s^{-1}.

Figure 6. Arrhenius plot of the k_2^o data listed in Table 11 for the reaction $CO_2 \rightarrow CO + O(^3P)$. o - This data, + - Experimental data of Burmeister and Roth (1990). solid line through the data is the linear least squares fit, $k_2^o(T) = 1.63x10^{-8} \exp(-122565/RT)$.

Figure 7. Comparison of selected rate constant data for the reaction $CO_2 \rightarrow CO + O(^3P)$. o - this study, □ - Burmeister and Roth (1990). Solid line —— Linear least squares fit: $k_2^o(T) = 1.63x10^{-8} \exp(-122565/RT)$. Dashed line is the expression of Wagner and Zabel (1974): $k^o(T) = 8.5x10^{-10} \exp(-110400/RT)$ cm^3 $molecule^{-1}$ s^{-1}, $3000K \leq T \leq 4600K$. Dotted line is the expression of Kiefer (1974): $k^o(T) = 5.5x10^{-10} \exp(-107200/RT)$ cm^3 $molecule^{-1}$ s^{-1}, $3600 \leq T \leq 6500K$.

Figure 8. Absorbance (ABS) for O-atom build-up in an experiment at 2150K: $X_{CO} = 1.13x10^{-3}$; $X_{O2} = 1.17x10^{-2}$; $\rho_5 = 3.23x10^{18}$ molecules cm^{-3}; [O] build-up rate (at t>1.57 msec) is 653.3 ABS s^{-1} which gives a value of $k_3 = 1.05x10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. This value of k_3 is about 3 times larger than that derived from the expression of Thielen and Roth,[13] as listed in Table IV.

Figure 9. Simulated [O] build-up vs. time using the reaction mechanism listed in Table IV: $\rho_5 \approx 3x10^{18}$ molecules cm^{-3}; $X_{CO} \approx 2000$ ppm; $X_{O2} \approx 2\%$; $X_{H2O} = H_{H2} = 1$ ppm; $[H]_o = 6.10^{11}$ atoms cm^{-3} (i.e. ≈ 0.2 ppm). A value of $k_3 = 1.8x0^{-17}$ cm^3 $molecule^{-1}$ s^{-1} is derived from the [O] build-up rate and this value is about 2 times larger than that computed from the expression of Thielen and Roth.[13]

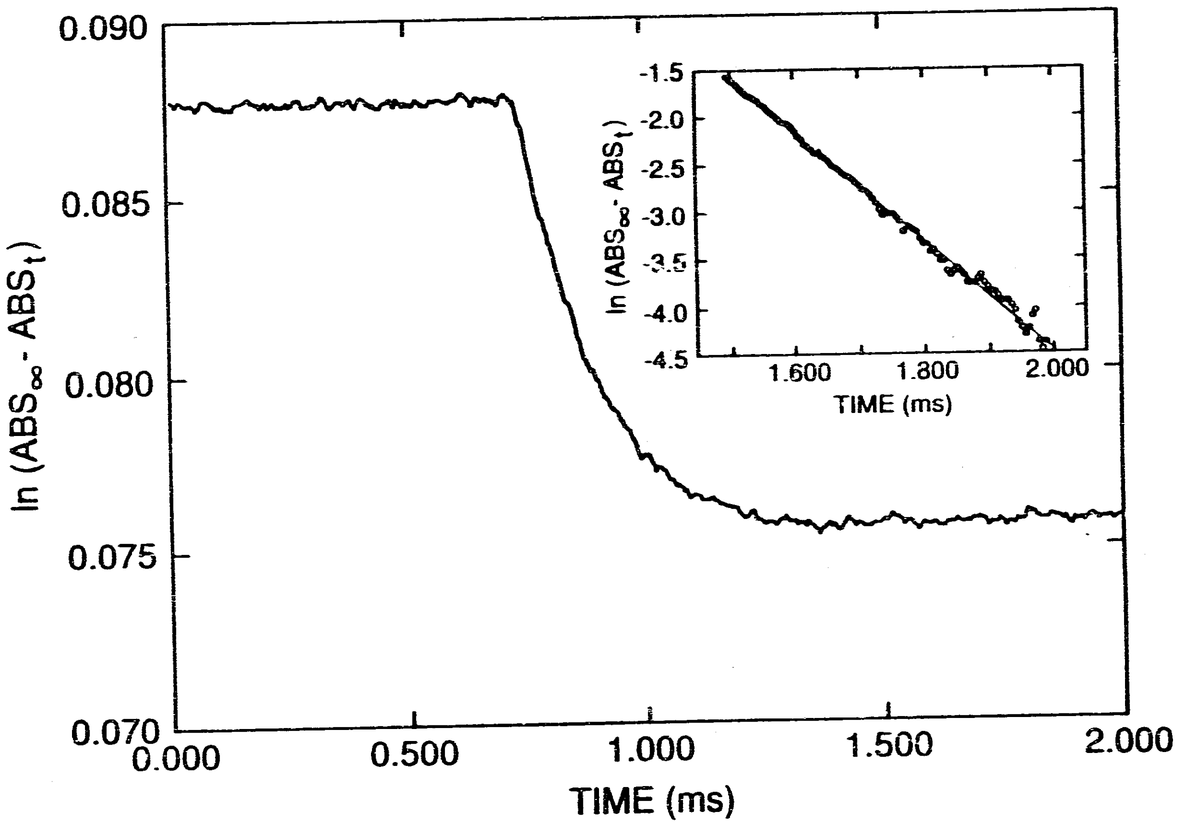
0.090
0.085
0.080
0.075
0.070
0.000
0.500
1.000
1.500
2.000
TIME (ms)
ln (ABS$_\infty$ - ABS$_t$)
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
1.600
1.800
2.000
TIME (ms)
ln (ABS$_\infty$ - ABS$_t$)

FIGURE 1.

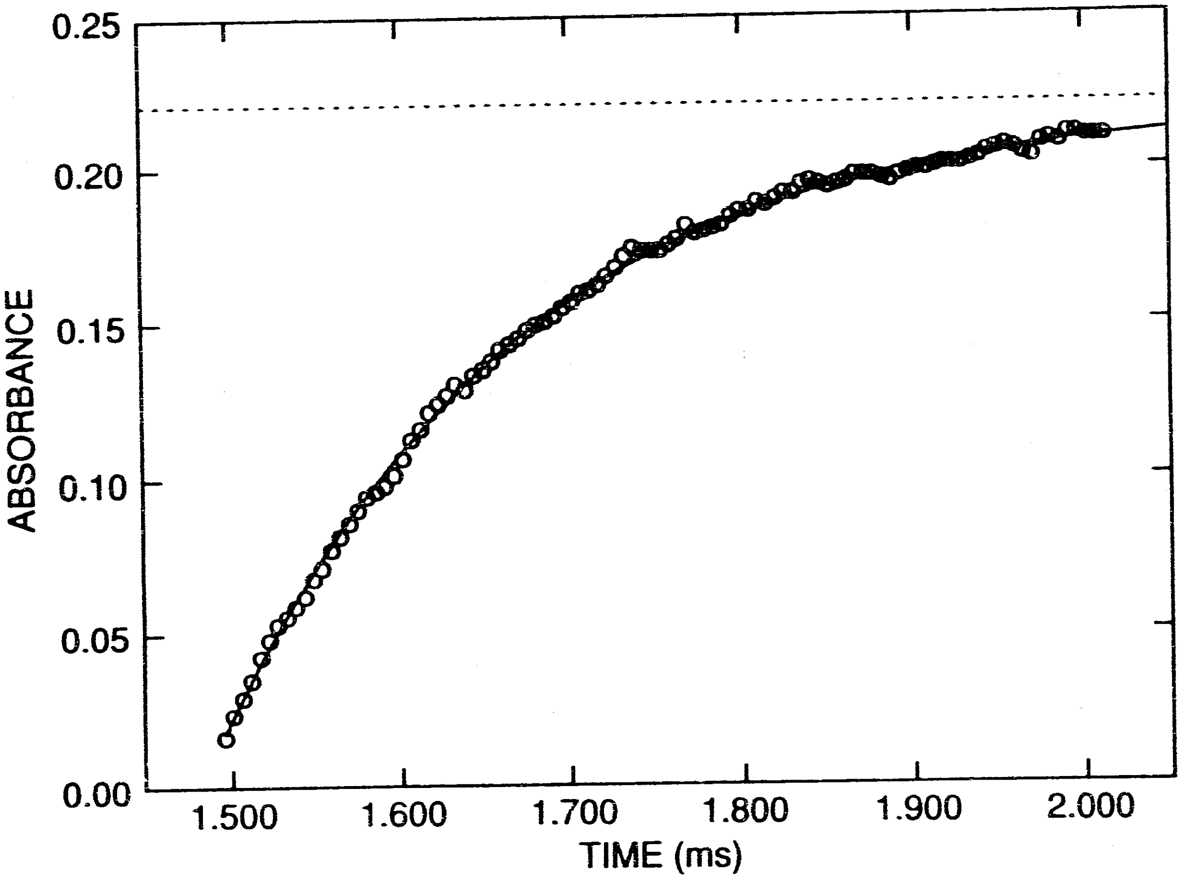
0.25
0.20
0.15
0.10
0.05
0.00
ABSORBANCE
1.500
1.600
1.700
1.800
1.900
2.000
TIME (ms)

FIGURE 2.

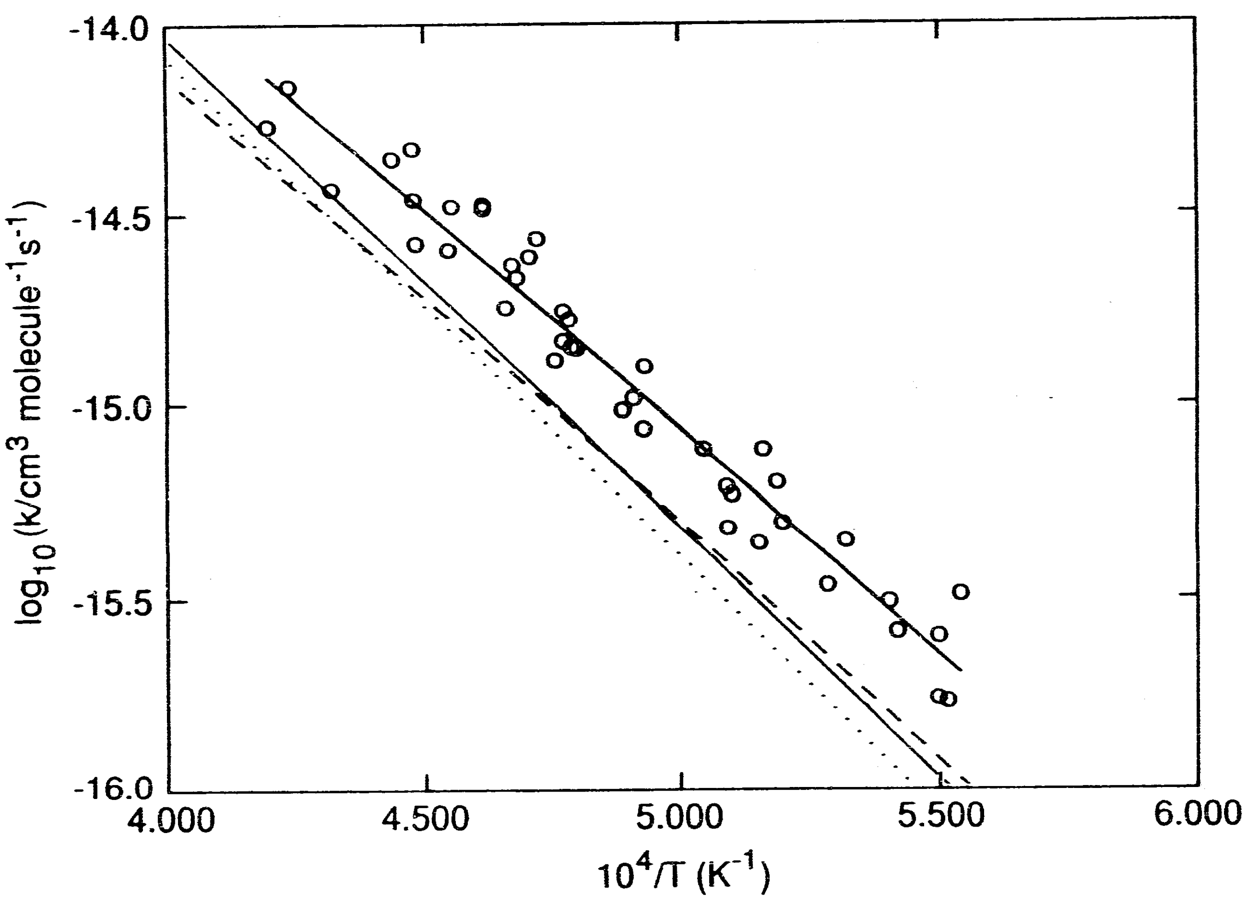
-14.0
-14.5
-15.0
-15.5
-16.0
$\log_{10}(k/cm^3 molecule^{-1}s^{-1})$
4.000
4.500
5.000
5.500
6.000
$10^4/T (K^{-1})$

FIGURE 3.

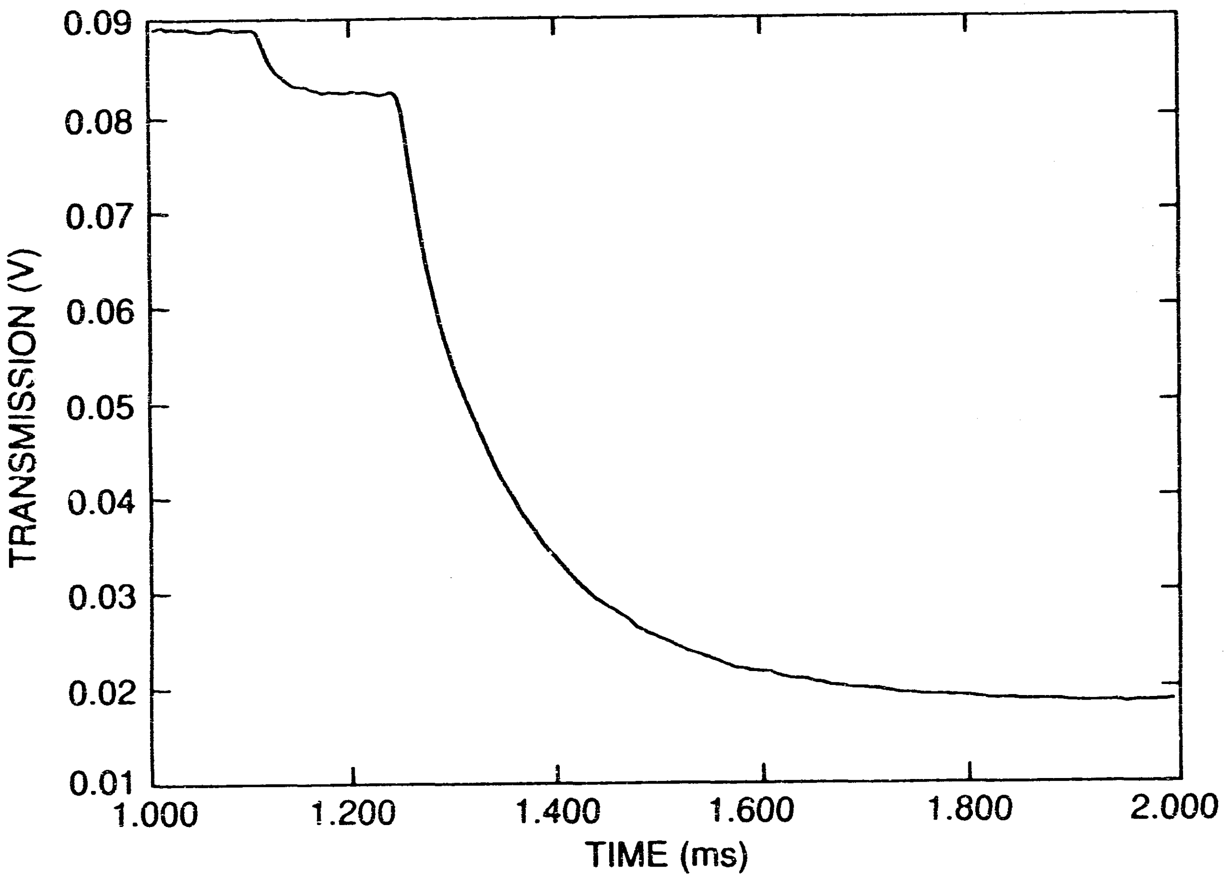
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
TRANSMISSION (V)
1.000
1.200
1.400
1.600
1.800
2.000
TIME (ms)

FIGURE 4.

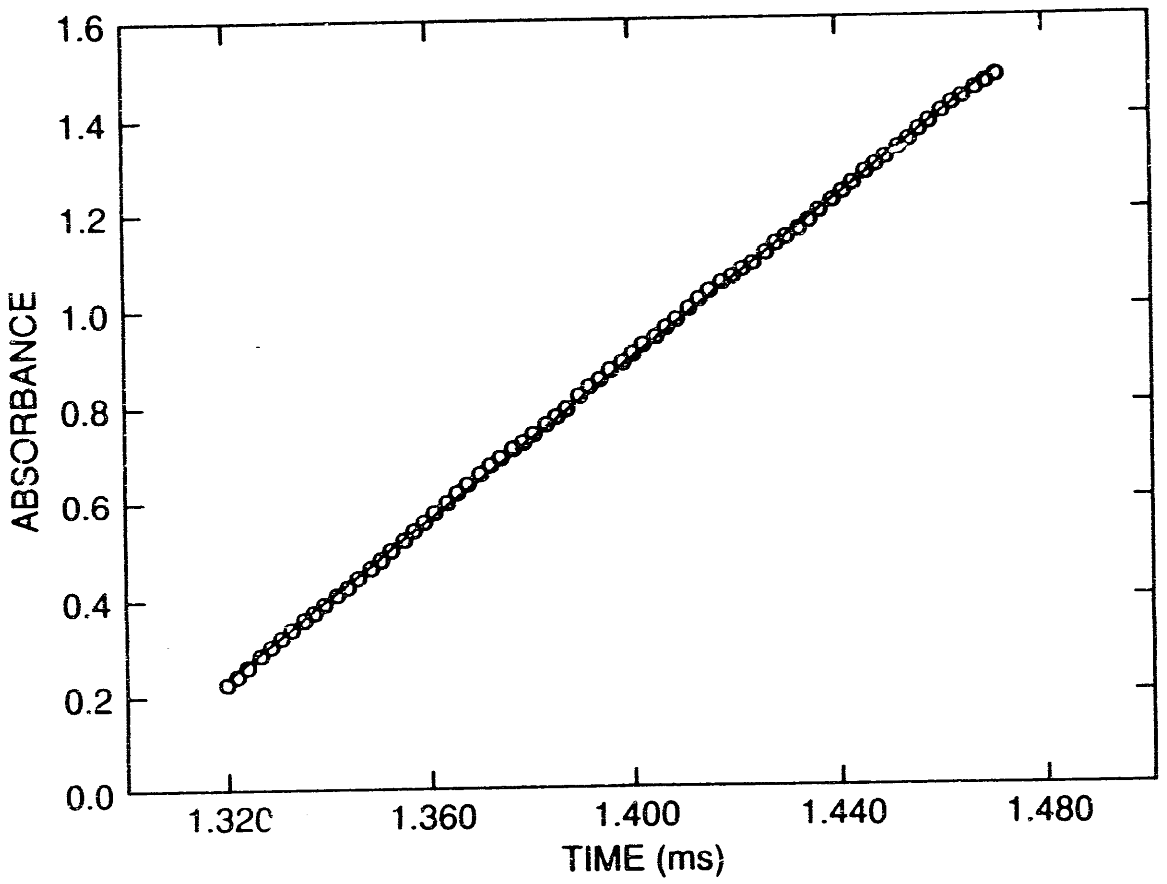
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
ABSORBANCE
1.320
1.360
1.400
1.440
1.480
TIME (ms)

FIGURE 5.

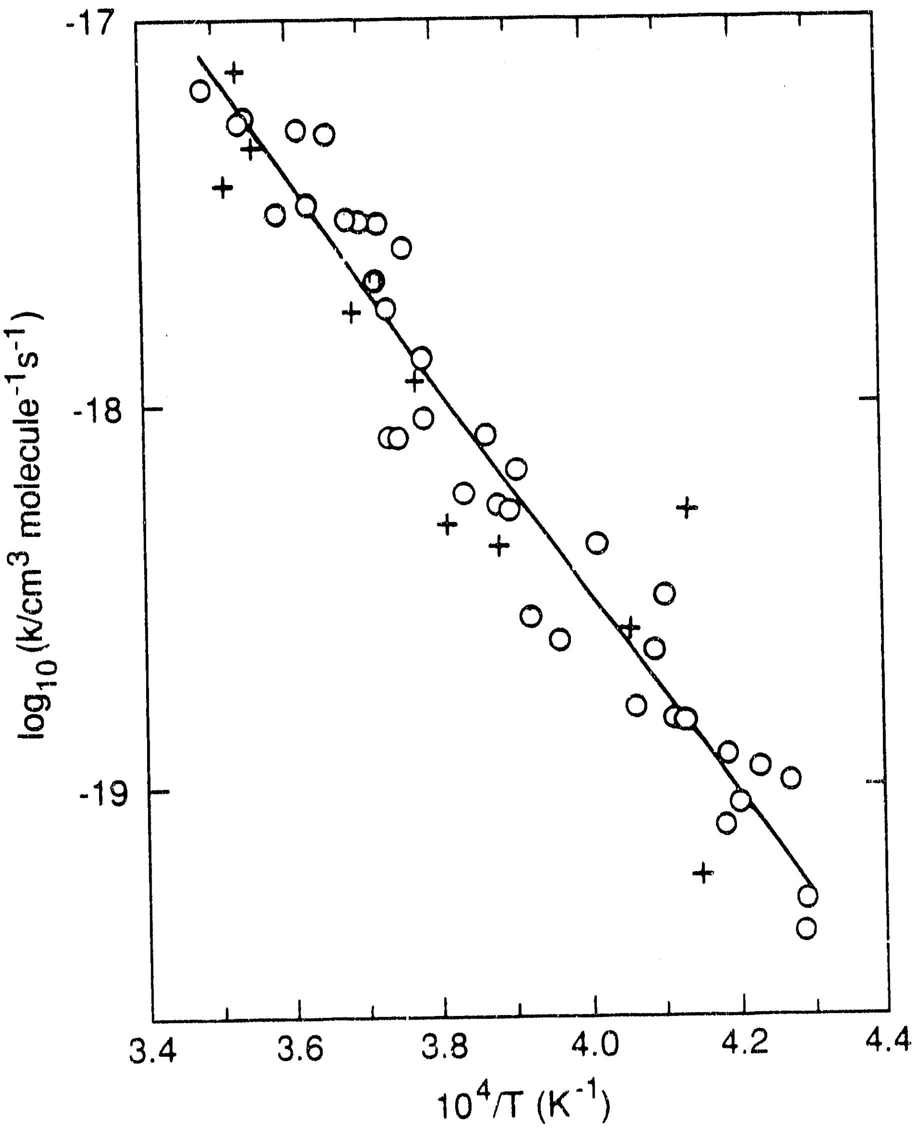
-17
-18
-19
$\log_{10}(k/\mathrm{cm^3\ molecule^{-1}s^{-1}})$
3.4
3.6
3.8
4.0
4.2
4.4
$10^4/T\ (K^{-1})$

FIGURE 6.

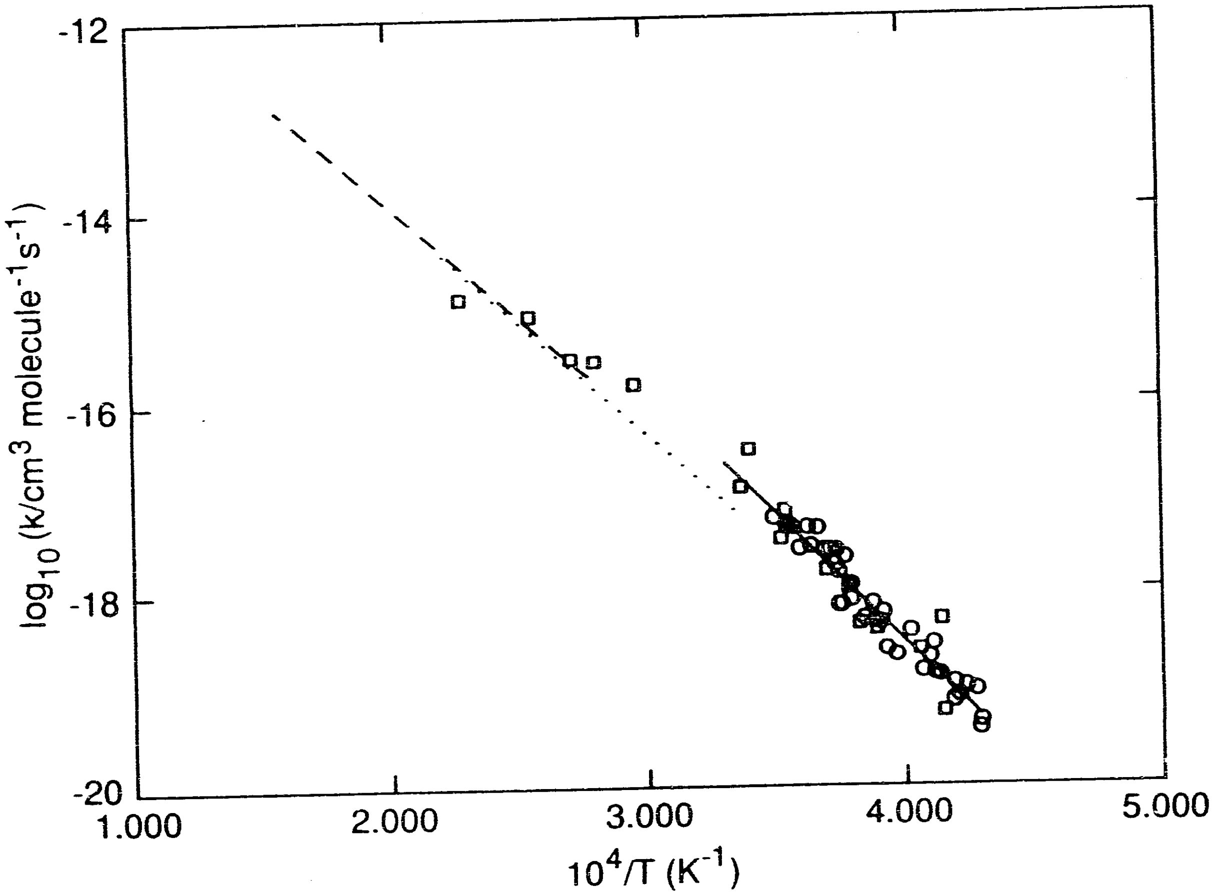
-12
-14
-16
-18
-20
1.000
2.000
3.000
4.000
5.000
$\log_{10}(k/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\mathrm{s}^{-1})$
$10^4/T\ (\mathrm{K}^{-1})$

FIGURE 7.

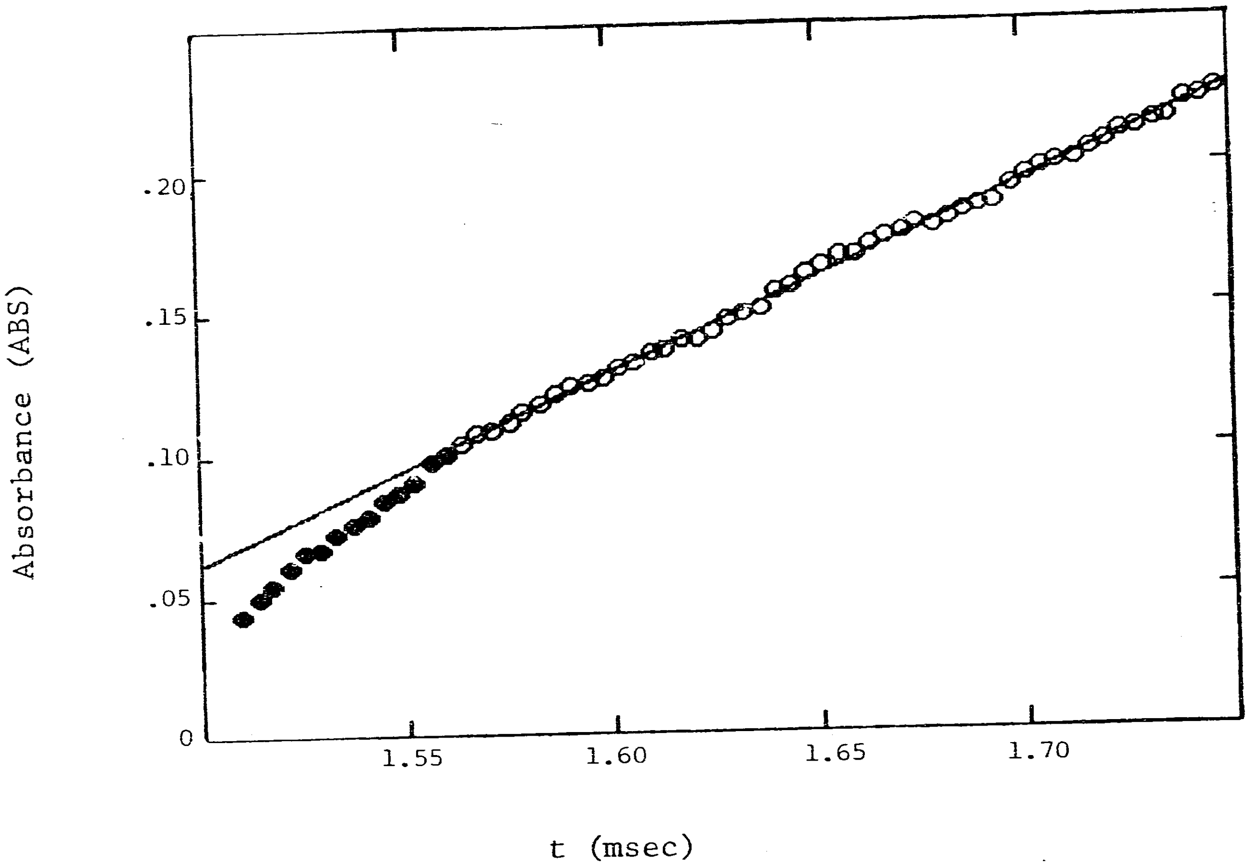

FIGURE 8.

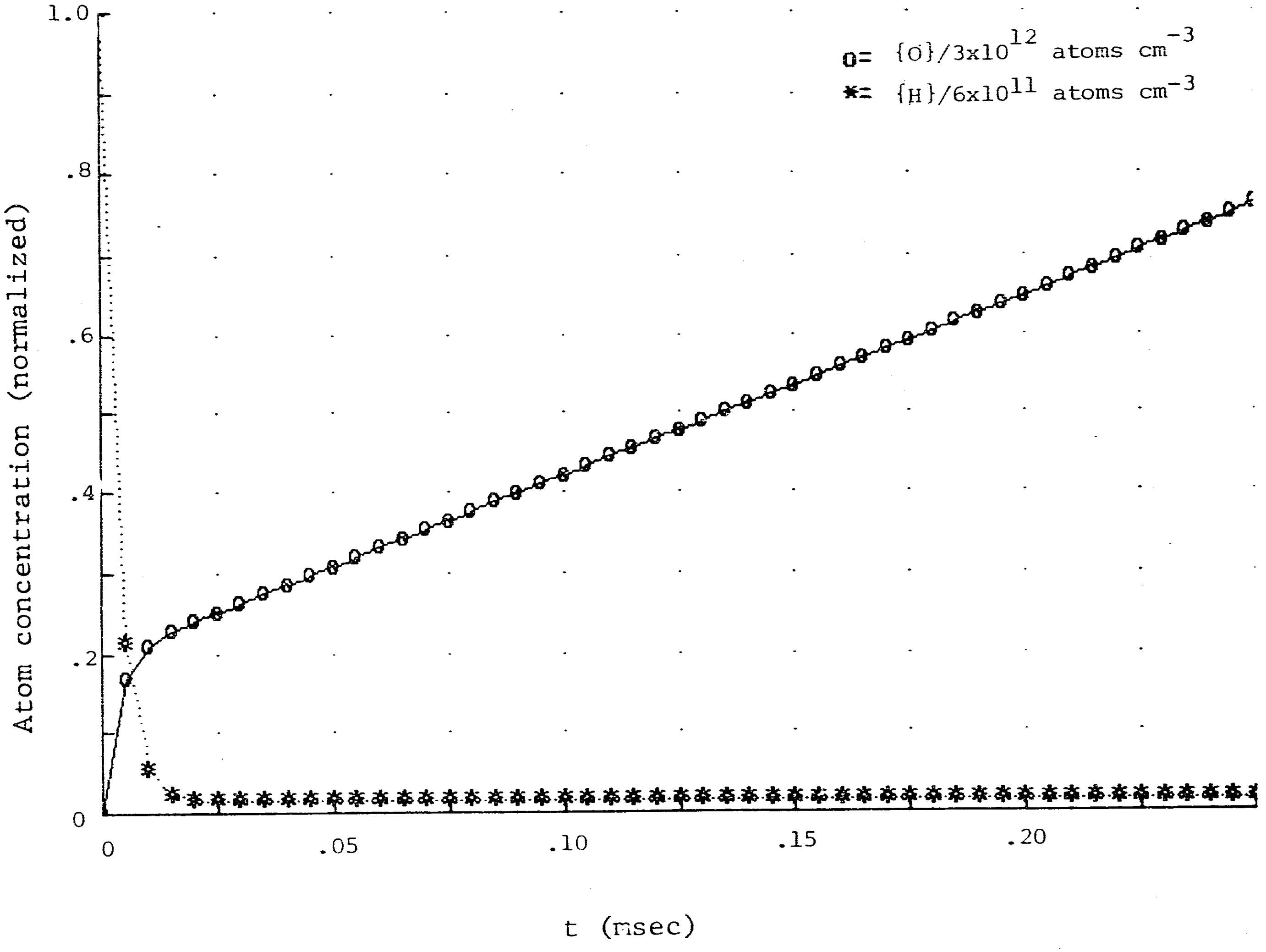1.0
.8
.6
.4
.2
0
0
.05
.10
.15
.20
t (msec)
Atom concentration (normalized)
O= {O}/3x10^{12} atoms cm^{-3}
*= {H}/6x10^{11} atoms cm^{-3}

FIGURE 9.

END

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