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MEASUREMENTS OF GAS-PHASE REACTION RATES INVOLVING N₂O AND CH₂O--ETC(U)
DEC 79 S S PENNER, K O SULZMANN, J M KLINE

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N00014-75-C-0261

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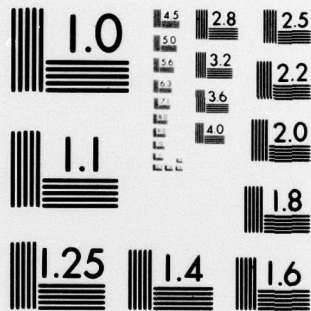
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1. REPORT NUMBER 9 FINAL REPORT	2. GOVT ACCESSION NUMBER	RECIPIENT'S CATALOG NUMBER 13
3. TITLE (and Subtitle) MEASUREMENTS OF GAS-PHASE REACTION RATES INVOLVING N_2O AND CH_2O		4. PERIOD OF REPORT FOR PERIOD ENDING 1979
5. AUTHOR(S) S.S. PENNER, et al K.G.P. / Sulzmann	6. PERFORMING ORG. REPORT NUMBER FINAL REPORT	7. CONTRACT OR GRANT NUMBER(S) ONR Contract No. N00014-75-C-0261
8. PERFORMING ORGANIZATION NAME AND ADDRESS UNIVERSITY OF CALIFORNIA/SAN DIEGO La Jolla, California 92093	9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11 31 dec 79	10. CONTROLLING OFFICE NAME AND ADDRESS LT. R.S. MILLER, Office of Naval Research Code 473, Arlington, VA 22217
11. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) AS IN 11	12. REPORT DATE December 31, 1979	13. NUMBER OF PAGES 9
14. DISTRIBUTION STATEMENT (of this Report) ONR DISTRIBUTION LIST	15. SECURITY CLASS. (of this report) UNCLASSIFIED	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N.A.
16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) ONR DISTRIBUTION LIST		
17. SUPPLEMENTARY NOTES LEVEL		
18. KEY WORDS (Continue on reverse side if necessary and identify by block number) GAS-PHASE KINETICS SHOCK-TUBE KINETIC STUDIES MEASUREMENTS OF RATE CONSTANTS 79 12 20 052 GAMMA NU		
19. ABSTRACT (Continue on reverse side if necessary and identify by block number) We have determined effective absorption coefficients for the NO γ -bands at 2259Å and for the ν_3 fundamental of N_2O at 4.52 μ . These data have been used for simultaneous measurements of rate constants for the three principal reaction steps in N_2O pyrolysis. An infrared He-Xe laser has been installed to monitor the rate of CH_2O decomposition behind reflected shock fronts by		

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absorption measurements. Preliminary results have been obtained on the rate of CH₂O pyrolysis.

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Annual Report (December 31, 1979)

on

Measurements of Gas-Phase Reaction

Rates Involving N_2O and CH_2O

under

ONR Contract No. N00014-75-C-0261

1. Publications

The following papers have been published during 1979: (a) K. G. P. Sulzmann, J. M. Kline and S. S. Penner, "Shock-Tube Studies of N_2O -Decomposition," Twelfth International Symposium on Shock Tubes & Waves, Hebrew University Press, The Hebrew University, Jerusalem, Israel, 1979. This paper contains very extensive modifications from the version that had been completed by the end of 1978. (b) K. G. P. Sulzmann, J. M. Kline and S. S. Penner, "Empirical Determinations of the Effective Absorption Coefficients for the NO γ -Bands at 2259 A and the ν_3 -Fundamental of N_2O at 4.52 μ ," JQSRT 21, 475-482 (1979).

2. Experimental Accomplishments

A. Measurement of Absorption Coefficients

Shock-Tube correlation-absorption data at 2259 A ($\Delta\lambda = 39$ A) of low-pressure (~ 5 torr) emission lines by high-pressure ($0.5 \leq p$, atm ≤ 2.1) and high-temperature

($905 \leq T, \text{ }^\circ\text{K} \leq 2015$) lines belonging to the (0, 0) band of the NO γ -system are described by using an effective absorption coefficient for emission lines of negligible width and line-center absorption by isolated Voigt-lines of common widths. The effective f-number differs by -26% from the preferred value. Modeling the system with narrow-line emission and absorption by a just-overlapping band system does not correlate the observed data.

Shock-tube emission data at 4.52μ ($\Delta\lambda = 0.083 \mu$) for N_2O in the ν_3 -fundamental for $975 \leq T, \text{ }^\circ\text{K} \leq 2300$ and $0.4 \leq p, \text{ atm} \leq 2.2$ are well described by the just-overlapping line model. The effective integrated band-intensity agrees within 9.4% with recent literature data.

The appropriate models are useful for concentration time-history measurements of NO and N_2O behind shock waves.

B. N_2O Pyrolysis

The thermal decomposition of nitrous oxide has been studied behind reflected shock waves for $1685 \leq T, \text{ }^\circ\text{K} \leq 2560$ and $1.7 \leq p, \text{ atm} \leq 4.6$ in Ar- N_2O mixtures containing 2% N_2O . Concentration-time histories have been determined for N_2O from emission at 4.52μ ($\Delta\lambda = 0.083 \mu$) and for NO by correlation spectroscopy at 2259 \AA ($\Delta\lambda = 39 \text{ \AA}$). Needed spectral absorption coefficients were obtained by the use of semi-empirical procedures.

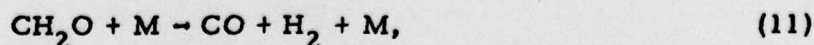
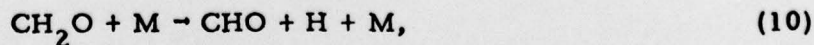
There is some delay before the O-atom concentrations attain steady-state values at low temperatures, for which the initial N_2O -decomposition is governed by the binary decomposition reaction $\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}$ with the rate coefficient

k_1 . At higher temperatures, the reactions $N_2O + O \rightarrow 2NO$ and $N_2O + C \rightarrow N_2 + O_2$ (with rate coefficients k_2 and k_3 , respectively) occur so rapidly that the O-atoms attain steady-state concentrations (within the experimentally achieved time resolution) immediately after reflected shock-heating. When a steady state obtains for the O-atom concentrations, the effective rate of N_2O -decomposition is double ($2k_1$) that for the one-step binary decomposition step. We find that $k_1 = (3.71 \pm 2.74) \times 10^{14} \exp[-(27,660 \pm 1,445)^\circ K/T] \text{ cm}^3/\text{mole-sec}$ and $k_3/k_2 \approx 1.09 \pm 0.10$ for $1685 \leq T, ^\circ K \leq 2560$. For $1685 \leq T, ^\circ K \leq 2000$, $k_2 + k_3$ was measured directly and yielded $k_2 = (4.07 \pm 3.26) \times 10^{13} \exp[-(12,350 \pm 2,380)^\circ K/T]$ and $k_3 = (4.43 \pm 3.97) \times 10^{13} \exp[-(12,350 \pm 2,380)^\circ K/T] \text{ cm}^3/\text{mole-sec}$.

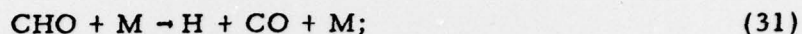
C. Preliminary Studies on CH_2O Pyrolysis

Formaldehyde pyrolysis has been studied by Dean et al (1978) and by Just (1979). Formaldehyde oxidation using N_2O or O_2 has been investigated by Dean et al (1979). Examination of these studies leads to the following conclusions.

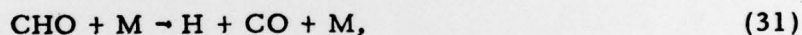
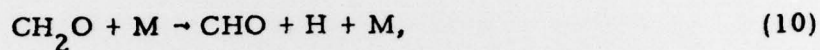
The initial step in CH_2O pyrolysis is believed to be the formation of two free radicals. The mechanism of Just (1979) includes the direct decomposition of CH_2O to CO and H_2 ,* i.e.



*The numbering system used for reaction processes corresponds to the numbering system used in our computer codes.



on the other hand, the mechanism of Dean et al (1978) requires a chain reaction for the production of H_2 and CO , i. e.



The estimated rate constants for the specified elementary steps are listed in Table 1.

Comparisons of pyrolysis and oxidation rates suggest to us that the rate of CH_2O decomposition, in the presence of N_2O , is initially determined by CH_2O pyrolysis [in particular by reaction (10)] and subsequently accelerates to values that are dominated by the presence of O atoms in the reacting mixture. In the limit, at sufficiently high temperatures, a value may be reached for the O-atom concentration that approaches the steady-state value encountered during N_2O pyrolysis. The corresponding rate of CH_2O removal is probably close to the highest rate that is achievable in CH_2O - N_2O mixtures.

Clarification and validation of the hypothesis presented in the preceding paragraph will represent the principal focus for our experimental studies during

Table 1. Rate constants for elementary steps in CH₂O pyrolysis.

Step	Just (1979)			Dean et al (1979)		
	A, cm ³ /mole-sec	Ea, cal/mole	k at 2000°K, cm ³ /mole-sec	A, cm ³ /mole-sec	Ea, cal/mole	k at 2000°K, cm ³ /mole-sec
10	1.9x10 ¹⁶	80,200	3.3x10 ⁷	3.31x10 ¹⁶	81,000	4.7x10 ⁷
11	8x10 ¹⁵	69,500	2.0x10 ⁸	-	-	-
14		assumed to be fast		3.31x10 ¹⁴	10,500	2.4x10 ¹³
31		assumed to be fast		1.55x10 ¹⁴	14,700	3.8x10 ¹²
37	-	-	-	1.99x10 ¹⁴	0	2.0x10 ¹⁴

the third contract year. A key measurement technique that will be used in this validation involves spectral absorption measurements for an He-Xe laser centered near 3.5μ , which coincides with an absorption line of CH_2O . In the oxidation studies of CH_2O by N_2O , we monitor the CH_2O concentration by absorption of the He-Xe line and the $(\text{CO})(\text{O})$ product by chemiluminescence at 3700 \AA in mixtures of CH_2O , N_2O and CO in Ar. It should be noted that direct measurement of CO emission is difficult because of N_2O emission at 4.8μ .

Rate constants for O-atom reactions will be evaluated with the aid of a chemical kinetics computer code.

In addition to the facilities described in our 1978 annual report, we have installed an He-Xe laser for absorption measurements on CH_2O .

The He-Xe laser was manufactured by Advanced Kinetics, Inc., of Costa Mesa, Calif. It consists of an 8 mm diameter, water-cooled discharge tube mounted in a 98 cm long optical cavity. The He-Xe mixture flows through the tube at a pressure of approximately 2 torr. The maximum power output of the laser is 3 mW. It may be operated in either a CW mode or a pulsed mode. Pulse rates between 40 and 1000 pulses per second may be achieved. In the pulsed mode, the laser output power may be feed-back stabilized.

The laser is mounted below the shock tube, and its beam is directed by two mirrors through the center of the shock tube observation windows and onto a liquid- N_2 -cooled InSb detector.

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5