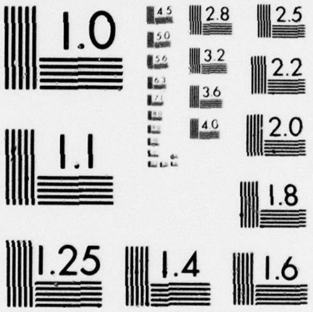
AD-A061 595 WASHINGTON UNIV SEATTLE DEPT OF CHEMISTRY F/G 7/3
VIBRATIONAL ENERGY TRANSFER IN THERMAL UNIMOLECULAR SYSTEMS BY --ETC(U)
NOV 78 E KAMARATOS, J D BURKHALTER, D G KEIL N00014-75-C-0690
UNCLASSIFIED NR092-549-TR08 NL

1 OF 1
AD
A061595

END
DATE
FILMED
1 -79
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

LEVEL II

(12)

SC

AD A061595

(6)

Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane.

(10)

E. Kamaratos, J. D. Burkhalter, D. G. Keil
and B. S. Rabinovitch

Department of Chemistry, BG-10
University of Washington
Seattle, WA 98195

(9) Technical rept.,

Prepared for publication in J. Phys. Chem.

(14)

Technical Report No. NR092-549-TR08

Contract N00014-75-C-0690, NR092-549

(15)

(11) 1 Nov[redacted]78

(12) 26p.

OFFICE OF NAVAL RESEARCH
Department of the Navy
Code 473
800 N. Quincy
Arlington, VA 22217

78 11 20 024

370 274

mt

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
NR092-549-TR08 ✓

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane.

5. TYPE OF REPORT & PERIOD COVERED
Technical

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
E. Kamaratos, J. D. Burkhalter, D. G. Keil and B. S. Rabinovitch

8. CONTRACT OR GRANT NUMBER(s)
N00014-75-C-0690 ✓
NR092-549

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Professor B. S. Rabinovitch
Department of Chemistry BG-10 ✓
University of Washington
Seattle, WA 98195

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research, Code 743
Department of the Navy
800 N. Quincy
Arlington, VA 22217

12. REPORT DATE
1 November 78

13. NUMBER OF PAGES
22

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To be submitted to J. Phys. Chem.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Bath Gases
Cyclopropane
Diffusion Cloud
Energy Transfer
Gas Reaction
Unimolecular Reaction
Vibrational Energy

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A study of vibrational energy transfer by the Diffusion Cloud Method has been made at temperatures from 975 K to 1175 K in the cyclopropane isomerization system. H_2, He, N_2 and CO_2 were studied as inert bath gases. Their relative efficiencies increase in that order. Values of $\langle \Delta E \rangle$ vary from 150 cm^{-1} to 1100 cm^{-1} at 975 K. These values tend to decline and the collisional efficiencies, β_c, decrease markedly with rise of temperature to 1175 K.

78 11 20 024

Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane[1]

by E. Kamaratos,[†] J. F. Burkhalter,[‡] D. G. Keil,[#]
and B. S. Rabinovitch[*]

Department of Chemistry
University of Washington
Seattle, WA 98195

Abstract

Little information is available regarding vibrational energy transfer involving highly excited polyatomic molecules at higher temperatures ($\gtrsim$ 1000 K). In an earlier paper (ref 6), we described some features of the point source diffusion cloud method which is here applied to the study of the thermal unimolecular isomerization of cyclopropane. The relative collisional energy transfer efficiencies β_c for the bath gases He, H_2, N_2 and CO_2 have been determined in the fall off region ($k/k_\infty \sim 0.02$-0.05) at 975 K. By calibration of absolute rate constants from earlier data, values of the average energy down-jump size $\langle\Delta E\rangle_d$ were determined. They are approximately 200, 150, 400, and 1100 cm^{-1}, respectively, and decrease with rise of temperature to 1175. β_c also decreases between 975 K and 1175 K. These findings have relevance for the interpretation of high temperature gas reactions such as shock tube systems and complement some earlier measurements (ref. 7b).

Introduction

Since the development of the point source diffusion flame method by M. Polanyi and co-workers,[2] it has been used extensively to study the kinetics of fast bimolecular reactions. Extended versions of the method have added flow transport to the diffusive transport and reaction.[3-4] Tal'rose has called this technique the diffusion cloud method.[5] In an earlier paper,[6] where a history of the method and a summary of recent experimental and theoretical developments was presented, we have examined theoretical and experimental aspects of the method using a non-reactive diffusive substrate, mercury. We proposed that the method should be applied to the study of unimolecular reactions and vibrational energy transfer and adopt Tal'rose's nomenclature for such applications.

Specifically, the diffusion cloud method may be employed advantageously to extend investigations to the lower region of elevated temperatures ($\gtrsim$ 1000 K) reached usually by shock tube methods. Interesting information regarding unimolecular reaction rate constants and collisional efficiencies for vibrational energy transfer may be obtained. Little information on vibrational energy transfer involving highly excited polyatomic molecules at high temperatures is available.[7]

The present paper presents data on the relative collision efficiencies of cyclopropane in N_2, CO_2, H_2, and He bath gases using the diffusion cloud technique. Temperature dependence of the rate has also been measured between 975 - 1175~~°~~ K. Since the diffusion constants increase at higher temperatures, it was necessary to extend the mathematical treatment presented in the earlier paper.[6] A model given by Nevrovskii[8] which employs reflections at the wall and a flat velocity (plug flow) profile has been considered. Efforts have been made to extend the treatment to the case of a laminar (parabolic) flow contour, with only partial success. However, the present results serve to illustrate the usefulness of this method for the study of unimolecular systems.

Recently, unimolecular reaction rate constants for the thermal decomposition of CF_2BrCF_2Br in N_2 were reported.[9] The experimental method used was an extended diffusion method with laminar flow; however, the reactant was not introduced from a point source. The method and mathematical treatment employed restricted the determination of rate constants to measurements made at large distances from the origin.

Experimental

The diffusion reaction chamber was a 5 ft length of 12 in. i.d. fused silica tube with a 0.5 in. wall. The polished ends of the tube were sealed with a brass inlet flange and a steel outlet flange with the use of 1/4 in. neoprene gaskets. The apparatus was pumped through a stainless steel liquid nitrogen trap by a Leybold-Heraeus WA 500 Roots-type pump, with displacement capacity of 160 ℓ sec^{-1}, and backed by a Leybold-Heraeus E150 two-stage pump.

The bath gas flow was measured with a precalibrated Manostat Tri-Flat flowmeter. The gas entered the reaction chamber through a stainless steel diffuser can, 11 in. diam., which served also as a preheater. The diffuser had 50 - 1/32 in. diam. holes, grouped so as to produce parabolic flow. Four 14-mesh stainless steel screens were attached with crossed meshes to the face of the diffuser to break up wakes due to the flow through the holes. The neoprene end gaskets were protected by copper water jackets around the ends of the quartz tube. The bath gas exited through a chevron optical baffle which screened the reaction area from a cooling baffle. The cooling baffle was a water-cooled hollow copper can, 11 in. diam., 1 in. thick, through which flow was conducted *via* 32 - 3/4 in. axially oriented copper tubes. The tubes were arranged so as to accept parabolic flow with minimum perturbation. Roughly 15% of the cooling baffles surface area consisted of tube openings.

A quartz-sheathed, vacuum-jacketed, water-cooled, stainless steel reactant inlet probe, 25 in. long, entered through the brass inlet flange along the wall of the quartz tube; the probe made a right angle and terminated in a water-cooled 11/32 in. diam. sterling silver spherical nozzle on the axis of the reactor. The nozzle was located 11 in. from the diffuser face and 16 in. upstream from the optical baffle. Each of the twenty nozzle holes on the sphere were located at the center of the face of an icosahedron. Input from the nozzle was designed to be not more than 5% of mass flow of atmospheric gas over the surface of the sphere, so as to minimize perturbations.

Two stainless steel axial collection tubes entered upstream and downstream of the nozzle, through cajon fittings in the end flanges. They were movable on axis at positions from 1/4 in. to 8 in. from the nozzle. The probes were vacuum-jacketed and water-cooled similar to the inlet probe and were fitted with truncated conical sterling silver tips having an approximately seven-thousandths in. orifice on an end flat ~1/32 in. in diam. The diameter of the collection probes was 1/4 in. for a length of 1 in. after which the probe tube expanded to 1/2 in. o.d. The samples were pumped through a stainless steel flexible tube to a liquid nitrogen-cooled trap.

Heat to the reactor was provided by a 3-zone Kanthal wire oven, controlled by an internal thermocouple. The output from a Partlow proportional time temperature controller could be reduced by a separate control for each zone. Proper adjustment permitted a relatively flat temperature profile. Over the reaction region, the effective maximum temperature drop near the ends of the reactor was approximately 10°.

Samples were analysed by glpc using a 1-ft column of Duropak followed by 10-ft of 15% squalane on 45-60 mesh Chromosorb P and a flame detector.

Results

Mathematical Treatment of Data. The equation of continuity for the concentration of reactant is

$$D\ \nabla^2 C - U(\rho)\frac{\partial C}{\partial z} - kC = 0 \qquad (1)$$

where D is the diffusion constant, C is the concentration, $U(\rho)$ is the velocity profile as a function of the cylindrical radial coordinate ρ, z is the axial distance from the origin of reactant, and k is the rate constant. The solution of this equation for a point source and $U(\rho)$ = constant has been given for an unbounded reactor.[4] At higher temperatures, where the diffusion coefficients become larger, i.e., low U/2D, the values of k computed from our data became unrealistically large and depended on the axial distance z from the nozzle. This is due to reflection from the wall. As a consequence, it is necessary to apply some boundary conditions for a cylindrical reactor of finite size,

$$\left.\frac{\partial c}{\partial \rho}\right|_{\rho=0} = 0 \qquad \text{and} \qquad \left.\frac{\partial c}{\partial \rho}\right|_{\rho=R} = 0 \quad ,$$

where R is the radius of the reactor. A solution with these boundary conditions has been given by Nevrovskii (eq. 16, ref. 8) as a limiting case of the more difficult problem in which the velocity field is taken as parabolic. We have independently solved the equation by integrating the time-dependent concentrations of instantaneous sources moving in a flat velocity field,[11,12]

$$C(\rho,z,k) = \frac{I}{2\pi R^2 D}\sum_{i=1}^{\infty}\frac{\exp\left[\frac{U}{2D}z - z\left(\frac{U^2}{4D^2} + \frac{k}{D} + \alpha_i^2\right)^{1/2}\right]}{\left(\frac{U^2}{4D^2} + \frac{k}{D} + \alpha_i^2\right)^{1/2}}\,\frac{J_0(\alpha_i\rho)}{J_0^2(\alpha_i R)} \qquad (2)$$

where α_i are the roots of $J_1(\alpha_i R)$. This expression for the concentration can be shown to be equivalent to that of Nevrovskii when an integral of Bessel functions given by him is evaluated.

The system under study is an isomerization reaction so that it is possible to make the useful and realistic simplification of taking the diffusion coefficients of reactant cyclopropane and product propene to be equal. The diffusion coefficient was calculated by a well-known relationship.[14] The rate constant k was evaluated from the data as the root of the equation

$$\frac{C(\rho,z,k)}{C(\rho,z,o)} = \frac{C'_{\text{reactant}}}{C'_{\text{reactant}} + C'_{\text{product}}} \qquad (3)$$

by using the IMSL Computer library probram ZBRENT, where the C' are experimentally determined concentrations. ZBRENT combines linear and quadratic inverse interpolation to determine the roots of an equation. Only the first 21 roots of $J_1\ (\alpha_i R)$ were employed in evaluating $C(\rho,z,k)$ and $C(\rho,z,o)$ and the value of k was usually determined with fewer than 10 iterations.

When applied to the data, the finite cylinder model with constant flow velocity eliminates the dependence of calculated k values on z and gives good agreement between values obtained from both upstream and downstream sample collection probes. Table I illustrates this behavior. The value of the constant velocity was set at the average for parabolic flow, $\overline{U} = U(0)/2$. This is a physically reasonable value. Moreover, comparison of the z part of terms in the solution for the constant velocity model with terms in the (partial) solution for laminar flow model (next paragraph) supports this assignment. As is brought out later, however, in the presentation of the results, our approximate mathematical treatment is not adequate in all respects.

It has already been noted[6] that eq. (1) has been solved in principle for a point source with laminar atmosphere flow and with reflection at the wall. Both analytical[8,9] and numerical[13] solutions have been given that apply at distances far from the source. However, for fast reactions the data must be taken at distances close to the source. The numerical method requires very small grain sizes and thus prohibitively long computer times for evaluation. The analytic solution holds the greatest promise, since it is only necessary to evaluate more terms to the series solution in order to obtain accurate results at the positions of interest. The difficulty arises in evaluating the coefficient for each term. Gershenzon et al. used a single term, which is only adequate for Z much larger than R. Nevrovskii used a truncated series of four terms, which is adequate only for axial distances greater than 0.6 R. In order to evaluate coefficients, it was necessary for Nevrovskii to use an orthogonalization routine for each set of functions ψ_i (eq. 4). This requires an increasing number of numerical integrations with each term added. It may be noted parenthetically that although Nevrovskii provided a limited analytical series solution of the point source in a finite cylinder with laminar flow, his subsequent experimentation[15] utilized only the unbounded piston flow model. We have succeeded in evaluating the first fifteen exponential eigenvalues λ_i and the radial functions $\psi_i(\rho)$ in the series:

$$C_{lam}(\rho,z,k) = \sum_i A_i \, \psi_i(\rho) \, e^{\lambda_i z} \qquad (4)$$

where the $\psi_i(\rho)$ is a product of an exponential and a confluent hypergeometric function;[8] $\psi_i(\rho) = 1$ for the special case $\rho = 0$. Our continuing work is directed toward developing a more efficient method of evaluating the coefficients, A_i, which avoids the intractably cumbersome orthogonalization routine of Nevrovskii. The inverse problem of finding rate constants from experimentally determined concentrations would then become tractable for the case of laminar flow.

Diffusion and Flow without Reaction. Several diffusion experiments were performed at room temperature in order to test the apparatus and to confirm our earlier results with Hg in nitrogen.[6] Diffusion of cyclopropane and butane in nitrogen was studied at total pressures around 1 torr. Samples were taken downstream of the spherical nozzle. For $r = z$, in the infinite cylinder model, $C(z) = I/4\pi Dz$, where I is the rate of input of the nozzle gas, for the case of diffusion and transport of a nozzle gas introduced from an axial point source into an atmospheric gas stream flowing with uniform velocity along the axis of the cylinder; $\bar{U}/2D$ is ~ 1. Plots of inverse concentration (1/C) vs axial distance z for each hydrocarbon followed the straight line relation.

Some typical behavior is illustrated in Fig. 1. Also, the ratios of linear least squares slopes curves were determined for the three hydrocarbons. The experimental ratios agreed with the predicted values, $C_i/C_j = D_j/D_i$, within 20%.

Diffusion, Flow and Reactions. Efficiencies of Bath Gases at 975 K. Exploratory data were obtained over the range from 800 - 1200 K. Most of the data were taken at 975 K and at 1175 K, with the former set being the most extensive. Rates at 975 K were measured at pressures around 0.5, 1, 2 and, in some cases, 7 torr for all four bath gases.

Most measurements were usually made at $\bar{U}$ values between 20 and 100 cm sec^{-1}. The type of reproducibility that could be obtained upon repetition of measurements in different runs under constant condition of pressure and flow velocity is illustrated in Table I. The data for He show excellent concordance, both in detail as a function of z, and between upstream and downstream measurements. The values for H_2 have more scatter and are typical of some runs; however, although the data does have some obvious dispersion (some of which is believed to have known experimental sources), nonetheless, the mean value has a standard deviation of only 10% in this case.

Deficiencies of the constant velocity finite cylinder model became evident in an apparent dependence of k on the experimental flow velocity. The dependence was particularly noticeable at the lower temperature. It is interesting to note that although not recognized by them and described only as random experimental error, a dependence of the unimolecular rate constants on the experimental flow velocity also appears in the work of Gershenzon[9] mentioned in the Introduction. In view of this dependence, it was not possible to determine absolute unimolecular reaction rates (although relative collision efficiencies of the bath gases could be determined under constant experimental conditions). We have employed an expedient adopted by shock tube exponents and have used the known rate of cyclopropane decomposition in order to calibrate, or to correct for the flow parameter approximation. Rate constants are recorded[7b] for the decomposition of cyclopropane diluted in He at 973 K and at pressures below 1 torr; the literature values are 0.035 and 0.065 sec^{-1} at 0.5 and 1 torr, respectively. These values coincide with the present measurements at 975 K for a constant value of $\overline{U}$, namely, 70 cm sec^{-1}. This value has been used as a reference for all other data and rate constants at this velocity have been obtained by interpolation from the measured data.

Values of rate constants for all bath gases at 975 K are summarized in Table II along with the relative collisional efficiencies, β_p; derived quantities are listed in Table III.

Efficiencies of Bath Gases at 1175 K, Decline of β_c with Temperature. Since the 1175°K data did not display any marked velocity dependence, no interpolation was needed. The rate data are presented in Table IV together with their statistical parameters. Some obvious inconsistency in the pressure dependence of k is evident. Nevertheless, the results, taken as a whole, indicate marked lowering of the observed activation energy for all gases which is beyond experimental error; values averaged over all pressures are (kcal $mole^{-1}$): CO_2=42; N_2=49; H_2=40; He=49, at a fixed value of ω corresponding to $k/k_\infty \simeq 0.03$ at 975 K.

Discussion

Relative efficiencies at 975 K. The pressure-per-pressure efficiencies, β_p , in Table II show a decrease along the series: $CO_2 > N_2 > H_2 \simeq He$. This trend accords with some other experiments reported in the literature at lower temperatures. Chan et al.[16] report β_p values for methylisocyanide of .32, .21, 0.28, .17, for CO_2, N_2, H_2 and He, respectively, at 550 K in the second order region. Pritchard et al.[17] gave for the cyclobutane system, 0.21, 0.10, 0.07 for N_2, H_2 and He bath gases, respectively, at 720 K in the fall off region. Volpe and Johnston[18] found low-pressure values, for NO_2Cl at 476 K, of 0.34, 0.15, and 0.15 for N_2, H_2, and He, respectively; a CO_2 value is not recorded but that for N_2O was 0.48.

Absolute efficiencies at 975 K. Absolute efficiencies on a collision basis, β_c, were obtained from the pressure (collisional rate ω) displacement by comparison of the data with calculated (App I) fall off curves (Fig. 2). The experimental fall off is displaced with respect to the strong collider curve and $\beta_c = \omega(sc)/\omega(wc)$; $k/k_\infty \simeq 0.03$. The collision cross sections of refs. 7b and 16 were used. The fall off curves were calculated for various assumed average energy-transfer step sizes and probability distribution model by a stochastic computation similar to that described earlier.[19] The value of $\langle\Delta E\rangle_d$ is also obtained, as well as the dimensionless parameter, $E' = \langle\Delta E\rangle_d/\langle E^+\rangle$, where $\langle E^+\rangle$ is the average energy of substrated molecules above E_0 as given by the Boltzmann distribution. It has beer shown[19] that β_c is a universal function of E', for a particular distribution model. Values of β_c are summarized in Table III. It appears[16,19] that the step ladder (or gaussian) model is an apt one for more efficient colliders while an exponential model may be more correct for weaker colliders.

The value of $\langle\Delta E\rangle_d$ measured here for H_2 gas is closely similar to that measured previously at the same temperature in the cyclopropane-d_2 system[7b] for He, which has comparable efficiency. The value 1100 cm^{-1} for CO_2, the most efficient gas studied here, is less than that measured previously[7b] for the more efficient parent cyclopropane substrate (1900 cm^{-1}). The $\langle\Delta E\rangle_d$ value for N_2 is intermediate at 450 cm^{-1}.

Temperature dependence of $<\Delta E>_d$ and β_c. Theoretical falloff plots at 1175 K were calculated for various assumed collisional energy transfer step sizes. These are similar to those in Fig. 2 and are given in ref. 12. By fitting the rate data of Table IV to the calculated curves, the appropriate values of $<\Delta E>_d$ were obtained (Table IV); the collision cross-sections of ref. 7b were employed.

The collisional efficiencies β_c were again evaluated, at a fall off value of $k/k_\infty \cong 0.01$, by comparison of the displacement of the experimental weak collider data on the collision rate axis with respect to the theoretical strong collider curve (Table IV).

By comparison of the 975° and 1175°K results, it is evident that β_c decreases markedly — particularly since <E> appears to decrease with rise of temperature. Such a decrease is predicted on theoretical grounds.[7a] The average activation energies, ∿ 45 kcal, are very low as a result of the decrease of β_c with temperature. The present data, although limited, provide a useful complement to the meager number of investigations of the collisional efficiencies for polyatomic molecules at higher temperatures.

It may be noted that earlier shock tube studies[7a] have yielded low values of the activation energy at elevated temperatures. It was suggested[7a] earlier that at least part of the reason for the low shock tube values of E_a could be attributed to a decline of the collisional efficiency with temperature.

Dedication

This paper is dedicated to Don Bunker.

Appendix I

Model for RRKM Calculations

Complex frequencies (cm^{-1}): 3020(5), 1430(3), 1100(4), 900(5), 550(3)

Molecule frequencies (cm^{-1}): 3050(6), 1460(3), 1080(7), 870(3), 735(2)

$d = 12$; $(I^{+}/I)^{\frac{1}{2}} = 1.24$

$E_o = 62.7$ kcal $mole^{-1}$

Table I. Illustrative Run Data; Rate constants k (sec^{-1})

A. He (2.14 torr); $\bar{U}$ = 40 cm sec^{-1}

Run\z(cm)		5.0	6.0	7.5	8.0	10	13	Run Average
1	u[a]	0.064		0.074		0.079[b]		0.074
						0.077		
	d	0.081			0.079	0.077		0.079
		0.077						
2	u	0.078		0.098		0.090		0.086
		0.078		0.084				
	d			0.081		0.093		0.093
				0.094		0.101		
				0.098				
3	u			0.071		0.062		0.074
				0.088				
	d	0.080		0.111				0.096
4	u	0.083		0.081		0.087		0.088
		0.092		0.085		0.097		
	d	0.095		0.101		0.103		
		0.089		0.092		0.109		0.098
5	u		0.092		0.104	0.153		
						0.114		0.116
	d		0.099		0.116			
			.102			0.118	0.130	0.113

Grand Average 0.092 ± .005[c]

Table I. (continued)

B. H_2 (2.14 torr); $\overline{U}$ = 90 cm sec^{-1}

Run	z(cm)	5.0	6.0	7.5	9.0	10.0	12.0	Run Average
1[d]	d	0.15 0.16		0.25 0.25		0.21		0.20
2[d]	d	0.19		0.22		0.22		0.21
3	u	0.11		0.10 0.08		0.12		0.10
	d	0.12		0.13 0.14		0.13		0.13
4	u					0.20	0.25	0.23
	d		0.26 0.26	0.32 0.33	0.27	0.32 0.16		0.27
5	u	0.20 0.15 0.16		0.18 0.17 0.18		0.15		0.17
	d	0.29		0.20 0.19 0.21 0.18		0.19 0.20		0.21

Grand Average 0.19 ± .02[c]

a u or d represents up or downstream measurements, respectively.

b Multiple entries represent repetitions at different times during a run.

c Standard deviation of the mean.

d No upstream measurements in this case.

Table II. Summary of Rate Constants[a] (sec^{-1}) and Efficiencies,[b] β_p , at 975 K.

β(torr)	0.53		1.0		2.1	
	k	β_p	k	β_p	k	β_p
CO_2	0.28 ±.08[c]	(1)	0.20 ± .05	(1)	0.39 ± .04	(1)
N_2	0.051±.020	0.18	0.13 ± .01	0.65	0.23 ± .02	0.59
H_2	0.035±0.001	0.13	0.069±.002	0.35	0.16±0.02	0.41
He	0.035	0.13	0.065	0.33	0.14 ± .01	0.36

a) Based on calibration described in text

b) Values relative to $CO_2 \equiv 1$

c) Standard deviation from fit of line

Table III. Values of β_c and $<\Delta E>_d$ (cm^{-1}) at 975 K.

	$<\Delta E>_d^{SL}$	$<\Delta E>_d^{EXP}$	E'^{a}	$\beta_c^{\ c}$
He	--	190[b]	0.16	0.010
H_2	--	150	0.14	0.009
N_2	450	400	0.37	0.02
CO_2	1100	--	1.0	0.09

a) $E' = <\Delta E>_d/<E^+>$, where $<E^+>$ is the average energy (1094 cm^{-1}) above E_0 for a Boltzmann distribution (Ref. 18).

b) Based on calibration of rate. See Text.

c) At $k/k_\infty \simeq 0.015$

Table IV. Summary of rate constants (1175 K), β_c and $\langle \Delta E \rangle_d$

	p (torr)	$\Delta \overline{U}$ [a] (cm sec^{-1}	k (sec^{-1})	$\langle \Delta E \rangle$ [d] (cm^{-1}) [d]	β_c [d,e]
CO_2	0.53		13.8 ± 2.0(4) [b]	450 ± 150	0.022
	1.02		8.0 ± 0.6(9)		
	2.14		14.2 ± 1.4(10)		
N_2	0.53		8.4 ± .6(6)	350 ± 150	0.013
	1.02		5.8 ± .4(8)		
	2.14	45-85	12.3 ± .8(4)		
H_2	2.14		5.6 ± .4 [c]	110	0.002
He	0.53	100-198	2.75 ± .05(6)	200 ± 50	0.006
	2.14	95-136	10.5 ± .8(12)		

a) Range of $\overline{U}$ in runs where $\overline{U}$ varied significantly.

b) Standard deviation of the mean of the number of run measurements shown in parenthesis.

c) Average of two measurements only.

d) Averaged over all pressures

e) At $k/k_\infty \simeq 0.01$

References

† Present address: Chemistry Department, Tougaloo College, Tougaloo, MS 39174

Present address: Chemistry Department, University of Pittsburg, Pittsburg, PA 15213

‡ NSF ERG Trainee

1. This work was supported by the Office of Naval Research.

2. M. Polanyi, "Atomic Reactions," Williams and Norgate Ltd., London, 1932; C.E.H. Bawn, Chem. Soc. Ann. Reps., 39, 36 (1942); E. Warhurst, Quart. Revs., 5, 44 (1951).
3. R. J. Cvetanovic and D. J. LeRoy, Can. J. Chem., 29, 597 (1951); K. J. Mintz and D. J. LeRoy, Can. J. Chem., 53, 1726 (1975).
4. J. F. Reed and B. S. Rabinovitch, J. Phys. Chem., 59, 261 (1955).
5. A. F. Dodonov, G. K. Lanrovskaya, V. P. Strunin, and V. L. Tal'rose, Kinet. Katal., 7, 693 (1966), et. seq.
6. D. G. Keil, J. F. Burkhalter, and B. S. Rabinovitch, J. Phys. Chem., 82, 362 (1978).
7. a) B. S. Rabinovitch, D. G. Keil, J. F. Burkhalter and G. B. Skinner, Tenth Intern. Shock Tube Sympos., Kyoto, 1975, p. 579; b) I. E. Klein and B. S. Rabinovitch, J. Phys. Chem., 82, 243 (1978), J. Chem. Phys., 67, 3833 (1977).
8. V. A. Nevrovskii, Kinet. Katal., 17, 51 (1976).
9. Y. M. Gershenzon, G. Y. Driker, A. M. Ryvkin, and N. A. Shwartsman, Kinet. Katal., 16, 596 (1975).
10. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," 2nd ed., Oxford University Press, 1959, p. 378.
11. V. A. Nevrovskii and L. B. Soroka, Kinet. Katal., 17, 551 (1976).
12. See J. F. Burkhalter, Ph.D. Thesis, University of Washington, for details.
13. R. L. Brown, Int. J. Chem. Kinet., 2, 495 (1970).
14. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1964.
15. V. A. Nevrovskii and L. B. Soroka, Kinet. Katal., 17, 551 (1976).

16. S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, J. Phys. Chem., 74, 3160 (1970).

17. H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, Proc. Roy. Soc., 218A, 416 (1953).

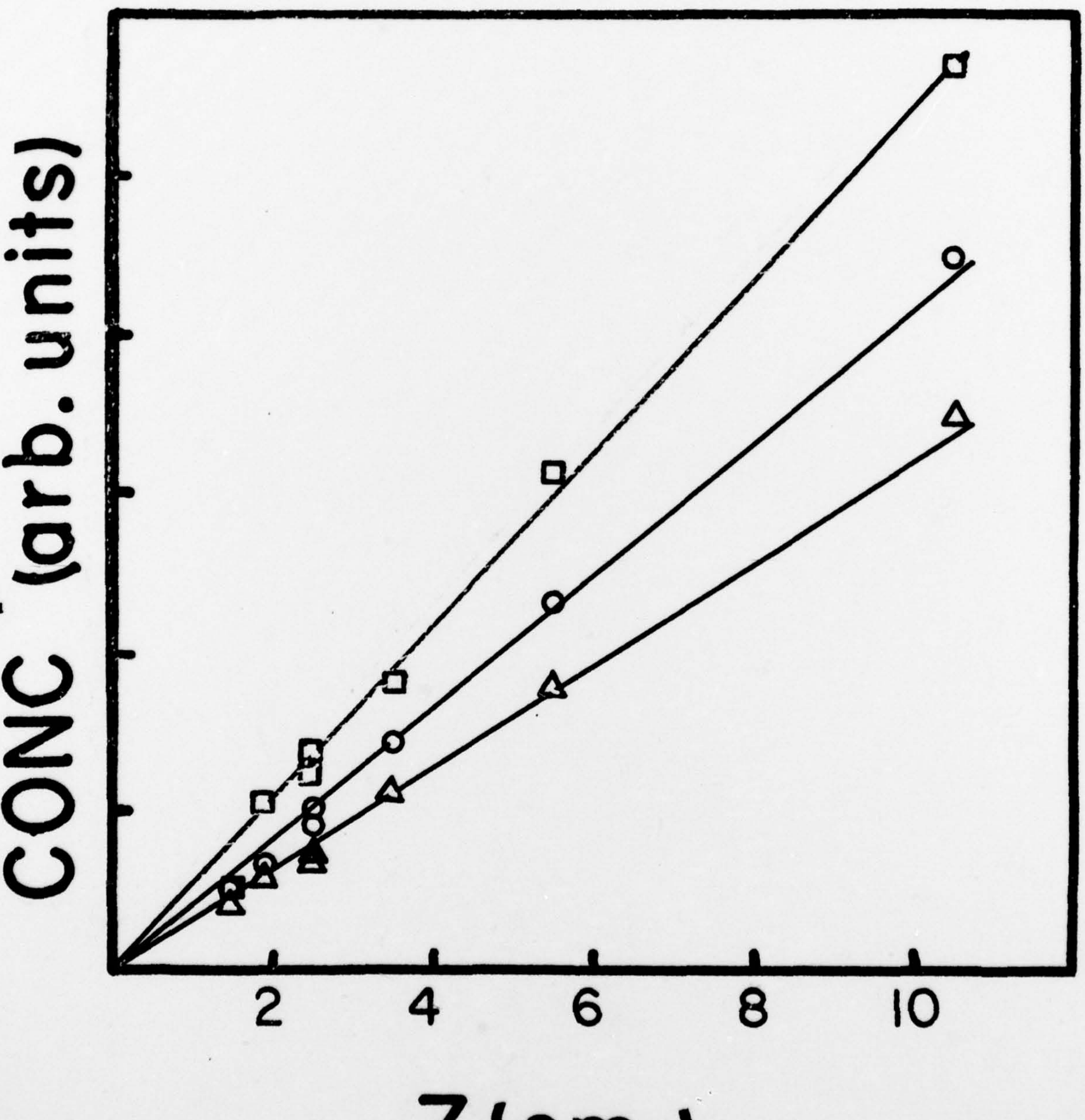
18. M. Volpe and H. S. Johnston, J. Am. Chem. Soc., 78, 3903 (1956)

19. D. C. Tardy and B. S. Rabinovitch, J. Chem. Phys., 48, 1282 (1968).

Figure Captions

Fig. 1 Plot of inverse concentration *vs* z at 25° for several gases △, butane; ○, cyclopropane; □, ethane. Slope ratios: butane: cyclopropane: ethane; experimental = 1.3:1:.78; theoretical: 1.1: 1:.84.

Fig. 2 Plot of log k/k_∞ *vs* log ω for cyclopropane-d_2 at 975 K for various bath gases: □ , CO_2; △ , N_2; ◇, H_2; ○ , He.


CONC^{-1} (arb. units)
2
4
6
8
10
Z (cm.)

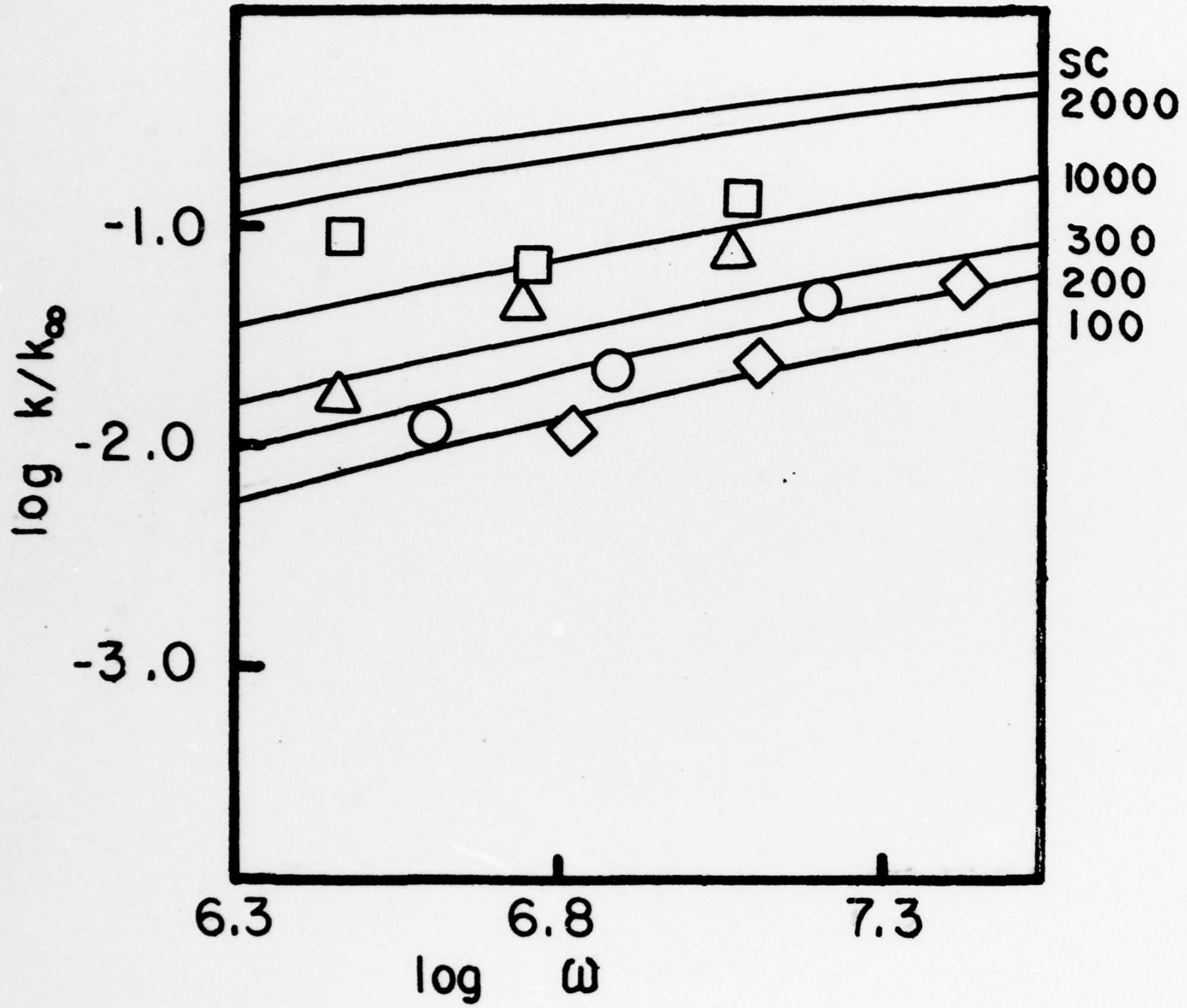


Fig. 2

DISTRIBUTION LIST

Contractor University of Washington NR 092-549

Contract Number N00014-75-C-0690 Date November 1, 1978

	No. Copies
Office of Naval Research Code 473 Arlington, VA 22217 Attn: Lt. Richard Miller	10
Office of Naval Research Branch Office 1030 East Green Street Pasadena, CA 91106 Attn: Dr. R. J. Marcus	1
Office of Naval Research Branch Office 536 S. Clark Street Chicago, IL 60605 Attn: Dr. J. Smith	1
Defense Documentation Center Bldg. 5 Cameron Station Alexandria, VA 22314	12
Office of Naval Research Branch Office 495 Summer Street Boston, MA 02210 Attn: Dr. L. H. Peebles	1
Office of Naval Research Resident Representative University of Washington 3710 Brooklyn Avenue NE, Unit 2 Seattle, WA 98195	1
U. S. Naval Research Laboratory Code 2627 Washington, D.C. 20375	6
Naval Research Laboratory Code 6100 Washington, D.C. 20375	1
Naval Air Systems Command Code 440 Washington, D.C. 20360 Attn: Dr. H. Rosenwasser	1

	No. Copies
Naval Sea Systems Command SEA-0331 Washington, D.C. 20362 Attn: Mr. J. Murrin	1
Naval Sea Systems Command SEA-0332 Washington, D.C. 20362 Attn: Dr. A. Amster	1
Naval Surface Weapons Center Research and Technology Dept.-WR Silver Spring, MD 20910	1
Naval Weapons Center Research Department Code 60 China Lake, CA 93555	1
Naval Weapons Center Code 608 China Lake, CA 93555 Attn: Ronald L. Derr	3
Air Force Office of Scientific Research Directorate of Aerospace Sciences Bolling Air Force Base Washington, D.C. 20332	1
Air Force Office of Scientific Research Directorate of Chemical Sciences Bolling Air Force Base Washington, D.C. 20332	1
Air Force Office of Scientific Research Directorate of Physics Bolling Air Force Base Washington, D.C. 20332	1
U.S. Army Research Office Chemistry Division P.O. Box 12211 Research Triangle Park, N.C. 27709	1
U.S. Army Research Office Physics Division P.O. Box 12211 Research Triangle Park, N.C. 27709	1
Professor S.N.B. Murthy Technical Director, Project SQID Purdue University Lafayette, IN 47907	5