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Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low-Pressure **Unimolecular Reaction**

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A technique has been developed, called the variable encounter method, for the study of gas-wall vibrational energy transfer in the transient region of a unimolecular reaction. The method was applied to the isomerization of cyclopropane to propylene. Molecules at room temperature were introduced into a hot reactor, and the accommodation to the final temperature of the reactor was monitored by measurement of the amount of reaction that occurred at various intervals during the energy relaxation process. Specifically, the amount of reaction following some (variable) mean number of collisions, m, between gas and reactor wall was measured. Temperatures in the range 900-1125 K were employed. Reactors having m values of 2.6, 8.5, and 27.2 were used. The average probability of reaction per collision, $P_{c}(m)$, for a given reactor, was deduced from the data and compared with a theoretical stochastic calculation based on both Gaussian and exponential models for the energy transfer probabilities. It is found that the efficiency of a seasoned quartz wall is greater than gas-gas collisions of substrate and that the efficiency declines with an increase of temperature. The steady state is closely approached (90%) in a comparatively small number of gas-wall collisions—10-20, approximately.

Introduction

Lindemann inspired the modern, systematic study of unimolecular reactions.¹ His mechanism proposed that molecules become vibrationally excited by collisions with other molecules, thereby establishing a population of critically energized molecules which may decompose to products if not deactivated by collisions. From this simple mechanism, the study of energy transfer in unimolecular reactions evolved.² At sufficiently low pressures, the rate of a thermal unimolecular reaction becomes the rate of critical energization of reactant molecules. The rate of energization depends upon the nature of the collision partners.³ The study of energy transfer is important for both practical and theoretical reasons. In thermal systems, such study has almost invariably been carried out under steady-state conditions.

The present report describes a study of energy transfer in a unimolecular reaction in which molecules experience

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collisions only with the wall of the reaction vessel. The objective was to study the energization process in the transient region prior to the establishment of a steady-state population of energized molecules. A stochastic treatment has been applied to unimolecular reactions by Shuler and Rubin and by Montroll and Shuler.⁴ Treatments of the "mean first passage time" (the average time required for a random walker to reach an absorbing barrier along an energy coordinate) have been developed by Kim⁵ and Widom.⁶ In principle, if one knows the matrix of transition probabilities among molecular energy levels and the initial population vectors, then one may calculate the mean first passage time and the transient behavior.

There has been very little experimental work done in the transient region. Dove, Nip, and Teitelbaum⁷ found an "incubation period," corresponding to ca. 3000 collisions, in the shock-heated N_2O decomposition. In an early VLPP paper, Benson and Špokes⁸ claimed that accommodation to an energy of 60 kcal mol⁻¹ occurred in ~ 80 collisions, but the basis of their treatment was inadequate to support their conclusions. In this paper we describe a

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new method, called the variable encounter method, for the study of the transient region and its application to cyclopropane isomerization. A preliminary account of the method has been given.⁹

Description of the Method

The variable encounter method (VEM) depends on the random entry of molecules into a hot reactor from a cold reservoir flask, under molecular flow conditions. A molecule leaving the hot zone experiences a large number of collisions with the cold wall of the reservoir before reentering the reactor. The molecules thus automatically recycle themselves through the reactor. The mean number of hot collisions that a molecule makes per encounter with the hot reactor, m, is a function of the shape of the hot zone. One may easily measure rather small reaction probabilities per encounter by using large experimental times.

Certain design features of the experiment are important. The ratio of cold surface area to hot surface must be sufficiently large to ensure that a molecule is cooled between encounters. The mean free path must be much larger than the reactor dimensions. The pressure must be low enough so that the system is well into the falloff region (ideally, in the second-order region). The mean free flight time between wall collisions in the hot zone should also be as large as possible compared to the mean reaction time of the activated molecules. Of course, the final exit flight involves a longer path length into the cold flask. The total amount of gas and the percent reaction are to be commensurate with the sensitivity of the analysis method.

The relation between the amount of reaction and the experimental time is expressed in eq 1, where R_t is the

$$-\ln\left(R_t/R_0\right) = k_{\rm obsd}t \tag{1}$$

amount of reactant at time t, and R_0 is the initial amount of reactant. The experimental rate constant k_{obsd} is related to the average probability of reaction per collision, $\bar{P}_c(m)$, for a given (m) reactor, and to the rate of entry of molecules from the reservoir into the reactor; the latter involves only simple mechanical and gas kinetic quantities.

The mean number of collisions m, per encounter, was calculated by a Monte Carlo method modeled on that of Davis,¹⁰ and the principle of the calculations is reviewed in ref 11. The cosine law of reflection was employed and is believed to be the appropriate model under the present condition. The cosine law distribution is characteristic of diffuse as opposed to specular reflections at a surface. The seasoned quartz surface employed is assumed to be microscopically rough. Microscopic roughness, as well as high temperatures, usually leads to diffuse scattering.¹² In any case, since initial entry into the hot reactor *does* follow a cosine law, even the extreme assumption of specular reflection thereafter, for the reactor shapes described in the Experimental Section, does not greatly perturb the calculated distribution of collisions.

Along with m and the distribution of collisions, the mean distance between collisions was also calculated.

Experimental Section

The apparatus consisted of a 2-L fused quartz reservoir sphere onto which were blown several cylindrical closed finger reactors of diameter 3.2 cm. The quartz bulb was connected to the system by a ground joint, which permitted each of the reactors to be rotated into position for heating. In order to heat a reactor, it was imbedded in a stainless steel block surrounded by a temperature-controlled furnace. Several thermocouples were cemented to the heated finger so that the temperature along the reactor could be monitored. Temperature fluctuations along the length of the finger amounted to less than 10 °C over most of the length.

The length of a particular finger determined the mean number and distribution of collisions that a molecule made on entering the reactor. Two types of reactor apertures were used, the first being the unconstricted opening to the reactor and the second being a blown circular constriction at the entrance to the cylinder. Reactors having m values of 2.6, 8.5, and 27.2 were used. Some data were collected in an m = 107 reactor but were more fragmentary; they are also believed to be less reliable, because the reactor was apparently not as well seasoned, and are not included here.

The relative sizes of the quartz sphere and the aperture of an attached reactor were such that the internal surface area of the sphere was more than 100 times the aperture area. Thus, after an encounter, molecules were cooled before reentering the hot reactor.

The quartz sphere was attached to a glass vacuum system that could be pumped below 10^{-6} torr. Provision existed for gas handling and measurement, sample introduction, and transfer to the analytical system.

Reaction mixtures were analyzed by gas chromatography. A squalane (28% on Chromosorb P) and phenyl isocyanate–Porasil C series column arrangement was used. In this arrangement, propene was eluted before the parent cyclopropane, with a concomitant advantage in sensitivity.

Cyclopropane (Matheson reagent, 99.0% minimum) was used, usually without further treatment for most experiments. Analysis revealed 0.3% propene as an impurity. For some experiments involving low-percent reaction, the propene was reduced below 0.05% by passage through a $HgSO_4-H_2SO_4$ column (1 cm³ of a 20% $HgSO_4-20\%$ H_2SO_4 aqueous solution per gram of Chromsorb W).

To perform a run, a measured aliquot of cyclopropane was admitted into a 2-L quartz bulb for a given time, after which the reaction mixture was pumped out through a liquid-nitrogen-cooled trap. The time required to pump out the vessel to 1/e of the initial pressure (~ 10 s) was entered into the run time with suitable weighting. Run pressures in the bulb ranged from 10^{-4} to 10^{-8} torr of Hg. Run temperatures ranged from 900 to 1126 K, and reaction times from 25 s to 4 h.

Results and Discussion

Experimental data were obtained by measuring the percent isomerization as a function of time for each reactor at each temperature. In most cases, three separate runs were made at a given run time, and three or four run times were used so that the determination of the experimental rate constant, and of the value of $\vec{P}_c(m)$, at a given temperature in a given reactor was the result of 9–12 runs. Plots of the log of the fraction of reactant remaining vs. run time gave straight lines. An illustrative plot is shown in Figure 1 for the reactor m = 8.5, T = 1012 K. The plots were found to be straight lines, as given by eq 1.

The primary quantity of interest in the present study is the mean probability of reaction per collision in a given reactor, $\bar{P}_c(m)$ (Table I). It is a quantity that is closely related conceptually to stochastic theories of chemical kinetics. Plots of $\bar{P}_c(m)$ vs. temperature are shown in Figure 2 for mean collision numbers m of 2.6, 8.5, and 27.2. It is noted that the values of $\bar{P}_c(m)$ tend to converge at lower temperatures; i.e., the wall becomes a stronger collider at lower temperatures.

The corresponding Arrhenius plots give slightly curved lines; there is no a priori reason that the plots should be straight lines in a nonequilibrium system. Average Arrhenius values are given in Table II.



Figure 1. Experimental decay curve at m = 8.5, T = 1012 K.

TABLE I: Average Probabilities of Reaction per Collision, $\overline{P}_{o}(m)$

m	<i>Т</i> , К	$10^{8}\overline{P_{\rm c}}(m)$
2.6	907	2.71
	993	9.40
	1081	40.4
8.5	891	7.1
	895	6.6
	931	15.8
	1012	65
	1117	512
27.2	906	11.0
	989	86
	1126	1650

TABLE II: Observed Activation Energies

m	E_{a} , kcal mol ⁻¹	
2.6	30	
8.5	39	
27.2	47	

The gas-wall energy transfer process may be described in terms of a probability matrix, where p_{ij} is the element for a molecule going from the *j*th to *i*th energy level upon collision. Once the functional form (model) of the downsteps of this matrix is specified, the corresponding upsteps may be calculated by detailed balance. The details of the construction of these matrices are given in ref 13. Two different models for the probability of a *downstep* of size ΔE were used:

exponential

$$P_{\Delta E} = A \exp(-\Delta E / \langle \Delta E \rangle) \qquad 0 \le \Delta E \le 9000 \text{ cm}^{-1}$$
$$= 0 \qquad \Delta E > 9000 \text{ cm}^{-1}$$

Gaussian

$$P_{\Delta E} = A' \exp[-(\Delta E - \Delta E_{\rm mp})^2 / 2\sigma^2]$$
$$0 \le \Delta E \le 9000 \text{ cm}^{-1}$$
$$= 0 \qquad \Delta E \ge 9000 \text{ cm}^{-1}$$

where A and A' are normalization constants which also include the upstep probabilities; $\langle \Delta E \rangle$, $\Delta E_{\rm mp}$ (mp signifies most probable), and σ are parameters of the model. The limitation of 9000 cm⁻¹ is a practical computational feature invoked to make the matrix of more tractable dimensions.



Figure 2. Dependence of $\overline{P}_{\rm c}(m)$ on T, for reactors of varying m: dotted curves are simple exponential, and dashed curves are simple Gaussian calculated curves for values of $\langle \Delta E \rangle$ and $\Delta E_{\rm mp}$, as in Table III, fitted to the m = 2.6 curve.

TABLE III: Average Values of $\langle \Delta E' \rangle$ (cm⁻¹) for Cyclopropane-Wall Collisions

<i>Т</i> , К	900	1000	1075
Gaussian ($\sigma = 0.35 \Delta E_{mp}^{a}$) exponential	$\begin{array}{c} 4900\\ 3200^{14}\\ b\\ 3035^{14} \end{array}$	3275 3000 ¹⁴ 3100 2775 ¹⁴	3000 2775 ¹⁴ 2850 2425 ¹⁴

^a ΔE_{mp} is same as $\langle \Delta E' \rangle$ within a few cm⁻¹. ^b Exponential model too inefficient; cannot give fit.

The details of how calculated $\bar{P}_{c}(m)$ curves are obtained from these models of energy transfer are given in ref 14. Because of the truncation feature, we also define an *effective* value of the average energy downstep, called $\langle \Delta E' \rangle$.

In all cases, the values of $\langle \Delta E \rangle$ or ΔE_{mp} were selected to fit the m = 2.6 reactor data, and $\bar{P}_c(m)$ values were then calculated for the other, larger, m reactors. The reason for this procedure is that the calculated value of $\bar{P}_{\rm c}(m)$ is somewhat more sensitive to the value of $\langle \Delta E \rangle$, or $\Delta E_{\rm mp}$, for smaller *m* values. The values of $\langle \Delta E' \rangle$ and $\Delta E_{\rm mp}$ used at various temperatures are given in Table III. It is seen that the amount of energy transferred upon collision is quite large (approaching strong collider) at lower temperature and decreases at higher temperatures (Table III). A decrease in efficiency with temperature has previously been observed in neat gas experiments¹⁵ where the ΔE values are significantly smaller. This same decrease has been observed in other VEM work^{9,14} and in some lowpressure pyrolysis studies.¹⁶ The ΔE values reported here are somewhat higher than those found for cyclopropane d_2^{14} (Table III). The difference is systematic, but within experimental error at the higher temperatures. The experimental procedures used here in early work, particularly seasoning, may have been somewhat less reliable than in the other studies. The present value is noticeably higher at 900 K although still qualitatively and semiquantitatively consistent. It is seen from the lack of fit at 900 K that an exponential mode is not as appropriate as a Gaussian model for very strong collisions. This is a well-founded conclusion.13

Conclusions

The results of the VEM experiments for cyclopropane indicate the following: (a) Below 900 K, vibrational energy accommodation is substantially complete in ~ 10 collisions; at higher temperatures, larger collision numbers are necessary for complete accommodation. (b) Wall collisions are more efficient than gas-phase¹⁵ collisions, with wall collisions approaching strong collider behavior at lower temperatures. (c) Collisional efficiency and $\langle \Delta E \rangle$ decline with increasing temperature, supporting similar findings from the homogeneous cyclopropane- d_2 system.¹⁵

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References and Notes

- (1) F. A. Lindemann, Trans. Faraday Soc., 17, 598 (1921).
- D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.*, **77**, 369 (1977).
 D. J. Wilson and H. S. Johnston, *J. Am. Chem. Soc.*, **75**, 5763 (1953).
 E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.*, **1**, 361 (1958).

- (5) S. K. Kim, J. Chem. Phys., 28, 1057 (1958).
 (6) B. Widom, J. Chem. Phys., 31, 1387 (1959); 34, 2050 (1961).
 (7) The recent work of J. E. Dove, W. Nip, and H. Teitelbaum, Symp.
- (Int.) Combust., [Proc.], **15**, 903–16 (1975) is an exception. (8) S. W. Benson and G. N. Spokes, J. Am. Chem. Soc., **89**, 2525 (1967).
- (1967).
 (9) D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, *J. Chem. Phys.*, **71**, 538 (1979).
 (10) D. H. Davis, *J. Appl. Phys.*, **31**, 1169 (1960).
 (11) B. D. Barton, Ph.D. Thesis, University of Washington, Seattle, WA, 1979.
- (12) S. T. Ceyer and G. A. Somorjai, Annu. Rev. Phys. Chem., 28, 477
- (1977).
 D. C. Tardy and B. S. Rabinovitch, J. Chem. Phys., 45, 3720 (1966).
 D. F. Kelley, L. Zalotal, and B. S. Rabinovitch, Chem. Phys., 46, 379 (1990). (13)(14)
- (15)I. E. Klein and B. S. Rabinovitch, Chem. Phys., 35, 439 (1978).
- (16) R. Gilbert and K. D. King, private communication.

Gas-Phase Photolysis of Sulfoxides. Tetramethylene Sulfoxide

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The reaction channels exhibited during the gas-phase photolysis of tetramethylene sulfoxide (TMSO) have been characterized. Whereas photolysis in the liquid phase produces no hydrocarbon products, photolysis in the gas phase produces ethylene, propylene, cyclopropane, 1-butene, cyclobutane, and small amounts of butadiene. The results are interpreted in terms of a mechanism which involves initial rupture of a C-S bond to form a diradical intermediate. The product composition appears to depend upon the internal energy content of the initially formed diradical. The results are compared to those for cyclopentanone photolysis.

Introduction

There is very little work in the literature that deals with the photochemistry of organic sulfoxides, and this is particularly true of the gas-phase photochemistry of these systems.¹ There has been interest in the thermal reactions of some systems, including dimethyl sulfoxide,² thietane S-oxide,³ and thiirane oxide.⁴ There is also some rather detailed work on elucidating the nature of the transition state in the thermolysis of acyclic sulfoxides.⁵ The work that is most related to our efforts is that which deals with elucidating the electronic state of SO that is produced when thiirane oxide is thermally decomposed.

We have initiated an exploratory study of the gas-phase photochemistry of trimethylene sulfoxide (TRMSO) and tetramethylene sulfoxide (TMSO). Since the gas-phase



photochemistry of these two systems differs, we are confining this report to the photochemistry of TMSO. In addition to simply answering the basic questions regarding what kind of chemistry sulfoxides exhibit subsequent to the absorption of light energy and to comparing their photochemistry to that which is observed in cycloalkanone photolysis, we are interested in these systems for an additional reason. We are interested in observing how the conservation of electronic spin and orbital angular momentum affects photochemical reaction channels. Since there are three energetically allowed electronic states of SO that might be produced during the photofragmentation of these cyclic sulfoxides^{4,6}—the ${}^{3}\Sigma$ ground state, the ${}^{1}\Delta$ state (18 kcal mol⁻¹ above the ground state), and the ${}^{1}\Sigma^{+}$

state (30 kcal mol⁻¹ above the ground state)—our hope is that these systems will display a product composition such that one can elucidate which electronic state of SO is produced in the primay process. These systems might provide a convenient route to generating electronically excited SO. It turns out that TMSO is not the system that yields unambiguous answers to questions of this nature.

Experimental Section

Materials. Tetramethylene sulfoxide was purchased through Aldrich Chemical and purified by fractional distillation under reduced pressure. Vapor pressure vs. temperature measurements carried out during distillation indicated that $\Delta H_v \sim 21$ kcal mol⁻¹. By using Trouton's rule to estimate ΔS_v , we estimate the vapor pressure of TMSO to be 7.6 \times 10⁻³ torr at 23 °C. TMSO has an onset in its UV absorption spectrum at about 240 nm. In methanol solution the spectrum is structureless, and it has a maximum at ~200 nm ($\epsilon_{\rm max}$ ~1600 L mol⁻¹ cm⁻¹). Other chemicals used as diluents were checked for interfering impurities before use. Products were identified by comparison of their GLC retention times with known samples.

Equipment. All gas handling was carried out on a conventional mercury-free vacuum apparatus fitted with greaseless stopcocks. Analyses were done on a gas-liquid chromatograph fitted with a flame ionization detector and a special inlet system for injecting gaseous samples. For the most part photolyses were carried out in cylindrical Suprasil quartz cells that were 40 and 425 cm³ in volume. Some experiments were carried out in a 475-cm³ commercial grade quartz cell. The mercury sensitization experiments were carried out in a 1000-cm³ spherical Vycor reactor. The light sources used in the photochemical experiments included Cd (228 nm), Zn (214 nm), and low-