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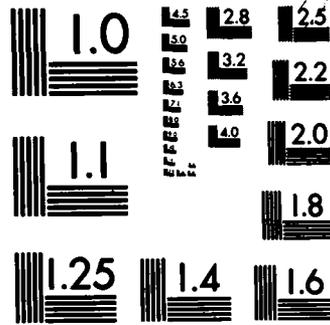
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ANNUAL SUMMARY REPORT, 1 August 1982 - 31 July 1983

High Temperature Gas Energy Transfer

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OFFICE OF NAVAL RESEARCH
Contract N00014-75-C-0690
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Study of the transfer of vibrational energy between molecules and surfaces was continued at high levels of vibrational excitation and high surface temperature. Past work is summarized. Results are outlined. Future work is indicated.		

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I. Summary of Progress. → In the period of this report, vibrational energy transfer studies have been carried out with three types of molecules that fall into the "energetic" category: these are nitromethane, azomethane and methyl nitrite. Apart from a propensity for more complex reaction mechanisms and catalytic behavior, the energy transfer properties of energetic materials at a surface seem to follow just the behavior expected from the intermolecular potential and not that of the intramolecular or reaction potential. More stable molecules can thus suffice to delineate the energy transfer properties expected for energetic materials.

The study of gas/surface energy transfer has been extended to metals, i.e. to various gold surfaces, which appear to be stronger energy transfer media than fused quartz. The behavior for cyclobutene on gold was studied up to 1250 K and strong collision behavior was found below 600 K. Extension to other metals is readily possible.

The examination of liquid metal surfaces as energy transfer agents is being investigated. Tin metal is being studied. Extension to other liquids will be made.

A theoretical model has been applied to the calculation of energy transfer amounts between molecules as a function of molecular size, energy level and ambient temperature. ←

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II. Complete Listing of Technical Reports:

1. Technical Report TR01, 7 January 1976.

Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures by B. S. Rabinovitch, D. G. Keil, J. F. Burkhalter and G. B. Skinner.

In this report a theoretical analysis was given of shock tube data for high temperature gas reactions. The data were analyzed to show that collisional energy transfer efficiency appears to decrease at high temperatures.

2. Technical Report TR02, 20 April 1976

Temperature Dependence of the Arrhenius Activation Energy. High Temperature Limit, J. F. Burkhalter and B. S. Rabinovitch.

In this report a conventional approximation to the high temperature vibrational partition function is shown to be defective, and the usual high temperature expression for the Arrhenius activation is in error. The variation of the activation energy for unimolecular reactions as a function of temperature is calculated for various representative systems.

3. Technical Report TR03, 15 October 1976

Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems, D. C. Tardy and B. S. Rabinovitch.

This report gives a comprehensive and detailed survey and analysis of energy transfer in thermal gaseous systems. The present status of the field is delineated and future areas of work indicated.

4. Technical Report TR04, 15 April 1977

On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations, S. E. Stein and B. S. Rabinovitch.

This report describes an algorithm for accurate state sum and density calculations and refutes an error in the literature.

5. Technical Report TR05, 15 August 1977

Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems by I. Oref and B. S. Rabinovitch.

In this report a simple theoretical model describing energy transfer probabilities is given. Conservation of angular momentum was imposed. The importance of completeness and detailed balance conditions and correction of an earlier model in the literature are illustrated. The model is applied to experimental data.

6. Technical Report TR06, 1 September 1977

Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method by D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch.

A theoretical and experimental study was made of flow and diffusion of a reactant in a low pressure gas stream. Connection is made with earlier theoretical analysis.

7. Technical Report TR07, 10 October 1978

Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically?
I. Oref and B. S. Rabinovitch.

The literature is surveyed and analyzed. A variety of excitation techniques including crossed molecular beam, laser, chemical activation, photochemical and thermal are considered. The answer to the title question is "yes." The relationship to the present work on intermolecular transfer is the following: multiphoton laser experiments frequently involve collisional heating of the gas. In order to understand the results, one must have a good basis for interpretation of data. In this survey, some suggested models for energy relaxation by molecular collisions are criticized and data reinterpreted in light of results obtained in this laboratory.

8. Technical Report TR08. 1 November 1978

Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane. E. Kamaratos, J. D. Burkhalter, D. G. Keil and B. S. Rabinovitch.

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. It was shown that these values decline, and the collisional efficiencies, β_c , decrease markedly with rise of temperature to 1175 K. This is only the second measurement of such a phenomenon.

9. Technical Report TR09. 15 March 1979

Collisional Relaxation of Non-Equilibrium Vibrational Energy Distributions in a Thermal Unimolecular System. Surface Collisions. D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch.

A novel, simple technique, the Variable Encounter Method, is described for obtaining information on energy transfer efficiency between a gas and a solid in the transient region, and as a function of temperature. The method is as powerful as it is simple. Results for cyclopropane are described. Decrease

in collisional efficiency $\langle \Delta E \rangle$ with rise of temperature is confirmed, and the form of the transfer probability matrix \underline{P} is discovered. This method and these results are considered to be some of the most innovative and important that have ever been made in this field.

10. Technical Report TR10. 15 June 1979

Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by VEM. M. C. Flowers, D. F. Kelley, F. C. Wolters, and B. S. Rabinovitch.

Extension of the VEM technique to cyclobutane is described. An exponential form of \underline{P} is required to fit the data. The value of $\langle \Delta E \rangle$ declines with rise of temperature.

11. Technical Report TR11; 15 September 1979

Collisional Relaxation of Transient Vibrational Energy Distributions in a Thermal Unimolecular System. The Variable Encounter Method. D. F. Kelley, L. Zalotai and B. S. Rabinovitch.

The Variable Encounter Method permits the study of the transient in the relaxation of an initial vibrationally cold ensemble of molecules in a vibrationally hot distribution by a known and variable number of successive collisions with a hot wall. The system studied was the isomerization of 1,1-cyclopropane- d_2 with a fused quartz wall temperature of 800 K to 1175 K, and average number of collisions from 2.3 to 22.3. The detailed theory of the experiment was presented, together with the method of data deconvolution. Various modified gaussian and exponential models of energy transfer were found to give agreement with the data. The average down-step size was found to decline from $\leq 3500 \text{ cm}^{-1}$ at the lowest temperature to $\sim 2500 \text{ cm}^{-1}$ at the highest on the basis of a gaussian model, but heterogeneous energy transfer is more efficient than homogeneous gas-gas collisional transfer. A mathematical analysis of the relation between mean first-passage times and incubation times is given. Incubation times increase from ~ 7 to ~ 12 collisions with increasing temperature. Transient population distributions and the sequential reaction probabilities as a function of collision number are calculated.

12. Technical Report TR12. 10 October 1979

Vibrational Energy Transfer in a Diffusion-Flow Cyclopropane- d_2 System. J. F. Burkhalter, E. Kamaratos, and B. S. Rabinovitch.

In this study, absolute rate constants for isomerization of cyclopropane- d_2 and high temperature homogeneous energy transfer were determined in a diffusion-flow system. The relative rates of the competitive isotopic isomerization channels

were measured for two bath gases, N_2 and He, at two temperatures, 973 K and 1073 K. Values of the average energy down-jump size $\langle \Delta E \rangle$ were computed from both the absolute rates and the isotopic relative rates by suitable modelling by a stochastic calculation. The results confirm earlier diffusion cloud measurements.

13. Technical Report TR13, 10 October 1979

Transients in the Vibrational Excitation of Cyclobutane Decomposition Using the Variable Encounter Method. M. C. Flowers, F. C. Wolters, B. D. Barton and B. S. Rabinovitch.

The probability of reaction of cyclobutane molecules in a fixed-time interval after experiencing a known number of collisions with a hot surface at temperatures between 749 K and 1126 K was determined using the Variable Encounter Method. Calculations utilizing exponential or gaussian models for energy transfer enabled the average amounts of energy transferred for deactivating collisions, $\langle \Delta E' \rangle$, to be estimated. The exponential model fits the experimental data best and, using this model, $\langle \Delta E' \rangle$ is 2430 cm^{-1} at 748 K and decreases to 1470 cm^{-1} at 1123 K. Surface collisions are more efficient than binary gas collisions; but cyclobutane is a less efficient partner than cyclopropane- d_2 (TR No. 11). The results follow from a quasi-statistical model of energy accommodation.

14. Technical Report TR14, 1 December 1979

A Crucial Demonstration of Strong Collisional Behavior of Vibrational Energy for Gas-Surface Collisions. M. C. Flowers, F. C. Wolters, D. F. Kelley and B. S. Rabinovitch.

Application of the VEM technique was made to the thermal cyclobutene decomposition system. Vibrational energy transfer in the cyclobutene - seasoned quartz surface system was studied. Collisional efficiency again declines with rise of temperature, but the occurrence of strong collisions was demonstrated in crucial manner at temperatures below 450 K. The wall appears to behave like a theoretical strong collider below 450 K. This is a very novel finding.

15. Technical Report TR15, 31 March 1980

Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low-Pressure Unimolecular Reaction. B. D. Barton, D. F. Kelley and B. S. Rabinovitch.

The Variable Encounter Method, for the study of gas-wall vibrational energy transfer in the transient region of a unimolecular reaction was applied to the

isomerization of cyclopropane to propylene. Temperatures in the range 900 K - 1125 K were employed. The average probability of reaction per collision, $\bar{P}_c(m)$, was deduced from the data and compared with a theoretical stochastic calculation based on both gaussian and exponential models for the energy transfer probabilities. The former model is more appropriate. The efficiency of a seasoned quartz wall was greater than gas-gas collisions of substrate and the efficiency declined with increase of temperature. The steady state is closely approached (90%) in a comparatively small number of gas-wall collisions - 10-20, approximately. The efficiency of transfer by cyclopropane is comparable with that by cyclopropane-d₂ (TR 11).

16. Technical Report TR16, 1 August 1980

Collisional Relaxation of Vibrational Energy Transients in the Methyl Cyclopropane System. D. F. Kelley, T. Kasai and B. S. Rabinovitch.

The variable encounter method has been used to study vibrational energy transients in the isomerization of methylcyclopropane to various butenes. This molecule, which has a hindered methyl rotation mode, has the highest vibrational energy level density of any molecule - cyclopropane, cyclobutene, cyclobutane - that has been studied so far in testing the variation of energy transfer efficiency with molecular structure. This system was studied with reactor surface temperatures of 800 to 1130 K and average numbers of collisions per encounter with the reactor of 5.6 and 20.0. An exponential model of energy transfer was found to give the best fit to the data with the average down step energy $\langle \Delta E' \rangle$ decreasing from 1860 to 1415 cm⁻¹ with increase of temperature over the range studied. Incubation times increased from 14 to 19 collisions with increase in temperature, and these times, together with values of the conventional relative collision efficiency β and values of $\langle \Delta E' \rangle$, are compared with those of other molecules studied by VEM. The calculated transient population distributions and the associated sequential reaction probabilities are also displayed. The energy transfer efficiency from the hot molecules in down-collisions is lowest in this system and hence the weakest model - exponential - gives a good fit. By contrast, the efficiency of up-transitions, i.e., energy transfer into the cold molecule measured in this work is higher than for other molecules. This is a consequence of the increased

eigenstate density and the important conclusion is reached that this verifies the suitability of a statistical model of energy accommodation to describe vibrational energy transfer involving high energy polyatomic molecules at these temperatures.

17. Technical Report TR17, 15 September 1980

A Reinvestigation of Transients in the Cyclopropane System by the Variable Encounter Method. M. C. Flowers, F. C. Wolters, D. F. Kelley and B. S. Rabinovitch.

The isomerization of cyclopropane to propene was reinvestigated under conditions identical to those used in a previously reported VEM study on cyclobutane. The simultaneous reaction of cyclobutane was also studied in the largest reactor. Some details of the method are amplified; the distribution functions for numbers of collisions in each reactor are displayed as are the contributions to reaction $R(n)$ as a function of the number of consecutive collision n . The present data are in essential agreement with those obtained by Kelley et al [TR 11], although the average size of an internal energy down transition ($\langle \Delta E' \rangle$) for cyclopropane molecules colliding with a hot surface is a little lower than previously estimated. The increasing efficiency of the surface in deactivating energized molecules as the surface temperature decreases is confirmed ($\langle \Delta E' \rangle = 2550 \text{ cm}^{-1}$ at 900 K, on a gaussian model for energy transfer, and $\langle \Delta E' \rangle = 2000 \text{ cm}^{-1}$ at $\sim 1100 \text{ K}$). The surface acts as a somewhat stronger collider for cyclopropane than for cyclobutane and is also a more efficient collider for cyclopropane than are gas-gas cyclopropane collisions. This accords with the results of TR16 and leads to the important conclusion that heterogeneous collision is more efficient than homogeneous collision, in general, for the deactivation of excited molecules.

18. Technical Report TR18, 15 October 1980

Transients in Thermal Isomerization of Cyclobutene by the Variable Encounter. Vibrational Energy Transfer and Relaxation at Lower Temperatures. F. C. Wolters, M. C. Flowers and B. S. Rabinovitch.

Vibrational energy transfer and relaxation in the thermal isomerization of cyclobutene to 1,3-butadiene was studied over the temperature range 429 K - 778 K using the Variable Encounter Method. Reactors characterized by various mean number of collisions, m , per encounter of a substrate molecule with the reactor ($m = 2.6, 5.9, 8.5$ and 27.2) were used. The

significant observation was made that strong collider behavior in collisions of substrate with a seasoned fused quartz wall is reached at lower temperatures (below 450 K), as evidenced by the coincidence of values of the probability of reaction per collision, $\bar{P}_c(m)$, obtained in VEM reactors having different m values. The average energy transferred to the wall per deactivating collision, $\langle \Delta E' \rangle$, increased strongly as temperature decreased, from $\langle \Delta E' \rangle = 2150 \text{ cm}^{-1}$ at 764 K to $> 6000 \text{ cm}^{-1}$ at 460 K. Various forms of models for the probability of energy transfer in down transitions were applied to data. The weak form - exponential - cannot apply, in contrast to the behavior that applies at higher temperatures for looser molecules (higher vibrational eigenstate densities) such as methyl cyclopropane (TR16).

19. Technical Report TR19, 15 March 1981.

Energy Transfer at High Temperatures in the Cyclopropane System. Temperature Dependence of $\langle \Delta E' \rangle$. T. Kasai, D. F. Kelley and B. S. Rabinovitch.

The study of collisional energy transfer between cyclopropane molecules and a seasoned silica wall by the Variable Encounter Method was extended over a range of more than 500° upward in temperature to 1325 K. The value of $\langle \Delta E' \rangle$, the average energy of a down-transition upon collision of the hot substrate molecule with the wall to decrease monotonically. The data provide the most accurate and well-documented display for a polyatomic molecule of the temperature trend of $\langle \Delta E' \rangle$ presently available. The rate of decrease in $\langle \Delta E' \rangle$ seems to be more rapid at lower temperatures. The data have been explained by the theory of Lin and Rabinovitch on a quasi-statistical accommodation model.

The behavior at still higher temperatures is considered to be not well known and must be considered as in quite unsatisfactory condition. It is of extreme practical and theoretical importance to detect the possible transition of the observed behavior from an attractive potential-dominated accommodation phenomenon to a Landau-Teller type repulsive potential-dominated impulsive phenomenon.

20. Technical Report TR20, March 15, 1981

Single-Collision Gas-Surface Vibrational Energy Transfer in a Reacting System. D. F. Kelley, T. Kasai and B. S. Rabinovitch.

Gas-surface vibrational energy accommodation in a reactive system has been studied under single collision conditions for the first time for polyatomic molecules. The reaction system was the isomerization of cyclobutene to 1,3-butadiene. Both seasoned pyrex and silica surfaces were used over the temperature ranges 400-775 K and 500-975 K, respectively. Strong collider behavior was observed below ~ 425 K. The vibrational energy accommodation coefficient was found to decrease with rise of temperature from ~ 1.0 to 0.2, while the relative collisional efficiency β_1 declined from ~ 1.0 to 0.008. A stochastic calculation was used to fit the data. This technique provides a more sensitive test between the various model forms for energy transfer than has been possible heretofore. It is clearly shown that a Gaussian or particularly a Boltzmann weighted exponential form provide the best fit.

21. Technical Report TR21, August 1, 1981

Pyrolysis of 1-Iodopropane by the Variable Encounter Method. F. C. Wolters, K.-J. Chao and B. S. Rabinovitch

The pyrolysis of 1-iodopropane has been studied by the Variable Encounter Method (VEM) at temperatures from 625 K to 840 K. Deactivating wall collisions are found to be stronger for this molecule than for the hydrocarbons previously studied in this temperature range. This is attributed to the increased strength of the attractive molecule-surface interaction due to the dipole moment and enhanced polarizability of the substrate molecule.

22. Technical Report TR22, October 20, 1981

Isotope Effect in Gas-Surface Vibrational Energy Transfer. Cyclopropane and Cyclopropane- d_6 Isomerization by the VEM Technique. W. Yuan, R. Tosa, K.-J. Chao, and B. S. Rabinovitch

The study of the effect of varying molecular structure upon the efficiency of vibrational energy transfer between initially cold molecules and a hot surface was extended to the reaction pair, cyclopropane/cyclopropane- d_6 . The latter member is somewhat less efficient in energy loss. This was interpreted in terms of molecular properties, namely, the latter's greater vibrational eigenstate

density. Conversely, the probability of energy up-transitions is enhanced. In thermal low pressure unimolecular reactions, this corresponds to the inverse statistical weight secondary isotope effect. Comparison was made with other molecules.

23. Technical Report TR23, November 25, 1981

Single Collision Gas-Surface Vibrational Energy Transfer in Reactive Systems. Variation of Initial Energy Distribution. R. Arakawa, D. F. Kelley, and B. S. Rabinovitch

The initial vibrational energy distribution of molecules that collide with a hot surface, which is an important parameter of the interaction, has been studied under single collision conditions. These experiments provide a more sensitive test of the relative suitability of various analytical forms for the collisional transition probability matrix, \tilde{P} . The reaction system is the isomerization of cyclobutene to 1,3 butadiene. A seasoned fused quartz surface was used over the temperature range $T_r = 600$ K - 900 K. Variation of the initial vibrational energy population vector of cyclobutene molecules was made by change of their initial temperature T_c in the range 273 K - 620 K. Gaussian or Boltzmann Exponential forms of \tilde{P} prove to be the most suitable to fit the data.

24. Technical Report TR24, January 15, 1982

Vibrational Energy Transfer and Pyrolysis of Nitromethane by the Variable Encounter Method. W. Yuan, B. S. Rabinovitch and R. Tosa

Nitromethane is of considerable interest because of its large dipole moment and importance in a variety of chemical systems. The pyrolysis of nitromethane has been studied by the Variable Encounter Method (VEM) at temperatures from 816 K to 1092 K with two reactors of differing geometry having fused silica surfaces. The probability of reaction per collision with the reactor surface was measured. The down energy transition jump size, $\langle \Delta E' \rangle$, was determined. It decreased with increasing wall temperature. A comparison is made of $\langle \Delta E' \rangle$ with previous results reported to date for other substrate molecules. Indeed, nitromethane is one of the more efficient energy transfer agents, as might be expected from the strength of the attractive interaction. However, in addition to the size (vibrational eigenstate density) and the polarity of the molecules, the nature of the hot surface seems also to play a role.

25. Technical Report TR25, June 1, 1982

The Isomerization of 1-Methyl Cyclobutene by the Single Collision Variable Encounter Method. R. Arakawa and B. S. Rabinovitch

The reaction probability, P_c , for 1-methylcyclobutene molecules energized at a hot silica surface was measured under single collision conditions over the temperature range $T_r = 480 \text{ K} - 800 \text{ K}$. The initial thermal vibrational energy population of the cyclobutene was varied from $T_c = 273 \text{ K} - 570 \text{ K}$. The reaction was isomerization to isoprene. These experiments provide a test of the relative suitability of various analytical forms for the collisional transition probability matrix \tilde{P} . Calculations with a Gaussian form provide the best overall fit to the data. The average amount of energy ($\langle \Delta E; >_{E_0}$) transferred from the hot molecules in a vibrational down transition from the reaction threshold energy level, E_0 , declined from 7220 cm^{-1} to 3890 cm^{-1} with increase in surface temperature from 600 K to 800 K. The experimental collisional efficiency, β_1 , declined from 0.39 to 0.035 over the combination temperature range $T_r, T_c = 600, 500$ to 800, 293. Strong collider behavior was observed for T_r less than 450 K.

The Following were submitted in the present report period:

26. Technical Report TR26, December 1, 1982

Vibrational Energy Transfer at a Gold Surface in Reacting Systems. Cyclobutene and Nitromethane. Wei Yuan and B. S. Rabinovitch

Single collision excitation probabilities were measured for cyclobutene and nitromethane on polycrystalline gold plane and wire surfaces. Transport above the reaction thresholds for isomerization and decomposition, respectively, for the two substrates was used as the criterion of vibrational energy transfer. Several different seasoning and processing procedures of the surfaces were tested. For cyclobutene, a defect from strong collider transition probabilities appeared only above 550 K - 600 K, which signifies that the energy transfer efficiency at a treated gold surface is greater than that at a seasoned silica surface. The vibrational energy transfer efficiency declined above 600 K and fell abruptly to a quasi-constant value in the range 900 K - 1100 K. Above 1100 K the differences between various conditioned surfaces diminished progressively. Unlike cyclobutene, and earlier studies of nitromethane on silica surfaces where reproducible non-catalytic behavior could be attained, nitromethane on gold showed apparent catalytic phenomena which the various conditioning treatments failed to repress.

27. Technical Report TR27, July 31, 1983

Study of Vibrational Energy Transfer at a Surface by a Time-of-Flight Method. Wei Yuan and B. S. Rabinovitch

A single collision, time-of-flight extension of the VEM method for the study of molecule-surface vibrational energy transfer is introduced. This refined technique helps election between possible alternative trial analytic forms of the collisional transition probability function. A gaussian form is preferred over a boltzmann-exponential form for cyclobutene isomerization to 1,3-butadiene energized by collisions at a seasoned silica surface at 800 K. The study illustrates the difference between conventional accomodation coefficient measurements, which examine average energy changes, and the present studies which explore the energy transport at high levels corresponding to chemical reaction thresholds. It confirms the hopes for refined exploration of the transition probability function expressed in section IVD of the Annual Report issued in August 1982.

III. Listing of Publications.

1. Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures, Proceed. Tenth Internat. Shock Tube Sympos. ed. G. Kamimoto, Kyoto, 1976.
2. Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems. D. C. Tardy and B. S. Rabinovitch, Chem. Revs. 77, 369 (1977).
3. On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations, S. E. Stein and B. S. Rabinovitch, Chem. Phys. Lett. 49, 183 (1977).
4. Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems. I. Oref and B. S. Rabinovitch, Chem. Phys. 26, 385 (1977).
5. Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method, D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch, J. Phys. Chem. 82, 355 (1978).
6. Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane. E. Kamaratos, J. F. Burkhalter, D. G. Keil and B. S. Rabinovitch, J. Phys. Chem. 83, 984 (1979).
7. Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically? I. Oref and B. S. Rabinovitch, Accts. Chem. Res. 12, 166 (1979).
8. Collisional Relaxation of Non-equilibrium Vibrational Energy Distributions in a Thermal System. Surface Collisions, D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, J. Chem. Phys. 71, 538 (1979).
9. Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by Variable Encounter Method. M. C. Flowers, B. D. Barton, F. C. Wolters and B. S. Rabinovitch. Am. Soc. Mass. Spectrom. Proceedings, ed. A. E. Harrison, 27, 661 (1979).
10. Collisional Relaxation of Transient Vibrational Energy Distributions in a Thermal Unimolecular System. The Variable Encounter Method. D. F. Kelley, L. Zalotai, and B. S. Rabinovitch. Chem. Phys. 46, 379 (1980).
11. Vibrational Energy Transfer in a Diffusion-Flow Cyclopropane-d₂ System. J. F. Burkhalter, E. Kamaratos, and B. S. Rabinovitch, J. Phys. Chem. 84 (1980) 476.
12. A Crucial Demonstration of Strong Collisional Behavior of Vibrational Energy for Gas-Surface Collisions. M. C. Flowers, F. C. Wolters, D. F. Kelley and B. S. Rabinovitch, Chem. Phys. Lett. 69, 543 (1980).
13. Transients in the Vibrational Excitation of Cyclobutane Decomposition Using the Variable Encounter Method. M. C. Flowers, F. C. Wolters, B. D. Barton and B. S. Rabinovitch, Chem. Phys. 47 (1980) 189.
14. Gas-Surface Vibrational Energy Transfer in the Transient Region of a Low-Pressure Unimolecular Reaction. B. D. Barton, D. F. Kelley, and B. S. Rabinovitch. J. Phys. Chem. 84, 1299 (1980).

15. Collisional relaxation of vibrational energy transients in the methyl-cyclopropane system. A variable encounter method study. D. F. Kelley, T. Kasai and B. S. Rabinovitch, 73, 5611 (1980).
16. Transients in Thermal Isomerization of Cyclobutene by VEM. Vibrational Energy Transfer and Relaxation at Lower Temperatures. J. Phys. Chem. 85 (1981) 589.
17. Surface-Gas Energy Transfer in the Cyclopropane/Cyclobutane Isomerization Systems by the Variable Encounter Method. M. C. Flowers, F. C. Wolters, D. F. Kelley, and B. S. Rabinovitch, J. Phys. Chem. 85 (1981) 849.
18. Single-Collision Gas-Surface Vibrational Energy Transfer in a Reacting System, D. F. Kelley, T. Kasai and B. S. Rabinovitch. J. Phys. Chem. 85 (1981) 1100.
19. Energy Transfer at High Temperatures in the Cyclopropane System. Temperature Dependence of $\langle \Delta E' \rangle$. T. Kasai, D. F. Kelley and B. S. Rabinovitch, Chem. Phys. Lett., 81, 126 (1981).
20. Pyrolysis of 1-Iodopropane by the Variable Encounter Method. F. C. Wolters, K.-J. Chao, and B. S. Rabinovitch. Int. J. Chem. Kin. 13, 1289 (1981).
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22. Single Collision Gas-Surface Vibrational Energy Transfer in Reactive Systems. Variation of Initial Energy Distribution. R. Arakawa, D. F. Kelley, and B. S. Rabinovitch, J. Chem. Phys. 76, 2384 (1982).
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25. Vibrational Energy Transfer at a Gold Surface in a Reacting System. Cyclobutene and Nitromethane. Wei Yuan and B. S. Rabinovitch, J. Phys. Chem. 81, 2167 (1983).

IV. Other Work Completed or in Progress and Future Work.

In addition to the accomplishment summarized in Technical Reports TR26 and TR27, the following work is presented.

A. Energetic Materials

1. Single collision activation of azomethane at a hot seasoned fused silica surface has been studied. Excitation above the critical threshold ($E_0 = 50.7 \text{ kcal mole}^{-1}$) was monitored by subsequent homogeneous decomposition. The collisional efficiency was examined over the range 700 K to 875 K. Both the magnitude of the energy transfer efficiency and an increase in efficiency with decrease of temperature are in line with previous results for other substrate molecules of comparable size and polarity. Obviously the thermodynamics of reaction chemistry do not affect the energy transfer properties which depend on the intermolecular, rather than the intra-molecular, potential. A technical report is in preparation.

2. The species, methyl nitrite, is heavily implicated in the mechanism of decomposition of nitromethane. We have made a particular effort to study the behavior of methyl nitrite. We have found that it is impossible to remove catalytic effects at low temperatures in studies on silica surface below 700 K. At higher temperature, catalysis is reduced in importance and methyl nitrite behaves more normally, i.e., collision efficiencies fall substantially below strong collider behavior. But it is evident that the system is a relatively complex one. Indeed, this is also true of the allegedly homogeneous decomposition studies reported in the literature. It appears that energetic materials, e.g., nitro- and azo-compounds, display energy transfer properties as expected from their intermolecular structure, functional group nature and intermolecular potential.

B. Liquid and Other Surfaces

It is of practical and theoretical interest to investigate energy transfer at other surfaces. There is very little work reported in the literature on molecule/liquid surface energy transfer. In 1937, Alty (Sci. Progr. 31 (1937) 436) reported that the accommodation coefficient α is unity for water(g)/water(l), Hg(g)/Hg(l), $\text{CCl}_4(\text{g})/\text{CCl}_4(\text{l})$, and $\text{C}_2\text{H}_5\text{OH}(\text{g})/\text{C}_2\text{H}_5\text{OH}(\text{l})$. Since then, in one study in 1967 (unpublished), Thomas has reported that α for He(g)/K(l) is less than unity.

All of the above work refers to temperatures near room temperature and, to our knowledge, high temperature energy transfer at liquid metal surfaces has not been studied. We have started such work with tin. We have just completed the design and construction of a new apparatus. In addition to metals such as tin and gallium,

similar considerations apply to liquid salt surfaces. We will pursue these studies with various substrate gas molecules.

We still wish to study other solid metal surfaces such as iron, silver, and copper which should be readily amenable using wires, as we have been doing with gold.

C. Theoretical Models and Calculations

In conjunction with Professor I. Oref of the Technion Institute, Haifa, Israel, we have defined a model for the energy transfer process and applied it to the interaction of two molecules (hot molecule and heat bath molecule). Parameters such as molecule size, molecule energy and temperature were examined. Graphic demonstration of the interplay between energy transfer amounts, both total and for up or down transitions are given. General relationships are presented that may be applied a priori to any pair of molecules of specified properties that obey the model. A solid surface represents the limiting strong collider case for a bath of infinite size. A report is being prepared.

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