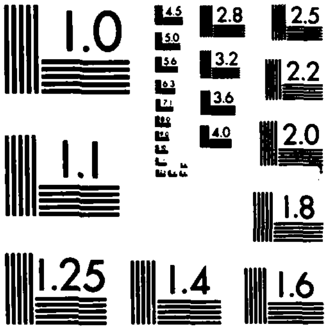
AD-A184 435 THE CALCULATION OF THERMAL RATE CONSTANTS FOR GAS-PHASE 1/1
AND HETEROGENEOUS (U) CHEMICAL DYNAMICS CORP UPPER
MARLBORO MD B C GARRETT 28 JUL 87 ARO-21301 30-CH-S
UNCLASSIFIED DAAG29-84-C-0011 F/G 21/2 NL



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

DTIC FILE COPY

AD-A184 435

Entered) MASTER COPY - FOR REPRODUCTION PURPOSES

2

DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER ARO 21301.30-CH-S	**2. GOVT ACCESSION NO.** N/A	**3. RECIPIENT'S CATALOG NUMBER** N/A

4. TITLE (and Subtitle)
The Calculation of Thermal Rate Constants for Gas-Phase and Heterogeneous Reactions in Combustion Processes

5. TYPE OF REPORT & PERIOD COVERED
FINAL, June 1, 1984 - May 31, 1987

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
Bruce C. Garrett

8. CONTRACT OR GRANT NUMBER(s)
DAAG-29-84-C-0011

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Chemical Dynamics Corporation
9560 Pennsylvania Avenue, Suite 106
Upper Marlboro, MD 20772

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

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE
July 28, 1987

13. NUMBER OF PAGES
11

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)

Approved for public release; distribution unlimited.

DTIC
ELECTE
SEP 1 1 1987
S D

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

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

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

chemical reaction, transition state theory, variational transition state theory, bimolecular gas-phase reactions, tunneling coorections, heterogeneous reactions, gas-surface reactions

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

This final report summarizes work performed on a three year research program to develop theoretical methods to aid in the interpretation and modeling of combustion processes. The methods developed are based upon variational transiton state theory and applied to gas-phase and heterogeneous reactions.

ARO 21301.30-CH-S

FINAL REPORT

THE CALCULATION OF THERMAL RATE CONSTANTS FOR GAS-PHASE AND HETEROGENEOUS REACTIONS IN COMBUSTION PROCESSES

to

U. S. Army Research Office
Research Triangle Park, NC

July 1987

Chemical Dynamics Corporation
9560 Pennsylvania Avenue
Upper Marlboro, MD 20772

Statement of Problem

The knowledge of the dynamics of elementary chemical reactions occurring in the gas phase and on surfaces is crucial to the understanding of the more complex mechanisms of decomposition of energetic materials. Heterogeneous reactions control the initial decomposition of solid propellants and explosives and can also play a role in combustion in closed environments in which wall-sensitive reactions are important. Gas-phase reactions in the primary flame zone immediately above the surface of the propellants and explosives control the heat conduction back to the solid material and thereby influence the stability and efficiency of the energetic materials. Exothermic gas-phase reactions of initial decomposition products release heat which is then absorbed by the solid, thus determining the burning-rate-versus-pressure characteristics of the combustion.

Major limitations in the understanding of the complex combustion mechanisms of the decomposition of energetic materials are the lack of knowledge of all the important reaction pathways, the lack of knowledge of dynamical constraints of individual elementary reactions, and the lack of accurate kinetic data of the elementary reaction steps. The goal of the research reported here is the development of theoretical methods to aid in the interpretation and modeling of gas-phase combustion processes. The methods are based upon variational transition state theory (VTST), which has been extensively tested for gas-phase reaction involving only a few atoms. The main thrusts of this research have been continued tests and development of the theory with the intent of extending the regions of applicability of the methods, extensions of the methods to treat reactions involving larger polyatomic species, and applications to systems of practical importance. The study of heterogeneous reactions has required further extensions of the methods. The aim in the study of heterogeneous reactions has been the qualitative understanding of the dynamics of reactions occurring on well characterized crystallographic surfaces and the systematic study of qualitative features of these processes.

Summary of Important Results

Exciting new advances have been made within this three year research program which have brought us closer to our goal of a practical, yet accurate method for computing rate constants for a wide variety of chemical reactions. This work is roughly divided into continuing tests of the accuracy of the methods of variational transition state theory (VTST), new theoretical developments and numerical methods, and applications to systems of fundamental importance.

Quantitative tests of VTST.

Although many quantitative comparisons have previously been made between rate constants computed using VTST and those obtained from accurate quantum mechanical calculations, most of these have been for model collinear reactions. With the advent of the new generation of supercomputers and the development of new methods of quantum scattering theory, there has been a recent flourish of activity in the area of accurate quantum calculations for realistic reactions in three dimensions. New quantum mechanical results for several isotopic variants of the reactions $H + H_2$ and $O + H_2$ have allowed further tests of our VTST calculations. These tests have once again confirmed the utility of VTST. Both sets of reactions have high classical barriers and are dominated by quantum mechanical tunneling at low temperatures. Even so, the methods were shown to be accurate to within about 40% even down to room temperature.

Perhaps the most interesting tests of VTST have been comparisons with reliable experimental rate constants. Such comparisons require accurate potential energy surfaces for carrying out the theoretical calculations. For the reaction of $O(^3P)$ with H_2 such a potential exists and VTST calculations have been carried out for the rate constants and deuterium kinetic isotope effects over a temperature range extending from below room temperature up to 2400K. Since then definitive experimental studies have been carried for this reaction measuring the thermal rate constant at low temperatures and also directly measuring the deuterium kinetic isotope effects. These measurements combined with recent shock tube measurements at higher temperatures have given a complete determination of the rates over an extremely wide temperature range. The comparison of the measured and theoretical rate constants have indicated the predictive powers of the theory. However, an even more exciting conclusion from these studies is the experimental confirmation that quantum mechanical tunneling plays a dominate role in this reaction at temperatures from room temperature to about 600K.

Hydrogen transfer reactions are typically facile and are ubiquitous in combustion of hydrocarbons and most conventional propellants and explosives. For the transfer of H between two heavy moieties, the angle between the bottom of the reactant valley and the bottom of the product valley in a mass weighted coordinate systems is small. A consequence of this small skew angle is that the reaction path must go through a highly curved region in proceeding from reactants to products. We have found that the effect of variationally optimizing the location of the generalized transition state dividing surface (the dynamical bottleneck for the reaction) can be very important for such small skew-angle, high reaction-path-curvature systems. The importance of the variational procedure has not been definitively tested in previous studies because in those studies the systems have had classical barriers which were high enough that quantum mechanical tunneling dominated the reaction over a wide temperature range. The reaction I + HI has been studied on a potential energy surface with a low classical barrier. For this reaction tunneling effects were found to be nominal and comparison with accurate quantum mechanical results have shown that the dynamical bottleneck must be positioned away from the symmetrically located saddle point to obtain quantitative agreement between the quantum mechanical and VTST results.

New theoretical and numerical developments

For reactions with moderate-to-large reaction path curvature in which quantum mechanical tunneling is important, the least-action ground-state (LAG) method was previously shown to provide insight into the dynamics of the reaction as well as an accurate method for computing a quantum mechanical tunneling correction factor. This method was previously tested for reactions which were nearly thermoneutral and for which the correction factor is dominated by contributions from tunneling from the ground vibrational state of reactants into the ground vibrational state of products. For exothermic reactions such as Cl + HBr there is a propensity to populate excited vibrational states of the products. The LA method was extended to treat this inherently vibrationally nonadiabatic process of tunneling into vibrationally excited states and successfully tested by comparison with accurate quantum mechanical calculations for the model collinear reaction Cl + HBr → HCl + Br.

Phenomenological models based upon conventional transition state theory with approximate tunneling correction factor have been widely used over the last 40 years to interpret kinetic isotope effects in hydride transfer reactions. The transfer of a light species between two heavy moieties manifests small skew angles and large reaction path curvature. The insight into such processes gained from our VTST studies including the LAG tunneling corrections have shown that these phenomenological models are based upon incorrect dynamical assumptions. However, we have shown how variational effects and large-curvature tunneling effects can be incorporated into a phenomenological model of kinetic isotope effects to give a more consistent picture of the underlying dynamics.

The calculation of thermal rate constants samples collision energies which are near to the maximum of the ground-state adiabatic barrier. Reactions involving vibrationally excited reactants sample higher collision energies and provide a probe of wider regions of the potential energy surface. In addition, these reactions provide a more stringent tests of the VTST methods. Approximate methods for treating excited state reactions have been developed based upon VTST and tested for several model and realistic reactions. It was found that an adiabatic description of the reaction in the reactant channel up to the first occurrence of large reaction-path curvature provided a convenient picture of the dynamics which is capable of semiquantitative accuracy.

Another area of crucial interest is the application of VTST to reactions involving larger polyatomic species which will be important in combustion processes. For these larger reaction systems global potential energy surfaces will generally not be available and methods were previously developed to allow accurate *ab initio* electronic structure information to be directly used in the VTST calculations. Methods for interpolating the *ab initio* information within the framework of the reaction path Hamiltonian (RPH) on a sparse grid allows the calculation of accurate rates from only a moderate amount of *ab initio* information. Quantitative tests of these RPH interpolation methods have only recently been carried out by comparing rate constants computed using a global potential energy surface with those computed using RPH interpolation of pseudo-*ab initio* information obtained from the global potential energy surface. These calculations indicate that rate constants for the four atom reaction $OH + H_2$ can be obtained to a numerical accuracy of about 25% at temperatures down to room temperature using information about the potential and its first and second derivatives at 8-10 points along the reaction coordinate.

Another concern in the use of RPH interpolation techniques is how accurate the reaction path (the minimum energy path in a mass-weighted coordinate system) is located. This is determined by the numerical integration scheme used to follow the path of steepest descents and the step size. We have made a comparison of several numerical integration algorithms and have found that to obtain a numerical accuracy of 15% the simplest fixed-step method allowed the largest steps to be taken. However, for much higher accuracy, 0.01-0.1%, a variable-step predictor-corrector algorithm was shown to be the most efficient. These algorithm were tested for the reactions $OH + H_2$ and $CH_3 + H_2$ using global potential energy surfaces and for the reactions $CH_3 + H_2$ and HCN → HNC using *ab initio* electronic structure information

The VTST methods have been extended to allow treatment of reactions occurring on surfaces. This includes simple processes such as hydrogen migration on surfaces and the more dynamically complex process of dissociative chemisorption. A major advantage of VTST over other dynamical methods for treating these systems is that the motion of the surface atoms can be easily included in the calculation, thereby incorporating the effect of phonons on the reaction process.

Applications

An exciting prospect for obtaining reliable rate constants for systems of practical importance in the study of energetic materials has been collaboration with quantum chemists to obtain *ab initio* electronic structure information as input into the VTST calculations Such a program is underway; in collaboration with Drs. Byron Lengsfield and George Adams at the Ballistic Research Laboratory at Aberdeen Provings Grounds we are currently studying the isomerization reaction HONO → HNO_2. HONO is known to be an important species in the decomposition of propellants and explosives containing nitro substituents. Currently the mechanism of depletion of HONO is not well understood and it has been suggested that the isomerization to form HNO_2 may be feasible. Preliminary indications from our studies indicate that the reaction rate is extremely small below about 600K but may be nonnegligible at higher temperatures. Because of the high classical barrier, even at 600K the reaction is dominated by quantum mechanical tunneling.

Progress has also been made in the study of reactions occurring on surfaces. A major difficulty in these studies is the lack of accurate information about the potential energy surface. Because of the extremely large number of atoms in the system the prospects of obtaining accurate *ab initio* electronic structure information in the near future is bleak. The most promising approach currently is provided by semiempirical potentials which are designed to have the correct topology and are empirically fit. This is similar in spirit to the approach taken to gas-phase reactions twenty years ago in which LEPS potentials were empirically adjusted to reproduce experimental results. These potential surfaces could then be used in theoretical calculations of other dynamical quantities and to provided insight into the dynamics of the reaction. A particularly fruitful approach to treating the bulk properties of metal surfaces has been the use of the embedded atom method (EAM) which is based upon density functional theory. This method has also been extended by Baskes, Daw, and Foiles to treat the interaction of adsorbates such as hydrogen with a metal surface. As a test of the accuracy of the semiempirical potential for

H interacting with bulk Ni, we have studied diffusion of H on the 100 and 111 surfaces of Ni and diffusion in bulk Ni. The computed rates are in quantitative agreement with the plentiful experimental measurements of bulk diffusion. For diffusion on the 100 surface the experimental measurements are much harder and less reliable, but our calculated results are in qualitative agreement.

The description of dissociative chemisorption such as H_2 on Ni(100) is complicated by the need to describe the covalent H_2 bond in the gas phase and the H interactions with Ni when it is chemisorbed. Covalent bonding is not easily described within density functional theory and therefore the EAM method by itself is not adequate for describing the potential. We have developed a general method of incorporating the EAM description of the metal-metal and metal-adsorbate interactions within a diatomics-in-molecules (DIM) framework that allows a flexible framework for semiempirically fitting the gas-surface potential. We note that the DIM model is equivalent to the LEPS potential when only two diatomic potentials are used to describe the atom-atom interactions. Thus, the embedded DIM method is just a natural extension of LEPS to treat gas-surface interactions. Work is now in progress to study H_2 chemisorbing on Ni(100)

Journal Publications

B. C. Garrett, D. W. Schwenke, R. T. Skodje, D. Thirumalai, T. C. Thompson, and D. G. Truhlar, "Adiabatic and Nonadiabatic Methods for Energies, Lifetimes, and Branching Probabilities of Bimolecular Reactive Scattering", in Resonances in Electron-Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics, ACS Symposium Series 263, ed. D. G. Truhlar (American Chemical Society, Washington, D.C., 1984), p. 375.

D. G. Truhlar, B. C. Garrett, P. G. Hipes, and A. Kuppermann, "Test of Variational Transition State Theory Against Accurate Quantal Results for a Reaction with Very Large Reaction-Path Curvature and a Low Barrier", J. Chem. Phys. **81**, 3542 (1984)

R. Steckler, D. G. Truhlar, B. C. Garrett, N. C. Blais, and R. B. Walker, "Characterization of Exit-Channel Barriers for Chemical Reactions Producing Specific Vibrational States", J. Chem. Phys. **81**, 5700 (1984).

F. B. Brown, R. Steckler, D. W. Schwenke, D. G. Truhlar, and B. C. Garrett, "An Improved Potential Energy Surface for F + H_2 --> HF + H and H + H'F --> HF + H", J. Chem. Phys. **82**, 188 (1985).

N. C. Blais, D. G. Truhlar, and B. C. Garrett, "Effect of Bending Potential on Calculated Product-State Distributions for the Reaction H + D_2 --> HD + H", J. Chem. Phys., **82**, 2300 (1985).

S. C. Tucker, D. G. Truhlar, B. C. Garrett, and A. D. Isaacson, "Variational Transition State Theory with Least-Action Tunneling Calculations for the Kinetic Isotope Effects in the Cl + H_2 Reaction: Tests of Extended-LEPS, Information-Theoretic, and Diatomics-in-Molecules Potential Energy Surfaces", J. Chem. Phys. **82**, 4102 (1985).

B. C. Garrett and D. G. Truhlar, "Nuclear-motion Corrections to Born-Oppenheimer Barrier Heights for Chemical Reactions", J. Chem. Phys. **82**, 4543 (1985).

R. Steckler, D. G. Truhlar, and B. C. Garrett, "Variational Transition State Theory Calculations of the Reaction Rates of F with H_2, D_2, and HD and the Intermolecular and Intramolecular Kinetic Isotope Effects", J. Chem. Phys. **82**, 5499 (1985).

B. C. Garrett and D. G. Truhlar, "Generalized Transition State Theory and Least-Action Tunneling Calculations for the Reaction Rates of H(D) + H_2 (n=1) --> H_2 (HD) + H", J. Phys. Chem. **89**, 2204 (1985).

B. C. Garrett, N. Abusalbi, D. J. Kouri, and D. G. Truhlar, "Test of Variational Transition State Theory and the Least-action Approximation for Multidimensional Tunneling Probabilities Against Accurate Quantal Rate Constants for a Collinear Reaction Involving Tunneling into an Excited State", J. Chem. Phys. **83**, 2252 (1985).

R. Steckler, D. G. Truhlar, and B. C. Garrett, "A High-barrier Potential Energy Surface for F + H_2 --> HF + H", J. Chem. Phys. **83**, 2870 (1985).

D. Thirumalai, B. C. Garrett, and B. J. Berne, "Evaluation of Microcanonical Rate Constants for Bimolecular Reactions by Path Integral Techniques", J. Chem. Phys. **83**, 2972 (1985).

D. G. Truhlar, F. B. Brown, D. W. Schwenke, R. Steckler, and B. C. Garrett, "Dynamics Calculations Based on *ab initio* Potential Energy Surfaces", in Comparison of *Ab Initio* Quantum Chemistry with experiment for Small Molecules, ed. R. J. Bartlett (Reidel, 1985), p. 85.

C. W. McCurdy and B. C. Garrett, "Quantum Mechanical Microcanonical Rate Constants from Direct Calculations of the Green's Function for Reactive Scattering", J. Chem. Phys. **84**, 2630 (1986).

B. C. Garrett, D. G. Truhlar, and G. C. Schatz, "Test of Variational Transition State theory and Multidimensional Semiclassical Transmission Coefficients Methods Against Accurate Quantal Rate Constants for H + H_2/HD, D + H_2, and O + H_2/D_2/HD, Including Intra- and Intermolecular Kinetic Isotope Effects", J. Am. Chem. Soc. **108**, 2876 (1986).

B. C. Garrett and D. G. Truhlar, "Thermal and State-Selected Rate Constant Calculations for $O(^3P) + H_2$ --> OH + H and Isotopic Analogs", Int. J. Quantum. Chem. **24**, 1463 (1986).

B. C. Garrett, D. G. Truhlar, J. M. Bowman, A. F. Wagner, D. Robie, S. Arepathi, N. Presser, and R. J. Gordon, "*Ab Initio* Predictions and Experimental Confirmation of Large Tunneling Contributions to Rate Constants and Kinetic Isotope Effects for Hydrogen-transfer Reactions", J. Am. Chem. Soc. **108**, 3515 (1986).

R. Steckler, D. G. Truhlar, and B. C. Garrett, "Tests of the Extension of Variational Transition State Theory to Calculate Reaction Rates for Molecules in Selected Excited Vibrational States", J. Chem. Phys. **84**, 6712 (1986).

M. M. Kreevoy, D. Ostovic, D. G. Truhlar, and B. C. Garrett, "Phenomenological Manifestations of Large-Curvature Tunneling in Hydride Transfer Reactions", J. Phys. Chem. **90**, 3766 (1986).

B. C. Garrett, D. G. Truhlar, J. M. Bowman, and A. F. Wagner, "Evaluation of Dynamical Approximations for Calculating the Effect of Vibrational Excitation on Reaction Rates. O + H_2 (n=0,1) --> OH(n=0,1) + H", J. Phys. Chem. **90**, 4305 (1986).

B. C. Garrett, D. G. Truhlar, A. J. C. Varandas, and N. C. Blais, "Semiclassical Variational Transition State Calculations for the H + H_2(v=0,1) and D + H_2(v=0,1) Reactions", Int. J. Chem. Kinetics **18**, 1065 (1986).

R. Steckler, D. G. Truhlar, and B. C. Garrett, "Dynamics Calculation of Kinetic Isotope Effects for the Reactions of Muonium Atoms with F_2, Cl_2, and Br_2", Int. J. Quan. Chem. Symp. **20**, 495 (1986).

B. C. Garrett, D. G. Truhlar, and R. Steckler, "Dynamics of Gas-Phase Reactions of Muonium", Hyperfine Interactions **32**, 779 (1986).

B. C. Garrett and D. G. Truhlar, "Reaction Rates for O + HD --> OH + D and O + HD --> OD + H", Int. J. Quan. Chem. **21**, 17 (1987).

D. G. Truhlar and B. C. Garrett, "Dynamical Bottlenecks and Semiclassical Tunneling Paths for Chemical Reactions", J. de Chimie Physique, in press.

B. C. Garrett, M. J. Redmon, R. Steckler, D. G. Truhlar, K. K. Baldridge, D. Bartol, M. W. Schmidt, and M. S. Gordon, "Algorithms and Accuracy Requirements for Computing Reaction Paths by the Method of Steepest Descent", submitted to J. Comp. Chem.

A. D. Isaacson, D. G. Truhlar, S. N. Rai, R. Steckler, G. C. Hancock, B. C. Garrett, and M. J. Redmon, "POLYRATE Program Manual, Version A", submitted to Comp. Phys. Comm.

J. Z. H. Zhang, Y. Zhang, D. J. Kouri, B. C. Garrett, K. Haug, D. W. Schwenke, and D. G. Truhlar, "L^2 Calculations of Accurate Quantal Dynamical Reactive Scattering Transition Probabilities and Their Use to Test Semiclassical Applications", submitted to Faraday Discussions 84: Dynamics of Elementary Gas Phase Reactions

Scientific Personnel

Bruce C. Garrett
Michael J. Redmon

END

10-87

DTIC