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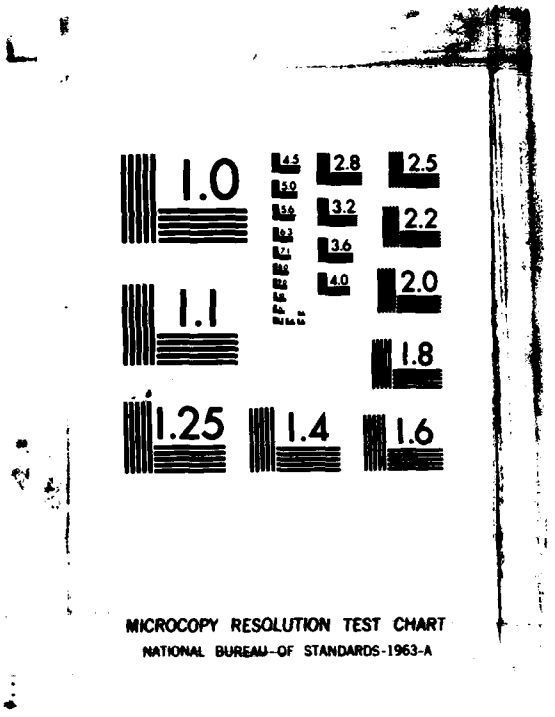

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chemical reaction, transition state theory, variational transition state theory, bimolecular gas-phase reactions, tunneling corrections to transition state theory.

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 transition state theory.

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FINAL REPORT

Prediction of thermal rate constants for combustion reaction

Contract number DAAG-29-81-C-0015

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Statement of Problem

The goal of the research carried out on this contract is the development of theoretical methods which will aid in the interpretation and modeling of gas-phase combustion processes. The methods are based upon variational transition state theory (VTST), which has been shown to be an efficient method of computing accurate rate constants for gas-phase reactions. The study of gas-phase reactions is an important step toward understanding complicated mechanisms of the combustion of energetic materials. Also, gas-phase rate data are needed as input for models of these combustion mechanisms.

The limitations in the accuracy of VTST arise from (1) a breakdown of the fundamental dynamical assumption of TST, (2) the ad hoc manner in which quantum mechanical effects are included in VTST, (3) the approximate methods for including anharmonic effects, and (4) inaccuracies in the potential energy surface information used as input into the theory. The major part of the research on this contract has included extension of the methods to surmount these limitations, validation of the new methods by testing them against accurate quantum mechanical methods on model collinear reactions, and extension of the methods to treat realistic reactions involving polyatomic molecules.

Summary of Important Results

Within the last few years we have made many advances in the application of VTST to gas-phase reactions. This research is roughly divided into five areas which are summarized below.

Classical recrossing effects. The fundamental dynamical assumption of TST assumes that classical trajectories cross the transition state or dividing surface only once. Breakdown of this assumption is termed "classical recrossing" of the dividing surface, and this recrossing leads to overestimation of the thermal rate constant in classical TST and VTST. The accuracy of TST can be improved, not only by minimizing the amount of classical recrossing by variationally optimizing the dividing surface location, but by estimating the amount of recrossing occurring at the variational dividing surface. We have proposed two new methods for estimating the amount of classical recrossing of the dividing surface - the canonical unified statistical (CUS) model and the unified dynamical (UD) model.

The CUS model is an extension of the unified statistical (US) model in which the amount of recrossing is estimated from the reactive flux through two variationally optimized dividing surfaces. In the canonical version (CUS) the microcanonical fluxes of the unified statistical model (which are related to the number of energetically accessible states in the TST approximation) are replaced by canonical fluxes (which are related to partition functions in the TST approximation).

In the more dynamically justified unified dynamical (UD) model, the amount of recrossing is estimated from quasiclassical trajectory calculations in which the trajectories are started at the VTST dividing surface.

Quantum mechanical effects on reaction-coordinate motion. Quantum mechanical tunneling effects are included in VTST by a multiplicative factor called the transmission coefficient. These effects are largest for low temperature reactions which involve hydrogen atoms. We have found that for some reactions the transmission coefficient can be as high as a factor of 36 at 300K and greater than a factor of 2 as high as 600K. Therefore, for accurate calculations of thermal rate constants, quantum mechanical tunneling effects must be considered.

Several methods of calculating the transmission coefficient have been suggested. Most of these are based upon the vibrationally adiabatic model, in which it is assumed that the vibrational and rotational motions are fast compared to the motion along the reaction coordinate. Within this framework, quantum mechanical transmission probabilities are computed for transmission through and above the one-dimensional ground-state adiabatic barrier (potential energy plus zero-point energies). The use of the ground-state adiabatic barrier alone is justified because at low temperatures (where tunneling is most important) a quantized system is in its ground state and at high temperature (where tunneling effects are unimportant) the transmission coefficient is one. During the last three years, we have thoroughly investigated vibrationally adiabatic models for three-atom collinear reactions, and have derived a validity criterion which limits the adiabatic approximation to systems with small reaction-path curvature. This work led to the development of a practical multidimensional tunneling method which is valid for systems with small reaction-path curvature (the small-curvature-tunneling semiclassical adiabatic ground-state SCTSAG method).

For systems with very large reaction-path curvature we have developed a large-curvature ground-state (LCG) tunneling method which does not

assume vibrational adiabaticity in the tunneling region. In this method, tunneling is assumed to proceed along the most direct path between the reactant and product valleys, through the actual potential barrier instead of the vibrationally adiabatic barrier. A more general tunneling method which is valid for systems with small, medium, or large reaction-path curvature is the least-action ground-state (LAG) tunneling method. In this method a parameterized set of tunneling paths is considered and the optimum path (the one with the least amount of exponential damping, i.e., the most tunneling probability) is selected using a variational procedure. In the limit of very small curvature the method is similar to the SCTSAG method, and in the limit of large curvature it is similar to the LCG method.

Anharmonicity in bound state energy levels. In order to obtain quantitatively correct rate constants it is necessary to include the effects of anharmonicity in the calculations of the energy levels of the bound degrees of freedom. This has been shown to be true for small systems with only a few degrees of freedom and also for large polyatomic systems. In this area, the most important recent advance has been in the treatment of anharmonicity in stretching vibration degrees of freedom. Our previous prescription was to include anharmonicities by fitting the potential in this degree of freedom to a Morse potential. This treatment was found to be inadequate for systems with very light reduced masses and for computing excited state rate constants. A new method was developed in which these energy levels are computed using a primitive WKB procedure. This procedure was found to give much better rate constants for a variety of reactions.

Tests of VTST. Two types of tests of VTST have been used: (1) comparisons of VTST rate constants to accurate quantum mechanical ones computed on

the same potential energy surface and (2) comparisons of VTST rate constants to experimental ones. Accurate quantal rate constants are available for several collinear reactions of atoms with diatomic molecules and for two three-dimensional atom-diatom reactions. VTST was compared with all of these results. In order to compare calculated rate constants to experimental ones, an accurate potential energy surface must be used. Comparisons of this type have been made for the H + H_2 reaction and isotopic variants using the accurate LSTH potential energy surface. The conclusions from these tests are as follows. (1) Variational optimization of the dividing surface is necessary to obtain quantitative agreement between the approximate and quantal rate constants. Errors as large as a factor of 13 were observed when the location of the dividing surface was not optimized. (2) For systems containing hydrogen, quantal effects on reaction-coordinate motion must be included for low temperatures (typically below 600K). The SCTSAG method works well for systems with small reaction-path curvature; the LAG method works well for systems with large reaction-path curvature; and the LCG method works well for a wide variety of systems. Neglect of tunneling can lead to errors in excess of two orders of magnitude at 200K. (3) The ICVT/LAG method typically gives errors of less than a factor of two at very low temperature (200K) and is accurate to within about 50% over the temperature range 300 to 1500K. (4) In comparisons with experiments the ICVT/SCTSAG method was accurate to within 20% for the temperature range 299 to 549K for H + H_2, and a kinetic isotope effect for the ratio of the rate for Mu + H_2 to the rate for H + H_2 was predicted to within 20%.

<u>Applying VTST to systems for which potential energy surface (PES) information is limited.</u> This topic can be further divided into two

subtopics, the use of a reaction-path interpolation technique and the semiempirical adjustment of potential energy surfaces.

One of the advantages of using VTST over dynamical methods for computing reaction rates is that with VTST a full potential energy surface (PES) is not needed. The regions of the PES that are the most important in controlling the rates of chemical reactions are the dynamical bottlenecks which can be identified as the locations of the variationally optimized dividing surfaces. It is upon these regions of the PES that the electronic structure calculations should focus; however, these regions cannot be identified until a VTST calculation is done, and a VTST calculation cannot be done until PES information is available. We have developed a new technique to interpolate the reaction-path Hamiltonian information needed as input into VTST calculations using the limited PES information that is available. Using this technique a VTST calculation can be performed to identify the bottleneck regions of the PES using PES information at a few locations along the reaction coordinate. Further electronic structure calculations can then be carried out to better describe these more critical parts of the PES. This procedure can be iterated (VTST calculations followed by more electronic structure calculations) to obtain better estimates of the rate constants.

For small systems, for which global potential energy surfaces can be expressed as analytic functional forms, attempts have been made to empirically adjust the parameters of the surface so that rate data computed using VTST methods agree with experimental rate data. We have carried out this procedure for the Cl + H_2 reactions and isotopic variants and work is in progress on the F + H_2 reaction. For Cl + H_2 there is a large body of experimental rate data including thermal rate constants and kinetic isotope effects. Several different functional forms for the PES have

been fit such that VTST gives the correct activation energy for the Cl + H_2 reaction for a limited temperature range. Using these various surfaces the kinetic isotope effects were computed and compared with experiment. This study pointed out the limitations of this type of procedure, as the agreement between the theory and experiment changed for the different functional forms used for the PES.

For the F + H_2 system, the surface was fitted semiempirically using a different type of experimental data. In this system we used information about thermal rate data and information about a reactive resonance. Reactive resonances are quasibound states which are trapped in the interaction region of the PES. If the resonances are sufficiently long lived, they can be used to probe the interaction region of the PES spectroscopically. We have developed approximate methods for locating and characterizing reactive resonances. For the F + H_2 system, the resonance does not appear to be sufficiently long lived for spectroscopic studies; however, it is observed in molecular beams scattering experiments. We are in the process of adjusting the F + H_2 surface to correctly describe the onset of the resonance feature as observed in the experiment of Neumark and Lee.

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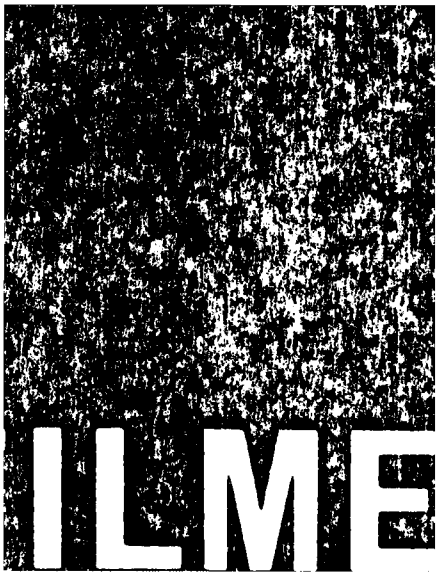
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