Theoretical and Experimental Rate Constants for Two Isotopic Modifications of the Reaction H + H_2

JOE V. MICHAEL, J. ROBERT FISHER, JOEL M. BOWMAN, QIYAN SUN

Theoretical rate constants for two isotopic modifications of the simplest possible chemical reaction, namely, $H + D_2 \rightarrow HD + D$ and $D + H_2 \rightarrow HD + H$, are presented. Experimental results, which have previously been obtained in the higher temperature regime by a shock tube technique, are combined with lower temperature results to give an experimental determination of the rate behavior over the large temperature range ~200 to 2000 K. It is now possible to assess the accuracy of ab initio potential energy surface calculations and to judge theoretical chemical kinetic methods.

THE THEORETICAL PREDICTION OF the rate behavior for gas-phase chemical reactions has been a major goal of physical chemists for over 50 years (*1, 2*). In the earliest work (*3*), the issues that are involved in this description were identified. In order to theoretically describe a thermally reacting system, the potential energy surface for the interaction of interest must be accurately known (*4*). Then, with the potential energy surface determined, a variety of dynamical methods might be used to deduce the behavior of the rate constants as a function of bulk quantities such as temperature and density.

With the rationale established, the theoretical estimation of potential energy surfaces has been a major area of research. In the recent "Frontiers in Chemistry" issue of *Science*, the current status of the development of ab initio methods for use in dynamical calculations was discussed (*5*) in terms of a consideration of three systems: the HCO radical, the OH + H_2 reaction, and the O + C_2H_2 reaction. With modern ab initio methods, it is now possible to theoretically determine the configuration of reacting systems; however, the calculation of relative energy is still accurate only to within about ±2 kcal/mol. Hence, within this range of uncertainty, it has been necessary to scale the energy in potential energy calculations, and these scaling factors then become parameters in the description of the potential energy of interaction. This unfortunate situation has existed in all known cases until quite recently.

The theoretical prediction of the ab initio potential energy surface for the most fundamental three-electron interaction, namely, the H + H_2 reaction, has now been determined with high accuracy by Liu (*6*) and Siegbahn and Liu (7). An analytic fit to their results has been given by Truhlar and Horowitz (*8*). Subsequently, a new and even more accurate representation of the ab initio potential energy surface has appeared (*9*). It is now true that the potential energy surface for this case is known with higher accuracy than for any other known chemical reaction, and this has prompted new theoretical predictions of the thermal rate behavior based on the variational transition-state method (*10*).

One of the weaknesses in the comparisons of theoretical to experimental rate data has been the paucity of data on the H + H_2 reaction and the isotopic modifications thereof. Experimental measurements of thermal rate constants in the higher temperature regime above ~1000 K would be particularly instructive because in this region quantum mechanical tunneling becomes less important, and the results could then provide direct information on the relative energetics of the potential energy surface for the interaction. Thermal rate data have now been obtained by the flash photolysis–shock tube (FP-ST) technique (*11, 12*) for the H + D_2 and D + H_2 reactions in the temperature range ~700 to 2000 K (*13, 14*). We review here these new data and combine them with lower temperature results (*15–21*). The experimental rate behavior for both reactions is now well understood over the very large temperature range from ~200 to 2000 K. In addition to these experimental results, new theoretical calculations are presented that use the newest and most accurate potential energy surface (*9*) as the basis. Hence, the theoretical predictions and their comparison to the experimental results constitute a stringent test of the theory of reaction rates.

There are several realistic dynamical methods currently in use for calculating thermal rate constants for A + BC reactions. These have recently been reviewed by Schatz (*22*). In the present work, one of these methods, which has been developed by Bowman (*23*) and Bowman and Wagner (*24*), is tested against the experimental data. This method is based on a solution of the Schrödinger equation in the reduced dimensionality space of (i) the distance of A to the center of mass of BC and (ii) the distance between atoms B and C. The internal angular (bending) motion is treated adiabatically. The calculated quantity is the cumulative reaction probability, that is, the reaction probability summed over all initial and final states of the reactants and products and also over all values of the total angular momentum. The rate constant is then given directly as a canonical (thermal) average of this probability. This general approach has been termed the reduced dimensionality theory of reaction rates (*23, 24*). However, even within this theoretical approach there are levels of approximation. For example, in the CEQB/G (collinear exact quantum bend) version of the theory, the cumulative reaction probability is calculated for the ground (G) bending state only. Then the probability for a given excited bending state at a total energy, E, is obtained from the ground bend probability evaluated at the energy, $E - E^{\dagger}_{nb}$, where $E^{\dagger}_{nb}$ is the nth bending energy for the transition state referenced to the ground bending state energy.

Recently two of us, along with co-workers, applied a more sophisticated version of the theory (labeled simply CEQB), in which the reaction probability has been explicitly calculated for each bending state, including all excited states. The method has been applied to a calculation of the cumulative reaction probability for the Cl + HCl reaction and has been tested by making comparisons to exact three-dimensional quantum scattering calculations with the same potential energy surface (*25*). The two theoretical methods agree with one another within the errors in numerical analysis associated with each. On the basis of this and other similar comparisons to exact calculations (*22–24*), it is expected that the CEQB method will provide accurate rate constants for the present reactions.

The CEQB method has recently been applied to the reactions (*26*)

$$H + D_2 \rightarrow HD + D \quad (1)$$

and

$$D + H_2 \rightarrow HD + H \quad (2)$$

J. V. Michael and J. R. Fisher, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.
J. M. Bowman and Q. Sun, Department of Chemistry, Emory University, Atlanta, GA 30322.

In this work, the less accurate potential energy surface of Liu (*6*) and Siegbahn and Liu (*7*) and Truhlar and Horowitz (*8*) was used at both the CEQB/G and CEQB levels of approximation. The more sophisticated CEQB method gave values for the rate constants of reactions 1 and 2 that were in good agreement with experimental values (*13–21*).

With the above-mentioned experience, it seems plausible that the best possible theoretical prediction to date for the rate behavior of reactions 1 and 2 would therefore be obtained with the use of the CEQB dynamical method, but incorporating the newer, more accurate double many-body expansion (DMBE) potential fit to the ab initio potential energy surface as reported by Varandas *et al.* (*9*). Accordingly, in this report, the CEQB method has been used to calculate cumulative reaction probabilities with the DMBE ab initio calculations for the H_3 system as the basis. The details of the implementation of the method are the same as described previously (*26*). Reaction probabilities for seven bending states were calculated for both reactions 1 and 2 at increments of 0.5 kcal/mol for total energies between 7 and 46 kcal/mol. Numerical tests indicate that the precision in the resulting rate constants is $\leq \pm 5\%$. Thermal rate constants have then been calculated for temperatures between 200 to 2000 K and 167 to 2000 K for reactions 1 and 2, respectively. The results of these theoretical predictions are shown in Table 1.

Thermal rate constants for reactions 1 and 2 have been measured by the FP-ST technique (*11, 12*) over the approximate temperature range 700 to 2000 K (*13, 14*). In this technique, a transient species is produced by the flash photolysis of a suitable source molecule, and then the time dependence of the transient species is followed with spectroscopic methods as reaction with an added reactant molecule proceeds. In the present cases, the source molecules are H_2O and D_2O, and the reactant molecules are D_2 and H_2, for reactions 1 and 2, respectively. The H or D atoms formed from the photodecompositions of H_2O or D_2O are monitored by atomic resonance absorption spectroscopy. Because the level of resonance light absorption is small, Beer's law is obeyed. The concentration of atoms is therefore directly proportional to the natural logarithm of the inverse of the transmittance; that is, $[H]_t$ (or $[D]_t$) = $(\ln T^{-1})/\sigma\ell$, where the proportionality constant σ is the effective absorption cross section, ℓ is the absorption path length, and the transmittance T is the ratio of the temporally transmitted intensity to the initial intensity of the resonance radiation. The quantity $\ell n T^{-1}$ is defined as the absorbance, $(\mathrm{ABS})_t$. The rate of atom removal, $R = -d[H]/dt$ (or $-d[D]/dt$), in reaction 1 (or 2) is equal to the product of the thermal rate constant times the concentrations of both the added reactant and the atom; that is, $R_H = k_1[D_2][H]$ (or $R_D = k_2[H_2][D]$). Because little reactant is consumed, the concentration of D_2 (or H_2) can be taken to be constant in time. With this approximation, the atomic concentration then follows a first-order rate law with the first-order decay constant, k_{first}, being equal to $k_1[D_2]$ (or $k_2[H_2]$); thus, $\ln[H]_t$ (or $\ln[D]_t$) = $-k_{\text{first}}t$ + const. Because the atomic concentration is proportional to absorbance, one can obtain the first-order decay constant simply by plotting the natural logarithm of $(\mathrm{ABS})_t$ as a function of time and calculating the negative slope.

Table 1. Theoretical rate constant predictions for H + D_2 and D + H_2 with the CEQB method and the DMBE ab initio potential energy surface.

T (K)	k_{H+D_2} (cm^3 molecule^{-1} s^{-1})	k_{D+H_2} (cm^3 molecule^{-1} s^{-1})
167		1.46×10^{-19}
200	2.53×10^{-20}	1.92×10^{-18}
256	1.79×10^{-18}	
300	1.92×10^{-17}	3.47×10^{-16}
400	7.09×10^{-16}	6.31×10^{-15}
500	6.84×10^{-15}	3.96×10^{-14}
600	3.28×10^{-14}	1.42×10^{-13}
700	1.04×10^{-13}	3.64×10^{-13}
800	2.56×10^{-13}	7.60×10^{-13}
900	5.26×10^{-13}	1.37×10^{-12}
1000	9.53×10^{-13}	2.25×10^{-12}
1100	1.57×10^{-12}	3.40×10^{-12}
1200	2.40×10^{-12}	4.86×10^{-12}
1300	3.47×10^{-12}	6.64×10^{-12}
1400	4.78×10^{-12}	8.73×10^{-12}
1500	6.34×10^{-12}	1.11×10^{-11}
1600	8.13×10^{-12}	1.38×10^{-11}
1700	1.02×10^{-11}	1.68×10^{-11}
1800	1.24×10^{-11}	2.00×10^{-11}
1900	1.48×10^{-11}	2.34×10^{-11}
2000	1.73×10^{-11}	2.69×10^{-11}

In order to obtain thermal rate constants from first-order decay constants, the concentrations of the reactants must be known. For this reflected shock wave experiment, the thermodynamic state of the hot stagnant gas in the reflected shock regime is calculated from the measured velocity of the incident shock wave through the well-known, one-dimensional hydrodynamic equations (*27*). Corrections for the nonidealities caused by boundary layer formation have also been applied (*12, 28*). Because the initial mole fractions of reactants are known and the reflected shock wave density and temperature are determined from the shock strength, the concentrations of either H_2 or D_2 can be determined for each experiment. Subsequent division of the measured k_{first} value by reactant concentration for a given experiment then provides a determination of either k_1 or k_2 at the conditions of total density and temperature for the experiment. The complete details of the experiments are given elsewhere (*13, 14*); however, the results for the two reactions are summarized as Arrhenius plots in Fig. 1. The specific temperature ranges for these new results are 724 to 2061 K and 655 to 1979 K for reactions 1 and 2, respectively.

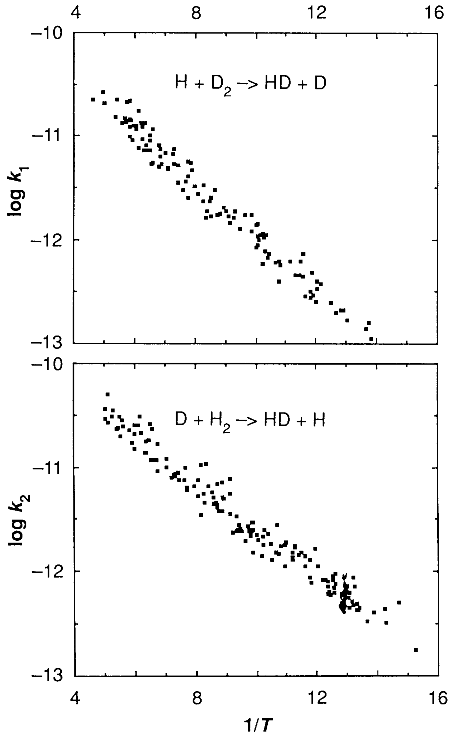

Fig. 1. Arrhenius plots, log(k) (where k is in units of cm^3 molecule^{-1} s^{-1}) versus ($1/T$) [where ($1/T$) is multiplied by 10,000 K in the figure], of the data for k_1 and k_2 from (*13*) and (*14*).

The lower temperature experimental results (*15–21*) have been obtained by traditional discharge-flow methods that have utilized either electron paramagnetic resonance atomic detection or reactant conversion to HD for the determination of the rate constants. The Arrhenius plots of the entire databases for reactions 1 and 2 are shown in Figs. 2 and 3, respectively. If all data are included (*13–21*), the temperature ranges for reactions 1 and 2 are 256 to 2061 K and 167 to 1979 K, respectively.

When the present predictions in Table 1 are compared to those obtained by the variational transition-state method (*10*), the agreement is satisfactory over the lower temperature range. Therefore, both methods agree on the extent of quantum mechanical tunneling. Tunneling is a large effect at 200 K, accounting for 97% and 98% of the overall reaction rate in reactions 1 and 2, respectively. The present theoretical predic-

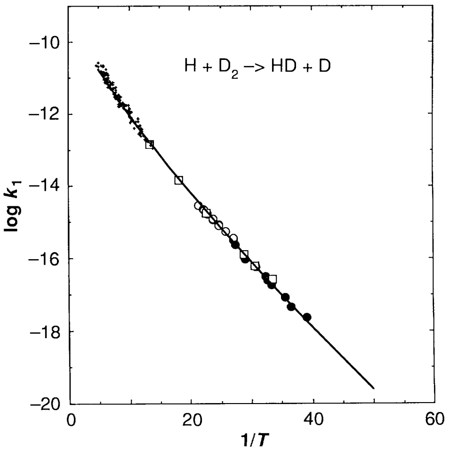

Fig. 2. Arrhenius plot of the thermal rate constants for k_1 (H + D_2) in comparison to the theoretical calculation; (•) Michael (*13*); (○) Schulz and Le Roy (*15*); (□) Westenberg and de Haas (*19*); (●) Jayaweera and Pacey (*20, 21*). The line shown is the CEQB theoretical calculation that is based on the DMBE potential energy surface as described in the text. Units are as in Fig. 1.

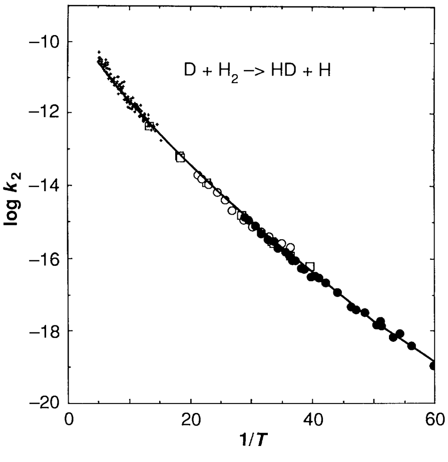

Fig. 3. Arrhenius plot of the thermal rate constants for k_2 (D + H_2) in comparison to the theoretical calculation; (•) Michael and Fisher (*14*); (○) Ridley *et al.* (*16*); (●) Mitchell and Le Roy (*18*); (□) Westenberg and de Haas (*19*). The line shown is the CEQB theoretical calculation that is based on the DMBE potential energy surface as described in the text. Units are as in Fig. 1.

tions are compared to the data in Figs. 2 and 3 where the Table 1 values are plotted as solid lines. This comparison confirms the tunneling phenomenon, and, therefore, the present demonstration argues strongly for its inclusion in all H-atom abstraction reactions.

When predictions obtained with the use of the variational transition-state method are compared to the data, the rate behavior for both reactions is underestimated by up to 20 to 40% in the high-temperature regime, 1000 to 2000 K (*13, 14*). However, it is obvious by inspection of Figs. 2 and 3 that the present CEQB calculations agree with experiment to within the attendant error of the experiments. The predictions diverge slightly from the mean of the data at high temperatures; however, this divergence is within the random error of the experimental FP-ST results.

The present comparisons confirm the original proposition of the earliest workers (*3*) in the theory of reaction rates, namely: If the potential energy of interaction is known with high enough accuracy, then the thermal rate behavior can be accurately evaluated with statistically averaged gas-phase chemical kinetic theory. The present comparisons firmly demonstrate that this proposition is completely true within the random error of the experimental data. In all earlier work, the proposition has only been an assumption in gas-phase chemical kinetics because the relative energetics in all other ab initio electronic structure calculations of potential energy surfaces are still not calculated accurately enough to allow for a first-principles comparison. In these cases, energy scaling and other parameterization schemes are always involved in the comparison of theory to experiment.

Lastly, even though the present methods have shown that CEQB theory (*23, 24*) coupled to the DMBE potential energy surface (*9*) is sufficient to give a high-quality prediction of the thermal rate behavior, rigorous quantum scattering calculations for describing the dynamics on this potential energy surface are becoming available (*22, 29*). This approach has recently been used to explain some of the state-to-state dynamical results (*30*). Indeed, in a very recent set of comparisons, this approach gave excellent agreement with experimental measurements of relative rotational state-to-state cross sections (*31*). These comparisons between rigorous theory and experiment are complementary to ours, especially since the state-to-state results (*30, 31*) have been obtained at single collision energies that are greatly in excess of the barrier to reaction. In contrast, the thermal rate data are most sensitive to the lower energy region below and near to the potential energy barrier maximum. In the future, we can expect that quantum scattering calculational methods (*22, 29*) will be applied to the thermally averaged case. Even though such calculations are clearly more involved, an even more fundamental estimate of the rate behavior will result when such a calculation becomes available.

REFERENCES AND NOTES

1. For reviews of earlier theoretical and experimental work, see: S. Glasstone, K. J. Laidler, H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941); K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1965); H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald, New York, 1966).
2. F. Kaufman, *Annu. Rev. Phys. Chem.* **20**, 45 (1969); D. G. Truhlar and R. E. Wyatt, *ibid.* **27**, 1 (1976).
3. F. London, *Probleme der Modernen Physik (Sommerfeld Festschrift)* (University of Leipzig, Leipzig, 1928), p. 104; *Z. Elektrochem.* **35**, 552 (1929); H. Pelzer and E. Wigner, *Z. Phys. Chem. Abt. B* **15**, 445 (1932); H. Eyring, *J. Chem. Phys.* **3**, 107 (1935); W. F. K. Wynne-Jones and H. Eyring, *ibid.*, p. 492; M. G. Evans and M. Polanyi, *Trans. Faraday Soc.* **31**, 875 (1935); *ibid.* **33**, 448 (1937); M. Polanyi, *J. Chem. Soc.* **1937**, 629 (1937).
4. D. G. Truhlar and R. E. Wyatt, *Adv. Chem. Phys.* **36**, 141 (1977). See also (*2*) for a discussion of earlier semiempirical and ab initio calculations.
5. T. H. Dunning, Jr., *et al.*, *Science* **240**, 453 (1988).
6. B. Liu, *J. Chem. Phys.* **58**, 1925 (1973).
7. P. Siegbahn and B. Liu, *ibid.* **68**, 2457 (1978).
8. D. G. Truhlar and C. J. Horowitz, *ibid.*, p. 2466.
9. A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, N. C. Blais, *ibid.* **86**, 6258 (1987).
10. B. C. Garrett and D. G. Truhlar, *Proc. Natl. Acad. Sci. U.S.A.* 76, 4755 (1979); *J. Chem. Phys.* **72**, 3460 (1980); ______, A. J. C. Varandas, N. C. Blais, *Int. J. Chem. Kinet.* **18**, 1065 (1986).
11. G. Burns and D. F. Hornig, *Can. J. Chem.* **38**, 1702 (1960); J. Ernst, H. gG. Wagner, R. Zellner, *Ber. Bunsenges. Phys. Chem.* **82**, 409 (1978); K. J. Niemitz, H. gG. Wagner, R. Zellner, *Z. Phys. Chem. (Frankfurt am Main)* **124**, 155 (1981).
12. J. V. Michael, J. W. Sutherland, R. B. Klemm, *Int. J. Chem. Kinet.* **17**, 315 (1985); J. V. Michael and J. W. Sutherland, *ibid.* **18**, 409 (1986).
13. J. V. Michael, *J. Chem. Phys.* **92**, 3394 (1990).
14. ______ and J. R. Fisher, *J. Phys. Chem.* **94**, 3318 (1990).
15. W. R. Schulz and D. J. Le Roy, *Can. J. Chem.* **42**, 2480 (1964); *J. Chem. Phys.* **42**, 3869 (1965).
16. B. A. Ridley, W. R. Schulz, D. J. Le Roy, *J. Chem. Phys.* **44**, 3344 (1966).
17. D. J. Le Roy, B. A. Ridley, K. A. Quickert, *Discuss. Faraday Soc.* **44**, 92 (1967); K. A. Quickert and D. J. Le Roy, *J. Chem. Phys.* **53**, 1325 (1970); *ibid.* **54**, 5444 (1971).
18. D. N. Mitchell and D. J. Le Roy, *ibid.* **58**, 3449 (1973).
19. A. A. Westenberg and N. de Haas, *ibid.* **47**, 1393 (1967).
20. I. S. Jayaweera and P. D. Pacey, *J. Phys. Chem.* **94**, 3614 (1990).
21. I. S. Jayaweera, thesis, Dalhousie University Halifax, Nova Scotia (1989).
22. G. C. Schatz, *Annu. Rev. Phys. Chem.* **39**, 317 (1988).
23. J. M. Bowman, *Adv. Chem. Phys.* **61**, 115 (1985).
24. ______ and A. F. Wagner, in *The Theory of Chemical Reaction Dynamics*, D. C. Clary, Ed. (Reidel, Boston, 1986), pp. 47–76.
25. Q. Sun, J. M. Bowman, G. C. Schatz, J. R. Sharp, J. N. L. Conner, *J. Chem. Phys.* **92**, 1677 (1990).
26. Q. Sun and J. M. Bowman, *J. Phys. Chem.* **94**, 718 (1990).
27. J. N. Bradley, *Shock Waves in Chemistry and Physics* (Wiley, New York, 1962).
28. J. V. Michael, *J. Chem. Phys.* **90**, 189 (1989).
29. R. T. Pack and G. A. Parker, *ibid.* **87**, 3888 (1987); M. Zhao *et al.*, *J. Am. Chem. Soc.* **111**, 852 (1989); T. J. Park and J. C. Light, *J. Chem. Phys.* **91**, 974 (1989); J. Z. H. Zhang and W. H. Miller, *ibid.*, p. 1528; D. E. Manolopoulos and R. E. Wyatt, *ibid.* **92**, 810 (1990). See also the references cited in these papers.
30. S. A. Buntin, C. F. Giese, W. R. Gentry, *J. Chem. Phys.* **87**, 1443 (1987); G. W. Johnston, B. Katz, K. Tsukiyama, R. Bersohn, *J. Phys. Chem.* **91**, 5445 (1987); J. Nieh and J. J. Valentini, *J. Chem. Phys.* **92**, 1083 (1990); D. A. V. Kliner and R. N. Zare, *ibid.*, p. 2107. See also the references cited in these papers.
31. D. A. V. Kliner, K.-D. Rinnen, R. N. Zare, *Chem. Phys. Lett.* **166**, 107 (1990).

32. We thank A. F. Wagner, L. B. Harding, and G. C. Schatz for a thorough reading of the manuscript and helpful suggestions. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contracts W-31-109-Eng-38 (Argonne National Laboratory) and DE-FG05-86ER13568 (Emory University).

21 February 1990; accepted 27 April 1990