ANL/CHM/CP--85844
CONF-950743--4

(submitted July, 1995)

RECENT ADVANCES IN THE MEASUREMENT OF HIGH TEMPERATURE BIMOLECULAR RATE CONSTANTS

by

J. V. Michael
Chemistry Division
Argonne National Laboratory, Argonne, IL 60439

presented at the International Symposium:

"Gas Phase Chemical Reaction Systems:
Experiments and Models 100 Years after Max Bodenstein,"
Internationales Wissenschaftsforum Heidelberg,
Universität Heidelberg, July 25-28, 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

(NOT PATENTABLE)

The submitted manuscript has been authored
by a contractor of the U. S. Government
under contract No. W-31-109-ENG-38.
Accordingly, the U. S. Government retains a
nonexclusive, royalty-free license to publish
or reproduce the published form of this
contribution, or allow others to do so, for
U. S. Government purposes.

This work was supported by the U. S. Department of Energy, Office of Basic Energy
Sciences, Division of Chemical Sciences, under Contract No. W-31-109-Eng-38.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED DT

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RECENT ADVANCES IN THE MEASUREMENT OF HIGH TEMPERATURE BIMOLECULAR RATE CONSTANTS

J. V. Michael

Chemistry Division, Argonne National Laboratory
Argonne, IL 60439 USA

Abstract. Recent advances in the measurement of high temperature reaction rate constants are discussed. The studies carried out by shock tube methods are particularly considered because these results are important not only in theoretical chemical kinetics but also in practical applications. The work on 5 chemical reactions are reviewed in detail. These are: $D + H_2$, $Cl + H_2$, $H + O_2$, $CH_3 + CH_3$, and $H + NO_2$.

1. Introduction.

The field of thermal gas phase chemical kinetics and, in particular, bimolecular reactions, has continually expanded since the first such study by Bodenstein ~100 years ago [1]. There are two main reasons for this continuing interest. First, most of these reactions occur with activation barriers that can be accurately determined from the thermal experiment. These barriers can then be compared to theoretical potential energy surfaces from modern *ab initio* electronic structure calculations that in turn can then serve as the basis for theoretically estimating the rate behavior with modern dynamical theories. Hence, the first reason for this type of study is to support theoretical chemistry and vice versa. However, there is a second and equally important motivation that is practical. A number of naturally occurring and anthropogenically altered environmental systems are now known to be influenced by the thermal rates of chemical processes. These include the earth's mesosphere, stratosphere, and troposphere; the various planetary atmospheres; interstellar clouds; air pollution; and high temperature incineration and, in general, combustion chemistry. Most gas phase kinetics investigations are currently being supported for use in developing mechanistic descriptions for these practical systems.

In this paper, current work in the field of high temperature bimolecular rate processes is considered. There have been two significant experimental developments in the past ~20 years, namely, the high temperature fast-flow reactor (HTFFR) method with the related high temperature photochemistry (HTP) option [2] and the flash or laser photolysis-shock tube (F/LP-ST) technique [3]. Both can be used for temperatures in excess of 1000 K; however, in favorable cases, the latter can be extended to ~2500 K. Hence, the combination of the F/LP-ST and the classic thermal shock tube experiment [4] has proven to be particularly powerful in providing rate constant data over very large temperature ranges. There are two recent reviews of high temperature bimolecular reactions studied in shock tubes that are particularly relevant [5,6].

In the remainder of the paper, selected examples of shock tube studies from our laboratory will be considered. In particular, the experimental and theoretical results on the simplest and most important reaction of all, namely $H + H_2$ (and deuterated analogs), will be discussed in order to illustrate the first motivation above. Subsequently, results on another important "theoretical test case" reaction, $Cl + H_2$ (and D_2) will be reviewed. In an attempt to illustrate the second motivation, recent results on the most important reaction in all combustion systems, $H + O_2 \rightarrow OH + O$, will be discussed. A vibrationally hot species is initially formed followed by a forward dissociation process that is higher lying than reactants. High temperature results will then be presented for two barrierless bimolecular rate processes that are also chemical activation cases, namely, $2CH_3 \rightarrow C_2H_5 + H$ and $H + NO_2 \rightarrow OH + NO$.

2. Experimental.

The F/LP-ST technique has been described previously [3,7]. Figure 1 shows a schematic diagram of the shock tube apparatus. He is used as the driver gas, and the test gas is mostly Ar (or Kr) with small quantities of added source and reactant molecules. The source molecule on photolysis gives the transient species that is spectroscopically measured as it reacts with the reactant

molecules. Two different molecules are generally used requiring accurate premixture determinations with capacitance manometers.

Experiments are performed behind reflected shock waves where the hot gas is effectively stagnant and not flowing. Flash or laser photolysis occurs after the reflected shock wave has traversed the spectroscopic observation station. Transient species are observed radially across the shock tube. Reflected shock pressure and temperature are kept low so that thermal decomposition is minimized. The initial transient species concentration is initiated by photolysis, and its decay is then totally determined by bimolecular reaction. Diffusion out of the viewing zone is negligibly slow on the experimental time scale. This experiment is then an adaptation of the static kinetic spectroscopy experiment with the reflected shock serving as a source of high temperature and density; i. e., shock heating is equivalent to a pulsed furnace.

Similar thermally induced experiments [4] can be carried out if a molecule exists that thermally decomposes to transients on a shorter time scale than that for transient decay through bimolecular reaction. Additionally, the reactant molecule must be thermally stable under thermodynamic conditions where the source has completely dissociated. In this type of experiment, the zero time is set by shock wave passage past the observation station. In both types of experiments, pressure transducers, mounted equidistant along the shock tube, are used to measure the incident shock wave velocity. Temperature and density in the reflected shock wave regime are calculated from incident shock velocities through relations and correction procedures [8] that account for boundary layer perturbations. Since the initial composition is known, the thermodynamic state of the system is fully determined.

In the atomic resonance absorption spectrometric (ARAS) adaptation of the methods, atomic species are spectroscopically monitored as a function of time. H- [7,9], D- [7,10], O- [7,11], N- [12], Cl- [13] and I-atom [14] reactions have been studied. Beer's law holds if absorbance, (ABS), is kept low, and then $(ABS) \equiv -\ln(I/I_0)$ (I and I_0 are transmitted and incident intensities of the resonance light, respectively) is proportional to the atomic concentration. If the decay of atom A is controlled by a bimolecular reaction, $A + R$, where R is the stable reactant molecule, then the decay rate is pseudo-first-order provided $[R] \gg [A]$. Because (ABS) is proportional to $[A]$, observation of $(ABS)_t$ is sufficient to determine the decay constant. Values for k_{bim} for each experiment are then determined by dividing the decay constant by $[R]$. The results from many experiments are usually displayed as Arrhenius plots. If a reaction is pressure dependent, experiments can also be carried by varying total density. Termolecular reactions can therefore be studied. In certain cases, chemical isolation is not possible, and numerical chemical simulations of the important chemical reactions then become necessary. In these cases, concentration profiles have to be derived, and this means that the atomic absorption curve-of-growth has to be carefully determined.

Lastly, we have recently modified the apparatus so that multi-pass optics can be incorporated into the photometric system [15]. The optical path length is 105 cm, and this technique has now been successfully applied to detect, CF_2 [16] and OH [17] radicals in two kinetics investigations.

3. Results and Discussion.

In the sections to follow, rate data for 5 bimolecular reactions are reviewed. The first two will be compared to theoretical calculations that use modern methods for both potential energy evaluation and dynamical estimation for thermal rate constants. The latter three involve the formation of vibrationally excited species that subsequently forward dissociate into products.

3.1 $D + H_2 \rightarrow HD + H$ and $H + D_2 \rightarrow HD + D$. FP-ST experiments have been carried out on these reactions over the temperature range, ~650 to 2200 K [9,10], and the absolute rate constant results have already been reviewed [6,7,18]. Because of the historical importance of these reactions in gas phase chemical kinetics, there are a large number of earlier lower temperature studies primarily due to Le Roy and coworkers [19], Westenberg and de Haas [20], and Jayaweera and Pacey [21]. All sets of data for $D + H_2$ have been combined to give the Arrhenius plot shown in Fig. 2. Both reactions have been evaluated

giving analytic expressions for the rate behavior over quite large temperature ranges [9,10].

Because these are the simplest reactions, they have served from the beginnings of gas phase chemical kinetics as a test case for theory. The theoretical potential energy surface for $\text{H} + \text{H}_2$ is known with sufficient accuracy that adjustments of vibrational frequencies and/or total electronic binding energy are not allowed; i. e., electronic structure and subsequent dynamics calculations can no longer be parameterized. *Ab initio* potential energy calculations are from Liu [22], Siegbahn and Liu [23], Truhlar and Horowitz [24], Varandas et al. [25], Diedrich and Anderson [26], and Boothroyd et al. [27] giving the LSTH [22-24], DMBE [25], and BKMP [27] surfaces. The LSTH surface has then been used in variational transition state theory (VTST) [28] and also in reduced dimensionality collinear exact quantum bend (CEQB) [29] calculations to estimate the thermal rate behavior for $\text{D} + \text{H}_2$ and $\text{H} + \text{D}_2$, and the results are in fairly good agreement with the experimental evaluations. Garrett et al. [30] calculated VTST rate constants for $\text{D} + \text{H}_2$ and Michael et al. [18] calculated CEQB rate constants for both reactions with the DMBE potential energy surface. These results show improvement over the original LSTH calculations particularly in the low temperature region where tunneling is dominate.

In addition to the thermal studies, researchers have also investigated the two processes using well established experimental dynamical methods [31]. These experiments involve hot hydrogen atoms and therefore sample the potential energy surface well above the potential barrier height. Several calculations using the LSTH surface have been carried out with modern quantum scattering theory, and one of the most notable explains the differential cross section data at 1.29 eV relative energy quite well if the geometric phase effect is taken into account [32]. This agreement suggests that the LSTH surface is relatively accurate above the barrier height.

Since the thermal results sample the potential energy surface below the barrier, we suggested [18] that quantum scattering theory should also be used to rationalize these data. Subsequently, studies have recently appeared by Park and Light [33] and Mielke et al. [34], and, in latter case, excellent agreement with the $\text{D} + \text{H}_2$ experiments is obtained if the DMBE surface is used. The newer BKMP surface gives worse agreement with experiment particularly in the lower temperature tunneling region. Mielke et al. also compare their cumulative reaction probabilities with Wang and Bowman's [35] modified J-shifted CEQB method on the DMBE surface. This theory-to-theory comparison is exceptionally good. Hence, the thermal rate behavior predicted by Wang and Bowman agrees well with Mielke et al. and also with experiment as seen in Fig. 2. It should be noted that the new CEQB results are almost identical to the earlier calculation on the DMBE surface [18] and also to DMBE surface based simple conventional transition state theory calculations with Wigner tunneling (CTST/W) from 300 to 2200 K [9,10].

The agreement between theory and experiment shown in Fig. 2 is impressive. If additional quantum scattering calculations were to be carried out on $\text{H} + \text{D}_2$ the CEQB-DMBE results [18] would undoubtedly be reproduced, and therefore, such calculations are probably not necessary. However, Fleming and coworkers have measured the T-dependence of $\text{Mu} + \text{H}_2$ and D_2 [36]. The Mu-atom has 1/9 the mass of H, and therefore, tunneling is still quite significant at higher temperatures than in $\text{H} + \text{D}_2$ and $\text{D} + \text{H}_2$. Even though VTST [37] and quantum scattering [38] calculations on the LSTH surface have already been reported, a rigorous quantum scattering calculation using the DMBE surface would be particularly interesting for rationalizing these data.

It is true that the theoretical $\text{H} + \text{H}_2$ work to date represents the most significant theoretical development in dynamics and kinetics since the first experiments by Bodenstein [1]. For nearly 70 years, countless theoreticians have been involved in this effort. The $\text{H} + \text{H}_2$ reaction served as the inspiration for transition state theory and for developing more accurate electronic structure calculational methods. To many experimentalists, the credibility of all other

theoretical advances in dynamics and kinetics has really rested on the solution to the $\text{H} + \text{H}_2$ problem. In view of the fact that good agreement has been obtained between the above mentioned experiments and theory, one is tempted to declare that the $\text{H} + \text{H}_2$ reaction is now solved. Clearly theoreticians should be congratulated on this major accomplishment.

3.2 $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ and $\text{Cl} + \text{D}_2 \rightarrow \text{DCl} + \text{D}$. Since the work of Nernst [39], this reactive system has also served as one of the test cases for thermal bimolecular reaction rate theory [40-42]. With the Cl-atom ARAS method bimolecular rate constants have been measured between 296 and 3000 K using both thermally and photochemically (LP-ST) produced Cl-atoms [43]. Equilibrium constants were also measured and were found to be in good agreement with JANAF values [44]. When combined with several lower temperature studies, the evaluated experimental results can be expressed by,

$$k_{\text{Cl},\text{H}_2} = 2.52 \times 10^{-11} \exp(-2214 \text{ K}/T) \text{ for } 199 \leq T \leq 354 \text{ K}, \quad (1)$$

$$k_{\text{Cl},\text{H}_2} = 1.57 \times 10^{-16} T^{1.72} \exp(-1544 \text{ K}/T) \text{ for } 354 \leq T \leq 2939 \text{ K}, \text{ and} \quad (2)$$

$$k_{\text{Cl},\text{D}_2} = 2.77 \times 10^{-16} T^{1.62} \exp(-2162 \text{ K}/T) \text{ for } 255 \leq T \leq 3020 \text{ K}, \quad (3)$$

all in molecular units. Arrhenius plots of these evaluations are shown in Fig. 3.

Tucker et al. [42] considered 11 potential energy surfaces, some of which had been previously derived using semi-empirical methods, in their improved canonical variational transition state theory with least action ground-state transmission coefficient (ICVT-LAG) calculations. These rate constant predictions were compared to the lower temperature experimental data obtained before 1985. In our work [43], we continued the comparison into the high temperature region (i. e., with eqns. (1)-(3)) using the CTST/W method. At this level of theory, none of the 11 surfaces from Tucker et al. can explain the data. Harding has performed new high level *ab initio* electronic structure calculations [45], and the CTST/W comparison to experiment is still unsatisfactory. CTST calculations using Eckart tunneling, CTST/E, were also carried out, and there was no significant improvement in predictions. The data summarized by eqns. (1)-(3) and plotted in Fig. 3 exhibits too little curvature, suggesting that the barrier height and/or bending or imaginary vibrations are in error for all 12 of the surfaces. Accordingly, these quantities are parametrically varied until good agreement is found for $\text{Cl} + \text{H}_2$ at the CTST/E level of calculation. For $\text{Cl} + \text{H}_2$, $V^\ddagger = 6.77 \text{ kcal mole}^{-1}$, $v_b = 782 \text{ cm}^{-1}$, and $v_i = 1000i \text{ cm}^{-1}$ gives the CTST/E theoretical prediction shown in Fig. 3. These saddle point properties are consistently transformed for $\text{Cl} + \text{D}_2$, and this prediction is also shown in Fig. 3. Even though the comparisons are excellent, the derived saddle point properties are not unique. Similar agreement can be obtained with other combinations of $V^\ddagger$, v_b , and v_i at the CTST/E level. Clearly, quite different conclusions about the saddle point and the reaction path might be found if these data and the new hot atom dynamical data of Alagia et al. [46] were to be considered using modern dynamical theory in exactly the same way as in the $\text{H} + \text{H}_2$ reaction. Such an approach might reconcile the experiments with the newest and most accurate potential energy surface by Harding [45].

3.3 $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ and $\text{D} + \text{O}_2 \rightarrow \text{OD} + \text{O}$. This reaction is the most important reaction in combustion. It is the principal branching reaction in the oxidation of H_2 but also occurs in the oxidation mechanisms of all hydrocarbons [47]. This branching reaction has the highest enthalpy of all reactions that significantly consume O_2 with most other O_2 consuming processes being linear propagation reactions. Because of this it is usually the most important "slow step" in combustion mechanisms and is therefore often rate controlling. Since it is so important, the rate data have been reviewed many times [48]. There are a number of notable experimental studies on $\text{H} + \text{O}_2$ dating from 1967 to the present [49,50]; however, there has been only one direct study [49m] reported

for $D + O_2$. As is to be expected, there is a substantial theoretical effort on these reactions [51].

The data and theoretical calculations up to 1992 have already been evaluated and reviewed [48d]; however, in the past three years there have been additional experimental work and developments. Ryu et al. [50] have made new measurements, have included new measurements by Yang et al. [49o], and have incorporated a new interpretation of earlier results by Yu et al. [49p] in an evaluation that takes into account all of the earlier direct studies [49]. This grand evaluation yields the result in molecular units,

$$k_{H,O_2} = 1.30 \times 10^{-10} \exp(-7105 \text{ K}/T) \text{ for } 960 \leq T \leq 5330 \text{ K}, \quad (4)$$

Schott's experiments [49c] and Miller's [51a-c] theory both suggested a negative T-dependence in the A-factor, and this catalyzed the new interest starting in ~1981. Quasiclassical trajectory calculations (QCT) [51a-c] on the Melius-Blint potential energy surface [52] were used to rationalize the negative T-dependence as being due to increased re-crossing as temperature increases; however, it has subsequently been shown that this surface is in error. More recently, Varandas and coworkers have used their DMBE IV surface in QCT, QCT-quantum mechanical threshold (labeled QMT), and QCT-internal energy quantum mechanical threshold (labeled IEQMT) calculations [51i,j], and their results at 5 temperatures ranging from 1000-3000 K indicate that re-crossing exists but has no major effect because their implied A-factor is not strongly T-dependent in agreement with eqn. (4). These workers have also theoretically examined the rate behavior for $D + O_2$ and find an isotope effect that is near to unity in agreement with experiment [49m].

Lastly, this new evaluation, eqn. (4), is only ~20-40% higher than the recommendation of Baulch et al. [48a]. This 1972 evaluation was based primarily on induction period and explosion limit measurements in the H_2/O_2 system showing that these early measurements were of high quality.

3.4 $CH_3 + CH_3 \rightarrow C_2H_5 + H$. This reaction was studied by observing H-atom formation rates using the ARAS technique in the thermal dissociation of CH_3I [53]. CH_3I dissociation is fast compared to the subsequent bimolecular dissociative recombination. In the analysis, all of the absolute $[H]_t$ results were fitted using numerical simulations on a mechanism that consisted of several reactions most of which were known. The main complication came from thermal cracking of CH_3 to give either $CH_2 + H$ or $CH + H_2$. These processes dominated above ~2100 K, and therefore, the useful temperature range for determining the rate behavior was limited to 1224-1938 K. Because the initially formed C_2H_5 -radical is thermally unstable above 1224 K, it rapidly decomposes to $C_2H_4 + H$ on a time scale that is short compared to the title reaction. Hence, the system effectively gives $C_2H_4 + 2H$ at the dissociative recombination rate. The rate constants can be expressed in Arrhenius form by,

$$k_{CH_3+CH_3} = (5.25 \pm 1.19) \times 10^{-11} \exp(-7384 \pm 312 \text{ K}/T), \quad (5)$$

in molecular units for $1224 \leq T \leq 1938 \text{ K}$. As can be seen in Fig. 4, eqn. (5) is only 15-25% lower than earlier results by Frank and Braun-Unkoff [54] (1320-2300 K) and is therefore in excellent agreement.

There is an important theoretical implication from eqn. (5). Using strong collision RRR theory for the CH_3 recombination, C_2H_6 formation rate constants are given by,

$$k_r = k_{add} \int_{E_0}^{\infty} \frac{\beta \omega f(\epsilon) d\epsilon}{(k_{fe} + k_{be} + \beta \omega)}, \quad (6)$$

where k_{add} , k_{fe} , k_{be} , β , ω , and $f(\epsilon)$ refer to (a) the high pressure rate constant for CH_3 recombination, (b) the RRR (or RRKM) rate constant for forward dissociation, (c) the RRR (or RRKM) rate constant for backward dissociation

at the threshold energy, ε_0 , (d) the collisional deactivation efficiency, (e) the collision rate constant, and (f) the RRK (or RRKM) normalized distribution function for a given temperature, respectively. Eqn. (6) shows that $k_\infty = k_{add}$. Rate constants based on H formation from $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{H}$ are,

$$k^{bi} = k_{add} \int_{\varepsilon_0}^{\infty} \frac{k_f f(\varepsilon) d\varepsilon}{(k_f \varepsilon + k_b \varepsilon + \beta \omega)}, \quad (7)$$

implying that at high temperature and low pressure, $k_{\text{lim } P \rightarrow 0}^{bi} \leq k_{add}$. The A-factor from eqn. (5) is $5.25 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is already the collision rate constant corrected for the electronic degeneracy ratio. In contrast, recombination experiments and analysis, based on eqn. (6), by Walter et al. [55] suggest decreasing k_{add} with increasing temperature. Their extrapolated estimate at 2000 K would be $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This disagreement will require a continuing theoretical assessment on this important reaction.

3.5 $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$. Rate constants were measured over the temperature range, 1100 to 2000 K, in reflected shock wave experiments using two different methods of analysis [17]. In both methods, the source of H-atoms was from $\text{C}_2\text{H}_5\text{I}$ decomposition followed by the faster subsequent dissociation of C_2H_5 . In the first method, absolute $[\text{H}]_t$ was measured with the ARAS technique. Experiments were performed under such low $[\text{C}_2\text{H}_5\text{I}]_0$ that the decay of H-atoms was strictly first-order. The second method utilized a multi-pass optical system [15] for observing the product OH-radical. A resonance lamp was used as the absorption source. Extensive calibration was required giving a modified Beer's law description of the curve-of-growth for use in converting absorption data to absolute $[\text{OH}]_t$ from which rate constants were determined. The combined results from the two methods give,

$$k_{\text{H},\text{NO}_2} = (1.61 \pm 0.41) \times 10^{-10} \text{ for } 1100 \leq T \leq 2000 \text{ K}, \quad (8)$$

in molecular units. These results have been compared to earlier work at lower temperatures [56], and the combined database yields the temperature independent value $k_{\text{H},\text{NO}_2} = (1.45 \pm 0.30) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $195 \leq T \leq 2000 \text{ K}$. The combined results are shown in Fig. 5 along with this T-independent value. We are currently carrying out a theoretical analysis using *ab initio* electronic structure calculations combined with modern dynamical theory in order to rationalize the surprising T-invariance [17].

4. Conclusions.

The field of chemical research started by Bodenstein [1] 100 years ago, gas phase chemical kinetics, is healthy. Experimental methods continue to mature, but the exciting field of theoretical kinetics and dynamics is still being formulated and tested against experimental results. Because these tests are always going to be necessary to assess success, chemical kinetics will remain a vibrant field in chemistry even though it is continually being de-emphasized in academic chemistry departments at least in the United States. Fortunately for theoretical chemistry, the need to model complex chemical systems in the practical disciplines has supplied intellectual support for continued work, and therefore, much of the current work is being carried out in departments of engineering in private and state supported laboratories and universities throughout the world. This trend will probably continue into the next century, and it is undoubtedly true that "advances in experimental chemical kinetics" will still be a topic of interest 200 years after Max Bodenstein.

5. Acknowledgments.

The author wants to thank former colleagues, J. R. Fisher and K. S. Shin, and present colleagues, Drs. K. P. Lim, S. S. Kumaran, M.-C. Su, and A. F. Wagner for thorough readings of the manuscript. This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-Eng-38.

6.0 References.

- 1 M. Bodenstein, Z. Physik. Chem. **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).
- 2 (a) A. Fontijn and S. C. Kurzius, Chem. Phys. Lett. **13**, 507 (1972); (b) W. Felder, A. Fontijn, H. N. Volltrauer, and D. R. Voorhees, Rev. Sci. Instr. **51**, 195 (1980).
- 3 (a) G. Burns and D. F. Hornig, Can. J. Chem. **38**, 1702 (1960); (b) J. Ernst, H. Gg. Wagner, and R. Zellner, Ber. Bunsen-Ges. Phys. Chem. **82**, 409 (1978); (c) K. J. Niemitz, H. Gg. Wagner, and R. Zellner, Z. Phys. Chem. (Frankfurt am Main) **124**, 155 (1981); (d) J. V. Michael, J. W. Sutherland and R. B. Klemm, Int. J. Chem. Kin. **17**, 315 (1985).
- 4 J. N. Bradley, *Shock Waves in Chemistry and Physics*, Wiley, New York, NY, 1962.
- 5 W. Tsang and A. Lifshitz, Annu. Rev. Phys. Chem. **41**, 559 (1990).
- 6 J. V. Michael and K. P. Lim, Annu. Rev. Phys. Chem. **44**, 429 (1993).
- 7 (a) J. V. Michael, *Advances in Chemical Kinetics and Dynamics*, Vol. 1, J. R. Barker, Ed., JAI Press, Greenwich, CT, 1992, p. 47. (b) J. V. Michael, *Isotope Effects in Gas-Phase Chemistry*, ACS Symp. Ser. 502, J. A. Kaye, Ed., American Chemical Society, Washington, 1992, p. 80.
- 8 (a) J. V. Michael and J. W. Sutherland, Int. J. Chem. Kinet. **18**, 409 (1986). (b) J. V. Michael and J. R. Fisher, *Seventeenth International Symposium on Shock Waves and Shock Tubes*; Y. K. Kim, Ed.; American Institute of Physics, New York, NY, 1989, p. 210.
- 9 J. V. Michael, J. Chem. Phys. **92**, 3394 (1990).
- 10 J. V. Michael and J. R. Fisher, J. Phys. Chem. **94**, 3318 (1990).
- 11 (a) J. V. Michael, J. Chem. Phys. **90**, 189 (1989). (b) M.-C. Su, K. P. Lim, J. V. Michael, J. Hranisavljevic, Y. M. Xun, and A. Fontijn, J. Phys. Chem. **98**, 8411 (1994).
- 12 (a) D. F. Davidson and R. K. Hanson, Int. J. Chem. Kinet. **22**, 843 (1990). (b) M. Koshi, M. Yoshimura, K. Fukuda, H. Matsui, K. Saito, M. Watanabe, A. Imamura, and C. Chen, J. Chem. Phys. **93**, 8703 (1990). (c) J. V. Michael and K. P. Lim, J. Chem. Phys. **97**, 3228 (1992).
- 13 S. S. Kumaran, K. P. Lim, J. V. Michael, and A. F. Wagner, J. Phys. Chem. **99**, 8673 (1995).
- 14 S. S. Kumaran, M.-C. Su, K. P. Lim, and J. V. Michael, Chem. Phys. Lett., in press.
- 15 M.-C. Su, S. S. Kumaran, K. P. Lim, and J. V. Michael, Rev. Sci. Instr., in press.
- 16 S. S. Kumaran, M.-C. Su, K. P. Lim, J. V. Michael, and A. F. Wagner, J. Phys. Chem., submitted.
- 17 M.-C. Su, S. S. Kumaran, K. P. Lim, A. F. Wagner, L. B. Harding, and J. V. Michael, in preparation.
- 18 J. V. Michael, J. R. Fisher, J. M. Bowman, and Q. Sun, Science **249**, 269 (1990).
- 19 (a) B. A. Ridley, W. R. Schulz, and D. J. Le Roy, J. Chem. Phys. **44**, 3344 (1966). (b) D. N. Mitchell and D. J. Le Roy, J. Chem. Phys. **58**, 3449 (1973). (c) W. R. Schulz and D. J. Le Roy, Can. J. Chem. **42**, 2480 (1964). (d) W. R. Schulz and D. J. Le Roy, J. Chem. Phys. **42**, 3869 (1965).
- 20 A. A. Westenberg and N. de Haas, J. Chem. Phys. **47**, 1393 (1967).
- 21 I. S. Jayaweera and P. D. Pacey, J. Phys. Chem. **94**, 3614 (1990).
- 22 B. Liu, J. Chem. Phys. **58**, 1925 (1973).
- 23 P. Siegbahn and B. Liu, J. Chem. Phys. **68**, 2457 (1978).
- 24 D. G. Truhlar and C. J. Horowitz, J. Chem. Phys. **68**, 2466 (1978).
- 25 A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, J. Chem. Phys. **86**, 6258 (1987).
- 26 D. L. Diedrich and J. B. Anderson, Science **258**, 786 (1992).
- 27 A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, J. Chem. Phys. **95**, 4343 (1991).
- 28 B. C. Garrett and D. G. Truhlar, Proc. Natl. Acad. Sci. **76**, 4755 (1979). (b) *ibid.*, J. Chem. Phys. **72**, 3460 (1980).

- 29 Q. Sun and J. M. Bowman, *J. Phys. Chem.* **94**, 718 (1990).
- 30 B. C. Garrett, D. G. Truhlar, A. J. C. Varandas, and N. C. Blais, *Int. J. Chem. Kinet.* **18**, 1065 (1986).
- 31 T. N. Kitsopoulos, M. A. Buntine, D. P. Baldwin, R. N. Zare, and D. W. Chandler, *Science* **260**, 1605 (1993), and references therein.
- 32 Y.-S. M. Wu and A. Kuppermann, *Chem. Phys. Lett.*, in press.
- 33 T. J. Park and J. C. Light, *J. Chem. Phys.* **94**, 2946 (1991); **96**, 8853 (1992).
- 34 S. L. Mielke, G. C. Lynch, D. G. Truhlar, and D. W. Schwenke, *J. Phys. Chem.* **98**, 8000 (1994).
- 35 D. Wang and J. M. Bowman, *J. Phys. Chem.* **98**, 7994 (1994).
- 36 I. D. Reid, D. M. Garner, L. Y. Lee, M. Senba, D. J. Arseneau, and D. G. Fleming, *J. Chem. Phys.* **86**, 5578 (1987).
- 37 D. K. Biondi, D. C. Clary, J. N. L. Connor, B. C. Garrett, and D. G. Truhlar, *J. Chem. Phys.* **76**, 4986 (1982).
- 38 G. C. Schatz, *J. Chem. Phys.* **83**, 3441 (1985).
- 39 W. Nernst, *Z. Elektrochem.* **24**, 335 (1918).
- 40 A. Wheeler, B. Topley, and H. Eyring, *J. Chem. Phys.* **4**, 178 (1936).
- 41 R. E. Weston, Jr., *J. Phys. Chem.* **83**, 61 (1979).
- 42 For a review see, S. C. Tucker, D. G. Truhlar, B. C. Garrett, and A. D. Isaacson, *J. Chem. Phys.* **82**, 4102 (1985).
- 43 S. S. Kumaran, K. P. Lim, and J. V. Michael, *J. Phys. Chem.* **101**, 9587 (1994).
- 44 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **14**, Suppl. 1 (1985).
- 45 L. B. Harding, private communication.
- 46 M. Alagia, N. Balucani, P. Casavecchia, E. H. van Kleef, and G. G. Volpi, 13th International Symposium on Gas Kinetics, paper A4, Dublin, Sept., 1994.
- 47 (a) C. K. Westbrook and F. L. Dryer, *Prog. Energy Combust. Sci.* **10**, 1 (1984). (b) J. A. Miller and C. T. Bowman, *ibid.* **15**, 287 (1989), and references therein.
- 48 (a) D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Data for High Temperature Reactions, Vol. 1*, Butterworths, London (1972). (b) N. Cohen, and K. R. Westberg, *J. Phys. Chem. Ref. Data* **12**, 531 (1983). (c) J. Warnatz, *Combustion Chemistry*, W. C. Gardiner, Jr., Ed., Springer-Verlag, New York, 1984. (d) J. V. Michael, *Prog. Energy Combust. Sci.* **18**, 327 (1992).
- 49 (a) D. Gutman and G. L. Schott, *J. Chem. Phys.* **46**, 4576 (1967). (b) D. Gutman, E. A. Hardwidge, F. A. Dougherty, and R. W. Lutz, *J. Chem. Phys.* **47**, 4400 (1967). (c) G. L. Schott, *Symp. (Int.) Combust.*, [Proc.] **12**, 569 (1968). (d) G. L. Schott, *Combust. Flame* **13**, 357 (1973). (e) K. M. Pamidimukkala and G. B. Skinner, *Thirteenth International Symposium on Shock Waves and Shock Tubes*, SUNY Press, Albany, 1981, p. 585. (g) P. Frank and Th. Just, *Ber. Bunsen-Ges. Phys. Chem.* **89**, 181 (1985). (h) N. Fujii and K. Shin, *Chem. Phys. Lett.* **151**, 461 (1988). (i) N. Fujii, T. Sato, H. Miyama, K. S. Shin, and W. C. Gardiner, Jr., *Current Topics in Shock Waves, Seventeenth International Symposium on Shock Waves and Shock Tubes*, Y. W. Kim, Ed., American Institute of Physics, New York, 1989, p. 456. (j) A. N. Pirraglia, J. V. Michael, J. W. Sutherland, and R. B. Klemm, *J. Phys. Chem.* **93**, 282 (1989). (k) D. A. Masten, R. K. Hanson, and C. T. Bowman, *J. Phys. Chem.* **94**, 7119 (1990). (l) T. Yuan, C. Wang, C.-L. Yu, M. Frenklach, and M. J. Rabinowitz, *J. Phys. Chem.* **95**, 1258 (1991). (m) K. S. Shin and J. V. Michael, *J. Chem. Phys.* **95**, 262 (1991). (n) H. Du and J. P. Hessler, *J. Chem. Phys.* **96**, 1077 (1992). (o) H. Yang, W. C. Gardiner, Jr., K. S. Shin, and N. Fujii, *Chem. Phys. Lett.* **231**, 449 (1994). (p) C.-L. Yu, M. Frenklach, D. A. Masten, R. K. Hanson, and C. T. Bowman, *J. Phys. Chem.* **98**, 4770 (1994).
- 50 S.-O. Ryu, S. M. Hwang, and M. J. Rabinowitz, *J. Phys. Chem.*, in press.

- 51 (a) J. A. Miller, *J. Chem. Phys.* **74**, 5120 (1981). (b) *ibid.* **75**, 5349 (1981). (c) *ibid.* **84**, 6170 (1986). (d) S. N. Rai and D. G. Truhlar, *J. Chem. Phys.* **79**, 6046 (1983). (e) C. J. Cobos, H. Hippler, and J. Troe, *J. Phys. Chem.* **89**, 342 (1985). (f) J. Troe, *ibid.* **90**, 3485 (1986). (g) D. C. Clary and H. J. Werner, *Chem. Phys. Lett.* **112**, 346 (1984). (h) M. M. Graff and A. F. Wagner, *J. Chem. Phys.* **92**, 2423 (1990). (i) M. R. Pastrana, L. A. M. Quintales, J. Brandão, and A. J. C. Varandas, *J. Phys. Chem.* **94**, 8073 (1990). (j) A. J. C. Varandas, J. Brandão, and M. R. Pastrana, *J. Chem. Phys.* **96**, 5137 (1992).
- 52 C. F. Melius and R. J. Blint, *Chem. Phys. Lett.* **64**, 183 (1979).
- 53 K. P. Lim and J. V. Michael, *Symp. (Int.) Combust., [Proc.]* **25**, 713 (1994).
- 54 P. Frank and M. Braun-Unkloff, *Proceedings of the Sixteenth Symposium on Shock Tubes and Waves*, VCH, Weinheim, 1988, p. 379.
- 55 D. Walter, H.-H. Grotheer, J. W. Davies, M. J. Pilling, and A. F. Wagner, *Symp. (Int.) Combust., [Proc.]* **23**, 107 (1990).
- 56 (a) W. A. Rosser and H. Wise, *J. Phys. Chem.* **85**, 532, 2227 (1961). (b) P. G. Ashmore and B. J. Tyler, *Trans. Faraday Soc.* **58**, 1108 (1962). (c) L. F. Phillips and H. I. Schiff, *J. Chem. Phys.* **37**, 1233 (1962). (d) H. Gg. Wagner, U. Welzbacher, and R. Zellner, *Ber. Bunsenges. Phys. Chem.* **80**, 1023 (1976). (e) M. A. A. Clyne and P. B. Monkhouse, *J. Chem. Soc. Faraday Trans. II* **73**, 298 (1977). (f) P. P. Bemand and M. A. A. Clyne, *J. Chem. Soc. Faraday Trans. II* **73**, 394 (1977). (g) J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *J. Phys. Chem.* **83**, 2818 (1979). (h) S. J. Wategaonkar and D. W. Setser, *J. Chem. Phys.* **90**, 251 (1989). (i) T. Ko and A. Fontijn, *J. Phys. Chem.* **95**, 3984 (1991).

Figure 1. Schematic diagram of apparatus

Figure 2. Data points from Ref. 10 and 19-21. Line is Theoretical from Ref. 35.

Figure 3. Solid lines are experimental evaluations (Ref. 43). Dashed lines are from CTST/E theory (see text).

Figure 4. Points are from Ref. 53. Dashed line is eqn. (5). Solid line is from Ref. 54.

Figure 5. Data points from Ref. 17, 56g-i. Line is the T-independent evaluation.