J. Phys. Chem. A **2000,** *104,* 1965−1967 **1965**

COMMENTS

Comment on Rate Constants for Reactions of Tritium Atoms with H_2, D_2, and HD

Jay Srinivasan and Donald G. Truhlar*

Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455

Received: October 8, 1999

A recent paper in this journal by Aratono et al.[1] stated that "though there are some studies on the theoretical calculation of rate constants for the abstraction of H or D with H_2, HD, or D_2, no report has been published on the rate constants of T with them." We called the attention of Aratono et al. to a 1983 paper[2] in this journal that reported calculations on all three reactions. The calculations employed improved canonical variational theory (ICVT) with Marcus−Coltrin-path vibrationally adiabatic ground-state (MCPVAG) transmission coefficients, which is appropriate for small curvature of the reaction path. References 1 and 2 employed the same potential energy surface, namely the LSTH surface.[3] Thus, it was of interest to compare the calculated rate constants. Fortunately, both studies reported results for 200 and 300 K, so such a comparison was possible.

We found that the differences between the two sets of results were surprisingly large. In four cases the rate constants of ref 1 were larger, and the average factor in these cases was 3.2. In the other four cases the rate constants of ref 2 was larger, and the average factor in these cases was 2.7. These comparisons and our new calculations reported below prompted Aratono et al. to re-check their calculations; they found an error and revised their results.[4] The comparison of the revised results[4] of Aratono et al. and the 1983 results of ref 2 is presented in the columns of Table 1 that are labeled ref 1 (revised) and 1983. These revised calculations show that in four cases the rate constants of ref 1 are larger, the average factor being 2.4 and that in four other cases the 1983 rate constants are larger, the average factor being 1.3. Thus, although the agreement is slightly better, there are still large quantitative differences.

Apparently, the H + H_2 reaction and its isotopic analogues still hold surprises and further work to understand the differences in various calculations would be valuable. We therefore performed new calculations in which we improved the 1983 treatment in three ways. (1) We used WKB anharmonicity[5] rather than Morse anharmonicity for the stretches. (2) We used quartic centrifugal oscillator (CO) anharmonicity[6,7] rather than uncoupled quadratic quartic (QQ) anharmonicity for the bends. (3) We used the least-action ground-state (LAG) approximation[8] for the transmission coefficient rather than MCPVAG transmission coefficients. This combination of methods (ICVT/LAG with WKB stretches and CO bends) has been widely validated against a large set of accurate quantal calculations.[9] Our new results with these three improvements are given in the final column of Table 1, and in the original version of this comment we noted that in four cases our new rate constant is larger than the value in ref 1 by an average factor of 2.3, and in four cases it is smaller by an average factor of 1.6. When Aratono et al. corrected their calculations in response to our results, their new results agreed very well with our new results. In three cases, their rate constant is smaller than ours by an average factor of 1.04, and in four cases their rate constant is larger than ours by an average factor of 1.13. These remaining differences are encouragingly small.

TABLE 1: Comparison of Calculated Rate Constants for the LSTH Surface in Units of cm^3 molecule^{-1} s^{-1}

reaction	*T*/K	ref 1 (revised)[a]	1983[b]	present[c]
T + H_2 → HT + H	200	1.8(−18)	1.01(−18)	1.87(−18)
	300	2.8(−16)	1.94(−16)	2.39(−16)
T + D_2 → DT + D	200	6.4(−20)	7.76(−20)	6.90(−20)
	300	2.9(−17)	3.49(−17)	2.62(−17)
T + HD → HT + D	200	4.1(−19)	1.04(−19)	4.15(−19)
	300	9.6(−17)	4.17(−17)	8.65(−17)
T + DH → DT + H	200	8.3(−20)	1.13(−19)	7.78(−20)
	300	2.6(−17)	3.20(−17)	2.22(−17)

[a] Taken from ref 4. [b] ICVT/MCPVAG with Morse stretches and QQ bends. [c] ICVT/LAG with WKB stretches and CO bends.

To ascertain which improvements made here are the most important, Table 2 gives results in which we made improvements in only two of these ways, but not all three. However, for convenience, rather than use the MCPVAG method for small-curvature tunneling, we employ the similar small-curvature semiclassical adiabatic ground-state[10] (SCSAG) method. Table 2 also gives results for the microcanonical optimized multidimensional tunelling[9,11] (μOMT) method, which has also been validated against a large set of accurate quantal results and which does almost as well on the average as the LAG method.[9] Finally, we double checked the effect of substituting the more recent double many-body expansion[12] (DMBE) potential energy surface for the LSTH one, and these results are presented in the last column of Table 2.

We draw several conclusions from Table 2. To make these conclusions quantitative, we will define the percentage unsigned deviation between any two numbers x and y as $200 \times |x - y|/(x + y)$. First of all, we note that the average deviation between SCSAG (Table 2) and MCPVAG (Table 1) is only 16%, and the average deviation between SCSAG and μOMT is only 7% (coming almost entirely from the largest curvature case, T + HD). The LAG method, however, differs from the μOMT method by 26% on average (and from the SCSAG method by 30% on average). In principle, the LAG method involves a greater degree of optimization than μOMT, and one might have expected that LAG would always yield more tunneling than μOMT. But LAG and μOMT involve quite different approaches to the small-curvature limit,[13] so neither is an automatic bound on the other.

The quadratic-quartic treatment of the bend agrees with the more accurate centrifugal oscillator treatment with an average deviation of 2%, but the WKB and Morse treatments of the bend differ on average by 23% when the LAG method is used for tunneling.

Finally, Table 2 shows only a 4% average unsigned deviation between the LSTH and DMBE surfaces.

The present LAG results, using the CO treatment for bends and WKB treatment for stretches, had a 53% average unsigned deviation from the old results of ref 1. Comparison to the revised

10.1021/jp993598+ CCC: $19.00

TABLE 2: Comparison of Calculated Rate Constants (in units of cm^3 $molecule^{-1}$ s^{-1}) with Various Combinations of Methods for Two Potential Energy Surfaces[a]

reaction	*T*/K	LAG WKB CO LSTH	SCSAG Morse QQ LSTH	SCSAG WKB CO LSTH	LAG WKB QQ LSTH	LAG Morse CO LSTH	μOMT WKB CO LSTH	LAG WKB CO DMBE
$T + H_2 \rightarrow HT + H$	200	1.87(−18)	8.16(−19)	1.52(−18)	1.87(−18)	1.32(−18)	1.53(−18)	1.70(−18)
	300	2.39(−16)	1.57(−16)	2.41(−16)	2.39(−16)	1.90(−16)	2.47(−16)	2.32(−16)
$T + D_2 \rightarrow DT + D$	200	6.90(−20)	6.58(−20)	8.68(−20)	6.91(−20)	5.37(−20)	8.72(−20)	6.96(−20)
	300	2.62(−17)	2.93(−17)	3.40(−17)	2.64(−17)	2.33(−17)	3.48(−17)	2.81(−17)
$T + HD \rightarrow HT + D$	200	4.15(−19)	1.16(−19)	2.27(−19)	4.15(−19)	2.95(−19)	2.89(−19)	3.88(−19)
	300	8.65(−17)	4.13(−17)	6.29(−17)	8.67(−17)	7.16(−17)	7.80(−17)	8.52(−17)
$T + DH \rightarrow DT + H$	200	7.78(−20)	9.12(−20)	1.24(−19)	7.79(−20)	6.26(−20)	1.24(−19)	7.70(−20)
	300	2.22(−17)	2.65(−17)	3.21(−17)	2.23(−17)	1.90(−17)	3.28(−17)	2.32(−17)

[a] In all cases, the overbarrier contribution is calculated by ICVT; the column headings specify the tunneling approximation, the methods used for stretch and bend anharmonicity, and the potential energy surface.

TABLE 3: Vibrationally Adiabatic Ground-State Barrier Heights (Relative to Zero Point Energy of Reactants) in kcal/mol for the LSTH Surface

location	stretches	bends	T + HD	T + DH
saddle point	harmonic	harmonic	8.68	8.76
	Morse I[a]	quartic[a]	8.76	8.80
	WKB	centrifugal oscillator	8.76	8.80
barrier maximum[b]	harmonic	harmonic	8.81	8.96
	Morse I[a]	quartic[a]	8.87	8.99
	WKB	centrifugal oscillator	8.77	8.94

[a] Method used in ref 2. [b] Maximum of vibrationally adiabatic ground-state potential energy curve.

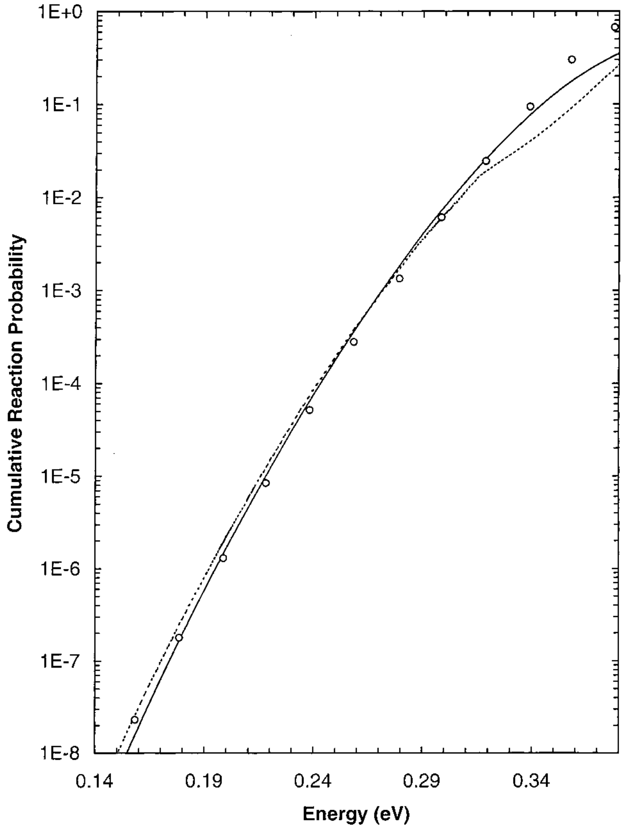

Figure 1. Comparison of quantum CRP (open circles, from ref 1) to the transmission probabilities calculated with WKB stretches and CO bends, for the $T + D_2$ reaction. Tunneling is treated using the SCSAG, μOMT, and LAG methods; the first two are indistinguishable to plotting accuracy and are shown as the solid line, and the LAG method is shown as a dashed line. The probabilities are shown as functions of total energy. The zero of total energy is placed at the zero point level of D_2. (In the present calculations the zero point energy of D_2 is 0.1878 eV). The transmission probabilities are for the first two states in the sum of eq 1, where the excited-state contribution is approximated by eq 2.

results[4] of Aratono et al. shows that this improves to 9% average unsigned deviation. Comparison of the revised results to our LAG calculations on the DMBE surface show that the average unsigned deviation in this case is also 9%.

Results using LAG, with CO for bends, but with Morse treatment for stretches, show a deviation of 29% from the revised results of ref 1. Results using WKB for stretches, but with QQ anharmonicity for bends show a deviation of 9% from the revised results of ref 1. Both these differences reflect the differences seen among the semiclassical calculations.

The average deviation of the present μOMT results from the revised calculations of ref 1 is 25%, showing that although μOMT has been shown[9] to be usually comparable to LAG, for the present case μOMT appears to be less accurate than LAG.

Aratono et al.[1] had reported that the vibrationally adiabatic ground-state barrier heights for the THD and TDH transition states and stated that the former is larger (by an unspecified amount). Reference 2 found that the latter is larger by 0.12 kcal/mol. Table 3 gives our own calculations of the ground-state vibrationally adiabatic barrier heights for $T + HD \rightarrow HT + D$ and $T + DH \rightarrow TD + H$. This table shows that, irrespective of whether one evaluates the vibrationally adiabatic barrier height at the saddle point or (more correctly) at the maximum of the vibrationally adiabatic ground-state potential curve[5,14] and whether one uses harmonic or anharmonic methods, TDH has (as expected) a higher value than THD. The new calculations of Aratono et al.[4] now agree with this result.

The cumulative reaction probability, *N*(*E*), may be defined as

$$N(E) = \sum_{\alpha} P_{\alpha}(E) \qquad (1)$$

where $P_{\alpha}(E)$ is the reaction probability for state α and is a function of the energy *E*. In the adiabatic theory of reactions, $P_{\alpha}(E)$ is replaced by the semiclassical probability of transmission through transition state level α.[15−17] The ground-state transmission probability, $P_0(E)$, provides an excellent estimate of the CRP for probability values less than 0.5. Figure 1 compares three of the present semiclassical methods to the quantal results of ref 1 for *N*(*E*) of the $T + D_2$ reaction at low energy. The present results include the first two terms in the sum with the first excited-state contribution approximated as

$$P_1(E) \cong P_0(E - (\epsilon_1 - \epsilon_0)) \qquad (2)$$

where ϵ_{α} is the energy of state α at its adiabatic transition state. For this reaction, we find that the SCSAG and μOMT transmission probabilities are identical over the whole energy range.

We find good agreement between the quantum and all semiclassical results for energies up to about 0.32 eV. The SCSAG data tend to agree better with quantum data than the

LAG results. Above 0.32 eV the semiclassical probability is less than the quantal CRP. This is consistent with the rate constant data where we see that, for T + D_2, the semiclassical result is slightly larger than the quantal result at 200 K and slightly smaller than the quantal result at 300 K. For the purposes of comparison, we note that the representative tunneling energy, i.e., the energy at which the quantity $P_0(E)$ exp($-\beta E$) is a maximum, is 0.313 eV at 200 K and 0.388 eV at 300 K for the LAG calculation, where E is the total energy relative to ϵ_0.

Acknowledgment. We thank Yao-Yuan Chuang for helpful discussions. This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences.

References and Notes

(1) Aratono, Y.; Matsumoto, T.; Takayanagi, T.; Kumada, T.; Komaguchi, K.; Miyazaki, T. *J. Phys. Chem. A* **1998**, *102*, 1501.

(2) Truhlar, D. G.; Grev, R. S.; Garrett, B. C. *J. Phys. Chem*. **1983**, *87*, 3415.

(3) Liu, B. *J. Chem. Phys*. **1973**, *58*, 1925. Siegbahn, P.; Liu, B. *J. Chem. Phys*. **1978**, *68*, 2457. Truhlar, D. G.; Horowitz, C. J. *J. Chem. Phys*. **1978**, *68*, 2457, **1979**, *71*, 1514 (E).

(4) Aratono, Y.; Matsumoto, T.; Takayanagi, T., Kumada, T., Komaguchi, K.; Miyazaki, T. Following reply. *J. Phys. Chem. A* **2000**, *104*, 1968.

(5) Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys*. **1984**, *81*, 309.

(6) Natanson, G. A. *J. Chem. Phys*. **1990**, *93*, 6589.

(7) Garrett, B. C.; Truhlar, D. G. *J. Phys. Chem*. **1991**, *95*, 10374.

(8) Garrett, B. C.; Truhlar D. G. *J. Chem. Phys*. **1983**, *79*, 4931.

(9) Allison, T. C.; Truhlar, D. G. In *Modern Methods for Multidimensional Dynamics Computations in Chemistry*; Thompson, D. L., Ed.; World Scientifc: Singapore, 1998; p 618.

(10) Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. *J. Phys. Chem*. **1981**, *85*, 3019.

(11) Liu, Y.-P.; Lu, D.-H.; González-Lafont, A.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc*. **1993**, *115*, 7806.

(12) Varandas, A. J. C.; Brown, F. B.; Mead, C. A.; Truhlar, D. G.; Blais, N. C. *J. Chem. Phys*. **1987**, *86*, 6258.

(13) Lynch, G. C.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys*. **1989**, *90*, 3102, **1989**, *91*, 3280 (E).

(14) Garrett, B. C.; Truhlar, D. G.; Grev, R. S.; Magnuson, A. W. *J. Chem. Phys*. **1980**, *84*, 1730, **1983**, *87*, 4554 (E).

(15) Miller, W. H. *J. Chem. Phys*. **1975**, *62*, 1899.

(16) Garrett, B. C.; Truhlar, D. G. *J. Phys. Chem*. **1979**, *83*, 1079.

(17) Chatfield, D. C.; Friedman, R. S.; Mielke, S. L.; Lynch, G. C.; Allison, T. C.; Truhlar, D. G. In *Dynamics of Molecules and Chemical Reactions*; Wyatt, R. E., Zhang, J. Z. H., Eds.; Marcel Dekker: New York, 1996; p 323.