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CLASSICAL AND QUANTUM REACTION PROBABILITIES
AND THERMAL RATE CONSTANTS FOR THE
COLLINEAR $H + H_2$ EXCHANGE REACTION
WITH VIBRATIONAL EXCITATION*

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Classical trajectory calculations for the collinear $H + H_2$ exchange reaction were performed using the same potential energy surface previously adopted for exact quantum mechanical calculations. Reactions of both ground state and vibrationally excited state reagent were considered, over a relative kinetic energy range sufficient to produce vibrational excitation of products. At energies close to threshold the classical and quantum mechanical reaction probabilities differ sufficiently to cause a major difference in the corresponding thermal rate constants at low temperatures. Effective reaction thresholds differ by 0.07 eV for ground state and 0.09 eV for excited state reagent. At energies substantially above threshold the quantum reaction probabilities oscillate around the corresponding classical ones. However, some classical curves

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also show oscillatory behavior, suggesting caution in the assignment of oscillations in the quantum curves to quantum effects.

Comparisons between exact classical and quantum mechanical calculations for the collinear $\text{H} + \text{H}_2$ exchange reaction have been previously reported. Mortensen [1] studied this collinear reaction and three of its isotopic variations classically and quantum mechanically. McCullough and Wyatt [2] reported a time-dependent quantum and classical calculation of this collinear reaction at four energies. In neither of these comparisons was the energy sufficiently high for a detailed comparison of the role of vibrational energy in classical and quantum calculations to be made.

In this paper we present such a comparison. We have performed quasi-classical trajectory calculations [3] and compare the results with the exact quantum calculations of Truhlar and Kuppermann [4]. The corresponding total reaction probability from the ground and first excited vibrational states of H_2 is compared, as well as reaction probabilities into individual vibrational quantum states of products. The relative collision energy was varied from 0.20 to 1.28 eV and 0.07 to 0.70 eV for collisions of the ground and first excited vibrational state of the diatomic reagent, respectively. At these energies the first three vibrational states of product H_2 are accessible. The potential energy surface used, identical in both the classical and quantum calculations, was a Wall-Porter [5] type, fit by Truhlar and Kuppermann [4] to the ab-initio H_3 surface of Shavitt, Stevens, Minn, and Karplus [6] and scaled to give the "correct" barrier height of 0.424 eV [7].

In a quasi-classical trajectory calculation one can choose to quantize the initial vibrational energy of the reactant diatom, but the final diatom energies are not quantized. One can, nevertheless, for purposes of comparison with the quantum mechanical results, assign a quantum number to the final diatom in several ways. We choose the following one. If $\Delta E(n) = E(n+1) - E(n)$ is the quantum mechanical energy difference between vibrational states $n + 1$ and n and E_{cl}^V is one of a continuum of classical final diatom vibrational energies such that $E(n) \leq E_{cl}^V < E(n+1)$, we assign to this diatom the quantum number $v = n$ if $E(n) \leq E_{cl}^V < \frac{1}{2}\Delta E(n)$, or $v = n + 1$ if $E(n) + \frac{1}{2}\Delta E(n) < E_{cl}^V \leq E(n + 1)$. If $E_{cl}^V \leq E(0)$, we set $v = 0$. Using this assignment we can obtain the probability P_{ij}^R for reaction from the i^{th} vibrational state of the reactant to the j^{th} vibrational state of the product from the quasi-classical trajectory calculations. This method of assignment optimized the agreement between classical and quantum results.

In Fig. 1 we exhibit the classical and quantum total reaction probability, P_0^R , for reactant H_2 in its $v = 0$ vibrational state as a function of relative collision energy. In this figure as well as in Figs. 2 and 3, the classical points are accurate to plus or minus 0.03 or better due to the statistical fluctuations associated with the trajectory calculation method [3]. The T1 and T2 marks on the abscissa correspond to relative collision energies at which vibrational excitation of H_2 to its $v = 1$ and $v = 2$ states respectively becomes energetically possible. As the collision energy exceeds

0.30 eV, both the classical and quantum reaction probability start to decrease with increasing energy. The classical curve drops monotonically, whereas the quantum one shows marked oscillatory structure and appears to oscillate about the classical curve. At energies between 0.28 and 0.30 eV the two curves are in good agreement, but at energies less than 0.28 eV, they diverge slowly.

The exact threshold energies at which $P_0^R = 0$ is zero for the quantum case and must equal or exceed 0.151 eV (at which value the classical kinetic energy at the saddle point is zero) in the classical one. However, if we arbitrarily define an "effective" threshold kinetic energy as that corresponding to $P_0^R = 0.01$, it is 0.19 eV for the quantum calculation and about 0.26 eV for the classical one, corresponding to a difference of about 0.07 eV (1.6 Kcal/mole).

In Fig. 2 we have plotted the classical and quantum total reaction probability, P_1^R , for reactant H_2 in its $v = 1$ vibrational state as a function of relative collision energy. The mark T2 designates the energy at which excitation to the $v = 2$ vibrational state becomes energetically accessible. At collision energies between 0.40 and 0.70 eV, the classical reaction probability displays, as before, the behavior of the oscillation-averaged quantum curve. From 0.20 to 0.40 eV, the two reaction probabilities show semi-quantitatively the same trend. At energies between 0.13 and 0.20 eV the dip in the classical reaction probability is qualitatively similar to, though more pronounced than, the one in the quantum reaction probability. We note that this curious oscillation in the reaction probability is manifestly not a quantum effect as it appears classically also. Thus,

one should be cautious when assigning oscillations in quantum results to quantum effects. At energies less than 0.13 eV the two curves show, as for the $v = 0$ case, a rapid decrease with decreasing energy, but in the present case they differ more from one another. In this case the quantum $P_1^R = 0.01$ effective reaction threshold is 0.02 eV and the classical one about 0.11 eV, although even at zero relative kinetic energy the total energy (0.79 eV) is sufficient for the reaction to proceed. Therefore, some kinetic energy is still necessary for the reaction probability to be appreciable, more in the classical case than in the quantum one. The difference in these effective threshold energies for $v = 1$ is now 0.09 eV, compared to 0.07 eV for the $v = 0$ case.

In Fig. 3 we have plotted four reaction probabilities, P_{00}^R , P_{10}^R , P_{11}^R , and P_{12}^R versus collision energy. The P_{00}^R , P_{10}^R , and P_{11}^R classical curves show decreasing monotonic behavior with increasing energy for collision energies greater than 0.30 eV and the corresponding quantum curves show pronounced oscillatory behavior about the classical ones. At the energies just above threshold the classical P_{10}^R and P_{11}^R curves show very rapid variation with energy. This indicates a very abrupt variation in the extent of non-adiabaticity in the reactive collisions. This effect is not seen quantum mechanically. We are uncertain as to how much credence should be given to this portion of the classical curves because of the way in which quantum numbers were assigned to classical vibrators.

For example, the classical reaction probability P_{12}^R is substantial at energies less than T_2 , because of this method of assignment. Again we see threshold differences of 0.07 to 0.09 eV.

Truhlar and Kuppermann [8] have recently calculated the thermal rate constant for this collinear reaction from their quantum reaction probabilities. Using the same expression for the rate constant, but replacing the quantum reaction probabilities with the corresponding classical ones, we calculated the classical thermal rate constant. Figure 4 shows a plot of the ratios of the classical to quantum rate constants as a function of $1/T$ for temperatures ranging from 150 to 1200°K. Table I shows this comparison more quantitatively. The classical activation energy, derived from the classical rate constant, is 0.30 eV, and the quantum activation energy is 0.299 eV [8]. The quantum results were reported with an accuracy of 2% or better and the present classical ones are accurate to about 10%. The two rate constants are seen to approach each other at high temperatures and to diverge significantly at temperatures below 250°K. The small difference in the quantum and classical reaction thresholds is responsible for this marked low temperature difference.

In summary, we have found that at the higher collision energies considered here, there is qualitative agreement between the classical and the oscillation-averaged quantum reaction probabilities discussed here. Quantitatively, however, a difference of a factor of two is not uncommon. In addition, a marked difference exists between

classical and quantum rate constants due to the difference between the corresponding reaction probabilities near threshold. We feel that, although these results were obtained from collinear calculations, the qualitative conclusions will still hold for 3-dimensional reactions.

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FIGURE CAPTIONS

- Figure 1. Classical (open circles) and quantum (full circles) total reaction probability, P_0^R , for the collinear reaction $H + H_2 (v = 0) \rightarrow H_2 (v = 0, 1, 2) + H$ as a function of relative collision energy E_0 .
- Figure 2. Classical (open circles) and quantum (full circles) total reaction probability, P_1^R , for the collinear reaction $H + H_2 (v = 1) \rightarrow H_2 (v = 0, 1, 2) + H$ as a function of relative collision energy E_1 .
- Figure 3. Classical (open circles) and quantum (full circles) reaction probabilities P_{ij}^R as a function of relative collision energy E_i .
- Figure 4. Ratio of classical to quantum rate constant as a function of $1/T$.

Table I. Exact quantum $k_{qm}(T)$ and classical $k_{cl}(T)$ rate constants in cm/(molecule-sec) and their ratio.*

$T(^{\circ}K)$	$k_{cl}(T)$	$k_{qm}(T)$	$k_{cl}(T)/k_{qm}(T)$
200	0.86(-2)	0.201(0)	0.43(-1)
300	0.19(1)	0.585(1)	0.32(0)
400	0.31(2)	0.593(2)	0.52(0)
500	0.17(3)	0.266(3)	0.64(0)
600	0.52(3)	0.752(3)	0.69(0)
700	0.12(4)	0.161(4)	0.74(0)
800	0.22(4)	0.290(4)	0.76(0)
900	0.37(4)	0.463(4)	0.80(0)
1000	0.55(4)	0.677(4)	0.81(0)
1100	0.77(4)	0.928(4)	0.83(0)
1200	0.10(5)	0.121(5)	0.83(0)

* The numbers in parentheses are powers of ten which multiply the numbers preceding them.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

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