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# Ab Initio Evaluation of the Barrier Height. Theoretical Rate Constant of the $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$ Reaction

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The rate constant of the  $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$  reaction was calculated using the nonvariational transition-state theory for the temperature range 500–2000 K. The quality of the theoretical barrier height depends on the amount of correlation energy taken into account, on the post-MP4 corrections, and on the spin decontamination when radicals are involved. The quadratic configuration interaction (QCI) method gives values higher than the perturbational post-MP4 SAC4/A1 method. The basis set superposition error and the sources of thermal corrections (theoretical or experimental) have minor importance. We found that the two rate constants using the SAC4/A1 and QCI barriers represent an upper and lower bound, respectively, to the available experimental values.

## Introduction

The past 30 years have seen substantial advances in understanding the  $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$  reaction. This reaction seems either to be extremely slow or to give no yield at all at low temperatures,<sup>1</sup> but at high temperatures it plays a significant role in the chemistry of ammonia pyrolysis and combustion.

Experimentally, Dove and Nip<sup>2</sup> made one of the first studies of this reaction at high temperatures using a shock tube technique. The expression they found for the Arrhenius rate constant was  $K(T) = (2.77 \pm 1.02) \times 10^{13} \exp[-(72.8 \pm 5.4) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , over the temperature range 1500–2150 K. Yamura and Asaba<sup>3</sup> found a slightly different expression over the temperature range 1860–2480 K. Michael et al.,<sup>4</sup> using a flash photolysis–shock tube technique, obtained improved kinetics for this reaction: for  $908 \leq T \leq 1777 \text{ K}$ , their Arrhenius expression was  $K(T) = (1.82 \pm 0.2) \times 10^{14} \exp[-(67.1 \pm 1.0)/RT]$ . This result is consistently higher than earlier values at all common temperatures. There were two parallel studies at lower temperatures. Hack et al.,<sup>5</sup> using a discharge flow system in the temperature range 673–1003 K, obtained a rate constant given by the Arrhenius expression  $K(T) = 8.1 \times 10^{13} \exp[-(60.9 \pm 4)/RT]$ . Marshall and Fontijn,<sup>6</sup> using a high-temperature photochemistry technique, found  $K(T) = (3.42 \pm 1.7) \times 10^{14} \exp[-(71.8 \pm 3.4)/RT]$  for 660–1140 K. Recently, Ko, Marshall, and Fontijn<sup>7</sup> have revised this expression. For the 490–960 K range, they found  $K(T) = 7.3 \times 10^{13} \exp(-57.5/RT)$ . When combined with two other sets of direct measurements,<sup>4,5</sup> they found a best-fit  $K(T) = (5.4 \times 10^5) T^{2.40} \exp(-4991/T)$  for the 490–1780 K range. These two expressions agree well with the Michael et al. study for the temperatures where they overlap. Excluding the first two expressions,<sup>2,3</sup> which are now seen to be wrong, and with the expression of ref 6 superseded by that of ref 7, it can be appreciated from this brief review that the pre-exponential factors differ by a factor of 2.5, and the activation energies are in the range 57–67 kJ mol<sup>-1</sup> (13.6–16.0 kcal mol<sup>-1</sup>).

The extensive experimental literature on the kinetics of this reaction contrast with the paucity of theoretical studies, of which, to the best of our knowledge, there have only been four reported. In the first, Gordon et al.<sup>8</sup> studied the reverse reaction,  $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$ , with a variety of methods, including MCSCF, POL-CI, UMP2, and UMP3. They conclude that the POL-CI method appears to be a consistently reliable approach for this type of reaction. In the second, Leroy et al.<sup>9</sup> studied the reaction

at the ab initio UHF/6-31G level, with energy properties computed at the configuration interaction level. At 913 K, their activation energy is near the lower limit of the experimental range, and the discrepancy between the theoretical and experimental results led them to draw up a semiempirical procedure to calculate the activation barriers. Melius,<sup>10</sup> using his BAC-MP4 method and geometries and frequencies obtained at the HF/6-31G(d) level, expressed the rate constant by a three-parameter equation for the range  $600 \leq T \leq 2600 \text{ K}$ . The result was in good agreement with the experimental values of Michael et al.<sup>4</sup> in the common zone of temperatures. Finally, Garrett et al.<sup>11</sup> computed the rate constant by using variational transition-state theory with a semiclassical ground-state adiabatic transmission coefficient for the 200–2400 K range. They conclude that, although the agreement with experimental values is good in general, the comparisons of experiment and theory indicate that the computed barrier height is overestimated.

As there is experimental interest in this reaction, we have carried out a broad theoretical study to determine its rate constant using the nonvariational transition-state theory (TST) for  $500 \leq T \leq 2000 \text{ K}$ . The use of TST is justified for three reasons. In the first place, as the greatest temperature ( $T \leq 2000 \text{ K}$ ) is not excessive and the activation barrier is high, we can assume that energy effects will dominate over entropy effects, and therefore the transition state will coincide with the saddle point. In the second place, as the bottom temperature ( $T \geq 500 \text{ K}$ ) is not excessively low we can assume that approximate and simple methods could give a reasonable description of the tunneling corrections. Finally, and in accordance with the previous two reasons, the TST requires less computational effort than the variational methodology used in the Garrett et al. paper.

## Method

Molecular calculations were carried out using the GAUSSIAN 90 system of programs.<sup>12</sup> The geometry of stationary points is optimized in restricted (R) and unrestricted (U) second-order Møller–Plesset perturbation theory,<sup>13</sup> MP2, with full electron correlation, using the 6-31G(d,p) basis set of Pople.<sup>14</sup> Then we use two levels of calculation.

**Level I. Perturbational Methods.** We make a single point calculation in fourth-order Møller–Plesset perturbation theory, MP4, with a frozen core (FC) approximation and single, double, triple, and quadruple replacements with a somewhat larger basis set: namely, 6-311+G(d,p).<sup>15</sup> The sp diffuse functions (+) are of great importance for molecules with free electron pairs.<sup>16</sup> We may denote this energy as

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(R or U)MP4sdtq(FC)/6-311+G(d,p)/(R or  
U)MP2(FULL)/6-31G(d,p)

However, it is well-known that the unrestricted Møller–Plesset perturbation theory converges slowly, especially in the case of free radicals.<sup>17</sup> In the present work, we use three economical options that were put forward with the aim of taking the post-MP4 energy into account:

(i) *The SAC4/A1 empirical method*,<sup>18</sup> in which the abbreviation SAC4/A1 denotes scaling all the correlation energy as estimated by Møller–Plesset theory of fourth-order, where the scaling factor (A1) is assumed to be independent of geometry for a given system:

$$E_{\text{MP-SAC4}} = E_{\text{UHF}} + (E_{\text{MP4}} - E_{\text{UHF}})/A1$$

(ii) *The theoretical fourth-order invariant* quantity of Feenberg<sup>19</sup> can be used as an upper bound to the perturbation series for the correlation energy,

$$E_{\text{Corr}} = E[2/1] + (E[2/1]/E_2)^2(E_4 - E_3^2/E_2)$$

where  $E[2/1] = E_2/(1 - E_3/E_2)$  is the Padé approximant and  $E_n$  denotes the  $n$ th-order perturbation correction to the electronic energy.

(iii) *The  $MP_\infty$  limit*<sup>20</sup> of the extrapolation of the  $MP_n$  series can be calculated by means of the formula

$$E_{\text{corr}} = (E_2 + E_3)(1 - E_4/E_2)^{-1}$$

In all calculations we use the spin projection operator as implemented in GAUSSIAN 90 to annihilate, or at least to reduce, the spin contamination. The energies after the spin decontamination will be  $PMP_n$ .

**Level II. Quasi-Variational Method.** We make a single point calculation to the quadratic configuration interaction level,<sup>21</sup> QCIsd(t), with a larger basis set, 6-311+G(2df,p). We may denote this energy as

QCIsd(t)/6-311+G(2df,p)/(R or  
U)MP2(FULL)/6-31G(d,p)

The harmonic vibrational frequencies were calculated at the MP2/6-31G(d,p) level at all stationary points. Such frequencies are known to be overestimated, and so they were uniformly scaled by a factor of 0.95.<sup>22</sup> With these frequencies, we can calculate the thermal corrections (TC) to the total energy using the classical formalism of statistical thermodynamics:<sup>23</sup>  $TC = ZPE + \Delta H(0 \rightarrow T)$ , where TC is the sum of the zero-point energy (ZPE) and the thermodynamic correction for temperature  $T$ .

Then, finally, we considered the kinetics of this hydrogen abstraction reaction, calculating the rate constant by means of the formalism of the nonvariational TST, including the tunneling correction via Wigner<sup>24</sup> and Eckart's<sup>25</sup> expressions. Although these latter tunneling models are very crude, they are sufficient for the present purpose (500–2000 K range). For example, the Wigner's factor is 2.41 and 1.09 at 500 and 2000 K, respectively.

## Results and Discussion

The geometric parameters of all stationary points are shown in Table 1. Figure 1 shows the optimized geometry of the saddle point. The total energies, with and without spin annihilation, are listed in Table 2, and Table 3 contains the harmonic vibration frequencies.

When comparison is possible, the MP2/6-31G(d,p) geometries are in excellent agreement with the experimental values. In the transition structure, the length of the bond that is broken ( $NH_1$ ) increases by 30%, and the length of the bond that is formed ( $H_1H_2$ )

TABLE 1: Geometric Parameters<sup>a</sup> of Reactants, Products, and Saddle Point

	NH <sub>3</sub> + H	NH <sub>3</sub>	H <sub>2</sub>	NH <sub>2</sub>
$d(NH_1)$	1.30 (1.24) <sup>b</sup>			
$d(H_1H_2)$	0.87 (0.95)		0.73 <sup>c</sup>	
$d(NH)$	1.02 (1.01)	1.01		1.02
$a(HNH)$	103.5 (105.3)	106.1		102.7
$a(HNH_1)$	99.1 (100.5)			
$a(NH_1H_2)$	158.5 (166.7)			
$a(HNH_1H_2)$	52.7 (53.7)			

<sup>a</sup> In Å and degrees. <sup>b</sup> In parentheses, Melius's theoretical values.<sup>10</sup> <sup>c</sup> Experimental values:<sup>32</sup> NH<sub>3</sub>:  $d(NH) = 1.012$ ,  $a(HNH) = 106.7$ ; H<sub>2</sub>:  $d(HH) = 0.741$ ; NH<sub>2</sub>:  $d(NH) = 1.024$ ,  $a(HNH) = 103$ .

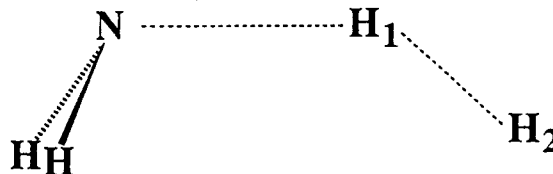


Figure 1. Definition of internal coordinates at the saddle point.

TABLE 2: Total Energies (hartrees) of the Stationary Points at Different Levels of Theory

	NH <sub>3</sub>	H	TS	NH <sub>2</sub>	H <sub>2</sub>
Level I: PMP4 = FC/6-311+G(d,p)/MP2/6-31G(d,p)					
UHF	-56.214 15	-0.499 81	-56.676 41	-55.581 72	-1.132 49
PUHF			-56.684 43	-55.584 66	
UMP2	-56.415 19		-56.878 44	-55.737 45	-1.160 26
PMP2			-56.883 91	-55.739 30	
UMP4	-56.434 23		-56.905 78	-55.757 93	-1.167 69
PMP4			-56.909 02	-55.759 03	
SAC4	-56.473 07		-56.948 65	-55.789 80	-1.173 90
PMP $\infty$	-56.435 03		-56.910 38	-55.759 79	-1.168 11
FEENB	-56.435 64		-56.911 93	-55.760 62	-1.168 26
Level II: QCIsd(t)/6-311+G(2df,p)/MP2/6-31G(d,p)					
	-56.462 13		-56.935 67	-55.785 17	-1.168 28

TABLE 3: Scaled Vibration Frequencies (cm<sup>-1</sup>) at the MP2/6-31G(d,p) Level<sup>a</sup> and Thermal Corrections (kcal mol<sup>-1</sup>) at Room Temperature

	TC	frequencies					
NH <sub>3</sub>	23.6	3535	3535	3386	1642	1642	1067
NH <sub>2</sub>	14.2	3417	3307	1516			
H <sub>2</sub>	8.2	4301					
H	1.5						
TS	22.5	3425	3314	1973	1530	1249	1089
		694	683	1920i <sup>b</sup>			

<sup>a</sup> Experimental values<sup>32</sup> (cm<sup>-1</sup>): NH<sub>3</sub>: 3577, 3577, 3506, 1691 1691, 1022; NH<sub>2</sub>: 3220, 3173, 1497; H<sub>2</sub>: 4405. <sup>b</sup> Other theoretical values: 2852i,<sup>9</sup> 2476i,<sup>10</sup> (1900–2600)i.<sup>11</sup>

increases by 20%. Moreover, the HNH angle is close to the value in the NH<sub>2</sub> product. The transition state becomes asymmetric,  $NH_1 > H_1H_2$ , and is formed late. This is the expected behavior since the reaction is endothermic (see Table 4). Our result differs from that of Melius,<sup>10</sup> who found the transition state to be more symmetric and to be formed earlier.

The saddle point was identified with one and only one negative eigenvalue of the Hessian matrix, and therefore, one imaginary frequency (Table 3). The corresponding eigenvector ( $V^*$ ) is associated with the reaction coordinate ( $V^* \approx 1/2^{1/2}[NH_1 - H_1H_2]$ ). When comparison is possible, the scaled MP2/6-31G(d,p) frequencies are in good agreement with the experimental values. Our imaginary frequency is 500–900 cm<sup>-1</sup> lower than other theoretical values in the literature.<sup>9,10</sup>

**Relative Energies.** The energy and enthalpy changes (reaction and activation) are presented in Table 4. The accuracy depends on several factors: (i) level of theory, (ii) spin contamination, (iii) basis set superposition error (BSSE), and (iv) quality of the thermal corrections.

**TABLE 4: Reaction and Activation Enthalpies at Room Temperature (kcal mol<sup>-1</sup>)**

method	$\Delta E_r$	$\Delta H_r^a$	$\Delta E^*{}^b$	$\Delta H^*{}^{a,c}$
UHF	-0.2	-3.6 (-2.8) <sup>d</sup>	23.7	20.7 (21.1) <sup>d</sup>
PUHF	-2.0	-5.5 (-4.7)	18.6	15.7 (16.1)
UMP2	10.8	7.4 (8.2)	23.4	20.5 (20.9)
PMP2	9.7	6.2 (7.0)	20.0	17.1 (17.4)
UMP4	5.3	1.8 (2.6)	18.2	15.3 (15.7)
PMP4	4.6	1.1 (1.9)	16.2	13.3 (13.6)
SAC4	5.7	2.3 (3.1)	15.7	12.8 (13.2)
PMP $\infty$	4.4	0.9 (1.7)	16.1	13.2 (13.5)
FEENB	4.1	0.7 (1.5)	15.5	12.6 (13.0)
QCISD(T)	5.3	1.8 (2.7)	16.8	13.9 (14.3)

<sup>a</sup>  $\Delta H_r = \Delta E + \Delta \text{TC}$ . Experimental value:<sup>32</sup>  $\sum \Delta H_r = 4.32 \pm 1.5$  kcal mol<sup>-1</sup> at room temperature for comparison. <sup>b</sup>  $\Delta E^* = \Delta E + \text{BSSE}$ . <sup>c</sup> For a bimolecular reaction:  $E_a = \Delta H^* + 2RT$ , so  $\Delta H^* = E_a - 2RT$ . For  $T = 298$  K, experimental  $\Delta H^*$  between 13.1 and 16.2 kcal mol<sup>-1</sup>. <sup>d</sup> Experimental TC at room temperature. In parentheses, theoretical TC.

(i) The introduction of the correlation energy is quite important. The perturbational methods, even at the MP2 level, give the correct sign of the reaction energy ( $\Delta E_r$ ), though its value is overestimated with respect to the experimental value (4.32 kcal mol<sup>-1</sup>). The introduction of the fourth-order of perturbation (MP4) corrects this value drastically, and the post-MP4 corrections behave differently depending on the approximation used. The QCI method behaves in the same way. Nonetheless, it is worth noting that the computations for the QCISD(t) energy took some 10 times longer than those for the PMP4 energy. With respect to the barrier height ( $\Delta E^*$ ), raising the order of the perturbational series drastically lowers this barrier (from 23.4 kcal mol<sup>-1</sup> at MP2 level to 16.2 at MP4 level). The effects of post-MP4 corrections are quantitatively smaller, though still in the same direction. At QCI level, the barrier is higher than that at post-MP4 levels ( $\approx 1$  kcal mol<sup>-1</sup> on average). This behavior has been described previously.<sup>26,27</sup>

(ii) The influence of the spin projection is noticeable although quantitatively smaller. Thus, at the MP4 level, annihilation of the lowest quartet from the unrestricted wave function lowers  $\Delta E_r$  by 0.7 kcal mol<sup>-1</sup> and  $\Delta E^*$  dramatically (by 2 kcal mol<sup>-1</sup>). This behavior has also been observed in earlier work.<sup>28,29</sup>

(iii) The BSSE to the barrier height ( $\Delta E^*$ ) was estimated as between 0.1 (UHF) and 0.5 kcal mol<sup>-1</sup> (MP4) for the 6-311+G(d,p) basis set, and 0.4 for the 6-311+G(2df,p) basis set (QCI), using the counterpoise method of Boys and Bernardi (CP).<sup>30</sup> When one uses a large basis set, the CP method gives good estimates of the BSSE.<sup>31</sup>

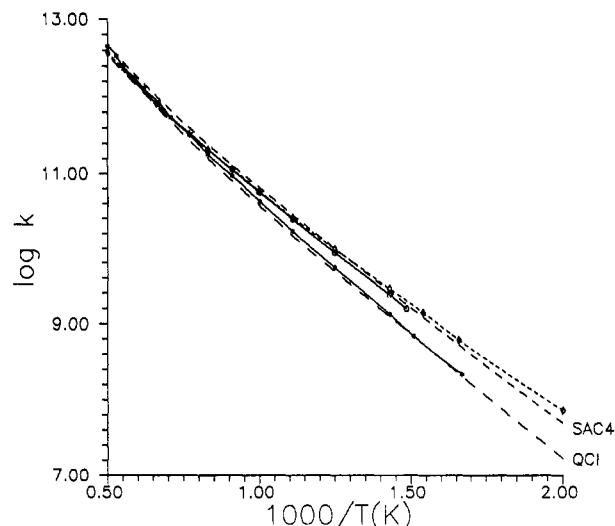
(iv) Finally, we analyzed the thermal corrections (TC). In the present work, by theoretical/experimental values we mean that both the ZPE and the thermodynamical corrections are calculated theoretically/experimentally. If we use either experimental values or theoretical ones, the difference in reaction and activation enthalpies is considerably less than 1 kcal mol<sup>-1</sup>.

We can hence conclude the following:

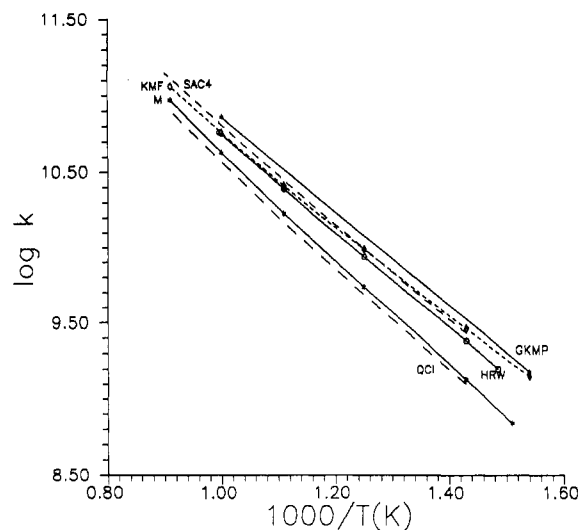
(a) For the reaction enthalpy (Table 4), the best value, obtained at SAC4/A1 with theoretical TC, is 3.1 kcal mol<sup>-1</sup>, near the experimental value ( $4.32 \pm 1.5$  kcal mol<sup>-1</sup>). The value obtained at QCI level is 2.7 kcal mol<sup>-1</sup>.

(b) For the activation enthalpy (Table 4), the three post-MP4 methods with BSSE give values of 13.5–13.0 kcal mol<sup>-1</sup>, when we take the theoretical TC, and of 13.2–12.6 kcal mol<sup>-1</sup> with the experimental TC. The difference between the mean values is less than 0.4 kcal mol<sup>-1</sup>. The agreement between the two predictions adds confidence to the calculated activation enthalpy. We propose a mean value of 13.0 kcal mol<sup>-1</sup> at room temperature. The value obtained at QCI level with BSSE is somewhat greater (14.3 kcal mol<sup>-1</sup> with theoretical TC).

**Analysis of the Kinetics.** The rate constant for the  $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$  reaction was calculated using the nonvariational



**Figure 2.** Arrhenius plot of  $\log_{10} K$  (cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) against the reciprocal temperature (K). Line SAC4: SAC4/A1 barrier + BSSE + theoretical TC + Wigner tunneling. Line QCI: the same but with QCISD(t) barrier. Line \*: Melius's<sup>10</sup> theoretical values. Line O: Hack et al.'s<sup>5</sup> experimental values. Line  $\diamond$ : Ko, Marshall, and Fontijn's<sup>7</sup> experimental values. Line +: Michael et al.'s<sup>4b</sup> experimental values.



**Figure 3.** Close-up of Figure 2 for  $650 \leq T \leq 1150$  K. Lines SAC4 and QCI, as in Figure 2. Line M: Melius's values.<sup>10</sup> Line HRW: Hack et al.'s values.<sup>5</sup> Line KMF: Ko, Marshall, and Fontijn's values.<sup>7</sup> Line GKMP: Garrett, Koszykowski, Melius, and Page's values.<sup>11</sup>

TST in the temperature range 500–2000 K. The variation of  $K(T)$  vs  $1000/T$  is given in Figure 2, where we use the barrier heights at SAC4/A1 and QCI levels for comparison. Also, in both cases, we used Wigner's tunneling correction, since the differences with Eckart's factor are negligible in the range of temperatures under study. Figures 3 and 4 are a close-up of the region  $650 \leq T \leq 1150$  K and  $1000 \leq T \leq 2000$  K, respectively, in the previous figure, so as to analyze more readily the differences between the distinct values.

It is notable that, while the SAC4 curve fits the experimental values of Hack et al.<sup>5</sup> and of Ko et al.<sup>7</sup> better, the QCI curve gives the better fit to Melius's results.<sup>10</sup> Our SAC4 and QCI curves represent a (practically) upper and lower bound, respectively, to the experimental rate constants. The theoretical curve of Garrett et al.<sup>11</sup> is in good agreement with our SAC4 curve in the 500–2000 K range, although slightly higher. However, the computational effort is considerably lower in our case. From Table VII of ref 11, we find that the variational effects are small in the 400–2400 K range (TST vs ICVT), and if we include our Wigner factor in their TST values, the differences of TST/W vs ICVT/SCSAG are also small. The good results obtained in the present

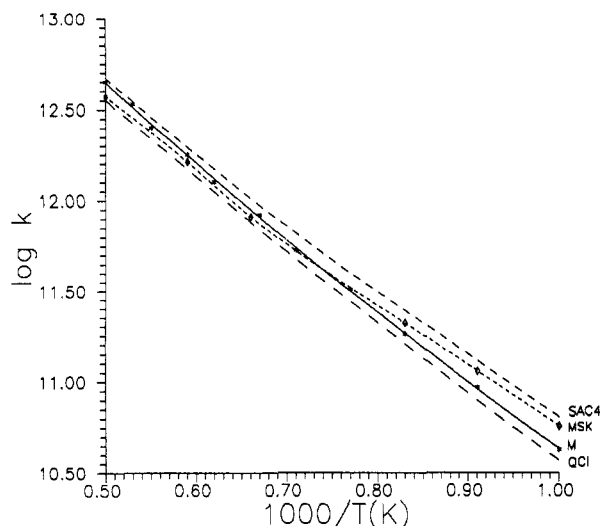


Figure 4. Close-up of Figure 2 for  $1000 \leq T \leq 2000$  K. Lines SAC4 and QCI, as in Figure 2. Line M: Melius's values.<sup>10</sup> Line MSK: Michael, Sutherland, and Klemm's values.<sup>4b</sup>

work reinforce the supposition made in the Introduction on the use of the nonvariational TST in this reaction. Given the variety of experimental results, it is difficult to choose between the SAC4 and QCI results. When confronted with the harsher test of the  $\text{H}_2 + \text{H}$  reaction (without doubt the most accurately known potential energy surface of any chemical reaction), we found our SAC4 curve fitted the available theoretical and experimental values better.<sup>27</sup> In both cases (SAC4 and QCI), we found in the present work that the Arrhenius plot is slightly nonlinear, in agreement with the experimental literature. The temperature dependence of the rate constant obtained from the fit of our SAC4 results is given by the expression

$$K(T) = (1.46 \times 10^7) T^{2.05} \exp(-5752/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

in the 500–2000 K range of temperatures.

## Conclusions

In the hydrogen abstraction reaction  $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$ , we have examined several factors affecting the barrier height. The introduction of the correlation energy, with either perturbation ( $\text{MP}_n$ ) or quasi-variational methods (QCI), has quite a major effect. The QCI method gives higher barriers than the  $\text{MP}_4$  method. Once at the  $\text{MP}_4$  level, spin projection and post- $\text{MP}_4$  correction have a quantitatively smaller influence. The BSSE raises this barrier between 0.1 and 0.5  $\text{kcal mol}^{-1}$ , depending on the method and the basis set used. The TC's tend to lower the barrier height by between 2.9 and 2.5  $\text{kcal mol}^{-1}$ , using either experimental or theoretical values, respectively. As one can see, the difference between the two forms of estimating the TC is less than 0.4  $\text{kcal mol}^{-1}$ .

On the basis of the calculation of the barrier height we have obtained the rate constant, using the nonvariational TST with Wigner's tunneling factor, in the temperature range 500–2000 K. We found that the rate constants with SAC4/A1 and QCI

barriers (with BSSE and theoretical TC) are in excellent agreement with the latest experimental and theoretical values.

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