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## Ab Initio Calculations of the Transition-State Geometry and Vibrational Frequencies of the $S_N2$ Reaction of $Cl^-$ with $CH_3Cl$

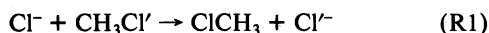
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We present ab initio geometries, energies, and frequencies at the MP2/6-31G\*\* level for three distinct stationary points on the  $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$  gas-phase reaction path. We compare the saddle point geometries and frequencies for several basis sets, with and without correlation energy, and we compare geometries, charge distributions, and energy differences for the two most reliable method/basis set combinations. Finally, we use the MP2/6-31G\*\* ab initio properties to evaluate the conventional transition-state theory rate constant at 300 K. Comparison with a classical calculation is used to test the validity of classical simulation techniques for this reaction. Comparison with the experimental rate constant yields a semiempirical estimate of the barrier height of 3 kcal/mol, in reasonable agreement with our best ab initio value of 4.5 kcal/mol.

### 1. Introduction

Bimolecular nucleophilic displacement ( $S_N2$ ) reactions have long played a fundamental role in organic chemistry. Reactions of this type involving halides and methyl halides have become prototypes of the class, and they have recently come under both theoretical and experimental scrutiny in studies using new techniques for gas-phase thermochemistry and kinetics of ions and for simulating reaction rates in solution. These studies show that the aqueous-phase rate coefficients are many orders of magnitude slower than the corresponding gas-phase ones for these reactions; thus they provide an interesting challenge for our ability to model solvent effects on reaction processes. In the present paper we study the chloride exchange reaction<sup>1-14</sup>



which has been modeled in aqueous solution, for example, by Monte Carlo simulation of the free energy of activation,<sup>1</sup> by

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generalized Langevin theory,<sup>3</sup> by the RISM integral equation method,<sup>4</sup> and by continuum solvation models<sup>5-7</sup> and in the gas phase by classical trajectory calculations.<sup>14</sup> Despite the many "solution-phase" theoretical studies of this reaction, there is still much to be learned. In order to fully understand the effects of solvation on this reaction, we must first have a clear picture of the gas-phase reaction process. It is with this in mind that we present a study of the gas-phase potential energy surface in the present article.

Ab initio calculations are one of the most useful tools for evaluating reaction profiles or reaction path Hamiltonians, which are critical components of dynamical models based on reaction paths.<sup>15-17</sup> For the gas-phase analogue of reaction R1, Chandrasekhar et al.<sup>1</sup> have shown that ab initio calculations at the Hartree-Fock (HF) level using a double- $\zeta$  plus-heavy atom polarization basis set (6-31G\*)<sup>18</sup> yield reasonable energy values, as compared to experiment,<sup>12,13,19,20</sup> for the stationary points on the reaction profile, and consequently they concluded that this is a good level of ab initio calculation to use for characterization of the reaction profile. A more complete consideration of the dynamics requires the frequencies orthogonal to the reaction path, in addition to the energy along it. Frequencies for reaction R1, however, have been calculated only at the HF/3-21G level,<sup>8</sup> which is unlikely to yield sufficiently accurate values. Thus, in the present article, we evaluate the energies and the frequencies of the chloride plus methyl chloride system at various orders of perturbation theory with various basis sets in order to determine the minimum level of electronic structure calculation which will provide reasonable values for both frequencies and energies along the reaction path. We find that Møller-Plesset second-order perturbation theory (MP2)<sup>18,21</sup> gives the frequencies of the reactant in good agreement with experimental values and it significantly changes the frequencies at the transition state as compared to HF theory. We then evaluate the properties of the reaction path stationary points at the MP2 level using two different basis sets. Finally, we evaluate conventional transition-state theory rate constants for our best ab initio geometries, energies, and frequencies. This allows us to make a semiempirical estimate of the classical barrier height.

## 2. Review of Experiments on Reaction Profile

Under ordinary conditions reaction R1 proceeds in both the gas phase and solution by back-side attack on the methyl chloride by the chloride ion (although front-side attack has been postulated for high translational energies<sup>12</sup>). The back-side mechanism implies a symmetric reaction path passing through a configuration with  $D_{3h}$  symmetry having the three heavy atoms on the  $C_3$  axis and the hydrogens in the  $\sigma_h$  plane. Experimentally measured gas-phase rate constants indicate the reaction passes through a transition state with a higher potential energy than the reactants by  $\sim 1$  kcal/mol.<sup>12</sup> We denote the transition state as  $\ddagger$ . In addition, these<sup>12</sup> and other<sup>13,19,20</sup> experiments have indicated that there is another stationary point which is bound with respect to reactants. We call this complex  $\mathcal{C}$ . In early work<sup>19</sup> the complex was associated with the  $D_{3h}$  point, but the currently accepted interpretation is that it is an ion-dipole complex between the transition state ( $\ddagger$ ) and the reactants ( $\mathcal{R}$ ). There is also a stationary point between  $\ddagger$  and the products, but this is equivalent to  $\mathcal{C}$  by symmetry. The stationary point  $\mathcal{C}$  is assumed to have  $C_{3v}$  symmetry. The most reliable experimental value for the stabilization of this complex relative to the reactants is 12.2  $\pm$

TABLE I: Saddle Point Geometries, Energies, and Vibrational Frequencies

method/basis set	$r_{\text{CCl}}$ Å	$r_{\text{CH}}$ Å	E, hartrees	$a_2''$ , $\text{cm}^{-1}$	$a_1'$ , $\text{cm}^{-1}$	$a_2''$ , $\text{cm}^{-1}$
HF/3-21G <sup>a</sup>	2.396	1.061	-954.060	322i	231	1220
HF/3-21G*	2.383	1.060	-954.242	384i	229	1221
HF/6-31G* <sup>b</sup>	2.383	1.061	-958.613	415i	214	1224
HF/6-31G**	2.385	1.062	-958.618	414i	213	1208
MP2/6-31G*// HF/3-21G <sup>a,c</sup>	2.396	1.061	-958.997			
MP2/6-31G*	2.307	1.072	-959.024	511i	233	1098
MP2/6-31G**	2.302	1.067	-959.048	516i	234	1086
MP2/6-31+G*	2.315	1.072	-959.042	527i	226	1110
MP-SAC2/6-31G**// MP2/6-31G**	2.302	1.067	-959.087			
HF/E <sup>d</sup>	2.391	1.06	-958.328			
CEPA/E//HF/E <sup>d</sup>	2.391	1.06	-958.776			

<sup>a</sup> From ref 8. <sup>b</sup> Geometry and energy for this level are from ref 1 (these values are also given in ref 8); the frequencies were calculated in our laboratory. A frequency of 684  $\text{cm}^{-1}$  for the  $a_1'$  asymmetric stretch was estimated in ref 2 from a harmonic fit to HF/6-31G\* energies as a function of the C-Cl distance. This method of obtaining the harmonic frequencies is less precise than diagonalization of the Hessian, as employed by the GAUSSIAN program used here. In addition, the frequency calculated from the fit differs from our value of 214  $\text{cm}^{-1}$  by so much that we suspect an error in the calculation. <sup>c</sup> // means "at the geometry computed by". <sup>d</sup> From ref 24.

2 kcal/mol,<sup>20</sup> although a previous measurement yielded a value of 8.6 kcal/mol.<sup>19</sup> The reaction profile is thus a symmetric double-well potential with three unique stationary points  $\mathcal{R}$ ,  $\mathcal{C}$ , and  $\ddagger$ .

Finally, we note that the experimental energy difference between  $\ddagger$  and  $\mathcal{R}$  has a large uncertainty. First, the rate coefficient from which the barrier was calculated is very small, and the absolute error of the rate constant at each energy was estimated<sup>12</sup> to be  $\pm 50\%$ . Second, the barrier was evaluated by Barlow et al.<sup>12</sup> using a RRKM transition-state theory approach<sup>22</sup> and is thus highly dependent upon the choice of vibrational mode frequencies at the barrier ( $\ddagger$ ) and perhaps also at a "loose" generalized transition state assumed between  $\mathcal{C}$  and  $\mathcal{R}$ . Barlow et al. do not indicate how these values were chosen. In accordance with these considerations, although Barlow et al. quote the barrier height as  $1 \pm 1$  kcal/mol, they accept this as being in good agreement with the HF/6-31G\* value of Chandrasekhar et al.<sup>1</sup> of 3.6 kcal/mol. The uncertainty in the classical barrier height deduced from experiment so far is at least a couple of kilocalories per mole.

## 3. Saddle Point Energy, Geometry, and Frequency Calculations

In order to test the sensitivity of various quantities to the order of perturbation theory and the size of the basis set, we performed geometry optimization and frequency calculations at the saddle point with four basis sets, including the previously applied 3-21G basis, at the Hartree-Fock level (HF) and with three basis sets using second-order Møller-Plesset perturbation theory. All calculations were carried out with the GAUSSIAN82<sup>23</sup> program. We used version revised-k on the Pittsburgh Supercomputing Center Cray X-MP and version revised-h on the Minnesota Supercomputer Institute Cray-2. The geometries, energies, and selected frequencies are given in Table I. For comparison, we have also included absolute energy values from an MP2/6-31G\* single-point calculation by Luke et al.<sup>8</sup> at the HF/3-21G optimized geometry and calculations by Keil and Ahlrichs<sup>24</sup> at the HF and coupled electron pair approximation (CEPA) levels with an extended double- $\zeta$  basis set denoted E; for C, H, and Cl, respectively, this basis set may be denoted (8s4p2d)[4s2p1d], (4s1p)[2s1p],-

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(10s,6p2d)[6s3p2d] in the standard Dunning<sup>25</sup> notation for segmented contracted basis sets.

We also calculated the MP-SAC2 (Møller-Plesset scaling all correlation energy second order)<sup>26</sup> correction to the MP2/6-31G\*\* energy (at the MP2/6-31G\*\* optimized geometry), and the result corrected this way is also in the table. The MP-SAC2 method is designed to correct for that part of the correlation energy not accounted for in an MP2 calculation with a given one-electron basis.<sup>26</sup> It is based on the assumption that the fraction of correlation energy accounted for in the MP2 calculation is constant across the whole potential surface. This fraction, called  $\mathcal{F}_2$ , is very high for this reaction compared to hydrogen atom transfers and hydrogen-bond-breaking processes that were studied with several basis sets<sup>26,27</sup> previously. For (R1) it equals 0.917. We evaluated this  $\mathcal{F}_2$  value by comparing the difference of the CH<sub>3</sub>Cl dissociation energy, at the MP2/6-31G\*\* optimized geometry, for an MP2/6-31G\*\* calculation and an HF/6-31G\*\* calculation, to the difference between the HF/6-31G\*\* calculation and the "experimental" value. The "experimental" dissociation energy,  $D_e$ , was evaluated from the experimental dissociation energy from the ground-state  $D_0$ <sup>28</sup> by

$$D_e = D_0 + \frac{hc}{2} [\sum_i \nu_i(\text{CH}_3\text{Cl}) - \sum_i \nu_i(\text{CH}_3)] \quad (1)$$

where  $h$  is Planck's constant,  $c$  is the speed of light, and  $\nu_i(x)$  is an experimental normal-mode frequency (in cm<sup>-1</sup>) for mode  $i$  of CH<sub>3</sub>Cl<sup>29</sup> or CH<sub>3</sub>.<sup>30,31</sup>

The HF-optimized geometries have carbon-chlorine distances,  $r_{\text{CCl}}$ , of  $\sim 2.4$  Å for all basis sets considered, whereas the MP2-optimized geometries have distances of  $\sim 2.3$  Å. We also see a systematic difference between the HF- and MP2-optimized carbon-hydrogen bond lengths, although this difference is very small,  $\sim 0.01$  Å. Furthermore the MP2/6-31G\* calculation yields a significantly lower energy than the MP2/6-31G\*\*//HF/3-21G<sup>9</sup> calculation (where the method and basis are given before the //, and the method and basis used to obtain the geometry are given after the //), indicating that the geometry change is energetically significant. The CEPA calculation in the table is a single-point energy calculation at the HF-optimized geometry,<sup>24</sup> and thus the geometry on which it is based has a carbon-chloride bond length that is too long by  $\sim 0.1$  Å and a carbon-hydrogen bond length that is too small by  $\sim 0.01$  Å. We also note that the absolute energies improve, as expected, both with increases in basis set completeness and with inclusion of correlation energy.

The three saddle point frequencies in Table I are those that are expected to most significantly affect the reaction dynamics, namely the  $a_2''$  imaginary frequency (corresponding to motion along the reaction path and thus providing an indication of the barrier width), the  $a_1'$  symmetric stretch frequency, and the  $a_2'$  hydrogen umbrella motion frequency. First we note that increasing the level of calculation systematically from HF to MP2 changes the values of the frequencies—raising the imaginary frequency by  $\sim 20\%$ , raising the symmetric stretch frequency by  $\sim 10\%$ , and lowering the umbrella frequency by  $\sim 10\%$ , although for the  $a_1'$  frequency there is a compensating basis set dependence which causes the HF/3-21G and HF/3-21G\* results to be similar to the MP2 values. The systematic effects of electron correlation on the vibrational frequencies mirror those seen for the geometric parameters, and we conclude that the MP2 method includes chemically significant effects not accounted for by HF theory.

The differences between the MP2/6-31G\* calculation and the MP2/6-31G\*\* calculation are minor. Still, the 6-31G\* basis set,

TABLE II: Stationary Point Energies (kcal/mol), Relative to Reactants

method/basis set	$\Delta E^e$	$\Delta E^*$
MP2/6-31+G*	-9.66	7.66
MP2/6-31G**	-10.96	4.55
MP-SAC2/6-31G**//MP2/6-31G**	-11.04	4.56
CEPA/E//HF/E <sup>a</sup>		9.67

<sup>a</sup>Reference 24.

TABLE III: Geometries and Charges at Stationary Points

method/basis set	MP2/6-31+G*	MP2/6-31G**
Properties at Saddle Point *		
$r_{\text{CCl}}$ , Å	2.315	2.302
$r_{\text{CH}}$ , Å	1.07	1.07
$q_{\text{Cl}}$	-0.704	-0.727
$q_{\text{C}}$	-0.434	-0.183
$q_{\text{H}}$	0.281	0.212
Properties at Complex $\mathcal{C}$		
$r_{\text{CCl}}$ , Å	1.81	1.81
$r_{\text{CH}}$ , Å	3.27	3.14
$r_{\text{CH}}$ , Å	1.08	1.08
$\angle \text{HCCl}$ , deg	108.9	109.1
$q_{\text{Cl}}$	-0.972	-0.970
$q_{\text{C}}$	-0.193	-0.236
$q_{\text{H}}$	-0.593	-0.341
$q_{\text{H}}$	0.253	0.182
Properties at Reactants Limit $\mathcal{R}$		
$r_{\text{CCl}}$ , Å	1.78	1.77
$r_{\text{CH}}$ , Å	1.09	1.08
$\angle \text{HCCl}$ , deg	108.9	109.0
$q_{\text{Cl}}$	-1.0	-1.0
$q_{\text{C}}$	-0.056	-0.104
$q_{\text{H}}$	-0.631	-0.397
$q_{\text{H}}$	0.229	0.167

which has 59 contracted (144 primitive) basis functions—as opposed to 71 (156 primitive) for the 6-31+G\* basis set and 68 (153 primitive) for the 6-31G\*\* basis set—shows a decrease in absolute energy of 0.024 hartree when p functions are added to the hydrogens to form the 6-31G\*\* basis set; thus we narrow our consideration for our final predictions to the MP2/6-31G\*\* calculation and the MP2/6-31+G\* calculation. For comparison, however, we also consider the MP-SAC2/6-31G\*\*//MP2/6-31G\*\* calculation, as well as the previous CEPA calculation.

#### 4. Reactants and Complex

In order to choose between the MP2/6-31G\*\* calculation and the MP2/6-31+G\* calculation, we performed geometry optimizations of both the van der Waals complex ( $\mathcal{C}$ ) and the reactants ( $\mathcal{R}$ ) with both of these basis sets. At each geometry, the absolute MP2 energy for the 6-31G\*\* basis set is lower than that for the 6-31+G\* basis set.

The well depth,  $\Delta E^e$ , and the saddle point height,  $\Delta E^*$ , where both values are referenced to the reactants as zero of energy, are tabulated for the two basis sets in Table II. We also evaluated the MP-SAC2 corrected energies at the MP2/6-31G\*\* optimized geometries for both  $\mathcal{C}$  and  $\mathcal{R}$ , and from these we computed MP-SAC2/6-31G\*\*//MP2/6-31G\*\* values for  $\Delta E^*$  and  $\Delta E^e$ . In Table II we also list for comparison  $\Delta E^*$  and  $\Delta E^e$  for the CEPA/E//HF/E<sup>24</sup> results. Both the 6-31G\*\* and the 6-31+G\* basis sets give energies for the ion-dipole complex which fall within the experimental range (see above);<sup>19,20</sup> however, the 6-31G\*\* value of -11.0 kcal/mol is closer to the more recent experimental value<sup>20</sup> of -12.2 kcal/mol. Although the "experimental" value of the barrier height<sup>12</sup> is uncertain (see section 2), the analysis of section 6 shows that the 6-31G\*\* value of 4.5 kcal/mol is probably more accurate than the value of 7.7 kcal/mol from the 6-31+G\* basis set. The barrier height calculation by the CEPA method, which often overestimates barrier heights, is even higher, at 9.7 kcal/mol.<sup>24</sup> We thus believe that the 6-31G\*\* basis set is an all-around better choice than the 6-31+G\* basis set. Finally, we note that the MP-SAC2 correction changes the MP2/6-31G\*\*

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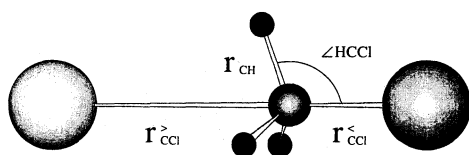


Figure 1. Geometry of the ion-dipole complex.

barrier height by only 0.01 kcal/mol, indicating that error in the barrier height due to the neglect of some correlation effects is very small. This lends further credence to the MP2/6-31G\*\* barrier height. Such cancellation of neglected correlation effects has been seen before in similar  $\text{S}_{\text{N}}2$  systems.<sup>32</sup>

In Table III we show the properties of the three stationary points as calculated by the most reliable of the method/basis-set combinations considered, MP2/6-31G\*\*. We also include values for the stationary points calculated at the MP2/6-31+G\* level for comparison. The definitions of the geometric parameters for  $\mathcal{R}$  and  $\ddagger$  are obvious; those for  $\mathcal{C}$  are defined in Figure 1. Comparing the geometric parameters, we see no significant difference between the two calculations. The charge values are taken from the Mulliken population analysis, which is inherently basis-set-dependent. We see that this dependence yields a significant variation in the resultant charge values. For example, the partial charges on the carbon and on the hydrogens at the reactant geometry are nearly a factor of 1.5 larger for the MP2/6-31+G\* calculation than for the MP2/6-31G\*\* calculation. We saw in previous work with the generalized Born model that such changes in the charge distributions can significantly affect solvation energies.<sup>7</sup> Thus, one should be especially cautious about using Mulliken charges in quantitative models of solvation.

## 5. Frequencies

In Table IV we give the normal-mode frequencies at the three stationary points,  $\mathcal{R}$ ,  $\mathcal{C}$ , and  $\ddagger$ , from the MP2/6-31G\*\* calculation. Comparison of the reactant frequencies with experimental frequencies for  $\text{CH}_3\text{Cl}$ <sup>29</sup> shows variations ranging from 4 to 7%. Various schemes for scaling some or all of the force constants have been suggested to correct for such errors.<sup>33</sup> In this spirit, we can generate more accurate results by scaling the frequencies. We scale all of the calculated frequencies by the same constant amount, this amount being chosen such that scaled frequencies for which there are known values agree with the known values. Choosing a scale factor of  $\eta = 0.94$ , i.e.

$$\nu_i^{\text{scaled}} = \eta \nu_i^{\text{ab initio}}$$

yields values for  $\nu_i^{\text{scaled}}$  at  $\mathcal{R}$  which deviate by less than 2.5% from the corresponding experimental values (see Table IV). We give the scaled values for the frequencies at  $\mathcal{C}$  and  $\ddagger$  in Table IV as well.

## 6. Rate Constants

Knowledge of the geometries and frequencies at  $\mathcal{R}$  and  $\ddagger$  and the energy difference between these two points is sufficient information for calculating rate constants by conventional transition-state theory<sup>34,35</sup> for this reaction. Because the transition state for the exchange reaction,  $\ddagger$ , is higher and tighter than the generalized transition state for association to the complex, we assume that a transition-state model with the single tight transition state  $\ddagger$  is a good model for the overall reaction. Under this assumption conventional transition-state theory (TST) may provide a reasonable estimate of the rate constant for two reasons. First,

TABLE IV: Frequencies (in  $\text{cm}^{-1}$ ) from MP2/6-31G\*\* Calculations and Experiment

	MP2/6-31G**	scaled ( $\eta = 0.94$ )	expt <sup>a</sup>
$\mathcal{R}$			
$a_1$	788	741	733
$e$	1082	1017	1018
$a_1$	1464	1377	1355
$e$	1545	1453	1488
$a_1$	3171	2981	2968
$e$	3289	3092	3044
$\mathcal{C}$			
$e$	72	68	
$a_1$	114	107	
$a_1$	695	653	
$e$	1033	971	
$a_1$	1396	1312	
$e$	1520	1429	
$a_1$	3225	3032	
$e$	3356	3155	
$\ddagger$			
$a_2''$	516i	485i	
$e'$	219	206	
$a_1'$	234	220	
$e''$	1007	947	
$a_2''$	1086	1021	
$e'$	1469	1381	
$a_1'$	3304	3106	
$e'$	3520	3309	

<sup>a</sup> Reference 29.

we are considering the exchange of two heavy atoms, via transfer of a methyl group, so tunneling should play only a small role, even at room temperature. Second, the net change in zero-point energy (of modes orthogonal to the reaction path) along the reaction path is small, with less than 100  $\text{cm}^{-1}$  difference between  $\mathcal{R}$  and  $\ddagger$ ; if the local variation of zero-point and entropic effects is also small then the variational transition state<sup>35</sup> should be at or close to the symmetric saddle point, at least at temperatures not too far above room temperature.

We evaluate the rate constants,  $k(T)$ , using the standard TST expression

$$k(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{\Phi^\mathcal{R}} e^{-\Delta E^\ddagger/k_B T}$$

where  $k_B$  is Boltzmann's constant,  $T$  is temperature,  $\Phi^\mathcal{R}$  is the reactant's partition function per unit volume, and  $Q^\ddagger$  is the transition-state partition function with the reaction coordinate removed. We calculate classical rotational partition functions from moments of inertia, which are calculated from the MP2/6-31G\*\* geometries at  $\mathcal{R}$  and  $\ddagger$ . Quantum mechanical vibrational partition functions are evaluated by the harmonic, independent-normal-mode approximation, using the scaled MP2/6-31G\*\* frequencies. Note that  $\Phi^\mathcal{R}$  also includes a relative translational partition function per unit volume. Using the MP2/6-31G\*\* barrier height,  $\Delta E^\ddagger$ , of 4.55 kcal/mol yields a thermal rate constant at 300 K of  $2.1 \times 10^{-15} \text{ cm}^3/(\text{molecule s})$ , a factor of 17 smaller than the experimental value of  $3.5 \times 10^{-14} \text{ cm}^3/(\text{molecule s})$ ,<sup>12</sup> indicating that the MP2/6-31G\*\* barrier is somewhat high. If we instead use the "experimental" barrier height of 1 kcal/mol (see section 2), but calculate the partition functions as before, we find a thermal rate constant of  $8.1 \times 10^{-13} \text{ cm}^3/(\text{molecule s})$ , a factor of 23 larger than the experimental value, indicating the experimental estimate of  $\Delta E^\ddagger = 1 \text{ kcal/mol}$  is quite low.

We find that adjusting the barrier height to 2.9 kcal/mol yields a conventional TST rate constant of  $3.3 \times 10^{-14} \text{ cm}^3/(\text{molecule s})$ , in agreement with the experimental value ( $3.5 \times 10^{-14} \text{ cm}^3/(\text{molecule s})$ ). Thus, if we ascribe the entire discrepancy between our calculated rate constants and the experimental rate constant to the use of incorrect barrier heights, we would estimate the true barrier to be 3 kcal/mol. However, although we have used frequencies which we believe to be reasonably accurate, we have made a (possibly significant) approximation in evaluating the vibrational

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partition functions, since we neglected anharmonicity and mode-mode coupling. Thus, we do not believe that the above adjustment is sufficient evidence for estimating the barrier height to better than  $\pm 1$  kcal/mol. It does indicate, however, that the MP2/6-31G\*\* value of 4.5 kcal/mol, while probably on the high side, is a more reasonable estimate of the barrier height than the 8–10 kcal/mol values in Table II.

In order to assess the importance of vibrational zero-point and quantization effects on this reaction, we also evaluate the completely classical TST rate constant at 300 K. This calculation differs from the calculation discussed above only in that the quantum mechanical vibrational partition functions are replaced by their classical analogues. (The zero-point energy difference between the transition state and reactants is not included in the classical calculation.) We find that the classical rate constant is only 20% slower than the rate constant computed with quantized vibrations at 300 K for this reaction.

## 7. Conclusion

On the basis of a comparison of calculated transition-state frequencies at seven ab initio levels for the gas-phase  $S_N2$  reaction of  $Cl^-$  with  $CH_3Cl$ , we conclude that second-order Møller-Plesset perturbation theory calculations with a 6-31G\*\* basis set provide

sufficiently reliable scaled frequencies and energies for creating a potential energy surface which will be useful in quantitative dynamical studies. The frequencies were improved somewhat by including a 6% correction at all geometries. This correction brings the calculated frequencies for  $CH_3Cl$  to within 2.5% of the experimental value for each mode. We saw that, for this reaction, the MP2 calculations account for a large fraction of the geometry-dependent part of the correlation energy ( $\mathcal{F}_2 = 0.917$ ), and that MP-SAC2 corrected energies, relative to the reactants energy, are very similar ( $\sim 0.01$  kcal/mol at the transition state) to the uncorrected MP2 values. Transition-state-theory rate constants calculated at 300 K and compared with experimental yield a semiempirical estimate of the barrier height of 3 kcal/mol, indicating that the MP2/6-31G\*\* value of 4.5 kcal/mol is reasonable, though probably a little high. Finally, we have tabulated our best estimates of geometries, charges, energies, and frequencies at the three stationary points on the reaction path.

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