

# *Ab initio* Calculations and RRKM/Master Equation Modeling of Chloroalkanes → Alkenes + HCl Reactions for Use in Comparative Rate Studies

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The computations reported in this paper were done in conjunction with an experimental study involving single pulse shock tube measurements of the thermal decomposition of three chloroalkanes, and that work is reported in an accompanying preceding paper. The overall aim of the combined work is to provide a well-defined and reliable set of rate constants over an extended temperature range (a self-consistent temperature standard) for use as reference reactions in comparative rate studies. In this largely computational work, we review the literature for thermochemical and chemical kinetic data for HCl elimination reactions from six alkyl chlorides: chloroethane, 1-chloropropane, 2-chloropropane, 2-chlorobutane, chlorocyclopentane, and chlorocyclohexane. We discuss the fundamental nature of these types of reaction (four-centered “semi-ion pair” transition states). We employ quantum chemical methods to compute the structure and energies of reactants, products, and transition states and employ this information, in conjunction with experimentally-determined rate constants, in RRKM/Master Equation modeling to develop a set of rate expressions which should be valid over a range of different pressures (low pressure to high pressure limits) and an extended range of temperatures.

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## Introduction

The thermal decomposition of haloalkanes to form alkenes and HX (X=F, Cl, Br, I) has been well studied for over half a century. When heterogeneous and free radical chemistry side-reactions are eliminated in experimental investigations, the fundamental process in thermal decomposition of the alkyl halides are HX eliminations, which can be considered unimolecular decompositions proceeding through a 4-centered transition state, and have been characterized as “semi-ion pair” reactions [see Maccoll (1969)].<sup>1</sup> The large electronegativity of the halogen atom, and the corresponding high dipole moment of hydrogen halides (HX), induce a dipole in the C=C double bond being formed upon HX elimination, and the barriers-to-elimination correlate well heterolytic bond energies ( $R-X \rightarrow R^+ + X^-$ ) for ion formation. In the transition states, the C–H bond is only slightly elongated, but the C–X bond is nearly broken with the carbon atom being very nearly  $sp^2$ -hybridized (product alkene-like).

These types of reactions have been the focus of many investigations over the years, both experimentally and computationally, because of the special nature of these reactions (semi-ion pair). Our interest in these reactions, however, is of a more practical nature type of reactions, as they are well-suited as reference (or standard) reactions for use in comparative rate studies. Because they have been well-studied, there are an extensive set of reliable rate constants for a variety of different reactions. In addition, employing different alkyl chlorides with different barriers-to-elimination (from about  $200 \text{ kJ mol}^{-1}$  to  $240 \text{ kJ mol}^{-1}$ ), the different chemical systems enable a range different temperature standards for comparative rate studies.

In this work, we briefly review the literature for experimental (and computational) studies where HCl elimination from chloroalkanes (dehydrochlorination) have been studied and identify systems where reliable rate constants are available. We also review thermochemical data available in the literature for the reactants and products of interest. This includes data measured the experimental component of this work and reported in an accompanying preceding paper.<sup>2</sup> The system studied are six chloroalkanes, three of which were subject of the experimental component to this work, and the other three have reliable constants reported in the literature. We then used several quantum chemical methods to compute the structure and energies of the transition states (along with that for reactants and products). These data, both experimental and computed, are used in RRKM/Master Equation modeling to provide rate expressions over a range of pressures and temperatures.

## Molecular Properties of Selected Species

### Overview.

Molecular properties and thermochemical functions impact RRKM/Master Equation (RRKM/ME) modeling used to extrapolate experimental rate expressions over a range of pressures and temperatures. This paper reviews selected relevant data for systems examined experimentally in this effort (2-chloropropane, chlorocyclopentane, and chlorocyclohexane), as well as those for the reference systems chloroethane, 1-chloropropane, and 2-chlorobutane. The experimental component of this work and the full analysis is given in an accompanying preceding paper.<sup>2</sup>

Table 1 reports pertinent thermochemical quantities  $\Delta_f H^\circ(\text{g}, 298 \text{ K})$ ,  $S^\circ(\text{g}, 298 \text{ K})$ ,  $C_p(\text{g}, 298 \text{ K})$  from our RRKM/ME models. Enthalpies of formation are from the literature as noted, while entropy and heat capacity values are based on our calculations. For comparison literature values of the latter quantities are also included in the table. Parameters used to treat hindered rotors (or pseudo-rotors) in the molecules and transition states are presented in Table 2. The barriers given therein were chosen to match the B3LYP/6-31G(d) torsional frequencies (also given) for each molecule. Given parenthetically in this table are values that would yield the literature result for the standard entropies,  $S^\circ(\text{g}, 298 \text{ K})$ , given in Table 1. The computed model entropies at standard state differed with the literature values by less than  $1 \text{ J mol}^{-1} \text{ K}^{-1}$ , except for 1-chlorobutane and 1-chloropropane where the differences were (2 to 5)  $\text{J mol}^{-1} \text{ K}^{-1}$ .

In Table 3, we provide a comparison between experimentally-derived enthalpies of reaction and computed values from our G3MP2B3 calculations. Differences are (2 to 4)  $\text{kJ mol}^{-1}$ , roughly on the order of the experimental uncertainties. On this basis we estimate the calculated enthalpies of reaction and barriers to reaction to be accurate to about (3 to 5)  $\text{kJ mol}^{-1}$ .

**Acyclic chloroalkanes: chloroethane, 1-chloropropane, 2-chloropropane, 2-chlorobutane.**

Thermochemical functions were calculated using a standard Rigid Rotator Harmonic Oscillator (RRHO) approach with inclusion of hindered internal rotations approximated as symmetric  $n$ -fold potentials as per the methodology of Pitzer.<sup>3, 4</sup> The general methodology has been discussed further and employed elsewhere in detail (see Benson<sup>5</sup> and Frenkel et al.<sup>6</sup>) and its application to non-cyclic monochloroalkanes is straightforward. Specific parameters are provided in Tables 1-3 and in Table S1 of the supplementary material.

## Cyclopentane and Chlorocyclopentane.

Cyclic structures have special considerations pertaining to ring modes. In this section, we discuss the cyclopentane and its derivatives, and in the next section, cyclohexane and its derivatives.

There has been a significant amount of work considering the structures and thermochemical properties of cyclopentane and its substituted derivatives. Much of the interest in this area dates to the early work by Kilpatrick, Pitzer, and Spitzer,<sup>7</sup> who recognized that the entropy and heat capacity of cyclopentane is more accurately predicted if one invokes a “pseudo-rotational” mode with an associated symmetry number of five. In cyclopentane, the most stable configuration is where four carbons are roughly in the same plane and the fifth carbon is out-of-plane. Through a pseudo-rotational mode, each carbon in turn moves out-of-plane around the ring (hence, a pseudo-rotation). However, the mode is not a rotation (around the ring), but involves in-of-plane and out-of-plane motions where the mode can be described as a low frequency asymmetric twist within the ring, rather than a higher frequency symmetric inversion mode. In the former, conversion from one conformer to another (indistinguishable) conformer proceeds through a low energy “twisted” configuration, while in the latter it proceeds through a higher energy planar configuration. In cyclopentane, the barrier-to-conversion is very small (on the order of a vibrational spacing or less) and the mode is essentially a “free pseudo-rotor” (“zero” barrier). The barrier-to-inversion through a planar configuration is more comparable to a torsional barrier in an alkane, *ca.* (20 to 30) kJ mol<sup>-1</sup>. The effective moment of inertia for the pseudorotation in cyclopentane was determined to be  $11.0 \times 10^{-47}$  kg m<sup>2</sup> by Durig and Wertz.<sup>8</sup>

If a substituent such as chlorine or methyl is placed on cyclopentane, the barrier to pseudo-rotation increases to *ca.* (5 to 10) kJ mol<sup>-1</sup>, but the process still occurs readily even at room temperature. In contrast to cyclopentane itself, the pseudo-rotational motion in substituted analogs interconverts distinguishable conformers; for example, *e*-chlorocyclopentane is where the chlorine atom is roughly in the plane (“equatorial”) and *a*-chlorocyclopentane is where the chlorine atom is roughly perpendicular to the plane (“axial”). The axial conformer is generally slightly more stable by about (1 to 2) kJ mol<sup>-1</sup> in substituted cyclopentanes. Loyd *et al.*<sup>9</sup> determined that the pseudo-rotational frequency of chlorocyclopentane from microwave studies to be 52 cm<sup>-1</sup>. This likely corresponds to the twist normal mode that puckers the ring and involves out-of-plane motions by

only methylene groups, rather than a conformational transition involving an out-of-plane motion by the chlorine atom.

Badawi *et al.*<sup>10</sup> determined that the equatorial conformer of chlorocyclopentane is less stable than the axial conformer by  $1.73 \pm 0.18 \text{ kJ mol}^{-1}$  ( $145 \pm 15 \text{ cm}^{-1}$ ) from the temperature dependence of the intensity of vibrational bands. Their measurements improve on earlier estimates of the energy difference of (1 to 3)  $\text{kJ mol}^{-1}$  by Ekejiuba *et al.*,<sup>11</sup> Harris *et al.*,<sup>12</sup> Durig *et al.* (1995),<sup>13</sup> and the molecular mechanics calculations of Shim *et al.*<sup>14</sup> The barrier-to-conversion between the conformers has been derived from experimental methods to be  $8.3 \text{ kJ mol}^{-1}$  and  $4.6 \text{ kJ mol}^{-1}$  by Hildebrand and Shen<sup>15</sup> and Durig *et al.* (1969),<sup>16</sup> respectively. The moment of inertia for the pseudorotation has been derived in various studies to be  $14.5 \times 10^{-47} \text{ kg m}^2$  by Durig *et al.* (1995),<sup>13</sup>  $16.0 \times 10^{-47} \text{ kg m}^2$  by Diky *et al.* (2001),<sup>17</sup> and another value by Diky *et al.* (2001)<sup>17</sup> of  $19.3 \times 10^{-47} \text{ kg m}^2$  given different assumptions. Badawi *et al.*<sup>10</sup> used quantum chemical calculations to predict a barrier-to-conversion of  $6.5 \text{ kJ mol}^{-1}$  and  $10.5 \text{ kJ mol}^{-1}$  using the B3LYP/6-311G(d,p) and MP2/6-311G(d,p) methods, respectively. Shim *et al.*<sup>14</sup> used molecular mechanics calculations to predict a similar barrier of about  $7.5 \text{ kJ mol}^{-1}$ . Altona *et al.*<sup>18</sup> using molecular mechanics estimated a barrier to pseudorotation of about  $5 \text{ kJ mol}^{-1}$ , and also computed the higher energy direct barrier to inversion (through a planar configuration) of about  $22 \text{ kJ mol}^{-1}$ . The most comprehensive and detailed study is that by Diky *et al.* (1993)<sup>19</sup> who measured the IR spectra, heat capacity, vaporization enthalpy, and determined the values  $C_{p,m}^{\circ}(\text{g}, 298.15 \text{ K}) = 98.86 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $S_m^{\circ}(\text{g}, 298.15 \text{ K}) = (339.54 \pm 0.29) \text{ J mol}^{-1} \text{ K}^{-1}$ . They also derived the thermodynamic properties of the gas phase species. Their values were adopted in the compilation of the Thermodynamics Research Center<sup>6</sup> and their vibrational assignment differs only slightly from the later work of Badawi *et al.*<sup>10</sup>

## Cyclohexane and Chlorocyclohexane.

Cyclohexane and substituted-cyclohexanes also have different conformers – the most stable form being a “chair” form and the less stable form being a “twist-boat”. A chair cyclohexane conformer has four carbon atoms (typically numbered 2, 3, 5, and 6) roughly in the same plane, and the two other opposing atoms (1, 4) “up” and “down” relative to the plane (*anti*). In the twist-boat conformer, the opposing atoms are roughly *cis* to each other (on the same side of the plane), while the four other atoms are twisted relative to a common plane. The barrier-to-conversion between the “chair” and “twist-boat” conformers of cyclohexane (see Ross and Troe<sup>20,21</sup> and Kakhiani et al.<sup>22</sup>) is significantly larger than that for interconversion of cyclopentane conformers and on the order of a large torsional barrier in an alkane, *ca.* (50 to 60) kJ mol<sup>-1</sup>. In a substituted-cyclohexane, there is an additional conformation consideration where the substituent can be either in an equatorial position (“in-plane”) or in an axial position (“out-of-plane”). The difference in energy between these two conformers is relatively small *ca.* (1 to 2) kJ mol<sup>-1</sup> and the equatorial configuration is slightly more stable. There is, however, a modest barrier (*ca.* 45 kJ mol<sup>-1</sup>) to conversion between the two forms; in addition, there are metastable “twist-boat” conformers *ca.* 24 kJ mol<sup>-1</sup> higher in energy than the chair form with a barrier to conversion of also about 45 kJ mol<sup>-1</sup>.

From the temperature dependence of the intensity of vibrational bands, Durig *et al.* (2008)<sup>23</sup> determined the axial conformer of chlorocyclohexane to be less stable than the equatorial conformer by  $1.58 \pm 0.16$  kJ mol<sup>-1</sup>. These measurements improved earlier determinations of (1.1 to 2.1) kJ mol<sup>-1</sup> by Stokr et al.,<sup>24</sup> Gardiner *et al.*,<sup>25</sup> Caminati et al.,<sup>26</sup> Bugay *et al.*,<sup>27</sup> and Diky *et al.* (1994).<sup>28</sup> Both Stokr *et al.* and Bugay *et al.* also determined the barrier-to-conversion to be about 45 kJ mol<sup>-1</sup>. A computed conformational energy difference of 1.9 kJ mol<sup>-1</sup> from *ab initio* calculations by Wiberg<sup>29</sup> is in good agreement with the experimentally-derived values. Molecular mechanics calculations by Shim *et al.*<sup>14</sup> also predicted a very similar conformational energy and barrier-to-conversion.

The enthalpy of formation and standard state entropy in the gas phase for chlorocyclohexane have been determined from experiment to be  $\Delta_f H^\circ(\text{g}, 298 \text{ K}) = -(164 \pm 2.0)$  kJ mol<sup>-1</sup> and  $S_m^\circ(\text{g}, 298.15 \text{ K}) = (348.0 \pm 2.3)$  J mol<sup>-1</sup> K<sup>-1</sup>, respectively, by Diky *et al.* (1994).<sup>28</sup> They combined this information

with other literature data to compute statistical values of the thermochemical functions for gaseous chlorocyclohexane. Our values are in close agreement (see Table 1).



## **Product Alkenes.**

Under our conditions, the thermodynamic properties of the product alkenes primarily affect calculated rate constants for the reverse HCl additions, with little effect on the RRKM results for dehydrochlorination. Values for the olefins are available in standard texts (see Frenkel *et al.*<sup>6</sup> and Stull *et al.*<sup>30</sup>). The thermochemical functions of propene are well established while those for cyclopentene and cyclohexene have slightly larger uncertainties because of the ring modes. Our values for the cycloalkenes are in good agreement with the recommendations of Frenkel *et al.*,<sup>6</sup> which are based on the evaluations of Dorofeeva *et al.*<sup>31</sup>

## Symmetry Numbers and Reaction Path Degeneracies due to Isomers.

It is important to correctly identify the symmetry numbers and reaction path degeneracies due to isomers associated with each of the molecules and transition states in the reactions under consideration. A general discussion of the issues can be found in Section 3.9 of Gilbert and Smith<sup>32</sup> and references cited therein. Brief overviews of specific systems are given below:

*Chloroethane.* Chloroethane has a symmetry number of 3 associated with the methyl torsion which is not present in the *Chloroethane-HCl* transition state. Inclusion of this symmetry number increases the pre-exponential factor by a factor of three, intuitively consistent with the existence of three equivalent reactive hydrogens.

*1-Chloropropane.* 1-Chloropropane has a symmetry number of 3 associated with the methyl torsion, but this is retained in the transition state (no net symmetry change). The transition state has a degeneracy of 2, due to the existence of a mirror plane in the structure (optical isomers). This increases the pre-exponential factor by a factor of two and is intuitively consistent with the existence of two equivalent reactive hydrogens.

*2-Chloropropane.* 2-Chloropropane has two methyl rotors with symmetry numbers of 3 and one of these rotors is lost in the transition state. The *2-Chloropropane-HCl* transition state is also optically active and has a degeneracy of 2, thereby accounting for six equivalent reactive hydrogens.

*2-Chlorobutane.* Both 2-chlorobutane and the transition state for 2-chlorobutane  $\rightarrow$  (*Z*)-2-butene + HCl have two methyl rotors plus mirror planes (thus, no net change in entropy due to isomers). Elimination of the alternate secondary hydrogen results in (*E*)-2-butene and is a separate reaction.

*Chlorocyclopentane.* Chlorocyclopentane has a symmetry number of 1 and degeneracy of 1. There is a low frequency inversion/pseudorotation (symmetry = 1) that must be considered in the molecule. The *Chlorocyclopentane-HCl* transition state is optically active (degeneracy=2) and there is a low frequency inversion (symmetry = 1) that must be considered.

*Chlorocyclohexane.* The degeneracies for chlorocyclohexane and the associated transition state for HCl elimination need to be carefully considered, because these depend on the models employed for the partition functions. Chlorocyclohexane has two low energy isomers, *e*-chlorocyclohexane

(equatorial) being more stable than *a*-chlorocyclohexane (axial) by about 2 kJ mol<sup>-1</sup>. [Multiple “twist-boat” conformations are also possible in this molecule, but are not considered because they are about 25 kJ mol<sup>-1</sup> higher in energy.] The barrier-to-isomerization between *e*-chlorocyclohexane and *a*-chlorocyclohexane is modestly large (about 45 kJ mol<sup>-1</sup>) and thus these should be considered to be distinct isomers. In computing thermochemical functions, we employed the most stable form *e*-chlorocyclohexane, considering it to have a “frozen” ring, and consequently employed a degeneracy of 2 to approximately account for the *a*-chlorocyclohexane isomer. The *Chlorocyclohexane-HCl* transition state has two slightly different transition states that correlate with (map to) the two optical isomers of the product cyclohexene. In addition, each of these transition states have (*R,S*) optical isomers. Thus, the overall degeneracy of the transition state is 4. The net ratio of the degeneracy in the transition state to the reactant is 2 – that is, a reaction path degeneracy of 2, consistent with what one might intuitively guess.

## Computational Methodology, Uncertainties, and General Discussion

### Computational Methodology.

The composite *ab initio* methods G3MP2B3 and G3B3,<sup>33, 34</sup> variants of the Gaussian-3 method (G3), were used to calculate thermochemical and chemical kinetic parameters for reactions of interest in this study. These variants use B3LYP/6-31G(d)<sup>35, 36</sup> geometries and zero-point energies instead of MP2/6-31G(d) geometries and HF/6-31G(d) zero-point energies used in standard G3 methods. Molecular geometries derived from B3LYP/6-31G(d) and other hybrid density functional theory (DFT) calculations have been observed to usually perform better than *ab initio* geometries for use in energy calculations, particularly where spin contamination in the wavefunctions may be present in open shell radical species or transition states. Vibrational frequencies for the various reactants, products, and transition states were computed using the B3LYP/6-31G(d) method and then scaled by 0.96 to approximate experimental values. This scaling factor is a “best fit” value determined from calculations of vibrational frequencies for a wide range of molecules.<sup>37</sup> All calculations were performed using Gaussian 03.<sup>38</sup>

For computing rate constants, in our RRKM/ME analysis, we used an estimated symmetric Eckert tunneling parameter of  $\alpha = V^*/h\omega^* = 2.0$ , and used an estimated exponential step-down energy transfer parameter of  $680 \text{ cm}^{-1}$ . The tunneling parameter was chosen, because it is an intermediate value<sup>39</sup> and consistent with that employed by McGrath and Rowland<sup>40</sup> based on their *ab initio* calculations of the potential energy surface near the barrier for HCl elimination from chloroethane. This resulted in tunneling corrections that increased the rate constants by about a factor of 2 at the lower end of the temperature range (600 K) and about 20% at the higher end (1000 K). We used the same tunneling function for all of the reactions considered. The step-size down parameter of  $680 \text{ cm}^{-1}$  used in this work is consistent with that typically needed to fit the falloff behavior of chlorinated species and was used for all of the reactions considered. Given that the reactions are all homologous and that there are many variables and uncertainties in the *ab initio* calculations and the RRKM/ME analysis, we deemed it statistically unwarranted to employ different tunneling and step-down parameters for the different systems without further evidence for such – and consequently, fixed the values at “reasonable” values.

### **Analysis of Uncertainties in the Calculations.**

Before presenting in detail the results of our calculations and comparing those computed data to experimentally-determined rate constants, it is instructive to consider uncertainties present in such computations. Our discussion of estimated uncertainties will use the reaction chlorocyclohexane  $\rightarrow$  cyclohexene + HCl as an example; similar analyses can be done for other reactions.

Given the uncertainty in the generic scaling factor ( $0.96\pm 0.022$ ) used to scale B3LYP/6-31G(d) vibrational frequencies, we computed a corresponding uncertainty of about  $3 \text{ kJ mol}^{-1}$  in the zero point energy  $E_{\text{ZPE}}$  of the transition state structure for HCl elimination from chlorocyclohexane and an uncertainty in the entropy at standard state  $S^\circ(\text{g}, 298 \text{ K})$  of about  $2 \text{ J mol}^{-1} \text{ K}^{-1}$ . However the uncertainty in the rate constant will be significantly smaller, since it is dependent on differences between the transition state and the reactants – not the absolute quantities. Considering this, we found that the uncertainty in the difference in zero point energies  $\Delta E_{\text{ZPE}}$  and  $\Delta S^\circ$  were about  $0.5 \text{ kJ mol}^{-1}$  and  $0.25 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively, which correspond to uncertainties of about (6 to 11)% and 3%, respectively, in the computed rate constants in the temperature range of interest (600 K to 1000 K).

We also considered the impact of uncertainties in structures and vibrational frequencies (due to different structures) of the reactants and transition states. We estimated these values in several different ways. First, we computed transition state structures using different levels of theory/electron correlation (HF, MP2, QCISD, B3LYP). Second, we considered the different isomeric forms of the reactants and transition states. We then employed the different structures and set of vibrational frequencies in an RRKM/ME model and computed rate constants in the temperature range of interest. Based on all of these considerations, we estimated the uncertainty in a rate constant due to the uncertainty in the structures and vibrational frequencies of a molecule or transition state was about (6 to 8)%.

The most significant uncertainty in the entropy is the magnitude in change of the low frequency modes from the reactants to the transition state. A low frequency “breathing” mode may change significantly (e.g., from  $120 \text{ cm}^{-1}$  to  $180 \text{ cm}^{-1}$ ) depending on other changes in the molecule (or transition state). We note that in such cases that the stiffening of one mode is often compensated by loosening of another, thus making it difficult to unambiguously assign the corresponding

uncertainty in a rate constant. Our empirical observations on a number of different systems suggest that (10 to 15)% is a reasonable estimate of the uncertainty in the derived rate constant from the uncertainty in the low frequency modes. For cycloalkanes, the inversion and twist modes may be part of a “frozen” (low entropy) structure at low temperatures, while converting the molecule to a “freely-puckering” (excess entropy) structure at higher temperatures. Uncertainties in systems with these more complicated modes are undoubtedly larger than for simple systems, and our empirical observation is that in these cases the uncertainty could be on the order of (25 to 50)%. Essentially, these “uncertainties” are related to the fact that one approximates these ring modes as “harmonic vibrations” (which they are not) and that they are not coupled (which they are not) – the fundamental uncertainty here is accurate partition functions for these internal modes.

One must also consider the uncertainty of tunneling on the computed rate constants. In this work, we employed an estimated symmetric Eckert tunneling parameter of  $\alpha = V^*/\hbar\omega^* = 2.0$ , a generic value chosen to be consistent with the work of McGrath and Rowland<sup>40</sup> for HCl elimination from chloroethane. If we assume the tunneling parameter has a value of  $\alpha = 2.0 \pm 0.4$ , we compute an overall uncertainty in the rate constants of about 40% at lower temperatures (600 K) and about 10% at higher temperatures (1000 K). This translates into an uncertainty of about  $\pm 3 \text{ kJ mol}^{-1}$  in the Arrhenius activation energy and 30% in the pre-exponential A-factor.

We also considered uncertainties in the computed barrier heights on the rate constants. This is possibly the largest (and “most uncertain”) uncertainty to consider – it is difficult to quantify such because there are no absolute references for comparison. We attempted, nevertheless, to estimate the uncertainty in the barrier in several ways. First, we computed G3MP2B3 energies for the transition state for HCl elimination from chlorocyclohexane using different optimized geometries. We found that a QCSID/6-31G(d) geometry gave the lowest transition state barrier ( $E_0 = 218.0 \text{ kJ mol}^{-1}$ ) with the B3LYP/6-31G(d), MP2/6-31G(d), and HF/6-31G(d) geometries giving barriers about  $1.0 \text{ kJ mol}^{-1}$ ,  $1.6 \text{ kJ mol}^{-1}$ , and  $7.6 \text{ kJ mol}^{-1}$  higher, respectively, than the that from the QCSID/6-31G(d) geometry. Secondly, we computed the barrier height from G3B3 and found it to be about  $3 \text{ kJ mol}^{-1}$  higher. Thirdly, we found an alternative transition state structure for this system (where the cyclohexane ring was skewed slightly different) that was about  $5 \text{ kJ mol}^{-1}$  higher in energy. Fourthly, as discussed earlier, we found the differences between the computed enthalpies of reactions and the experimental values to be on the order of (2 to 4)  $\text{kJ mol}^{-1}$  (roughly

the experimental uncertainties in these values). Based on these combined observations, we consider the uncertainty in the computed barriers to be on the order of (3 to 6)  $\text{kJ mol}^{-1}$  for HCl eliminations from monochloroalkanes. An uncertainty in the energetics of about 4  $\text{kJ mol}^{-1}$  translates into an uncertainty of about 70% (a factor of 1.7) in the rate constant over the temperature range of interest in this work. We note, however, that there are typically compensation effects in the computed pre-exponential terms and the barriers to reaction: a tighter transition-state is likely to have a lower barrier. This highlights the need to consider the uncertainty in the free energy change ( $\Delta G$ ), and not treat the entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) changes as fully separable quantities. Consequently, for the presently considered reactions, which appear to be computationally well behaved, a more realistic estimate of the uncertainty in a computed rate constants is likely on the order of (25 to 35)%. Coincidentally, this is similar to the experimental uncertainties. Of course, one should not generalize the above uncertainty estimates to rate constants computed for unrelated reactions.

## General Features of Hydrogen Halide (HX) Eliminations from Haloalkanes.

To put in context the results of our calculations and for making comparisons with rate constants from experimental determinations, we first provide a general overview of HX (hydrogen halide) eliminations from alkyl halides.

Four-centered HX eliminations from alkyl halides have been characterized as “semi-ion pair” reactions based on early work by Benson and coworkers<sup>41, 42</sup> who drew upon earlier observations by Maccoll and Thomas.<sup>1, 43</sup> The basic concept of the semi-ion pair model is that the hydrogen halides, having high dipole moments, will upon addition to an unsaturated site in an alkene induce a dipole in the C=C double bond resulting in a polar four-center transition state with significant charge separation. This model is in accord with the observation that barriers to elimination are correlated with heterolytic bond energies ( $R-X \rightarrow R^+ + X^-$ ) for ion formation and not with homolytic bond energies ( $R-X \rightarrow R\cdot + X\cdot$ ) for radical formation. Several researchers have proposed variations of this basic model, including Benson and coworkers,<sup>41, 42</sup> Tschuikow-Roux and coworkers,<sup>44, 45</sup> and Setser and coworkers.<sup>46, 47</sup> An excellent review of the work in this area up to 1994 is provided by Toto *et al.*,<sup>48</sup> who also conducted some of the first high level *ab initio* calculations for these types of reactions. Their calculations qualitatively support the semi-ion pair model, but differ in details of the charge separation in the transition state.

Computed transition state structures for HX eliminations show that the C–X bond is nearly broken and that the halide-binding carbon has become largely  $sp^2$ -hybridized (the local configuration is nearly planar), while the reacting C–H bond is only partially elongated and its carbon atom largely remains  $sp^3$ -hybridized (having a pyramidal structure). These effects are illustrated in Table 4 which shows relevant computed bond lengths for reactants, products, and transition states (TS) for HCl elimination from chlorocyclohexane. Note that the C–Cl bond distances in the transition states are over 0.9 Å longer than in starting chlorides (the covalent bond is essentially broken), that the C–C bond distances in the transition states are only 0.04 Å longer than in cyclohexene (the new pi bonds are significantly formed), and that the C–H bond distances in the transition states are only slightly stretched (about 0.04 Å) relative to those in the chlorides (indicating the bonds are largely intact). Inspection of the bond angles in the transition state reveals that the CH bond on the “C–Cl” carbon atom is only about 10° out-of-plane (that containing the adjacent carbon atoms) - or quasi- $sp^2$ -hybridized, while the CH bond on the



adjacent “C–H” carbon atom in the elimination site is about 30° out-of-plane – or quasi-sp<sup>3</sup>-hybridized. The two transition state structures for HCl elimination from chlorocyclohexane are shown in the Figure 1, and clearly show the elongated C–Cl bond and the sp<sup>2</sup>-hybridized nature of the “C–Cl” carbon atom involved in the four-center elimination. The semi-ion pair nature of the transition state is further elucidated by examining computed Mulliken charge populations for reactants and transition states. From the MP2/G2MP2large calculation in the G3MP2B3 method, we found Mulliken charge populations of:

$$a=\{-0.35,+0.75\}; \{H,Cl\}=\{+0.03,-0.55\} \quad [\text{chlorocyclohexane}]$$

$$\{C_H,C_{Cl}\}=\{-0.31,+0.38\}; \{H,Cl\}=\{+0.34,-0.89\} \quad [\text{chlorocyclohexane-HCl TS}]$$

Here, {C<sub>H</sub>,C<sub>Cl</sub>} denotes the two carbon atoms connected to the hydrogen and chlorine atoms, denoted {H,Cl}, that are involved in the reaction. The computed Mulliken charges clearly show a significant weakening in the C–Cl bond where the magnitude of the charge on the chlorine atom has significantly increased (-0.55 → -0.89) concurrent with a significant decrease of the charge on the adjacent carbon atom (+0.75 → +0.38) and also shows the beginning of formation of an H–Cl bond where the charge on the hydrogen atom has significantly increased (+0.03 → +0.34). In addition, we see a minimal change in the charge on the one carbon atom where the C–H bond has only been slightly weakened (-0.35 → -0.31).

For all of the reactions considered in this work, we found a single transition state structure for elimination of HCl with two exceptions, one general and the other more specific. First, a number of the transition states can be considered optically active. This leads to a reaction path degeneracy of 2 for these reactions, where the two transition states are identical except that they are mirror images of each other. Second, for HCl elimination from chlorocyclohexane, we found two slightly different transition state structures. These two structures (Figure 1) are most easily visualized by considering the reverse addition of HCl to cyclohexene, which exists as an optically active non-planar molecule in which the two carbons opposite the double bond are twisted out of the plane, one “up” and one “down”.<sup>31, 49, 50</sup> The distinct transition-states arise depending on whether the Cl adds opposite the “up” or “down” –CH<sub>2</sub>– (methylene) group. We found a quasi-symmetric (in the ring) higher energy conformer where the Cl atom is *cis* to the opposing puckered methylene group and an asymmetric lower energy conformer where the Cl atom is *trans*. The computed difference

in energy of the transition-states is about  $5.0 \text{ kJ mol}^{-1}$  from the G3MP2B3 calculations. Although not shown in this figure, the structure of the ring in the cyclohexene molecule itself is very similar to the asymmetric lower energy transition state structure – with the exception that the both H-atoms (rather than just one) are fully in the plane defined by the C=C double bond.

Table 5 shows the dependence of the transition state structure on the level of theory and conformational geometry for the chlorocyclohexane  $\rightarrow$  cyclohexene + HCl reaction. Computed values of the C–Cl, C–H, H–Cl, and C–C bond distances are given and may be compared with those in the reactants and products. Key things to note are that the C–Cl bond is significantly lengthened in the transition state, that the C–C bond is very product-like, and that the C–Cl bond length is sensitive to the level of theory and the details of the structure, while other bond distances are relatively unaffected.

## Computed *ab initio* Barriers and RRKM/ME Rate Expressions

### Systems Studied.

In the experimental component of this work, we measured the rates of HCl elimination from chloropropane, chlorocyclopentane, and chlorocyclohexane. In the computational component of this work, we used *ab initio* quantum chemical calculations to compute the structures and barriers of transition states for these reactions, and then employed RRKM/master equation methods to predict the rates of reactions at the experimental conditions, as well as extrapolated these values to the high pressure limit. To assist in ascertaining the validity of such quantum calculations for computing barriers and rate constants for these three molecules, we also computed barriers to HCl elimination for a number of reference reactions where there are experimental data for comparison. These additional reactions are: chloroethane  $\rightarrow$  ethane + HCl, 1-chloropropane  $\rightarrow$  propene + HCl, and 2-chlorobutane  $\rightarrow$  (*Z*)-2-butene + HCl. Table 6 summarizes the computed *ab initio* barriers and the computed rate expressions from the corresponding RRKM/ME analyses, and compares the results to experimental values in the literature.

## HCl Eliminations from Chloroethane, 1-Chloropropane, and 2-Chlorobutane.

*Chloroethane.* In Table 6 we reference several experimental values and one computed value by Rowland and coworkers. There are other values from quantum calculations at lower levels that can be found in the literature including work by Toto *et al.* (1994),<sup>47</sup> by Rajkumar (2003),<sup>51</sup> and by Allen (2004).<sup>52</sup> Our computed rate constants are about 20% higher and 15% higher than the respective rate constants measured in the low temperature static experiments of Heydtmann *et al.*<sup>53</sup> and the high temperature shock tube experiments of Evans *et al.*<sup>54</sup> Based on our RRKM/ME analysis, the low temperature measurements at 100 torr (0.133 bar)<sup>52</sup> are at about 90% of the high pressure limit, while the high temperature measurements at 7 atm (7.1 bar)<sup>53</sup> are at about 80-90% of the high pressure limit. In our analysis of the low temperature experiments, where the bath gas was the reactant chloroethane, we used an energy transfer parameter of 2000 cm<sup>-1</sup>. At 755 K this leads to rate constants at 1 torr (1.33x10<sup>-3</sup> bar) that are about 40% of those at 0.133 bar, which is consistent with the fall-off observed by Heydtmann *et al.*

*1-Chloropropane.* The decomposition of 1-chloropropane has been studied experimentally by static methods near 700 K and 0.5 bar, and in shock tubes at near 1030 K and 7 bar. Our RRKM/ME analysis indicates the measured rate constants are near their respective high pressure limits. Although our calculations suggest activation energies (5 to 7) kJ mol<sup>-1</sup> larger than experiment, this is offset by a slightly larger pre-exponential factor and the calculated rate constants are only (10 to 15)% lower than the experimental values.

*2-Chlorobutane.* For 2-chlorobutane, we considered the HCl elimination channel that produces (*Z*)-2-butene, which is similar with regard to both the chemical groups and the geometric orientation to the HCl eliminations from chlorocyclopentane and chlorocyclohexane. Based our RRKM/ME model, the experimental rate constants reported by Heydtmann and Rinck<sup>55</sup> appear to be at the high pressure limit. Our calculated rate constants are about 30% lower than the reported values and the computed rate expression has an activation energy ( $E_a$ ) about 2.2 kJ mol<sup>-1</sup> higher than the experimentally-derived value, which itself has a reported uncertainty of about 2 kJ mol<sup>-1</sup>. Lowering the computed barrier by 1.5 kJ mol<sup>-1</sup> provides good agreement between the computed

and experimental rate constants. Adjusting either the low frequency modes or the torsional barriers in the molecule and/or the transition state by 10-25% can also account for the difference.

For the above three reference systems the level of agreement between the computed and experimental values is excellent, and better than expected based on typical reported experimental uncertainties of 25% and our estimate of computational uncertainties (see prior section) of (25 to 35)%.

## HCl Eliminations from 2-Chloropropane, Chlorocyclopentane, and Chlorocyclohexane.

Also provided in Table 6 are comparisons of the computed and experimental rate constants for HCl elimination from 2-chloropropane, chlorocyclopentane, and chlorocyclohexane, the primary molecules of interest in this study. As discussed in more detail below, we again find excellent agreement between the computed values and experimental data – coincidentally close, we believe given the limitations in computing rate constants based upon *ab initio* computed transition states. The only difference outside an estimated confidence level of 10-25% is for chlorocyclohexane, and this is discussed below.

*2-Chloropropane.* We computed the rate constants for 2-chloropropane  $\rightarrow$  propene + HCl in the range 585 K to 1025 K using molecular structures and vibrational frequencies (scaled by 0.96) for the reactants, products, and transition state from B3LYP/6-31G(d) calculations. For the reactant 2-chloropropane, the transition state, and the product propene, we replaced the appropriate torsional frequencies of the CH<sub>3</sub>- (methyl) hindered rotors having three-fold potentials with moments of inertia (I) derived from the computed structures and barrier heights ( $V_3$ ) that were chosen to replicate the torsional frequencies. The data are given in Table 2. We employed a reaction path degeneracy of 2 (the transition state has two optical isomers), a barrier height of  $E_0 = 220.9 \text{ kJ mol}^{-1}$  (from G3MP2B3 calculations), used an estimated symmetric Eckert tunneling parameter of  $\alpha = V^*/h\omega^* = 2.0$ , and used an estimated exponential step-down energy transfer parameter of  $680 \text{ cm}^{-1}$ . As mentioned earlier, the tunneling parameter was chosen because it is an intermediate value<sup>39</sup> and consistent with that employed by McGrath and Rowland<sup>40</sup> based on their *ab initio* calculations of the potential energy surface near the barrier for HCl elimination from chloroethane. In the 2-chloropropane system, use of this parameter resulted in tunneling corrections of about 2.0 at 600 K, 1.45 at 800 K, and 1.21 at 1100 K. The energy transfer parameter of  $680 \text{ cm}^{-1}$  was chosen in accordance with other work with chlorinated hydrocarbons.

As can be seen in Table 6, the computed pre-exponential is within 10% of the experimentally-derived quantity and the computed activation energy is within about  $1 \text{ kJ mol}^{-1}$ . For 2-chloropropane, one can obtain the equivalent rate expressions by increasing a low frequency vibrational mode by about 10% from  $114 \text{ cm}^{-1}$  to  $125 \text{ cm}^{-1}$  (simultaneously increasing  $E_0$  by  $0.6 \text{ kJ}$

mol<sup>-1</sup> to 221.5 kJ mol<sup>-1</sup>) or by decreasing the step-down size from 680 cm<sup>-1</sup> to 620 cm<sup>-1</sup> (while increasing E<sub>0</sub> by 1.0 kJ mol<sup>-1</sup> to 221.9 kJ mol<sup>-1</sup>).

From the RRKM/ME analysis, we found that the rate constant at 1025 K was at about 70% of the high pressure limit, and at 700 K it was essentially at the high pressure limit. The high pressure rate expression relative to that at 2 bar can be described by with a pre-exponential A-factor that is about 2 times higher and a effective activation energy that is about 4.0 kJ/mol higher. The computed overall rate expressions in Arrhenius and extended-Arrhenius form are given in the accompanying preceding paper.<sup>2</sup>

We also estimated the uncertainty in the predicted high pressure rate expression relative to the experimentally-derived rate expression at (1 to 3) bar and found an uncertainty of about 10% in the relative pre-exponential A-factors (i.e., A<sub>∞</sub>/A<sub>2 bar</sub> = 2±0.2) and a uncertainty of about 25% in the relative activation energies (i.e., E<sub>∞</sub> - E<sub>2 bar</sub> = 4±1 kJ mol<sup>-1</sup>).

In computing the overall uncertainty, we assumed 25% uncertainties in the barriers of the torsional modes and one additional low frequency mode in both the molecule and the transition state, a 25% uncertainty in the step-down parameter, and a 25% uncertainty in the symmetric Eckert tunneling parameter  $\alpha$ . The total uncertainty was dominated by roughly equal contributions from the step-down energy transfer parameter and those for the torsions/low frequency modes. However, considering the absolute values of the rate constants, we found that the tunneling parameter had the largest effect – effectively decreasing the pre-exponential by about a factor of 2 and decreasing the activation energy by about 6 kJ mol<sup>-1</sup>. Next in importance, we find that decreasing the step-down parameter from by 150 cm<sup>-1</sup> decreases the pre-exponential by about (10 to 15)% and the activation energy by about (0.5 to 1.0) kJ mol<sup>-1</sup>. Increasing the torsional barriers or low vibrational frequencies in the molecule by 25% increases the pre-exponential by about (10 to 15)% and decreases the activation energy only (0.2 to 0.3) kJ mol<sup>-1</sup>.

*Chlorocyclopentane.* Rate constants based on *ab initio* transition states for HCl elimination from chlorocyclopentane were computed using the same procedure as for 2-chloropropane: torsional frequencies were replaced with equivalent hindered rotors, an estimated symmetric Eckert tunneling parameter of  $\alpha = V^*/h\omega^* = 2.0$  was used, an estimated exponential step-down energy transfer parameter of 680 cm<sup>-1</sup> was employed, and the barrier height (E<sub>0</sub> = 202.9 kJ mol<sup>-1</sup>) was taken from the G3MP2B3 calculations. Again, we find fortuitously good agreement (within 15%)

between the computed and measured rate constants with a difference about 25% in the pre-exponential and within 1 kJ mol<sup>-1</sup> for the activation energy. Comparisons between the computed values and the experimental data are given in Table 6.

The RRKM/ME model indicates that the rate constant is at the high pressure limit at the lower end of the experimental temperature range (590 K) and at about 95% of the high pressure limit at the highest temperature (1020 K). To force agreement between the computed and experimental rate expressions, we decreased  $E_0$  a small amount from 202.9 kJ mol<sup>-1</sup> to 202.1 kJ mol<sup>-1</sup> and increased two low frequency vibrational modes by 15% from {166, 217} cm<sup>-1</sup> to {190, 250} cm<sup>-1</sup>. The RRKM/ME model predicts a high pressure pre-exponential A-factor that is about 10% higher and an activation energy about 0.6 kJ mol<sup>-1</sup> higher than the effective parameters at 2 bar. The computed overall rate expressions in Arrhenius and extended-Arrhenius form are given in the accompanying preceding paper.<sup>2</sup>

*Chlorocyclohexane.* Our calculated rate constants (see Table 6 and discussion below) based on B3LYP/6-31G(d) computed molecular structures (and frequencies) and *ab initio* computed barriers are in only fair-to-acceptable agreement compared to the experimental rate constants for HCl elimination from chlorocyclohexane: depending on the parameters employed, the computed rate constants may be a factor of (1.2 to 1.7) times lower, computed pre-exponentials a factor of (1.4 to 2.0) higher, and the computed barriers (3 to 6) kJ mol<sup>-1</sup> higher. This contrasts somewhat with the other five reactions considered in the computational part of this work where general agreement to within about (10 to 25)% for rate constants and within about 2 kJ mol<sup>-1</sup> for barriers was observed. Although the differences for this reaction are not significantly higher than our uncertainty estimates (see earlier discussion), nevertheless, the computed rate constants are not in as good agreement as for the other reactions.

The source could be traceable to the three largest sources of uncertainties: 1) the computed barrier height, 2) the tunneling correction, and 3) low frequency ring modes. We now consider and discuss some of these concepts.

We explored the transition state calculations for this system to determine if there are alternative, lower energy pathways. A summary of these results are given in Table 6. First, we computed the transition state structure at different levels of theory (electron correlation) using HF, MP2, B3LYP, and QCISD methods (all using 6-31G(d) basis sets) and then employed these structures in the



G3MP2 calculations. We found that the barriers using the MP2 and QCISD structures were within about 1 kJ mol<sup>-1</sup> of the G3MP2/B3LYP barriers, while the HF/6-31G(d) structure yielded a barrier that was (unsurprisingly) nearly 7 kJ mol<sup>-1</sup> higher. Second, we also computed the barrier using the more computationally expensive and generally more accurate G3B3 method and found it to be within about 3 kJ mol<sup>-1</sup> of the G3MP2B3 barrier. Third, we found an alternative transition state structure where the cyclohexane ring was quasi-symmetric. This transition state was about 5 kJ mol<sup>-1</sup> higher in energy than the more stable “skewed” transition state structure – both of which are illustrated in Figure 1. In short, we found no lower energy alternative pathways for HCl elimination from chlorocyclohexane..

It is possible that the difference with experiment is simply due to inaccuracy in the *ab initio* barrier for this system – and a difference of 4-6 kJ mol<sup>-1</sup> is not unreasonably large – but larger than observed for the other reactions studied here. It is also possible the source of the difference may be traceable to a differing tunneling function for this reaction. As outlined earlier, we employed the same tunneling parameters ( $\alpha = 2.0 \pm 0.4$ ) for all of the reactions – which translates into estimated uncertainties in the rate constants of (10 to 40)%, in the pre-exponential of about 30%, and in the activation energy of about 3 kJ mol<sup>-1</sup>. Another possible explanation, and the one that we favor, is that the RRHO model used here may be inadequate because of peculiarities that are not present in the other reactions considered here.

In particular, chlorocyclohexane, like cyclohexane, has two fundamental forms that interconvert with modest barriers. The lowest energy conformer is a “chair” configuration where four carbon atoms in the ring are in a plane with the other two carbon atoms opposing each other in the ring and *trans* relative to the plane (“up” and “down”). The higher energy conformer is a “twist-boat” configuration where two opposing carbon atoms are *cis* relative to the plane, while the other four carbon atoms are twisted (or buckled alternatively) out of the plane. It has been estimated and calculated that “twist-boat” conformer in chlorocyclohexane is about 25 kJ mol<sup>-1</sup> higher in energy and there is an isomerization barrier of about 45 kJ mol<sup>-1</sup>.<sup>28</sup> In addition, there are two different “chair” conformers depending upon whether the chlorine atom is substituted in an equatorial (in the plane) or axial (out of the plane) position. The axial conformer is about 2 kJ mol<sup>-1</sup> higher in energy with a barrier-to-isomerization of about 45 kJ mol<sup>-1</sup>. With regard to the barrier to HCl elimination, we found two different transition states differing in energy by about 5 kJ mol<sup>-1</sup> – the

difference in structure being largely a “right-handed” versus “left-handed” twisting (or buckling) of the ring.

A consequence of the above is that at lower temperatures, the molecular conformers may not readily interconvert (are effectively “frozen”), while at higher temperatures the ring puckering modes may be partially active. These modes are not accurately described by either harmonic oscillators or hindered rotors (or pseudo-rotors) and we cannot readily model the complicated partition functions. Qualitatively, the net result will be “excess” entropy at higher temperatures as the modes become active, and therefore lower rate constants in comparison to the “frozen” ring model. From a practical perspective one can model the system and obtain agreement between the computed and measured rate expressions by simply adjusting the *ab initio* barriers and the computed vibrational frequencies. To accomplish this we decreased  $E_0$  by 5.5 kJ mol<sup>-1</sup> (from 219.0 kJ mol<sup>-1</sup>) and increased two low frequency modes by 5% from {68, 122} cm<sup>-1</sup> to {71, 128} cm<sup>-1</sup>. Changing  $E_0$  by this amount effectively roughly doubles the rate constants and increases the rate at lower temperatures (590 K) proportionally more (about 60%) than at the high temperatures (1020 K). Using these adjusted parameters, we found that rate constant at the lower end of the experimental temperature range was about 95% of the high pressure limit – and as for chlorocyclopentane, we found that the high pressure limiting rate had a pre-exponential that was about 10% higher and an activation energy about 0.6 kJ mol<sup>-1</sup> larger. The computed overall rate expressions in Arrhenius and extended-Arrhenius form are given in the accompanying preceding paper.<sup>2</sup>

## Summary

In this paper, we have presented results for computed rate expressions using RRKM/ME analysis employing computed barriers from *ab initio* calculations for six different reactions involving HCl eliminations from the acyclic alkyl chlorides: chloroethane, 1-chloropropane, 2-chloropropane, 2-chlorobutane, and from the cyclic alkyl chlorides: chlorocyclopentane and chlorocyclohexane. Three of the molecules (2-chloropropane, chlorocyclopentane, and chlorocyclohexane) were used in an experimental study reported in an accompanying preceding paper as standards for providing a self-consistent temperature scale for use in comparison of rate expressions derived from kinetic measurements using different methods and temperature ranges. Decomposition reactions involving the other three molecules (chloroethane, 1-chloropropane, and 2-chlorobutane) were used in this computationally study as additional reference reactions because good experimental rate expressions are available for these systems.

In general, in this study, we found good agreement (10-25)% between the computed rate constants and those either measured in the experimental component of the present work, or from earlier work found in the literature. The only exception was the rate constants for HCl elimination from chlorocyclohexane where a “higher barrier” was computed than would be consistent with the experimental determinations. We propose that either the *ab initio* calculations are either slightly inaccurate for this reaction, or that the model used to describe the thermochemical properties of the molecule and/ or transition state is inadequate given the possibility that cyclohexane ring in the molecule may be intermediate between a “frozen” and “floppy” structure – that is, the ring may be more rigid at lower temperatures, but more readily isomerizes at higher temperatures.

**Table 1.** Standard thermochemical quantities used for species considered in this work. Enthalpies of formation  $\Delta_f H^\circ$  were taken from the literature (reference given). Entropies  $S^\circ$  and heat capacities  $C_p$  are those derived from our calculations. Values given parenthetically are those from TRC,<sup>6, 56</sup> except for chlorocyclopentane and chlorocyclohexane where the values are from Diky.<sup>19, 28</sup> See text for more details.

Species	$\Delta_f H^\circ(\text{g}, 298 \text{ K})$	$S^\circ(\text{g}, 298 \text{ K})$	$C_p(\text{g}, 298 \text{ K})$	Reference for $\Delta_f H^\circ(\text{g}, 298 \text{ K})$
	$\text{kJ mol}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	
chloroethane	$-112.1 \pm 0.7$	277.2 (275.9)	63.4 (62.6)	Manion (2002) <sup>57</sup>
1-chloropropane	$-132.5 \pm 0.9$	320.2 (318.6)	86.0 (85.3)	Fletcher (1971) <sup>58</sup>
2-chloropropane	$-145.0 \pm 0.9$	306.8 (306.1)	88.6 (87.6)	Fletcher (1971) <sup>58</sup>
2-chlorobutane	$-166.7 \pm 1.0$	348.1 (351.5)	111.1 (110.2)	He (1992) <sup>59</sup>
chlorocyclopentane	$-119.7 \pm 2$	339.9 (339.5)	105.1 (98.9)	Diky (1993) <sup>19</sup>
chlorocyclohexane	$-164.2 \pm 2$	345.9 (345.6)	123.3 (121.1)	Diky (1994) <sup>28</sup>
ethene	$52.4 \pm 0.5$	219.5 (219.3)	43.3 (42.9)	Gurvich (1991) <sup>60</sup>
propene	$20.2 \pm 0.4$	267.2 (266.7)	65.1 (64.3)	Burcat (2005) <sup>61</sup>
(Z)-2-butene	$-7.7 \pm 1.3$	300.4 (301.3)	83.1 (80.2)	Prosen (1951) <sup>62</sup>
cyclopentene	$36 \pm [3]$	292.3 (291.4)	83.1 (81.3)	Allinger (1982) <sup>63</sup>
cyclohexene	$-4.3 \pm 1.0$	311.6 (310.6)	102.0 (101.5)	Steele (1996) <sup>64</sup>
HCl	$-92.3 \pm 0.1$	186.9 (186.6)	29.1 (29.1)	Cox (1984) <sup>65</sup>

**Table 2.** Torsional moments of inertia, barriers, and frequencies for reactants, products, and transition states. The values of the barriers and torsional frequencies given parenthetically are those that would yield the literature result for the standard entropies,  $S^\circ(\text{g}, 298 \text{ K})$ , given in Table 1.

Species	<b>I</b>	<b>Barrier (<math>V_3</math>)</b>	<b>Torsions</b>
	$10^{-47} \text{ kg m}^2$	$\text{kJ mol}^{-1}$	$\text{cm}^{-1}$
chloroethane	4.6	14.3 (18.5)	255 (290)
1-chloropropane	4.5, 22	10.9, 13.4 (16, 24)	226, 113 (273, 151)
1-chloropropane-HCl	5.1	16.9	265
2-chloropropane	5.1	13.6, 16.4 (16, 16)	237, 260 (257, 257)
2-chloropropane-HCl	5.2	6.3	160
2-chlorobutane	5.1, 5.2, 30	12.4, 14.3, 18.3 (15, 16, 23)	225, 245, 113 (248, 255, 127)
2-chlorobutane-HCl	5.1, 5.2	4.7, 4.7	97, 132 (138)
chlorocyclopentane	16	$V_2=10$	67 (76)
chlorocyclopentane-HCl	26	$V_2=30$	96 (104)
propene	3.9	7.5 (9)	201 (220)
(Z)-2-butene	4.9, 4.9	3.7, 5.0 (4.3, 6.4)	126, 145 (136, 156)
cyclopentene	16	35	139 (143)

**Table 3.** Experimental and computed enthalpies of reaction for HCl elimination.

Species	$\Delta_r H^\circ(\text{expt})$	$\Delta_r H^\circ(\text{calc})$	diff
	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$
chloroethane $\rightarrow$ ethene + HCl	$72.2 \pm 0.9$	67.2	-5.0
1-chloropropane $\rightarrow$ propene + HCl	$60.4 \pm 1.0$	57.0	-3.4
2-chloropropane $\rightarrow$ propene + HCl	$72.9 \pm 1.0$	71.3	-1.6
2-chlorobutane $\rightarrow$ ( <i>Z</i> )-2-butene	$66.7 \pm 1.6$	68.3	+1.6
chlorocyclopentane $\rightarrow$ cyclopentene + HCl	$63.4 \pm 3.6$	60.3	-3.1
chlorocyclohexane $\rightarrow$ cyclohexene + HCl	$67.6 \pm 2.2$	68.6	+1.0

**Table 4.** Characteristic bond lengths for chlorocyclohexane  $\rightarrow$  cyclohexene + HCl from B3LYP/6-31G(d) optimizations.

<b>TS/Reactants/Products</b>	<b>C-Cl / Å</b>	<b>C-H / Å</b>	<b>H-Cl / Å</b>	<b>C-C / Å</b>
chlorocyclohexane-HCl (TS)	2.77	1.21	1.94	1.42
chlorocyclohexane	1.84	1.10	—	1.53
cyclohexene	—	—	—	1.38
HCl	—	—	1.29	—

**Table 5.** Relevant bond distances for chlorocyclohexane → cyclohexene + HCl for different transition-state structures and from different optimizations using 6-31G(d) basis sets.

Calculation	Conformer	C-Cl / Å	C-H / Å	H-Cl / Å	C-C / Å
Transition-state structures:					
HF	skew	2.93	1.19	2.08	1.39
B3LYP	quasi-sym	2.82	1.19	1.99	1.42
B3LYP	skew	2.77	1.21	1.94	1.42
B3LYP	planar	2.76	1.20	1.97	1.41
QCISD	skew	2.74	1.20	1.97	1.41
MP2	skew	2.63	1.21	1.99	1.41
Reference structures: reactants or products as indicated					
B3LYP	reactants	1.84	1.10		1.53
B3LYP	products			1.29	1.38



**Table 6. Comparison of experimental and calculated rates for selected hydrodechlorination reactions.**

Reaction	Method	Temp. K	A s <sup>-1</sup>	E <sub>a</sub> kJ mol <sup>-1</sup>	k <sub>calc</sub> /k <sub>exp</sub> <sup>a</sup>	Ref.
CD <sub>2</sub> (Cl)CH <sub>2</sub> D → ethene- <i>d</i> <sub>3</sub> + HCl	Static	663-743	7.8E12	225.8	-	Choi (1994) <sup>66</sup>
[ <i>chloroethane</i> ]* → ethene + HCl	Chem Act	Chem Act	1.2E13	229.7	-	Ferguson (2005) <sup>67</sup>
chloroethane → ethene + HCl	Shock Tube	820-1000	1.5E13	236.1	-	Tsang (1964) <sup>68</sup>
	Static	714-767	2.1E13	235.3	-	Heydtmann (1975) <sup>53</sup>
	Shock Tube	960-1100	6.2E13	241.5	-	Evans (1978) <sup>53</sup>
	G3MP2B3	750 <sup>b</sup>	3.4E13	237.4	1.15 to 1.20	This Work
	G3MP2B3	750 <sup>c</sup>	4.6E13	238.0	1.10 to 1.15	This Work
	G3MP2B3	0	-	239.9	-	This Work
	G3B3	0	-	243.0	-	This Work
	CCSD/pVnZ	0	-	241.4	-	McGrath (2002) <sup>40</sup>
[ <i>1-Cl-propane</i> ]* → propene + HCl	Chem Act	Chem Act	2.7E13	225.9	-	Ferguson (2005) <sup>66</sup>
1-Cl-propane → ethene + HCl	Static	672-734	3.2E13	230.0	-	Hartmann (1964) <sup>69</sup>
	Shock Tube	989-1094	2.8E13	229.0	-	Okada (1988) <sup>70</sup>
	Shock Tube	960-1100	2.713	227.0	-	Evans (1978) <sup>53</sup>
	G3MP2B3	700 <sup>d</sup>	5.6E13	234.1	0.85 to 0.9	This Work
	G3MP2B3	1030 <sup>e</sup>	7.1E13	234.9	0.90 to 0.95	This Work
	G3MP2B3	0	-	232.8	-	This Work
2-Cl-butane → Z-2-butene + HCl	Static	589-666	7.1E13	212.0	-	Heydtmann (1961) <sup>54</sup>
	G3MP2B3	630 <sup>f</sup>	3.8E13	214.7	1.05 to 1.10	This Work
	G3MP2B3	0	-	217.9	-	This Work
2-Cl-propane → ethene + HCl	Evaluation	623-1021	9.6E13	218.0	-	This Work
	G3MP2B3	2 bar <sup>g</sup>	1.0E14	217.2	1.15 to 1.20	This Work
	G3MP2B3	0	-	220.9	-	This Work
CCP <sup>h</sup> → cyclopentene + HCl	Evaluation	591-1021	4.5E13	204.3	-	This Work
	G3MP2B3	2 bar <sup>i</sup>	5.8E13	205.2	1.05 to 1.15	This Work
	G3MP2B3	0	-	202.9	-	This Work
CCH <sup>j</sup> → cyclohexene + HCl	Evaluation	590-1020	2.15E14	215.8	-	This Work

	G3MP2B3	2 bar <sup>k</sup>	2.4E14	221.1	0.6 to 0.8	This Work
	G3MP2B3	0	-	219.0	-	This Work
	G3MP2B3//QCI	0	-	218.0	-	This Work
	G3B3	0	-	222.0	-	This Work
	G3MP2B3//MP2	0	-	219.6	-	This Work
	G3MP2B3//HF	0	-	225.6	-	This Work
(higher energy conformer)	G3MP2B3	0	-	224.0	-	This Work
(planar conformer)	G3MP2B3	0	-	272.1	-	This Work

<sup>a</sup> Values from an RRKM/ME model for the experimental pressure and temperature when employing parameters computed at the indicated level of theory. See text for details.

<sup>b</sup> pressure = 0.13 atm;

<sup>c</sup> pressure = 7 atm;

<sup>d</sup> pressure = 0.5 atm;

<sup>e</sup> pressure = 7 atm;

<sup>f</sup> pressure = 0.6 atm;

<sup>g</sup> pressure = 2 bar;

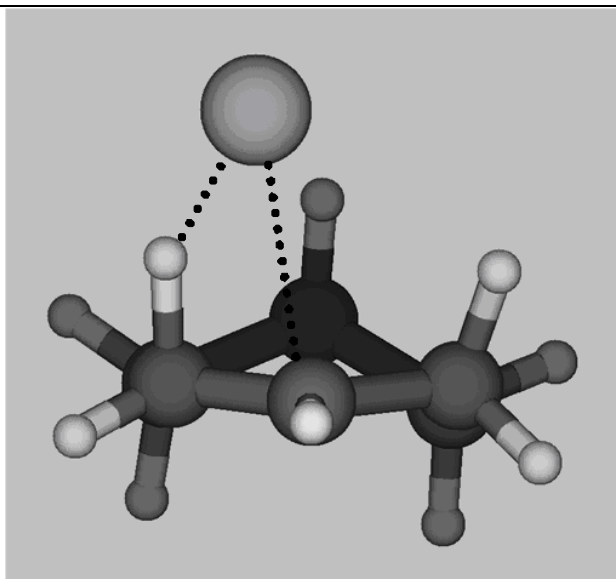
<sup>h</sup> CCP = chlorocyclopentane;

<sup>i</sup> pressure = 2 bar;

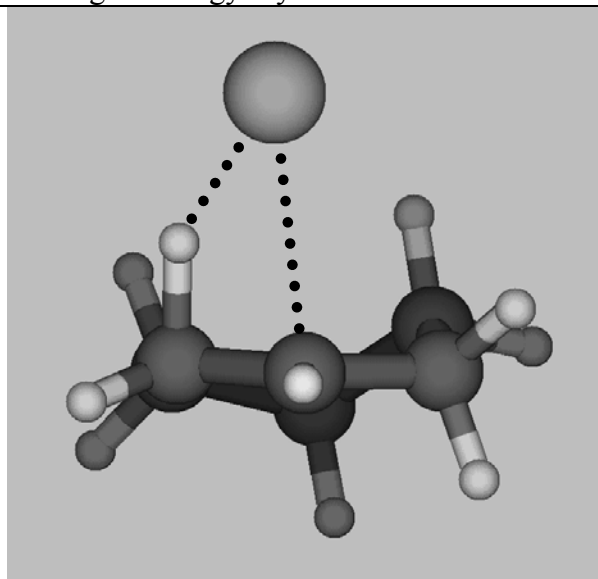
<sup>j</sup> CCH = chlorocyclohexane;

<sup>k</sup> pressure = 2 bar.

**Figure 1.** Transition state structures for chlorocyclohexane  $\rightarrow$  cyclohexene + HCl from B3LYP/6-31G(d) optimizations.



Higher energy “symmetric” conformer



Most stable “skewed” conformer

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