Standard Reactions for Comparative Rate Studies: Experiments on the Dehydrochlorination Reactions of 2-Chloropropane, Chlorocyclopentane and Chlorocyclohexane

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Single pulse shock tube studies of the thermal dehydrochlorination reactions (chlorocyclopentane \rightarrow cyclopentene + HCl) and (chlorocyclohexane \rightarrow cyclohexene + HCl) at temperatures of 843 to 1021 K and pressures of 1.4 to 2.4 bar have been carried out using the comparative rate technique. Rate constants have been measured relative to (2-chloropropane \rightarrow propene + HCl) and the decyclization reactions of cyclohexene, 4-methylcyclohexene, and 4-vinylcyclohexene. Absolute rate constants have been derived using *k*(cyclohexene \rightarrow ethene + butadiene) = $1.4 \times 10^{15} \exp(-33500/T) \text{ s}^{-1}$. These data provide a self-consistent temperature scale of use in the comparison of chemical systems studied with different temperature standards. A combined analysis of the present results with literature data from lower temperature static studies leads to:

$$k(2\text{-chloropropane}) = 10^{(13.98 \pm 0.08)} \exp(-26225 \pm 130) \text{ K/T} \text{ s}^{-1}; 590 \text{ K to } 1020 \text{ K}; 1 \text{ to } 3 \text{ bar}$$

$$k(\text{chlorocylopentane}) = 10^{(13.65 \pm 0.10)} \exp(-24570 \pm 160) \text{ K/T} \text{ s}^{-1}; 590 \text{ K to } 1020 \text{ K}; 1 \text{ to } 3 \text{ bar}$$

$$k(\text{chlorocylohexane}) = 10^{(14.33 \pm 0.10)} \exp(-25950 \pm 180) \text{ K/T} \text{ s}^{-1}; 590 \text{ K to } 1020 \text{ K}; 1 \text{ to } 3 \text{ bar}$$

Taking systematic uncertainties into consideration, expanded standard uncertainties in these rate constants are estimated to be about 15% near 600 K rising to about 40% at 1000 K. At 2 bar and 1000 K the reactions are only slightly under their high pressure limits, but fall-off effects rapidly become significant at higher temperatures. On the basis of computational studies and RRKM/Master Equation modeling of these and reference dehydrochlorination reactions, reported in more detail in an accompanying article, the following high pressure limits have been derived:

$$k_{\infty}$$
 (2-chloropropane) = 5.74x10⁹ T^{1.37}exp(-25680/T) s⁻¹; 600 K to 1600 K
 k_{∞} (chlorocylopentane) = 7.65x10⁷ T^{1.75}exp(-23320/T) s⁻¹; 600 K to 1600 K
 k_{∞} (chlorocylohexane) = 8.25x10⁹ T^{1.34}exp(-25010/T) s⁻¹; 600 K to 1600 K

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1. Introduction

When heated, chloroalkanes undergo decomposition to form HCl and the corresponding olefin. This process has been studied for many decades. In their early study of the decomposition of *tert*-butyl chloride Brearley *et al.*¹ concluded that in properly seasoned vessels the mechanism for this compound was a homogeneous molecular process. Later, in a series of papers published almost sixty years ago Barton and coworkers²⁻⁷ studied the decomposition of a number of alkyl chlorides and showed that, depending on conditions, both free radical and homogenous processes play roles in dehydrochlorination. They were able to provide structure-based rules showing when one could expect molecular and free radical processes to dominate. In laboratory vessels, it was found that the free radical process could be suppressed by suitably conditioning the walls of the reactor with pyrolysis products and by the addition of a free radical scavenger such as toluene. In the 1950s and 1960s a number of workers investigated structural factors controlling the rates of HX elimination and the reverse addition to double bonds.^{3,8-11} It became apparent that the unimolecular reaction rates scale with the ionization energy of the molecule and this led to the now generally-accepted proposition by Benson and Bose¹⁰ that the transition state for the 4-center elimination process is semi-ionic in nature. Much of the early literature has been discussed by Maccoll¹² in his 1969 review.

In the intervening years, dehydrochlorination reactions have received only limited attention. Most of the recent experimental work has been on specific industrially important compounds, such as 1,2-dichloropropane,¹³ or on less studied aspects of the reaction, such as the elimination of HCl from alkenyl chorides,¹⁴ where the focus has been on the effect of the double bond and the branching ratio for competing channels.

We report herein on the kinetics of the elimination of HCl from 2-chloropropane and two chlorocycloalkanes (cyclic alkylchlorides): chlorocyclopentane (CCP) and chlorocyclohexane (CCH). Our interest is prompted primarily by our desire to utilize the latter two reactions as temperature standards in our shock tube studies at temperatures in the range of 850 K to 1020 K. Their utility for such purpose arises from the expectation that these reactions proceed as clean molecular processes with no significant competing channels, and that the olefin products are both stable on the time scale of our experiments and are difficult to form in any other manner.

A particular need in our case is our ability to determine the rate constants in comparison with other reactions that we use as temperatures standards. We wish to obtain accurate relative rates both for compounds reacting with very similar rates, as well as for those compounds reacting an order of magnitude or so slower. The point of the latter work is to overlap with standards suited for covering higher temperature ranges. A goal is to assure that studies with different standards are interchangeable and that we have a broad, accurate, and consistent temperature scale.

The thermal decompositions of chlorocyclopentane (CCP) and chlorocyclohexane (CCH) have received little study in the past, and only at temperatures lower than considered in the present In 1958, Swinbourne¹⁵ reported experiments on the dehydrochlorination of work. chlorocyclohexane using a static system at temperatures of 591 K to 658 K and initial pressures of 40 torr to 400 torr (5.3 kPa to 53.3 kPa). Results using packed and unpacked reactors with and without free radical scavengers led him to conclude that he was able to isolate the homogenous process in properly seasoned vessels. He determined the kinetics of the reaction by following the pressure rise in the system. Two years later he published¹⁶ a related article on chlorocyclopentane at temperatures of 582 K to 649 K and initial pressures of 40 torr to 400 torr (5.3 kPa to 53.3 kPa) using the same apparatus and technique. In the latter work, he slightly updated his original results on chlorocyclohexane after adding a small correction for dead volume in his apparatus. Herndon et al.¹⁷ studied the decomposition of chlorocyclohexane using a stirred flow reactor at temperatures of 623 K to 749 K and initial pressures of about 750 torr (100 kPa). They determined the kinetics by following the production of cyclohexene using gas chromatography with flame ionization detection. The absolute rate constants are in close agreement with those of Swinbourne over the range of temperature overlap, but exhibit a slightly larger activation energy. Benson and O'Neal¹⁸ subsequently evaluated the data on both chlorocyclopentane and chlorocyclohexane as part of their 1970 review of the kinetics of more than 600 gas phase unimolecular reactions.

In the present work we use the comparative rate shock tube technique to obtain kinetic data on these reactions at temperatures significantly higher than heretofore examined. The results are compared with the lower temperature data from the literature. Rate expressions suitable for our shock tube studies and high pressure limiting values are recommended. We have also explored the reactions with computational methods and carried out a Rice Ramsberger Kassel Marcus/Master Equation (RRKM/ME) analysis of the data. The theoretical work, reported in detail in an accompanying article¹⁹ allows a more accurate extrapolation of the results over a wide temperature

and pressure range, as well as provides some indication of the current accuracy of *a priori* predictions for these reactions.

2. Experimental²⁰

Chemicals. Chlorocyclohexane (99%, Aldrich), chlorocyclopentane (99%, Aldrich), 2-chloropropane (99+%, Aldrich), cyclohexene (99+%, Aldrich), 4-methylcyclohexene (99%, Aldrich), 4-vinylcyclohexene (99%, Aldrich), 1,3,5-trimethylbenzene (135TMB, 99% Aldrich), and argon (Praxair, 99.999%), were the primary chemicals used. Chemicals were used without further purification other than degassing during preparation of the mixtures.

Apparatus and Gas Chromatographic/Mass Spectral Analysis. Experiments were carried out in a heated single pulse shock tube. The apparatus is described more completely elsewhere²¹ and only a brief overview is given here. Compositions of the gas mixtures (detailed later) were typically composed of 100 μ l/l of the substrates under study and 10,000 μ l/l of the free radical scavenger 1,3,5-trimethylbenzene in argon. Mixtures were prepared by vapor pressure and/or direct injection of liquid samples through a septum into the heated 15 L sample holding tanks. Compositions were confirmed by gas chromatographic analysis. Temperatures in the reflected shock ranged from 843 K to 1021 K; shock pressures were typically 1.3 bar to 2.4 bar, although a few experiments were conducted at pressures as high as 7 bar. Heating times derivable from the shock pressure traces were (500 ± 50) μ s. As shown by Tsang,²² errors due to uncertainty in the exact heating time are small in comparative rate studies of the present type. There is a complete cancellation of errors if the activation energies are identical, while a 20% difference in activation energy and a 20% uncertainty in heating time leads to an error of about 4% in the derived relative rate.

Following the shock, samples were extracted by opening a port 5 cm from the end of the shock tube to admit the test gas into a narrow (4.6 mm i.d.) evacuated tube with an approximate volume of 200 ml and connected to two switching valves (Valco) outfitted with 1 ml sample loops [electroformed nickel, 2.16 mm (0.085 in) i.d.] near the far end of the sampling system. Helium introduced at the near end of the sampling system serves to compress the test gas in the loops to a pressure of 1 bar (note that the helium does not dilute the gas in the sample loops because of the length of the 200 ml tube). Automated switching of the valves injects the loop volumes onto two

separate columns in an Agilent 6890N gas chromatograph (GC) for analysis. One column was optimized for separation of light gases while the second was utilized primarily for heavier components. The GC was equipped with both flame ionization detection (FID) and an Agilent Technologies 5973 Inert mass spectrometer (MS). The sample eluting from the heavy products column was quantitatively split using an Agilent Technologies Dean's Switch to allow simultaneous FID and mass spectral analyses. Agilent Technologies ChemStation software was used to control the GC/MS and carry out peak area integrations.

Product separations utilized a J & W Scientific 30 m x 0.53 mm internal diameter (i.d.) DB-1 (100% dimethypolysiloxane) fused silica capillary column for the separation of C5 and higher molecular weight products and a Restek 30 m x 0.53 mm i.d. Rt-Alumina (aluminum oxide porous layer) capillary column for C1 to C4 species. The GC was set up for cryogenic operation with the oven temperature programmed from -60 °C to 180 °C and the carrier gas set to the constant flow mode. Although the Rt-Alumina column is superior to the DB-1 for separation of light components, the use of cryogenic operation allowed the DB-1 column to successfully separate many C1 to C5 species, often giving us a duplicate analysis. In these cases concentrations from the two analyses agreed within a few percent.

Molar FID responses of all the starting substrates and product olefins were determined from standard samples. The C2-C6 *n*-alkenes and *n*-alkanes were calibrated with commercial samples (Scott Gases) containing 100 μ l/l of each component. To confirm these calibrations and determine response factors for other species, measured vapor pressures of appropriately degassed components were used to prepare a number of in-house mixtures. In these cases vapor pressures were measured with calibrated pressure transducers (MKS Instruments, Inc. and Mensor Corp.). The response factors so determined include ethene, ethane, propene, 1,3-butadiene, cyclopentene, cyclohexene, 4-vinylcyclohexene, 4-methylcyclohexene, 2-chloropropane, chlorocyclopentane, and chlorocyclopexane. Each component was present in multiple mixtures and cross checks of the values obtained showed good agreement. Overall we estimate the standard uncertainty (1 σ) in our analyses for the above components to be about 3%.

3. Experimental Results

The reactions under consideration are given below:

$$(1)$$

$$\bigvee_{CI} \rightarrow \bigvee + HCI$$
⁽²⁾

$$\overset{\text{CI}}{\longrightarrow} \longrightarrow + \text{HCI}$$
(3)

$$\longrightarrow \qquad + \qquad \parallel$$
(4)

$$(5)$$

$$(6)$$

The first three reactions are HCl eliminations from (cyclo)chloroalkanes, while the remainder are "retro-ene" reactions: cycloeliminations. The decompositions of chlorocyclohexane and chlorocyclopentane are the reactions of interest as new temperature standards, while the others have been used in this laboratory as temperature standards in earlier work. The compositions of the mixtures studied are given in Table 1.

3.1 Products and General Observations.

The only significant products detected from the decompositions of chlorocyclopentane, chlorocyclohexane, and 2-chloropropane were the corresponding olefins: cyclopentene, cyclohexene, and propene, respectively. No attempt was made to detect HCl. Rates of HCl elimination from the three chlorides were similar and followed the order chlorocyclohexane \approx chlorocyclopentane > 2-chloropropane. As expected on the basis of the kinetics literature,²³ the alkyl chlorides were found to decompose much faster than the cycloalkenes. This disparity means that there is a limited temperature region over which the rate constants overlap sufficiently to obtain accurate rate comparisons. At high conversions, boundary effects in the shock tube limit the accuracy of the relative rate determinations, while at very low conversions we are variously limited by our analytical sensitivity, trace impurities, or secondary sources of products.

Cyclohexene and the substituted analogs used here undergo decyclization to give 1,3-butadiene and a second olefin as indicated in reactions (4-6). The two products should be formed in a 1:1

ratio based on the stoichiometry of the reaction. This is in agreement with our analyses for both cyclohexene and 4-methylcyclohexene except at extremely low degrees of conversion (see discussion of Mixtures 3 and 5, below). 4-Vinylcyclohexene gave 1,3-butadiene as the only detectable product. The mechanism of the reaction of 4-vinylcyclohexene has been much discussed in the literature²⁴⁻²⁷ and has been suggested to involve a biradical or a direct molecular process. 1,5-cyclooctadiene has been reported as a product in the dimerization of 1,3-butadiene at lower temperatures²⁸ and is known to isomerize to 4-vinylcyclohexene.²⁴ In the present studies 1,5-cyclooctadiene was specifically sought but not found.

Mixture 1: CCP, CCH, Argon. Despite containing no free radical inhibitor, this mixture gave a clean product spectrum containing cyclopentene and cyclohexene as the only significant organic products. We noted no evidence of ring-opened species or other products that might be expected from free radical processes. For both substrates the amount of product olefin was equal to the reacted chloride within about 2%. Substrate conversions ranged from 6% to 60%. Measured relative rate constants from this mixture were not discernibly different from those of the other mixtures, again indicative of the molecular nature of the reaction.

Mixture 2: CCP, CCH, 2CP, 135TMB, Argon. The only significant products observed were the olefins expected from the molecular elimination of HCl from the respective substrates, reactions (1-3). An experimental test for the presence of H atoms is the formation of *m*-xylene (1,3-dimethylbenzene) from 1,3,5-trimethylbenzene via the displacement reaction (H + 135TMB \rightarrow *m*-xylene + CH₃). We observed no increase in the amount of *m*-xylene over that present as a small impurity in 1,3,5-trimethylbenzene.

Mixture 3: CCP, 2CP, CH, 135TMB, Argon. The starting mixture contained very small backgrounds of propene and cyclopentene. At the lowest conversion studied this amounted to a correction to the peak areas for these products of 9% and 5%, respectively. Assuming even a 10% error in these corrections, the effect on the measured rate constants should be negligible. These impurities were the primary factor limiting our ability to go to very low degrees of conversion. Conversion of cyclohexene (reaction 4) ranged from 0.007% to 1.9%. In most cases the ratio of ethene to 1,3-butadiene was equal to (1 ± 0.02) but at conversions less than about 0.06% the ethene to 1,3-butadiene ratio became larger than 1, approaching a value of 5 at the lowest degree of conversion, presumably because of secondary sources of ethene. There are many possible

pyrolytic sources of trace ethene, but 1,3-butadiene is much harder to make. For this reason rate constants for cyclohexene decomposition were based on 1,3-butadiene formation.

Mixture 4: CCP, CCH, 2CP, 4VCH, 135TMB, Argon. Reaction of 4-vinylcyclohexene was much slower than that of the chlorides with the conversion of 4-vinylcyclohexene varying between 0.1% and 4.5%. Peak areas for cyclopentene and cyclohexene were corrected by up to 9% due to the presence of a small background of these species.

Mixture 5: CCP, CCH, 4MCH, 135TMB, Argon. Conversion of 4-methylcyclohexene ranged from 0.007% to 1.5%. The ratio of the product olefins propene and 1,3-butadiene was equal to (1 ± 0.05) except at conversions less than 0.03% where the ratio increased gradually, ultimately reaching a value of about 1.6 at the lowest temperature studied. This was attributed to a small secondary source of propene and rate constants were calculated on the basis of 1,3-butadiene formed. Corrections of up to 8% and 16%, respectively, were made for the peak areas of cyclopentene and cyclohexene due to the presence of a small background in the starting mixture.

3.2 Kinetic Analyses.

All of the reactions considered here are first order unimolecular decompositions. The alkenes formed in reactions (2) through (6) are quite stable on the 500 μ s time scale of our experiments. In the case of reaction (1), the cyclohexene formed in the initial step can subsequently decompose via reaction (4) and this system should strictly be analyzed using the equations for consecutive first order reactions. This proved unnecessary, however, because $k_1 \gg k_4$: as a result of boundary effects in the shock tube, we find that the practical conversion limit to obtain accurate rate constants for a unimolecular process is around 65%; at that point the correction to cyclohexene formation due to the occurrence of reaction (4) is only 0.2%, an order of magnitude smaller than our analytical accuracy. Consequently all reactions could be analyzed using simple first order kinetics. Rate constants are derivable from the expression $k/s^{-1} = -(1/\tau) \ln(c_i/c_f)$ where τ is the residence time of about 500 μ s and c_i and c_f are the initial and final concentrations of the substrate. At low degrees of conversion, concentrations based on loss of substrate will have low precision since they are derived from the difference of two large numbers. At conversions of less than 10% the degree of reaction is therefore calculated on the basis of the products formed. At conversions > 10% the values derived from products formed and substrate reacted agreed within a few percent and the average value was selected. Total mass balances were within a few percent in all cases.

3.3 Comparative Rate Plots.

Figure 1 shows a comparative rate plot in which we have plotted the log k(CCH) vs the log k(CCP). The basis for such relative rate plots has been discussed in detail by Tsang in the previous literature.^{11,22,29,30} If the rate constants follow the Arrhenius form $k = A \exp(-E/T)$, where A is the pre-exponential factor, E the activation energy in K, and T the temperature in Kelvin, and using k_1 and k_2 to refer to the rate constants, one expects a straight line of the form

$$\log k_2 = m \log k_1 + b$$

where m is the slope and b is the intercept. This leads to the relations

$$E_2 = mE_1$$

and

 $\log A_2 = m \log A_1 + b/\ln(10)$

When the data are obtained in direct competitive experiments where the molecules have experienced exactly the same time and temperature history, for example as in the present shock tube experiments, an advantage of such plots is that knowledge of the temperature of the system is not required to obtain accurate relative rates. If one studies a series of compounds, the accurate determination of the temperature dependent expression for any one of the rate constants is then sufficient to place them all on an absolute scale.

Plots for the other systems studied are presented in Figure 2, Figure 3, and Figure 4, with the rate data from individual experiments summarized in Table 2. To identify the reaction conditions, this table also presents temperatures that have been derived after converting the relative rates to a consistent set of absolute values on the basis of our final analysis; this information is not necessary for the comparative rate plots. The temperatures have subsequently been used to calculate the shock pressures on the basis of the ideal gas shock equations.³¹ The comparative rate results from all mixtures are summarized in Table 3.

4. Computational Results and RRKM/ME Analysis

To assess the importance of pressure effects on the rate constants, and to provide a framework for the extrapolation of the present data, the dehydrochlorination reactions of chlorocyclopentane, chlorocyclohexane, 2-chloropropane, and several reference systems were explored with quantum chemical computational methods and Rice Ramsberger Kassel Marcus/Master Equation (RRKM/ME) analyses were performed on the systems of interest. The RRKM/ME calculations were performed with the NIST ChemRate program.³²⁻³⁴ Below we present a summary of the results; full details of the models used and more discussion may be found in the accompanying article.¹⁹

Molecular properties of the molecules and transition-states used in the RRKM/ME analyses were derived using composite *ab initio* methods G3MP2B3 and G3B3,^{35,36} which are variants of the Gaussian-3 method (G3).³⁷ Only modest changes in the properties were observed at different levels of theory. All species were treated with a modified Rigid Rotator Harmonic Oscillator (RRHO) approach in which internal rotations and pseudo-rotational modes were approximated as *n*-fold (symmetric) hindered rotors. Molecular properties and the calculated thermochemical functions were found to be in good agreement with the available literature data (see accompanying article¹⁹). Energy transfer was treated with an exponential down model using a step-size down in argon of 680 cm⁻¹. This value is somewhat larger than that typically used for hydrocarbons but is consistent with that typically needed to fit the falloff behavior of chlorinated species.³⁸⁻⁴⁰ The effect of tunneling was approximated using a symmetric Eckert potential using a tunneling parameters selected to be consistent with the tunneling corrections employed by McGrath and Rowland⁴¹ in their analysis of HCl elimination from chloroethane and d₅-chloroethane.

Unadjusted rate constants derived from the calculations were found to be in remarkably good agreement with the experimental data (from our work and others), with deviations of the calculated rate constants from evaluations of experimental values (see Discussion) typically being less than 25%. The largest deviation occurred for chlorocyclohexane where we propose that the difference may be a consequence of transitioning from "frozen" to "ring-puckering" conformations and the associated change in entropy impacting the rate constants (relative to the RRHO model employed). Based on our assessment of uncertainties in the calculations,¹⁹ this level of agreement gives confidence in the calculations and kinetic models.

Falloff behavior. Calculated falloff curves at 2 bar, expressed as values of k/k_{∞} , are shown in Figure 5 for 2-chloropropane, chlorocyclopentane, and chlorocyclohexane. These curves were derived after making small iterative adjustments to the transition-state properties so as to match, within 1%, the least-square fits of the experimental rate constant data. All systems were found to

be essentially at their high pressure limits under the conditions of the lower temperature static studies reported in the literature. Under the conditions of our shock experiments, the measured rate constants are calculated to be within about 5% of their high pressure limits for chlorocyclopentane and chlorocyclohexane, whereas 2-chloropropane is found to be slightly more in the falloff regime, with deviations of about 30% at our highest temperatures. These results are consistent with expectations based on molecular size.

With respect to our relative rate measurements, our values of k(CCP)/k(CCH) should be within a few percent of their high pressure limiting values, whereas deviations of up to about 30% are expected for the comparative rates of the cyclic chlorides with 2-chloropropane at 1000 K and pressures near 2 bar. For comparison, a few experiments were done at pressures near 6 bar (Table 2, runs 3-12 to 3-14). These experiments lead to values of k(CCP)/k(2CP) that are lower by about 10% than the line determined by the other data. This difference is about at the limit of our experimental precision and is not fully conclusive, but is in good agreement with the predictions of our model for these pressures.

5. DISCUSSION

5.1 Comparison of shock tube results with static system studies of dehydrochlorination.

In several cases our experimental results may be compared with those obtained from studies at lower temperatures. The literature data for selected systems are collected in Table 4. In the case of the cyclic chlorides, relative rates at lower temperatures may be derived by combining the chlorocyclopentane¹⁶ for and independent absolute measurements of Swinbourne chlorocyclohexane¹⁵ and those of Herndon et al.¹⁷ for chlorocyclohexane. The data are plotted in Figure 6, together with the present measurements. To reduce errors of extrapolation, we plot the low temperature data only in the region over which the measurements overlap. The shock tube data extrapolate to near-perfect agreement with the lowest temperature results of Swinbourne, agreeing within 3% at 591 K; at 649 K the deviation is 13% for the Swinbourne/Swinbourne data and 10% for the relative values derived from the Swinbourne/Herndon et al. results. This level of agreement but gives confidence to the data sets. Extrapolation of the may be fortuitous Swinbourne/Swinbourne results to our conditions is slightly less satisfactory, leading to relative

rates about a factor of two smaller than our directly measured values. A least squares fit to the combined low and high temperature data leads to:

 $\log k(\text{CCH}) = (1.0562 + 0.0008)\log k(\text{CCP}) - (0.0857 + 0.0021); 591-1021 \text{ K}; 1 \text{ bar to 3 bar}$

Errors are given as the standard 1σ uncertainty derived from the statistical fit. Overall, we estimate the relative rates should be accurate to about 10% at the one sigma level of confidence.

Figure 7 shows a similar comparative rate plot for chlorocyclopentane and 2-chloropropane. We have again derived the relative rates at the lower temperature from independently measured absolute rates. For chlorocyclopentane, the data of Swinbourne are the only available values, while there are several studies of the decomposition of 2-chloropropane. The data of Barton and Head,³ Howlett,⁸ Chytrý *et al.*,⁴² and Heydtmann *et al.*⁴³ are in excellent agreement while the results of Asahina and Onozuka⁴⁴ are about a factor of 2.5 larger. We note that in the latter work the authors do not report taking any precautions to avoid free radical or heterogeneous processes. The other researchers used seasoned reactors and/or inhibitors in their studies and this may account for the discrepancy. For this reason the data of Asahina and Onozuka were not used in our final analysis. The high and low temperature results are again in excellent agreement: even after an extrapolation of over four orders of magnitude in rate, the shock tube measurements are within about 15% of the derived low temperature results. A combined fit to the low and high temperature data leads to:

 $\log k(\text{CCP}) = (0.9369 + - 0.0014)\log k(2\text{CP}) + (0.5491 + - 0.0033);$ 591-1021 K; 1 bar to 3 bar where the uncertainties are those from the statistical fit; the overall uncertainty in the relative rates

should be similar to that estimated earlier, about 10% at the one sigma level of confidence.

5.2 Comparison with previous comparative rate experiments.

Tsang³⁰ has previously carried out comparative rate shock tube studies of the decomposition of 2-chloropropane relative to decyclization of cyclohexene and 4-vinylcyclohexene. These systems have been repeated in the present work and the results are compared in



Figure 3. In both cases the results from the previous work are indistinguishable at the upper end of the rate range, but there are small discrepancies in the measured slope. Figure 4 presents a similar relative rate plot for the decomposition of chlorocyclopentane and 4-methylcyclohexene. The individual data points and solid line are from the present comparative rate experiments. For this reaction there are no previous comparative rate studies and values have been derived on the basis of the absolute rate parameters. Data for chlorocyclopentane are as recommended later in this work; those for 4-methylcyclohexene were derived two ways, directly from literature-reported³⁰ comparative rate expression for 4-methylcyclohexene and cyclohexene [using the 1981 recommendation²² for *k*(CH)] and using the 1981 recommendation²² of Tsang for *k*(4MCH). The slight difference reflects the consideration of other comparative rate studies in the latter work. The results are indicated as dashed lines. The present results fall between the literature values at the upper end of the rate range but again show some variation in the slope.

The differences in the slopes of the comparative rate plots noted above are suggestive of small systematic errors in the various studies and are not altogether surprising given the difficulties alluded to earlier in comparing reactions with very different rates.

5.3 Absolute Rate Parameters.

In previous works Tsang and others have used the decyclization of cyclohexene as the primary standard and have derived absolute rates on this basis. In the present instance there is a large disparity in rate between the dehydrochlorination reactions of chlorocyclopentane and chlorocyclohexane and the decomposition of cyclohexene. Such a disparity increases the experimental difficulties and limits the temperature range over which reliable rate comparisons can be made. This reduces the accuracy of the result; in general the most accurate relative temperature dependencies are to be expected when the reactions to be compared have similar pre-exponential factors and activation energies. In this sense the data comparing chlorocyclopentane, chlorocyclohexane, and 2-chloropropane are to be preferred. The comparative rate plots shown in Figure 6 and Figure 7 provide well-defined relative rates for these species over an extended rate range, and can be used to derive absolute rates for the substrates of interest if a reliable absolute rate expression for 2-chloropropane is available.

In Figure 8 we present the extant data on the dehydrochlorination reaction of 2-chloropropane (see also Table 4). The preferred results from static systems at lower temperatures were discussed in Section 4.2; at higher temperatures there are several comparative rate studies and one absolute determination. In the latter Swihart and Carr⁴⁵ used pulsed Laser Powered Homogeneous Pyrolysis (LPHP) to study the reaction, deriving temperatures using a time dependent thermal lensing effect⁴⁵⁻⁴⁷ that relates signal delay times with heating of the gas and the speed of sound in the heated gas. They have discussed in detail the uncertainties in this technique.⁴⁵ Depending on the reactor used and assumptions made, derived temperatures varied by up to \pm 75 K; they validated their preferred configuration by carrying out comparative rate studies of 2-chloropropane and ethyl acetate and in this configuration the absolute temperatures matched those of the comparative rate studies within *ca*. \pm 20 K. While these experiments are of confirmatory value, we do not feel they are sufficiently validated to supersede shock tube based comparative rate measurements. With respect to the comparative rate results, the data of Swihart and Carr,⁴⁵ Tsang,³⁰ and this work are

all in excellent agreement. An additional comparative rate measurement has been reported by Cadman *et al.*,⁴⁸ but Tsang⁴⁹ has pointed out that the residence times derived in that work are impossibly short and those data are therefore not considered further.

In our final analysis we make use of the preferred static system results^{3,8,42,43} and the two comparative rate shock tube studies which utilized cyclohexene as the standard. The original result of Tsang,³⁰ when combined with his updated expression for k(CH),²² extrapolates to a value of k(2CP) that is about 50% larger than found in the lower temperature static studies. The present study of the same system extrapolates to values of k(2CP) about 20% smaller than the low temperature measurements. Our recommended expression is derived from a least squares fit to these two sets of results together with the aforementioned static system data and leads to:

 $\log k(2\text{CP})/\text{s}^{-1} = (13.98 \pm 0.08) - (26225 \pm 130)/2.303\text{T}$; 590 K to 1020 K; 1 bar to 3 bar

Our RRKM/ME analysis¹⁹ enables us to provide a rate expression in extended Arrhenius form as: $k(2\text{CP}) = 1.98 \times 10^{23} \text{ T}^{-2.80} \text{exp}(-28360/\text{T}) \text{ s}^{-1}$

The two expressions agree to within \pm 5 % over the experimental temperature range of 590 K to 1020 K.

At higher temperatures these rate expressions are directly linked to our preferred absolute rate constant for cyclohexene decyclization through the comparative rate shock tube experiments, but consideration of the static system data should provide a more accurate estimate of the temperature dependent behavior by virtue of the broader temperature range considered.

The uncertainty is given as the standard value (1σ) derived from the statistical fit and represents precision only. Systematic errors are more significant in almost all kinetic studies; at low temperatures these are typically errors resulting from surface and radical chain induced chemistry while in shock tube studies knowledge of the absolute temperature is a primary consideration. Taking the systematic uncertainties into consideration, we estimate the expanded standard uncertainty in *k* to be about 15% near 600 K rising to about 40% at 1000 K. This translates to about a factor of three in the pre-exponential factor and 6 kJ mol⁻¹ in the activation energy.

When combined with the comparative rate data of Figure 6 and Figure 7 the following expressions are derived:

log $k(CCP)/s^{-1} = (13.65 \pm 0.10) - (24570 \pm 160)/2.303T$; 590 K to 1020 K; 1.5 bar to 3 bar log $k(CCH)/s^{-1} = (14.33 \pm 0.11) - (25950 \pm 180)/2.303T$ 590 K to 1020 K; 1.5 bar to 3 bar

The extended Arrhenius forms of these rate expressions from our RRKM/ME analyses are:

$$k(\text{CCP}) = 3.99 \times 10^8 \,\text{T}^{1.52} \exp(-23400/\text{T}) \,\text{s}^{-1}$$

 $k(\text{CCH}) = 6.70 \times 10^{10} \,\text{T}^{1.05} \exp(-25150/\text{T}) \,\text{s}^{-1}$

Differences between the simple and extended Arrhenius expressions in the experimental temperature range are less than ± 3 %.

The major contributor to the overall uncertainty in the absolute expressions for these two reactions is the uncertainty in the standard reaction (cyclohexene decyclization) rather than error in the relative rate determinations. Accordingly, the expanded uncertainties are similar to that estimated for 2-chloropropane, about 15% near 600 K rising to about 40% at 1000 K.

Our RRKM/ME analysis allows us to extrapolate the above results to their high pressure limits. In the accompanying article¹⁹ we discuss and provide an estimate of the uncertainty in the extrapolated values. We found the following rate expressions to well represent the reactions at the high pressure limit when expressed in the Arrhenius format:

log $k(2CP)_{\infty} / s^{-1} = (14.36) - (26784)/2.303T$; 620 K to 1020 K log $k(CCP)_{\infty} / s^{-1} = (13.75) - (24714)/2.303T$; 590 K to 1020 K

 $\log k(\text{CCH})_{\infty} / \text{ s}^{-1} = (14.41) - (26070)/2.303\text{T}$ 590 K to 1020 K

and in extended Arrhenius form:

 $k(2\text{CP})_{\infty} = 5.74 \text{x} 10^9 \text{ T}^{1.37} \text{exp}(-25680/\text{T}) \text{ s}^{-1}$; 600 K to 1600 K

 $k(\text{CCP})_{\infty} = 7.65 \times 10^7 \text{ T}^{1.75} \exp(-23320/\text{T}) \text{ s}^{-1}$; 600 K to 1600 K

 $k(\text{CCH})_{\infty} = 8.25 \times 10^9 \text{ T}^{1.34} \exp(-25010/\text{T}) \text{ s}^{-1}$; 600 K to 1600 K

The above expressions covering a broad temperature range agree with the simple Arrhenius expressions over the entire range to within $\pm 5\%$ and agree with the rate constants *in the temperature range of interest* (590 K to 1020 K) to within $\pm 1\%$.

For instances where rate constants are needed in the pressure dependent regime, Tables 5, 6, and 7 provide tabulated values of k/k_{∞} for selected pressures and temperatures covering 0.01 bar to 1 bar and 600 K to 1600 K. These data can be parameterized as needed if analytical expressions are desired.

5.4 Parameters for dehydrochlorination

In 1970 Benson and O'Neal¹⁸ evaluated the data on chlorocyclopentane and chlorocyclohexane based on the data from static systems. While accepting the absolute rates reported in the studies of Swinbourne^{15,16} and Herndon *et al.*,¹⁷ they slightly modified the reported Arrhenius parameters, and suggested that the A-factor of chlorocyclopentane should be significantly lower than that of chlorocyclohexane. Their rationale was based on comparisons with data for other alkyl halides, and the expectation that chlorocyclopentane will experience a greater loss of entropy in the transition state due to freezing of pseudorotational modes. Remarkably, our measurements suggest a value of 4.8 for the ratio of A-factors in comparison with the Benson and O'Neal estimate of 5.0. The calculated result (without any corrections) is about 5.1 (see accompanying article¹⁹).

When placed in an Arrhenius format, the parameters derived from the combined experimental data from low and high temperatures for the dehydrochlorination reactions of 2-chloropropane, chlorocyclopentane, and chlorocyclohexane uniformly indicate slightly higher pre-exponential factors and activation energies in comparison with the results from lower temperature static studies and the evaluations of Benson and O'Neal. The computational results imply that this arises primarily from non-Arrhenius behavior and a relatively larger contribution from tunneling at lower temperatures. Our analysis of uncertainties in the computations (see accompanying article¹⁹) indicates the high level of agreement between the computations and experiments is partly fortuitous, but nonetheless suggests that there are no major errors in the absolute rate constants derived from the comparative rate shock tube studies. As these are ultimately linked to the rate parameters for decomposition of cyclohexene, our primary temperature standard, there appear to be no compelling reasons to think that the cyclohexene rates are in need of revision. A stronger confirmation of this conclusion would require the development of a demonstrably precise and accurate method of absolute temperature determination in high temperature kinetic studies.

5.5 Standard Temperature Scale

The dehydrochlorination reactions considered here are most useful as temperature standards at the lower end of the typical temperature range covered by shock tubes, roughly 840 K to 1020 K. Using the recommended data and calibrated GC analytical methods, temperatures derived from the chlorocyclopentane, chlorocyclohexane, and 2-chloropropane standards should be equal within a few degrees Kelvin. The present data also provide a direct link to the decyclization reaction standards that are most useful from roughly 1000 K to 1170 K. Near the overlap temperature of around 1000 K the temperatures derived by following the above dehydorchlorinations or the decyclization of cyclohexene should again agree within a few degrees Kelvin. When combined with techniques we have developed to study radical reactions of interest, such as the addition of H atoms to unsaturated compounds, or the decomposition of alkyl radicals, the consequence is that a much larger temperature range can be covered with accuracy. This can significantly increase the accuracy of the temperature dependent results and thus the ability to extrapolate results to the full range of interest and applicability, *e.g.* the use of reaction rate data in combustion simulations.

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Mixture	Components in mixtures (μ L/L)						
No.	CCP ^a	CCH ^b	2CP ^c	CH ^d	4MCH ^e	4VCH ^f	135TMB ^g
1^{h}	100	100	—	_	_	_	_
$2A^{h}$	100	100	100	_	—	-	8,400
$2B^{i}$	100	100	100	_	—	-	2,400
3 ⁱ	100	_	100	1000	—	_	10,300
4^{i}	100	100	100	_	—	200	10,000
5	100	100	—	_	500	-	9,800

Table 1. Gas mixtures used in the present experiments. The remaining balance is argon.

^a CCP = chlorocyclopentane; ^b CCH = chlorocyclohexane; ^c 2CP = 2-chloropropane; ^d CH = cyclohexene; ^e 4MCH = 4-methylocyclohexene; ^f 4VCH = 4-vinylcyclohexene; ^g 135TMB = 1,3,5-trimethylbenzene (inhibitor); ^h C1-C4 species analyzed on a HayeSep N column; ⁱ C1-C4 species analyzed on an Alumina PLOT column under cryogenic conditions (see text).

Mixture -	<i>k</i> ČČP	k CCH	k 2CP	k CH	<i>k</i> VCH	k MCH		
Run No.	s ⁻¹	s ⁻¹	s ⁻¹	s ⁻¹	s ⁻¹	s ⁻¹	T/K	P / bar
1-1	121	128	-	-	-	-	922	1.43
1-2	185	200	-	-	-	-	937	1.48
1-3	351	407	-	-	-	-	960	1.55
1-4	736	871	-	-	-	-	989	1.65
1-5	975	1159	-	-	-	-	1000	1.68
1-6	1575	1909	-	-	-	-	1020	1.75
2A-1	15.0	14.7	4.91	-	-	-	857	1.45
2A-2	21.9	21.7	7.39	-	-	-	868	1.49
2A-3	59.5	63.3	20.8	-	-	-	899	1.59
2A-4	89.1	95.6	31.0	-	-	-	911	1.63
2A-5	111	119	39.8	-	-	-	919	1.66
2A-6	214	241	80.1	-	-	-	942	1.76
2A-7	246	281	90.9	-	-	-	947	1.78
2A-8	315	365	120	-	-	-	956	1.81
2A-9	443	522	169	-	-	-	968	1.86
2A-10	501	591	195	-	-	-	974	1.89
2A-11	540	630	201	-	-	-	975	1.89
2A-12	600	702	227	-	-	-	979	1.00
2A-13	633	745	236	-	-	_	981	1 92
2A-14	977	1172	383	-	-	-	999	1.99
2A-15	1142	1370	463	-	-	-	1006	2.02
2A-16	1618	1951	686	-	-	_	1021	2.02
2R-1	9.06	8 55	3.00				843	1.26
2B-2	53.8	55.6	18.5				895	1.20
2B-3	69.2	73.2	23.8				903	1.41
2B-3	791	941	308				990	1.43
2B-4	782	941	308			_	990	1.73
2D-5 3-1	39.6	542	13.5	0.0670		_	801	1.75
3-2	71.6	_	25.1	0.0070		_	9091	1.00
3-3	130	_	50.0	0.130		_	909	1.00
3-4	360	_	1/2	1.231		_	920	1.70
3-5	434	_	163	1.25		_	900	1.92
3-6	806	_	359	3.49		_	906	2.05
3-7	1008	_	405	4.05		_	1000	2.03
3-8	1210	_	505	5.43		_	1000	2.07
3-0	2283	_	1024	13.45		_	1038	2.11
3-10	(3310) ^a	_	1654	26.9		_	1050	2.24
3-10	(3906) ^a	_	2109	38.0		_	1073	2.00
3-12	(3300)	_	68.2	0.401		_	936	5 37
3-12	2151	_	1016	12.1		_	1034	6.67
3-14	(3/31) ^a	_	1868	28.1	_	_	1062	7.06
J-14	52.0	54.2	17.0	20.1	- 2 17	-	804	1.00
4-1 1_2	52.0	55.2	18.5	-	2.17	-	805	1.02
4-2	32.0 86.0	03.0 03.0	30.0	-	2.10	-	030	1.02
4-3 A_A	120	33.0 1/1	<u> </u>	-	5.57	-	025	1.09
4-4	261	208	106	-	127	-	920	1.75
4-5	<u> </u>	290 556	100	-	25.6	-	932	1.00
4-0 Λ_7	4// /79	561	102	-	25.0	-	072	1.95
4-8	9/5	11/2	381	-	60.4		1000	2.07
4-0	340	1140	501	-	00.4	-	1000	2.07

Table 2. Summary of the rate constants determined in the present work.

4-9	1179	1431	500	-	79.5	-	1009	2.11
4-10	1287	1561	532	-	87.1	-	1012	2.13
4-11	1298	1573	544	-	92.3	-	1013	2.13
5-1	52.7	52.4	-	-	-	0.139	898	1.59
5-2	70.1	70.2	-	-	-	0.219	909	1.64
5-3	91.7	95.4	-	-	-	0.262	913	1.66
5-4	201	226	-	-	-	0.716	939	1.76
5-5	227	255	-	-	-	0.979	948	1.80
5-6	546	640	-	-	-	2.40	972	1.90
5-7	702	833	-	-	-	3.56	984	1.95
5-8	773	922	-	-	-	3.70	985	1.95
5-9	876	1053	-	-	-	4.91	993	1.99
5-10	1111	1344	-	-	-	6.66	1002	2.03
5-11	1407	1707	-	-	-	8.62	1010	2.06
5-12	1444	1748	-	-	-	8.92	1011	2.07
5-13	1555	1883	-	-	-	11.7	1019	2.10

^a Values given parenthetically are derived from substrate conversions greater than 65% and are of lower accuracy and expected to exhibit systematic errors associated with boundary effects.

T/K	Comparative rate expressions ^a	Source
894-1021	$\log k(CCH) = (1.0506 + - 0.0016)\log k(CCP) - (0.0714 + - 0.0041)$	TW - All data
591-1021	$\log k(CCH) = (1.0562 + - 0.0008)\log k(CCP) - (0.0857 + - 0.0021)$	High and Low T
880-1020	log k(VCH) = (1.214 +/- 0.008)log k(2CP) - (1.36 +/- 0.015)	1965TSA
843-1021	$\log k(CCP) = (0.9481 + - 0.0032)\log k(2CP) + (0.5255 + - 0.0068)$	All ST Data
591-1021	$\log k(CCP) = (0.9369 + - 0.0014)\log k(2CP) + (0.5491 + - 0.0033)$	High and Low T
843-1021	$\log k(CCH) = (9966 + - 0.0051)\log k(2CP) + (0.4908 + - 0.0109)$	Mix 2
891-1073	$\log k(2CP) = (0.7966 + - 0.0094)\log k(CH) + (2.107 + - 0.009)$	Mix 3
894-1013	$\log k(CCH) = (1.0472 + - 0.0015)\log k(CCP) - (0.0602 + - 0.0038)$	Mix 4
894-1013	log k(CCH) = (0.9896 +/- 0.0050)log k(2CP) + (0.491 +/- 0.011)	Mix 4
894-1013	$\log k(2CP) = (0.9050 + - 0.0096)\log k(VCH) + (0980 + - 0.013)$	Mix 4
898-1019	$\log k(CCH) = (1.0597 + - 0.0040)\log k(CCP) - (0.0991 + - 0.0107)$	Mix 5
898-1019	$\log k(CCP) = (0.7902 + - 0.0126)\log k(MCH) + (2.401 + - 0.0089)$	Mix 5
919-1046	$\log k(CH) = (1.304 + - 0.009)\log k(2CP) - (2.816 + - 0.02)$	1965TSA
891-1073	$\log k(CH) = (1.2532 + -0.015)\log k(2CP) - (2.640 + -0.037)$	Mix 3

Table 3. Summary of the rate relations determined for the reactions considered.

^a CCH = chlorocyclohexane; CCP = chlorocyclopentane; 4VCH = 4-vinylcyclohexene; 2CP = 2-chloropropane; 4MCH = 4-methylcyclohexene; ^m CH = cyclohexene

Reaction	<i>k</i> / s ⁻¹	Temp. (K)	Pressure (bar)	Method	Ref.
$CCP^{a} \rightarrow cyclopentene + HCl$	2.95x10 ¹³ exp(-24305/T)	582-649	0.053-0.53	Static	1960Swi
	1.26x10 ¹³ exp(-23853/T)	580-650	NS ^b	Review	1970Ben
	6.06x10 ¹³ exp(-24449/T)	843-1021	1.4 - 2.4 bar	ST-CR ^{c.d}	This Work
	4.47x10 ¹³ exp(-24570/T)	591-1021	1-3 bar	Evaluation	This Work
	5.62x10 ¹³ exp(-24714/T)	591-1021	HPL ^e	Evaluation	This Work
$CCH^{e} \rightarrow cyclohexene + HCl$	3.16x10 ¹³ exp(-24753/T)	591-658	0.053-0.53	Static	1960Swi
	7.59x10 ¹³ exp(-25262/T)	623-749	1.0	Stirred flow	1963Her
	6.30x10 ¹³ exp(-25161/T)	590-750	NS ^b	Review	1970Ben
	2.56x10 ¹⁴ exp(-25687/T)	843-1021	1.4 - 2.4 bar	ST-CR ^{c,} f	This Work
	2.15x10 ¹⁴ exp(-25950/T)	590-1020	1-3 bar	Evaluation	This Work
	2.57x10 ¹⁴ exp(-26070/T)	590-1020	HPL ^e	Evaluation	This Work
$2CP^{g} \rightarrow propene + HCI$	2.51x10 ¹³ exp(-25378/T)	640-675	0.052-0.17	Static	1950BAR
	1.59x10 ⁻⁰³	680	0.005-0.18	Static	1952HOW
	1.10x10 ¹¹ exp(-21288/T)	623-648	0.013-0.27	Static	1964ASA
	2.51x10 ¹³ exp(-25257/T)	625-669	0.056-0.061	Static	1970CHY
	3.55x10 ¹³ exp(-25600/T)	637-690	0.00013-0.13	Static	1975HEY
	5.99x10 ¹³ exp(-25690/T)	919-1046	0.5-1.6	ST-CR [°]	1965TSA
	3.63x10 ¹³ exp(-25618/T)	1140-1510	NS ^b	ST-CR ^{c, h}	1970CAD
	6.30x10 ¹³ exp(-25664/T)	960-1160	0.133	ST-CR ^{c, i}	1996SWI
	2.00x10 ¹³ exp(-25618/T)	960-1160	0.133	ST-Abs	1996SWI
	3.98x10 ¹³ exp(-25714/T)	640-940	NS ^b	Review	1970Ben
	3.63x10 ¹³ exp(-25618/T)	891-1073	1.5 - 2.4 bar	ST-CR [°]	This Work
	9.63x10 ¹³ exp(-26225/T)	623-1021	1-3 bar	Evaluation	This Work
	2.29x10 ¹⁴ exp(-26784/T)	623-1021	HPL ^e	Evaluation	This Work
$4VCH^{j} \rightarrow 2$ butadiene	2.51x10 ¹⁵ exp(-31100/T	900-1150	1.7 - 5	ST-CR [°]	1981TSA
				Evaluation	
$4MCH^k \rightarrow propene + butadiene$	2.0x10 ¹⁵ exp(-33400/T	900-1150	1.7 - 5	ST-CR °	1981TSA
	45			Evaluation	
$CH' \rightarrow ethene + butadiene$	1.41x10 ¹⁵ exp(-33500/T)	900-1150	1.7 - 5	ST-CR [°]	1981TSA
				Evaluation	

Table 4. Summary of experimentally-derived kinetic data for selected dehydrochlorination and retro-ene reactions.

^a CCP = chlorocyclopentane; ^b Not stated ^c Shock Tube-Comparative Rate ^d 2CP standard ; ^e high pressure limit based on our RRKM/ME extrapolation of the experimental data ^f CCH = chlorocyclohexane; ^g CCP standard; ^h 2CP = 2-chloropropane; ⁱ bromoethane standard; ^j ethyl acetate standard; ^k 4VCH = 4-vinylcyclohexene; ¹ 4MCH = 4-methylcyclohexene; ^m CH = cyclohexene

T/K	$k(P)/k_{\infty}$				
	0.01 bar	0.1 bar	1 bar	10 bar	
600	84.1%	95.8%	99.4%	99.9%	
700	64.9%	85.9%	96.9%	99.6%	
800	44.0%	69.2%	90.3%	98.2%	
900	26.8%	49.4%	78.2%	94.5%	
1000	15.1%	31.7%	61.8%	87.0%	
1100	7.99%	18.5%	44.5%	75.3%	
1200	4.09%	10.1%	29.4%	60.7%	
1300	2.05%	5.30%	18.1%	45.5%	
1400	1.02%	2.72%	10.6%	32.0%	
1500	0.51%	1.39%	6.01%	21.3%	
1600	0.26%	0.73%	3.39%	13.8%	

Table 5. Deviations from the high pressure limit, expressed as $100^* k/k_{\infty}$, for the reaction 2-chloropropane \rightarrow propene + HCl.

Table 6. Deviations from the high pressure limit, expressed as $100*k/k_{\infty}$, for the reaction chlorocyclopentane \rightarrow cyclopentene + HCl.

10 bar
100.0%
100.0%
99.9%
99.7%
98.8%
96.2%
90.4%
80.3%
66.6%
51.6%
38.0%

Table 7. Deviations from the high pressure limit, expressed as $100^* k/k_{\infty}$, for the reaction chlorocyclohexane \rightarrow cyclohexene + HCl.

	<i>k</i> (P)/ <i>k</i> ∞					
T/K	0.01 bar	0.1 bar	1 bar	10 bar		
600	99.6%	99.9%	100.0%	100.0%		
700	96.9%	99.5%	99.9%	100.0%		
800	87.7%	96.9%	99.6%	100.0%		
900	69.6%	88.3%	97.8%	99.7%		
1000	47.2%	71.2%	92.0%	98.7%		
1100	27.5%	49.0%	79.6%	95.6%		
1200	14.2%	29.0%	61.2%	88.2%		
1300	6.83%	15.3%	41.5%	75.5%		
1400	3.18%	7.67%	25.5%	59.0%		
1500	1.49%	3.79%	14.8%	42.3%		
1600	0.72%	1.91%	8.4%	28.4%		

Figure Captions

Figure 1. Comparative rate plot from shock tube studies of Chorocyclohexane \rightarrow cyclohexene + HCl and Chorocyclopentane \rightarrow cyclopentene + HCl. Symbols are as given in the legend with mixture compositions given in Table 1.

Figure 2. Comparative rate plot from shock tube studies of *chorocyclopentane* \rightarrow *cyclopentene* + *HCl* relative to 2-*chloropropane* \rightarrow *propene* + *HCl*. Symbols are as given in the legend with mixture compositions given in Table 1.

Figure 3. Comparative rate plot for the decyclization reactions of 4-vinylcyclohexene and cyclohexene relative to 2chloropropene \rightarrow propene + HCl). Symbols: **•**, cyclohexene/2-chloropropene, this work; \Box , cyclohexene/2chloropropene, 1965 Tsang³⁰; •, 4-vinylcyclohexene/2-chloropropene, this work. The solid lines show the least squares fits to the present data while the dashed lines indicate the rate relations reported by Tsang.

Figure 4. Comparative rate plot for the decyclization reactions of 4-methylcyclohexene relative to *chlorocyclopentane* \rightarrow *cyclopentene* + *HCl*. The solid line shows the least squares fit to the present data; the dashed lines have been derived from the non-competitive absolute measurements, taking *k*(CP) from this work and *k*(4MCH) from 1981Tsang²² (upper dashed red ine) or derived from the data of 1965Tsang³⁰ (lower dotted line); see text, Section 4.2.

Figure 5. Falloff curves derived from our RRKM/ME model at a pressure of 2 bar expressed as values of k/k_{∞} for 2-chloropropane, chlorocyclopentane, and chlorocyclohexane.

Figure 6. Extended range comparative rate plot for *chorocyclohexane* \rightarrow *cyclohexene* + *HCl* relative to *chorocyclopentane* \rightarrow *cyclopentene* + *HCl*. Data with log $k/s^{-1} > 0$ pertain to the direct competitive studies of the present work while smaller values have been derived from the non-competitive absolute measurements.¹⁵⁻¹⁷ Symbols are as given in the legend. The solid line shows the least squares fit to all data while the dotted red and black lines show the respective extrapolations of the present results and those of Swinbourne.^{15,16}

Figure 7. Extended range comparative comparative rate plot for *chorocyclopentane* \rightarrow *cyclopentene* + *HCl* relative to 2-*chloropropene* \rightarrow *propene* + *HCl*. Data with log $k/s^{-1} > 0$ pertain to the direct competitive studies of the present work while smaller values have been derived from the non-competitive absolute measurements.^{7,16,42,43} Symbols are as given in the legend. The solid line shows the least squares fit to all data while the dotted line is the extrapolated fit from the present shock tube studies.

Figure 8. Arrhenius plot for the reaction 2-*chloropropane* \rightarrow *propene* + *HCl*. The lower temperature results are from static systems while those at high temperatures are from shock tubes or pulsed Laser Powered Homogeneous Pyrolysis. Symbols are as given in the legend. The solid black line shows the fit to the preferred data (see Section 5.3 of text) and corresponds to $k/s^{-1} = 9.63 \times 10^{13} \exp(-26225/T)$.



Figure 1. Comparative rate plot for Chorocyclohexane \rightarrow cyclohexene + HCl and Chorocyclopentane \rightarrow cyclopentene + HCl. Symbols are as given in the legend with mixture compositions given in Table 1.



Figure 2. Comparative rate plot for *chorocyclopentane* \rightarrow *cyclopentene* + *HCl* relative to 2-*chloropropane* \rightarrow *propene* + *HCl*. Symbols are as given in the legend with mixture compositions given in Table 1.



Figure 3. Comparative rate plot for the decyclization reactions of 4-vinylcyclohexene and cyclohexene relative to 2chloropropene \rightarrow propene + HCl). Symbols: **•**, cyclohexene/2-chloropropene, this work; \Box , cyclohexene/2chloropropene, 1965 Tsang³⁰; •, 4-vinylcyclohexene/2-chloropropene, this work. The solid lines show the least squares fits to the present data while the dashed lines indicate the rate relations reported by Tsang.



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