Thermal decomposition of 2-bromopropene, and 2-chloropropene

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2-Chloropropene and 2-bromopropene have been decomposed in single pulse shock tube experiments. The only products under all conditions are propyne and allene. The high pressure rate expressions are

$$k(2\text{-}BrC_3H_5 \Rightarrow \text{propyne/allene} + HBr) = 10^{14.9}\exp(-32\,830/RT) \text{ s}^{-1}$$

$$k(2\text{-}ClC_3H_5 \Rightarrow \text{propyne/allene} + HCl) = 10^{14.8}\exp(-34\,200/RT) \text{ s}^{-1}$$

in the temperature range 1100 to 1250 K and pressures of 150 to 800 kPa. The propyne to allene ratios are 1.8 and 1.6 for the brominated and chlorinated compounds respectively with minimal temperature dependence. Results are compared with those for the alkyl compounds and *ab-initio* calculations on 2-chloropropene. Differences in energy transfer efficiencies for 2-chloropropene and 4-methylcyclohexene decompositions are explored.

Introduction

Dehydrohalogenation reactions have long been of interest to kineticists.[1] This is largely due to the analogies that exist between gas phase and solution phase reaction rate constants in polar media.[1] It is therefore always of interest to expand the database of relevant reactions. Furthermore, advances in theory promise to offer new insights into the details of the reactions. Table 1 summarizes some of the existing data[2–6] on the elimination of hydrogen halide from organic halides. We have divided the results into alkyl halide and vinylic halide categories. Most of the results involve alkyl halides where the hydrogen halide is ejected by 1,2 elimination. Note the greater

Table 1 Summary of data on hydrogen halide elimination from alkyl and vinyl halide compounds. The alkyl halide results are from single pulse shock tube studies. The vinyl halides are from all available results

1,2-Alkyl halide eliminations[1] (experiments) [rate constants at 1000] s^{-1}

$k(CH_3CH_2Cl \rightarrow CH_2=CH_2 + HCl) = 10^{13.3}\exp(-28\,330/T)$ [9.9]
$k(CH_3CH_2Br \rightarrow CH_2=CH_2 + HBr) = 10^{13.3}\exp(-26\,900/T)$ [41.5]
$k((CH_3)_2CHCl \rightarrow CH_3CH=CH_2 + HCl) = 10^{13.8}\exp(-25\,600/T)$ [457]
$k((CH_3)_2CHBr \rightarrow CH_3CH=CH_2 + HBr) = 10^{13.7}\exp(-24\,000/T)$ [1887]
$k((CH_3)_2CHI \rightarrow CH_3CH=CH_2 + HI) = 10^{13.8}\exp(-22\,600/T)$ [9185]
$k((CH_3)_3CCl \rightarrow (CH_3)_2C=CH_2 + HCl) = 10^{13.9}\exp(-22\,400/T)$ [14\,960]
$k((CH_3)_3CBr \rightarrow (CH_3)_2C=CH_2 + HBr) = 10^{14.0}\exp(-20\,800/T)$ [92\,610]
$k((CH_3)_3CI \rightarrow (CH_3)_2C=CH_2 + HI) = 10^{13.9}\exp(-19\,070/T)$ [417\,921]

Vinylic halide eliminations (experiments)
$k(C_2H_3Cl = C_2H_2 + HCl) = 10^{14}\exp(-34\,880/T)^3$ [0.071]
$k(C_2H_3Cl = C_2H_2 + HCl) = 10^{14}\exp(-34\,880/T)^4$ [0.071]
$k(C_2H_3Br = C_2H_2 + HBr) = 10^{15.2}\exp(-32\,960/T)^5$ [7.3]

Vinylic halide eliminations (theory)
$k(2\text{-}ClC_3H_5 = p\text{-}C_3H_4 + HCl) = 10^{15.15}\exp(35\,090/T)^6$ [0.81]
$k(2\text{-}ClC_3H_5 = a\text{-}C_3H_4 + HCl) = 10^{15.03}\exp(35\,300/T)^6$ [0.51]

stability of the chlorides in comparison to the bromides and iodides and the increase in rate constants with methyl substitution. These effects all arise from changes in the activation energies. The *A*-factor appears to be dependent only on the number of hydrogen atoms available. The activation energies are found to be about 0.28 of the ion dissociation energy ($\Delta H = (RX \Rightarrow R^+ + X^-)$.[2] The general subject has been reviewed[1] and there is a consensus that the transition state must be semi-ionic in character. Nevertheless, the rate data results maybe dependent in part on some contributions from the homolytic bond energies.

The only experimental thermal results on hydrogen halide elimination from unsaturated compounds are those for HCl and HBr elimination from vinyl chloride and bromide. Clearly rate constants are much smaller than those of the saturated species. This makes experiments more difficult since there is the added possibility of contributions from other channels. The smaller rate constants are mostly due to large increases in the activation energy, although the *A*-factors also appear to be larger. Note that for all these species there is also the possibility that hydrogen halide elimination will be through a three centered transition state (1,1 elimination).[7] This means that the rate constants given above may be the maximum possible if one wishes to consider only contributions from 1,2 elimination. The data on alkyl halide decomposition are all from single pulse shock tube experiments. The data from the vinyl halides are from a variety of methods. Interestingly, two of these determinations lead to exactly the same rate expressions. This is probably accidental. The review by Maccoll[1] showed that results from static and flow systems on the alkyl halides lead to much larger spreads of rate parameters. Also included in Table 1 are results from recent *ab initio* calculations.[6]

Recently, Mueller *et al.*[8] described experiments where a beam of 2-chloropropene was crossed with laser light at 193.3 nm. From the translational energy distribution they inferred that molecular elimination of HCl from the ground state molecule, resulted in the formation of both propyne and allene with the former predominating. This is contrary to the strengths of the C–H bond being broken, which differs

by about 90 kJ mol^{-1}.[2] We were sufficiently intrigued by their observations in demonstrating that the course of reaction is completely uninfluenced by homolytic bond cleavage considerations that we have now carried out single pulse shock studies on the thermal decomposition of 2-bromo and chloropropenes where the halides are adjacent to the double bonds. Nevertheless, Maccoll[1] has pointed out that the rate constant for elimination of an allylic hydrogen is only marginally increased in comparison to a normal secondary hydrogen. For that case the 50 kJ mol^{-1} (a factor of 150 in rate constants if directly reflected in the activation energy at 1100 K) difference has minimal effects on rate constants for elimination.

Single pulse shock tube studies provide an ideal means of studying the thermal decomposition of polyatomic molecules.[2] This is due to a combination of short reaction times, the capability of working at very low concentrations, and the use of chemical inhibitors. Thus it is possible to eliminate surface and radical induced contributions to the decomposition process. The only possible molecular destruction mechanism is that of unimolecular decomposition. These considerations can be strikingly demonstrated when one recalls that at typical reaction conditions of 200 kPa and 500 μs residence time there are in fact only a few million collisions. Indeed when one works at dilute concentrations, of the order of a few hundred parts per million, and in the presence of large quantities of a radical scavenger, it is easy to show that induced decomposition is impossible. By comparison, it is well known that in classical static or flow systems special measures must be taken to eliminate surface contributions to the decomposition process. Single pulse shock tube experiments under the conditions described here can therefore unambiguously establish in a quantitative manner the thermal cracking pattern for most polyatomic organic molecules.

This ability to isolate individual unimolecular reactions for study means that one can simultaneously study several reactions at the same time. If the rate expression for decomposition for one of these reactions is well established, then this reaction can serve as an internal thermometer. This circumvents the main problem in obtaining truly quantitative results from shock tube studies, the uncertainty in the reaction temperature that is determined from the shock velocity. This is the basis of the comparative rate method and extremely accurate rate expressions can be obtained. Finally by varying inhibitor to reactant ratios it is possible to demonstrate unambiguously the correctness of the proposed mechanism.

The high pressure thermal rate expression contains all kinetically useful experimental information on the nature of the transition state for a particular reaction. It is difficult to determine accurately since it is dependent on a slope measurement and correct results can be obfuscated by the mechanistic problems in static experiments. Single pulse shock tube experiments of the type described here have proved to be the one of the few consistent sources of such information. A possible source of error is that at sufficiently high temperatures, unimolecular reactions may no longer be at the high pressure limit. There are some indications that this may be a problem in the present work and will be discussed subsequently. The direct formation of molecules in thermal decomposition is of particular interest since unlike straightforward bond breaking, predictive capabilities are not satisfactory. We are therefore particularly interested in comparing the present results with the theoretical calculations of Parsons *et al.*[6] on the transition state structure and hence the high pressure rate expression for 2-chloropropene.

Experimental

The experimental studies are carried out in a heated single pulse shock tube. Details of the shock tube and the experimental procedures can be found in earlier publications.[2] The heated aspect of the shock tube enables us to study a much larger range of compounds than is possible with a room temperature instrument as well as use larger organic molecules with lower vapor pressures as inhibitors. When working at low concentrations, it also guarantees that adsorption on the walls will not deplete reactants or products. The experimental temperatures ranged from 1000 K–1250 K and reaction pressures between 1.5 bar to 12 bar pressure. The heating times were in the 500 μs range.

Product analysis utilized a dual column Hewlett Packard 6890 GC[9] equipped with flame ionization detection (FID). Except for hydrocarbons smaller than C4, most organics were well-separated on a Restek 30 m × 0.053 mm (530 μm) id Rtx-624 fused silica column (a crossbonded 6% cyanopropylphenyl/94% dimethyl polysiloxane). Hydrocarbons up to about C7 and C1 and C2 species containing up to three chlorines were separable on a 1 m × 1 mm id Hayesep S followed by a 1 m × 1 mm id Hayesep Q column (Restek). We have found this combination generally gives good separation of isomeric hydrocarbons as well as those differing only in degree of unsaturation. The GC was operated in the temperature programmed mode with constant carrier gas flow and gave good separation of all species of interest.

The chemical inhibitors used in these studies were a number of the methylbenzenes. They remove reactive radicals *via* the reactions

$$R^* + C_6H_3(CH_3)_n \Rightarrow RH + C_6H_3(CH_3)_{n-1}CH_2{}^*$$
$$\Rightarrow CH_3{}^* + C_6H_4(CH_3)_{n-1}$$
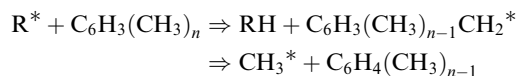
where n is less than 3. Given the overwhelming amount of the methylbenzenes, the consequence of these reactions is to substitute a relatively unreactive benzyl radical for any more reactive radicals. In the present environment, the benzyl radical can only react with other radicals in the system through fast combination reactions. In particular, it cannot attack the compounds whose decomposition characteristics we are attempting to determine. Thus the benzyl radicals are themselves extremely effective inhibitors of chain processes. The reactions being studied do not produce radicals. The presence of the inhibitor assures that any radicals from minor channel impurities will not alter the mechanism by inducing pathways to decomposition. As it turns out the reactions studied do not involve radicals. Thus inhibitors are probably not necessary. Nevertheless their presence guarantees that radical induced decomposition cannot occur. Furthermore note that for bromopropene decomposition reactions were carried out with wide variations in inhibitor to reactant concentrations. The failure to observe any systematic deviations provides the strongest validation for the postulated mechanism.

The reaction temperature was determined from the reverse Diels–Alder reaction of methylcyclohexene and in a few cases cyclohexene. These reactions involve the direct formation of stable molecules and therefore cannot contribute reactive radicals to the system. The rate expressions are[2]

$$k(C_6H_{10} \Rightarrow C_2H_4 + 1,3\text{-}C_4H_6)$$
$$= 10^{15.15}\exp(-33\,500\ \text{K}/T)\ \text{s}^{-1}$$
$$k(CH_3C_6H_9 \Rightarrow C_3H_6 + 1,3\text{-}C_4H_6)$$
$$= 10^{15.3}\exp(-33\,400\ \text{K}/T)\ \text{s}^{-1}$$

where the uncertainties in the A-factors are estimated to be a factor of 1.3 and the activation energy 3 kJ mol^{-1}. The temperature was determined through a measurement of the extent of reaction of the internal standard. Thus if the rate expression for the decomposition of one of the compounds is known to be

$$k_{\text{uni}} = A\exp(-E/RT)$$

where A is the pre-exponential factor, E the activation energy, R the gas constant and T the reaction temperature, then from the extent of decomposition of the standard reaction, the temperature can be determined or

$$\{\ln[1/t]\ln(C_0/C) - A\}R/E = 1/T$$

where t is the heating time and has been found to be about 500 μs for the present range of conditions. Since the molecules are suffering through the same time as well as temperature and pressure history, there is cancellation of errors. We have earlier given a detailed analysis of the uncertainties from these types of experiments.[2] Indeed, if the activation energies are the same then there is exact cancellation. Since it is difficult to carry out experiments with widely different activation energies, the discrepancies that can arise are small. Unimolecular decomposition rate constants are calculated in the standard manner

$$k_{uni}(\text{2-halopropene})$$
$$= (1/t)[\ln(1-(\text{propyne} + \text{allene})/\text{halopropene})]$$

The propyne and allene are lumped together since, as will be shown below, the ratio of the two products is invariant over the conditions studied. k_{uni}(2-halopropene) is thus the total rate constant for product formation. Rate expressions for the individual channels can be determined by multiplying the rate expression by the constant factors $\alpha/1 + \alpha$ and $1/1 + \alpha$ for propyne and allene respectively where α is the ratio of propyne to allene.

The 2-halopropenes, cyclohexene and 4-methylcyclohexene were obtained from Aldrich Chemicals and were used without further purification. Gas chromatographic analysis indicated impurities were below 0.1%. The argon is Ultra-Pure carrier grade from Air Products.[9]

Results

For the two secondary halides studied here, the primary products are propyne and allene. Propyne is the predominant product. The propyne to allene ratios are virtually constant over the entire range of experimental conditions. The values are 1.8 for the bromide and 1.6 for the chloride. On a per hydrogen basis the values are 2.7 and 2.4 respectively. However, if one assumes that the hydrogens in the methyl groups are equivalent (free rotor) and that 1,2-dehydrohalogenation can only occur from the *cis* configuration then the ratio would be 5.4 and 3.6. This constant ratio is maintained to the highest extent of decomposition or approximately 0.80 mole fraction for the bromide. All of these experiments are carried out under conditions where the isomerization reaction propyne ⇔ allene do not make any contributions. We have verified this by separate studies for this reaction.

Most of the experimental work deals with the decomposition of 2-bromopropene. Conditions were varied to establish unambiguously that the reaction is truly hydrogen bromide elimination. The results are summarized in Fig. 1 and include studies over a six-fold range of the concentration of the bromide. Changes in inhibitor to reactant ratio range from 50 to 1000 to one and pressures from 180 kPa to 1200 kPa. As can be seen from Fig. 1, the results show no significant trends with changes in these variables and it can be concluded that true unimolecular rate expressions are being determined. The best fit of these results leads to the rate expression.

$$k(\text{2-BrC}_3\text{H}_5 \Rightarrow \text{propyne/allene} + \text{HBr})$$
$$= 10^{14.92 \pm 0.16}\exp(-32\,830 \pm 400 \text{ K}/T) \text{ s}^{-1}$$

The stated uncertainties reflect the precision of the measurements. In absolute terms, the uncertainties in the standard rate
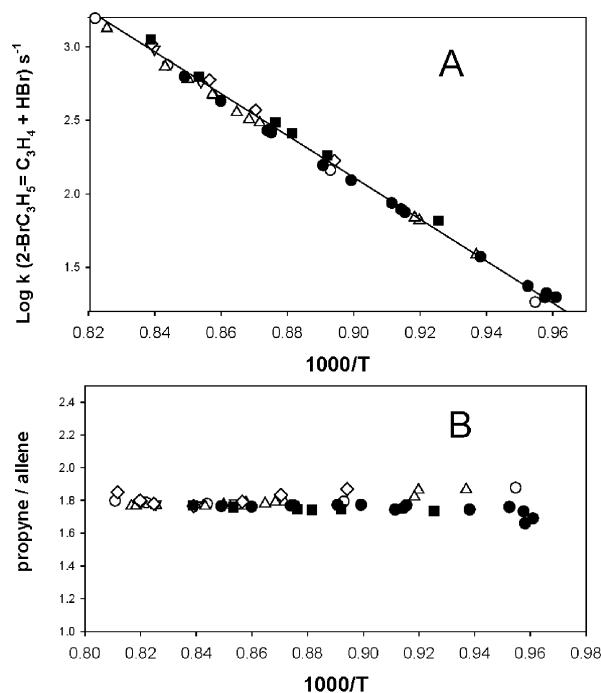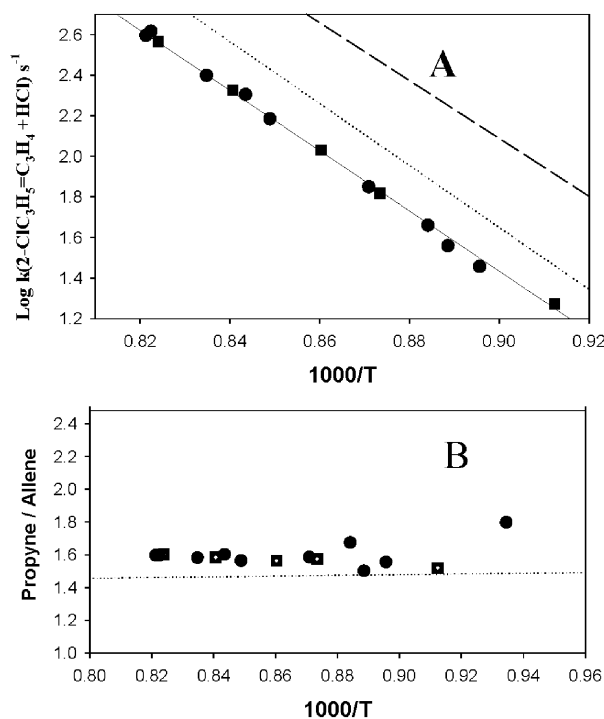
Fig. 1 A: Arrhenius plot for the elimination of HBr from 2-bromopropene. The rate constants are for the sum of the two products. B: Ratio of propyne and allene from 2-bromopropene decomposition. (1) Filled circles are experiments at 2 bar. Closed squares are experiments at 8 bar. Mixture composition: 200 ppm 2-bromopropene and 200 ppm 4-methylcyclohexene in 1% 1,3,5-trimethylbenzene. (2) Open circles are for experiments at 1.6 bar. Mixture composition: 100 ppm 2-bromopropene and 100 ppm cyclohexene and 0.5% *meta*-xylene. (3) Open triangles (up) are for experiments at 1.6 bar. Mixture composition: 100 ppm 2-bromopropene, 100 ppm 4-methylcyclohexene and 0.5% *meta*-xylene. (4) Open triangles (down) are for experiments at 2.5 bar. Mixture composition: 80 ppm 2-bromopropene, 80 ppm 4-methylcyclohexene and 5% *meta*-xylene. (5) Open diamonds are for experiments at 6 bar. 50 ppm 2-bromopropene, 50 ppm 4-methylcyclohexene and 3% *meta*-xylene. The least squares fit of the data for the propyne to allene ratio is $1.92 \pm 0.15\exp(-177 \pm 140/RT)$.

constants and expression leads to possible errors of 20% in the rate constants and factors of 2 in the A-factor and 6 kJ mol^{-1} in the activation energy. Note that this includes the uncertainty in the standard reaction.

One problem with these results is the possibility of a pressure dependence. Results at 2 bar and 8 bar from the same mixture are in fact different by a factor of 1.10. By working with the same mixture, errors from differences in mixture preparation are eliminated. The overall dependence is of the order of $p^{0.1}$ and in terms of the precision of the measurement is probably no more than factors of 2 or 3 larger then the scatter of the results. Since it is difficult to carry out experiments that encompass greater ranges of pressure the data has been treated as if it were at the high pressure limit. If this is not the case then the limiting rate parameters should be somewhat larger. Fig. 1B contains data pertinent to the propyne/allene ratio. Note the invariance with temperature.

Results on the decomposition of 2-chloropropene can be found in Fig. 2. In this case there does not appear to be any pressure dependence. Note that the reaction pressures are varied by the same amount as in the case of 2-bromopropene. Also included in Fig. 2 are the results from the 2-bromopropene study. It can be seen that the rate constants for the chloro compound are about a factor of 5 smaller than those for the bromo compound. The rate expression is

$$k(\text{2-ClC}_3\text{H}_5 \Rightarrow \text{propyne/allene} + \text{HCl})$$
$$= 10^{14.8 \pm .2}\exp(-34\,190 \pm 500 \text{ K}/T) \text{ s}^{-1}$$

Fig. 2 A: Arrhenius plot for elimination of HCl from 2-chloropropene. The rate constants are for the sum of the two products. B: Ratio of propyne to allene from 2-chloropropene decomposition. Filled squares are for experiments at 8 bar. Filled circles are for experiments at 2 bar. Mixture composition: 200 ppm 2-chloropropene and 200 ppm 4-methylcyclohexene in 1% 1,3,5-trimethylbenzene. Dotted lines are results derived from the transition state properties from Parsons *et al.* Dashed line are results for 2-bromopropene. The least squares fit of the data for the propyne to allene ratio is $1.27 \pm 1.4\exp(262 \pm 300/T)$ with a scatter of 4%.

Data pertaining to the propyne and allene ratios can be found in Fig. 2B. As with the bromo compound results are independent of pressure and temperature.

Discussion

The rate constants derived here are in quite good agreement with the calculated results of Parsons *et al.*[6] based on *ab initio* calculations. This is a very impressive demonstration of the capability of such calculations. Nevertheless it is possible that the degree of agreement may partly be due to the compensation of errors in the *A*-factor and activation energies. Unlike the experimental situation where rate constants are the directly measured quantities, the calculated rate parameters are in some sense independent of each other. This will be discussed below.

An important issue is the degree that the rate expressions given here represent high pressure values. The high temperatures utilized in effecting decomposition will always require examination of energy transfer effects.[10] For this purpose it will be necessary to consider contributions from the decomposition of the standard as well as the target reaction. Table 2 summarizes results of fall-off calculations[11] for 4-methylcyclohexene decomposition for step sizes down of 250 cm^{-1} and 500 cm^{-1} in the temperature range covered by these experiments. This range of step-sizes down is characteristic of hydrocarbon systems in this temperature range.[12] It is clear that experiments are near the high pressure limit. The transition state is based on that derived by Huang *et al.* for cyclohexene.[13] Thus the rate constants for 4-methylcyclohexene are high pressure values and derived temperatures are correct. Nevertheless these small differences are sufficient to have significant effects

on the high pressure rate expression. For example for the 500 cm^{-1} step down case the deviations from the high pressure rate constants would lead to a lowering of the activation energy by 7 kJ mol^{-1}.

However, if the deviation from the high pressure value of the target reaction is the same, then cancellation of the fall-off effects means that the use of the high pressure rate expression for the standard will lead to high pressure rate expression for the target. This would appear to be the case here. Nevertheless the halopropenes are much smaller molecules than the 4-methylcyclohexene used as a standard. Since the rate expressions are not that different it is difficult to reconcile similar pressure dependence unless both reactions are well into the high pressure region. The data in Table 2 suggest that this is not the case. Results for step sizes down of 500 cm^{-1} and 1000 cm^{-1} and the rate parameters from the *ab-initio* calculations of Parsons *et al.* can be found in Table 3. The conclusion is that with the *ab-initio* rate expression a pressure dependence of the rate constants should have been observed unless the step-size down parameter is larger than that used here. It can be seen that the agreement in the degree of fall-off can only be attained when the step-size down parameter for 2-chloropropene decomposition is considerably higher than that for 4-methylcyclohexene or alternatively if they are the same the rate expressions must be in the $10^{14}\exp(-32\,000/T)$ range. This is beyond the range of errors from the present experiments. The larger step size down parameter necessary to fit results on chlorinated compounds is in accord with the observations of Lim and Michael.[14] There is therefore a clear difference in the energy transfer characteristics of hydrocarbons and chlorinated compounds.

Table 4 contains results of calculations using the rate expression that was obtained in the present study and a step size down of 1000 cm^{-1}. It can be seen that under such conditions the pressure dependence will be below detectable limits. We have also carried out calculations with the reaction threshold reduced to that for 2-bromopropene. Due to the lower threshold we are slightly more into the fall-off region. This will be further accentuated by the somewhat looser structure of the bromo compound. In the present work the rate expression at the highest pressures of 800 kPa (from an Arrhenius fit of the 800 kPa results) is in fact very close to that given here. The consequence is that the present experiments are probably sufficiently near the high pressure limit so that the experimental rate expressions reported here are valid for such situations.

Table 2 Calculated k/k_∞ for 4-methylcyclohexene decomposition as functions of pressure, temperature and step size down

Temp (K)/ pressure (bar)	Step size down = 250 cm^{-1}			Step size down = 500 cm^{-1}		
	2	4	8	2	4	8
1100	0.94	0.97	0.98	0.98	0.99	0.99
1160	0.90	0.93	0.95	0.95	0.97	0.99
1200	0.82	0.88	0.92	0.92	0.95	0.97

Table 3 Calculated k/k_∞ for 2-chloropropene decomposition as functions of pressure, temperature and step size down. Results are based on the rate expression derived from the results of Parsons *et al.*

Temp (K)/ pressure (bar)	Step size down = 500 cm^{-1}			Step size down = 1000 cm^{-1}		
	2	4	8	2	4	8
1100	0.70	0.78	0.85	0.82	0.88	0.92
1160	0.61	0.71	0.79	0.75	0.82	0.88
1220	0.54	0.63	0.72	0.68	0.76	0.83

Table 4 Calculated k/k_∞ for 2-chloropropene decomposition as functions of pressure and temperature for a step size down of 1000 cm based on the rate expression derived from present work and that for 2-bromopropene decomposition

| | 2-Chloropropene | | | 2-Bromopropene | | |
| | $10^{14.8}\exp(-34\,190/T)$ s^{-1} | | | $10^{14.92}\exp(-32\,830/T)$ s^{-1} | | |
Temp (K)/pressure (bar)	2	4	8	2	4	8
1100	0.90	0.94	0.96	0.87	0.92	0.95
1160	0.86	0.91	0.94	0.82	0.88	0.91
1220	0.81	0.87	0.91	0.75	0.83	0.89

The rate constants for the bromo- and chloropropenes are each about two orders of magnitude smaller than those for isopropyl bromide and chloride. This suggests that the effect of halogen substitution in 1,2 elimination is not significantly affected by the double bond. It would thus appear that the rate expression for 2-iodopropene could be estimated by the data in Table 1. The effect of methyl substitution is less certain. Extrapolation of the published result on Shilov and Sbirova[5] for vinyl bromide decomposition leads to rate constants very similar to those for the 2-bromopropene from the present work. This is contrary to the situation for the chloro compounds. Vinyl chloride is much more stable than 2-chloropropene and the difference is in fact similar to that observed for the analogous alkyl chlorides. We have preliminary data that suggest that for 1-bromopropene, rate constants are in fact smaller than for 2-bromopropene. There is a question as to the contribution of a three centered transition state to these rate expressions. We hope to carry out some studies on vinyl bromide in the near future.

It is clear that the correlations developed for alkyl halide decomposition are not applicable upon the introduction of the double bond adjacent to the halide. The activation energy is larger than that calculated on the basis of the correlation between ion dissociation energy and the activation energy developed for the alkyl halides. The A-factor is about an order of magnitude larger and is indicative of a looser transition state. It is independent of the number of available H-atoms. Parsons *et al.* have interpreted the propensity for propyne formation in terms of the locking of the motion of the H-atoms in the internal rotor required for allene formation. These results must however be crucially dependent on the nature of the cation in the semi-ionic transition state. It is unfortunate that the calculations of Parsons *et al.* did not examine this aspect of the problem. In addition, a particularly interesting results would be similar calculations on the isopropyl chloride and a comparison of the semi-ionic transition state structures for the two cases.

Summary

2-Bromo- and 2-chloropropene have been decomposed in single pulse shock tube experiments. The mechanism involves unimolecular dehydrohalogenation. High pressure rate expressions have been obtained. The results confirm the observation of Muller *et al.* regarding the predominance of propyne to allene in 2-chloropropene decomposition. The rate expressions and constants are in fair agreement with the *ab-initio* calculations of Parsons *et al.* The effect of energy transfer on the relative rate constants for 4-methylcyclohexene and the 2-halopropenes have been considered. It is concluded that the latter must be more easily activated.

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