

STUDIES OF UNIMOLECULAR REACTIONS OF CHEMICALLY ACTIVATED
CHLOROALKANES AND IDENTIFICATION OF REACTIONS OF
SINGLET METHYLENE WITH CHLOROALKANES

by 503

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INTRODUCTION

The purpose of this work was threefold. The first objective was to investigate a method of producing a relatively pure singlet methylene system. Methylene has two low energy electronic states (a 1A_1 and a $^3\Sigma_g^-$) and it is necessary to be able to distinguish between these states to characterize the reactions of this singlet methylene with chloroalkanes. The second objective of this work was to use this pure singlet methylene system and other complementary methods to study the unimolecular decomposition of some highly vibrationally excited chloroalkanes.

The highly vibrationally excited chloroethanes studied in this work were produced by the recombination of thermalized alkyl and chloroalkyl radicals. These radicals were produced by two methods. The method of primary interest was the abstraction reaction of singlet methylene with a chloroalkane to produce the needed radicals. The second method was mercury (6^3P_1) photosensitization of a mixture of chloromethanes, which produced the desired radicals.

The Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular breakdown was applied to these vibrationally excited systems. Of particular interest was the effect of vibrational anharmonicity upon the rate constants and upon the nonequilibrium kinetic isotope effect. The unimolecular decomposition of a series of chloropropanes and chlorobutanes was also investigated, using the RRKM Theory.

THE REACTION OF METHYLENE WITH DICHLOROMETHANE IN THE PRESENCE OF CARBON MONOXIDE

The formation of methylene by the photolysis of ketene has been known for many years¹, but its electronic structure was determined only recently by Herzberg.² He was able to show from the far ultraviolet spectrum that there are two low energy electronic states, a $^3\Sigma_g^-$ and a 1A_1 , in agreement with earlier theoretical predictions.^{3,4,5} Herzberg's spectroscopic work also showed that the $^3\Sigma_g^-$ state is the ground state of methylene, even though he was unable to determine the limits of the two Rydberg series, which prevented determination of the separation energy.² Theoretical calculations indicated that the energy difference between these two states is between 10 and 16 kcal mole⁻¹,^{4,5} and based on comparison with known systems⁶, these calculations may be too high by about a factor of 2. This gives 5-8 kcal mole⁻¹ for the energy difference between the lowest triplet and lowest singlet states of methylene. This value is also in agreement with estimates of 2.5-12 kcal mole⁻¹ from experimental systems of various workers.⁷ There are various estimates of the heat of formation of ground state, triplet methylene, ranging from 67 to 95 kcal mole⁻¹, as determined by a variety of experimental methods. These early values are summarized by Frey.¹ The most recent determination, by mass spectrometric methods, is 91.9 kcal mole⁻¹.⁸

There are four general types of chemical reactions that methylene commonly undergoes.¹ The most studied of these reactions is the addition of methylene to a carbon-carbon double bond to form various derivatives of cyclopropane. Another common reaction is the insertion into carbon-X bonds; X is commonly a hydrogen atom or an alkoxy group in an ether. The insertion into Si-H bonds has also been studied.^{4,7} Insertion into a carbon-carbon single bond has

never been observed. The third common methylene reaction is abstraction of a hydrogen or halogen atom from various alkanes, alkenes, and alkyl halides. The fourth observed methylene reaction is the displacement of an olefin from an ether.^{1a,b} There are only a few examples of this reaction known. An example is the reaction of methylene with diethyl ether to form ethyl methyl ether and ethene. The first three of these general reactions have been known to occur simultaneously in a reaction system, unless steps are taken to specifically eliminate one of them. An example of this is the well known reaction of methylene with *cis*-2-butene,^{9,10} where both isomeric 1,2-dimethylcyclopropanes, 2-pentenes, and ethane are formed, among other products. The relative rate of addition into a carbon-carbon double bond by singlet methylene is about five times as fast as the rate of insertion into a carbon-hydrogen bond in an alkane,²³ while triplet methylene adds to a carbon-carbon double bond about 500 times as fast as it abstracts a hydrogen atom from an alkane.¹¹ Measurement of relative rates of addition to a double bond and abstraction of a halogen atom from a haloalkane is one of the topics of this work. These reactions of methylene are of particular importance as chemical activation systems for unimolecular decomposition studies. The decomposition of cyclopropane derivatives formed by the addition of methylene across a double bond has been studied extensively by B.S. Rabinovitch and co-workers.^{9,10,11} The decomposition of haloalkanes formed by the recombination of radicals from from the abstraction of a hydrogen or halogen atom from halomethanes and haloethanes has been studied extensively by D. W. Setser and co-workers,¹²⁻¹⁸ and others.^{19,20}

It has been shown that the photolysis of ketene by 3130 Å light produces a mixture of singlet and triplet methylene. The ratio of singlet to triplet

has been estimated to be 15% to 30%.^{10,28} Four methods of producing electronically pure systems of methylene have come into general use since it was realized that both low energy electronic states of methylene are produced during the photolysis of ketene, and that these states may have different reactivities toward various substrates. Relatively pure triplet methylene is produced by two methods: mercury (6^3P_1) photosensitization of ketene²¹ and by adding large amounts of inert gases, like nitrogen, argon or tetrafluoromethane to the reaction system.^{22,24,30} Recently, Carr has shown that the method of adding large amounts of inert gas, which relies on the intersystem crossing of singlet to triplet methylene, may produce only 93% triplet methylene, due to a thermal equilibrium between singlet and triplet methylene.²⁵ The mercury (6^3P_1) system has two problems. The first is intersystem crossing of CH_2 ($^3\Sigma_g^-$) to CH_2 (1A_1), or between the singlet and triplet manifold of the excited CH_2 CO. The second problem is that direct photolysis of ketene occurs by the 2537 Å light used in mercury photosensitization, to form almost pure singlet methylene. These two considerations lead to estimates of 3%^{26,27} to 13%²⁹ singlet methylene formed during the mercury (6^3P_1) photosensitization of ketene. The most commonly used method of producing relatively pure singlet methylene systems is by adding traces of oxygen or nitric oxide.^{22,30} However, it is useless for studying the singlet methylene reactions (abstraction reactions) in the system of interest to this study, because oxygen or nitric oxide removes all the doublet radicals formed by singlet methylene. Recently, DeGraff and Kistiakowsky³¹ showed that carbon monoxide reacts much more rapidly with triplet methylene than with singlet methylene and could be used to produce nearly pure singlet systems, without the problems caused by oxygen or nitric oxide. This reaction has been successfully used by Bamford,²⁰ in

his study of the reaction of methylene with chloroethane. This reaction is the subject of the first part of this work, and will be discussed in detail after the presentation of the experimental results.

The primary interest in producing pure singlet or triplet methylene systems is to isolate the various different reactions for each electronic state. One of the first reactions in which the difference in reactivities was noted was the reaction of methylene with *cis*-2-butene.^{9,10,30} Singlet methylene was observed to give stereospecific addition to the double bond, to form only *cis*-1,2-dimethylcyclopropane, while triplet methylene gave a mixture of *cis*- and *trans*-1,2-dimethylcyclopropanes. It has been found that singlet methylene shows a degree of selectivity toward insertion into primary, secondary and tertiary hydrocarbon bonds, the relative rate ratios being 1:1.2:1.5, respectively.⁴² A recent study of Mazac and Simons⁴⁷, showed that singlet methylene inserts into Si-H bonds about nine times faster than into C-H bonds. Triplet methylene was found to be nonspecific, because it reacted by forming radicals, rather than by direct insertion.⁴² There have been numerous studies on the relative rates of attack of triplet or singlet methylene on various hydrocarbon systems,^{26,11} but no one has been able to determine the relative rate of triplet to singlet reaction in a single system. The reaction of dichloromethane with methylene in the presence of carbon monoxide appears to give a value for this rate constant ratio in an abstraction system, and to give an indication of why singlet methylene reacts specifically with certain bonds.

EXPERIMENTAL

A. Reagents

The carbon monoxide used in this study was CP grade and obtained from The Matheson Co. Mass spectral analysis showed it to have less than one part per thousand of oxygen. Ketene was prepared by pyrolyzing acetone at approximately 700°C, purified by trap-to-trap distillation from an acetone-Dry Ice bath to liquid nitrogen, and then passed through a 20 feet x 1/4" column of Fluoropak in Tygon tubing at Dry Ice temperature on a GC.¹³ It was stored on the vacuum line in a blackened vessel at liquid nitrogen temperature. Dichloromethane was spectral grade and was obtained from the Fisher Scientific Co.. It was thoroughly outgassed on the vacuum line by several freeze-pump-thaw cycles. A sample was analyzed by GC on the analytical column used for this work and found to be free of any impurities. The cis-2-butene used was Phillips research grade (99.9%). It was treated in the same manner as the dichloromethane and found to be free of any trans-2-butene and other impurities.

The reagents used for calibrating the GC were ethane (The Matheson Co., CP grade), chloroethane (Eastman Organic Chemicals), 1,1-dichloroethane (Eastman Organic Chemicals), and 1,2-dichloroethane (Matheson, Coleman and Bell). A mixture of cis- and trans-1,2-dimethylcyclopropane was obtained from Columbia Organic Chemicals. A sample was separated into the pure components on the analytical column used for this work. These isomers were stored on the vacuum rack, and thoroughly outgassed before use, by the above procedure. Samples of approximately the same size used in calibrating the GC, were analyzed on the analytical columns used, and found free of any impurities.

B. EXPERIMENTAL PROCEDURES

1. Measurement of the ethane:1,2-dichloroethane ratio

For runs to determine the ethane to 1,2-dichloroethane ratio as a function of added CO, a vacuum rack employing greased stopcocks was used. All reagents were measured out in a mercury gas burette and frozen into the small, stopcocked Pyrex reaction vessels. No attempt was made to keep mercury out of the samples, as Pyrex would cut out any short wavelength light that would result in mercury photosensitization of the sample. Carbon monoxide was measured by loading the vessel with the necessary pressure of CO at liquid N₂ temperature to give the desired CO:CH₂Cl₂ ratio when the sample was warmed to room temperature. A constant ketene: dichloromethane ratio of 1:7 was used throughout this work, and the pressure in the reaction vessel was maintained at 35±5 cm.

After photolyzing the samples for one hour with the unfiltered light of a General Electric AH-6 high pressure mercury arc, the sample was frozen down with liquid N₂ and the CO and other noncondensables produced were slowly pumped off through a packed glass trap held at liquid nitrogen temperature. After all the noncondensables were removed, the remaining reaction products were transferred to the same packed glass trap, after being passed through a 8 cm long tube of Chromosorb P to remove any unreacted ketene. From the trap the sample was transferred to the GC inlet and analyzed. A rough calculation, using the lamp output parameters and the optical properties of ketene and Pyrex, showed that 98% of the methylene formed came from photolysis by the 3200±200 Å band of the lamp. (See Appendix A for details of this estimate.)

A 16 feet x 1/4" column of Porapak S was used for analysis of the reaction products.¹³ The initial column temperature was 28±2°C. After 12 min., it was programmed to 145±5°C. The retention times of the major reaction products

observed were: ethene, 6 min.; ethane, 8 min.; dichloromethane, 24 min.; and 1,2-dichloroethane, 36 min. The GC was calibrated using a mixture of known composition that closely resembled the reaction mixtures in sample size and composition.

2. Measurement of the chloroethane: 1,2-dichloroethane ratio

Several modifications of the equipment were made for this determination and all work that follows. The vacuum system was rebuilt, using only greaseless stopcocks in the gas measuring sections (Hoke Co bellows seal valves and G. Springham Co. bellows valves equipped with Viton A rubber diaphragms). The ground glass caps on the ends of the manifolds were sealed on with a minimum amount of Apiezon W sealing wax. The only grease in this part of the system was on the standard taper joints used as outlets. The vacuum system was equipped with a spiral gage and several calibrated volumes, which were used for measuring gas samples of less than 1 cc (at 76 cm Hg and 298⁰K). The procedures previously described were used for filling the photolysis vessels, photolyzing, and loading the samples into the GC.

For analysis, two columns, consisting of 3 feet x 1/4" of Porapak S and 6 feet x 1/4" of Porapak T, respectively, were used in series. The column temperature was held constant at 141-142⁰C during analysis. The relative retention times of the compounds of interest were: chloroethane, 9.5-10.5 min.; dichloromethane, 14 min.; and 1,2-dichloroethane, 46-54 min. Due to the widely varying retention times of chloroethane and 1,2-dichloroethane, their calibrations were checked at least once daily, and two different calibration mixtures were used. The amounts of these reaction products were determined by correlating their retention times with those of the corresponding compounds from the calibrations.

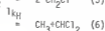
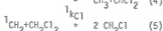
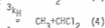
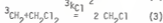
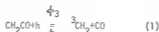
3. The reaction of methylene with a mixture of cis-2-butene and dichloromethane in the presence of carbon monoxide.

The samples were made up, photolyzed, and injected into the GC as described before. Usually, the cis-2-butene: dichloromethane ratio was 1:1, and the total substrate: ketene ratio was 7:1. For this study, two analytical columns were used: (1) 7 feet x 1/4" of Porapak S in series with 4 feet x 1/4" of Porapak T, and (2) 15 feet x 1/4" of 12% diisodecylphthalate on Chromosorb P in series with 15 feet x 1/4" of 40% silver nitrate saturated ethlene glycol on Chromosorb P. The initial column temperature was 110°C; after 38 min., the temperature was raised to 170°C. The portion of the sample eluted during the first 10 min. was trapped. By this analysis scheme the relative retention times were: cis-2-butene, 24 min.; chloroethane, 34 min.; and 1,2-dichlorethane, 78 min. The C₅H₁₀ products and dichloromethane were trapped and then run through the second column at room temperature. The relative retention times were: trans-1,2-dimethylcyclopropane, 18 min.; cis-1,2-dimethylcyclopropane, 26 min.; 2-pentene and 2-methyl-2-butene, 36 min.; and dichloromethane, 84 min.. As before, the columns were calibrated with a mixture of the desired products that closely resembled the reaction mixtures in size and composition. The second column was calibrated by trapping the same fraction of the standard samples as was trapped from the reaction mixture and then running it through the second column. As a check on the trapping procedure, a few samples were analyzed directly on the second column, and no differences in calibration factors were noted.

RESULTS

A. The reaction of methylene with dichloromethane in the presence of carbon monoxide.

The reaction of methylene with dichloromethane has been studied extensively in our laboratory. The primary photochemical processes are the formation of singlet and triplet methylene, which may react either by H or Cl abstraction.¹²⁻¹⁸ On the basis of previous data, it was not possible to eliminate any of the four following reactions, although reactions 4 and 5 were thought to be most important.



These radicals can recombine in all possible binary combinations, but the relevant recombinations for this study are:



The ethane: 1,2-dichloroethane ratio measured at high pressure directly gives $k_9 [\text{CH}_3]^2 / k_7 [\text{CH}_2\text{Cl}]^2$. It is known that $k_7 = k_9$, as these radical re-

combinations have a very low activation energy, ~ 0 ,¹⁶ and approximately the same preexponential factors. At infinitely high pressure, the chloroethane: 1,2-dichloroethane ratio directly gives $k_8[\text{CH}_3] / k_7[\text{CH}_2\text{Cl}]$. In this case, $k_8 = 2k_7$, as reaction 8 is statistically favored over reaction 7, since it is a radical cross combination. The relative radical concentrations measured by this technique are only the steady state approximations to the true radical concentrations, since the integration of the rate ratios to give product ratios in this manner assumes that the radical concentrations do not vary with time.

The molecules formed in steps 7-9 are highly vibrationally excited, 90 kcal mole⁻¹, but at the pressure used in these experiments, 35±5 cm, the vibrationally excited 1,2-dichloroethane formed in step 7 is completely stabilized,¹²⁻¹⁸ since it has a half-quenching pressure of 1.7 cm in an efficient gas. The pressure is too high for the ethane to dissociate,¹⁷ into methyl radicals. Since the half-quenching pressure of highly vibrationally excited chloroethane is 35 cm¹³ in an efficient quenching gas, about half of the highly vibrationally excited product would decompose to form HCl and ethene, at the pressure used in these experiments.^{13,17}

The decomposition of the highly vibrationally excited chloroethane was corrected in the following manner. The half-quenching pressure for 1,2-dichloroethane with carbon monoxide as a bath gas has been measured as 2.65 cm.³² This gives a quenching inefficiency of 1.54 for CO, relative to that of CH₂Cl₂. It was then assumed that CO has the same quenching inefficiency toward chloroethane as it does for 1,2-dichloroethane. This gives the ratio of decomposition product concentration, D, to stabilization product concentration, S, as $(\frac{D}{S}) (\frac{\gamma_{\text{CO}}}{\gamma_{\text{CH}_2\text{Cl}_2}}) \frac{k_8}{P}$, and then $[\text{C}_2\text{H}_5\text{Cl}]_{\text{eq}} = (\frac{D}{S}) S + S$, where γ is the

mole fraction of the respective bath gases, α is the quenching inefficiency of CO relative to dichloromethane, k_a is the apparent half-quenching pressure of CH_2Cl_2 for chloroethane, $[\text{C}_2\text{H}_5\text{Cl}]_\infty$ is the calculated yield of chloroethane at infinite pressure, P is the total pressure, and S is the measured stabilization product.

A series of experiments was done in which the ratio of $\text{CO}:\text{CH}_2\text{Cl}_2$ was varied, and the product ratio, $\text{C}_2\text{H}_5\text{Cl} : 1,2\text{-C}_2\text{H}_4\text{Cl}_2$, was measured. These data, corrected for the decomposition of chloroethane, are plotted in Fig. 2, and are listed in Table 1. The values for chloroethane: 1,2-dichloroethane found here, with no added CO, agrees well with the high pressure value of 0.8 ± 0.1 measured by Hassler and Setser for this reaction.¹⁶

Fig. 2 and Table 2 show the corresponding data for the ethane: 1,2-dichloroethane ratio. This curve was not carried out very far, since as the amount of CO added increased, the amount of methyl radicals in the system decreases rapidly, since the ethane yield varies as the square of methyl radical concentration. The amount of ethane being measured rapidly reached the limits of the thermal conductivity detector of the GC being used for this study and for that reason the data show a lot of scatter. Even so, the curve shows the same general features as the corresponding curve for the chloroethane: 1,2-dichloroethane ratio, and the intercept for no added CO is the same as found by the earlier work of Hassler and Setser.¹⁶

As can be seen from Fig. 1 and 2, CO drastically reduces the amount of methyl radicals formed in the system. This is an indication that reaction 5 is favored over reaction 6, and reaction 4 is favored over reaction 3. This conclusion is reached because the amount of chloromethyl radicals remained constant as CO was added, and it will be shown later that CO is removing triplet methylene from the reaction system.

Table 1 Chloroethane and 1,2-dichloroethane yields from the reaction of methylene with dichloromethane as a function of added carbon monoxide.

CH_2Cl_2 , cc ^a	$\frac{\text{CO}}{\text{CH}_2\text{Cl}_2}$	$\text{C}_2\text{H}_5\text{Cl}$ cc x 10 ⁻³	$1,2\text{-C}_2\text{H}_4\text{Cl}_2$ cc x 10 ⁻²	P_{Total} , cm Hg
1.70	0.00	16.3	4.1	34.4
1.60	0.76	7.7	8.7	31.9
1.80	1.28	8.0	9.1	34.9
1.70	12.09	4.6	6.2	35.3
1.75	0.00	16.6	3.9	28.5
1.70	4.22	2.8	4.4	35.7
1.60	22.25	2.3	5.7	36.3
1.70	59.01	0.7 ^b	2.2	159.9
1.60	55.05	0.7 ^b	2.7	157.8
1.60	38.01	1.5	6.6	36.7
2.80	35.65	1.8	8.9	161.2
1.40	0.17	9.2	4.9	27.2
2.10	0.10	18.8	6.1	36.3
2.05	0.33	15.0	10.8	52.9
2.05	0.23	19.7	11.7	31.9

a. cc gas at 76 cm Hg pressure and 298°K

b. estimated, as the amount observed was at the limits of detection of the GC

c. these are the measured yields, not the yields corrected to infinitely high pressure

Table 2. Ethane and 1,2-dichloroethane yields from the reaction of methylene with dichloromethane as a function of added carbon monoxide.

CH_2Cl_2 , cc ^a	$\frac{\text{CO}}{\text{CH}_2\text{Cl}_2}$	C_2H_6 cc x 10 ⁻³	$1,2\text{-C}_2\text{H}_4\text{Cl}_2$, cc x 10 ⁻²	P_{Total} , cm Hg
2.10	0.00	3.4	5.3	36.8
2.090	1.08	0.9	12.9	36.6
2.092	1.13	11.3	12.0	37.4
2.084	3.45	0.5	9.6	38.1
2.09	0.54	0.9	10.9	35.6
2.09	0.25	1.2	13.6	44.8
2.09	0.76	0.9	8.3	31.3
2.10	0.52	1.0	10.7	35.2
2.09	0.23	1.7	7.0	44.0
2.08	0.78	3.6	6.0	31.6
2.09	3.10	0.5	6.9	35.3

a. cc gas at 76 cm Hg and 298⁰k

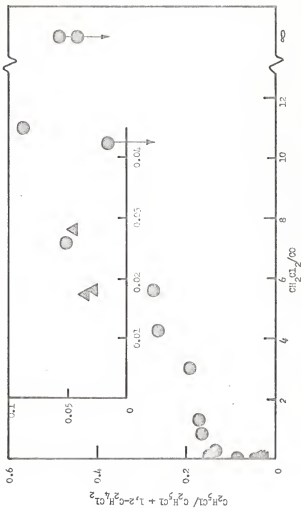


FIG. 1. Effect of adding CO to the reaction of CH_2 with CH_2Cl_2 . Circles, $P_{Total} \approx 35$ cm, triangles, $P_{Total} \approx 160$. Insert shows the region around the origin in more detail.

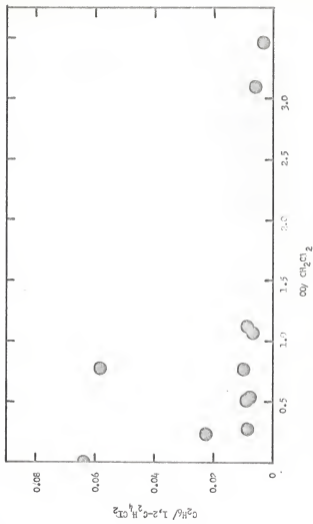
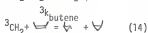
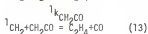
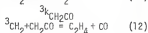


Fig 2. Effect of adding Co to the reaction of CH₂ with CH₂Cl₂.

B. The effect of carbon monoxide on the reaction of methylene with dichloromethane and cis-2-butene.

The reaction of methylene with cis- or trans-2-butene has been used by various workers as a method for estimating the relative amount of triplet methylene in various systems.^{1,9,10,21,22,24,26,27,29,30,31} In order to be able to compare our system to their work, a few runs with various ratios of dichloromethane to cis-2-butene were carried out. These runs were analyzed for cis- and trans-1,2-dimethylcyclopropane, as a measure of the relative amount of triplet methylene. Even though Frey³³ has raised some objections to this procedure, it is felt that this measurement will give a valid basis for comparison with published values of the relative amount of triplet methylene in such systems as studied here.

DeGraff and Kistiakowsky³¹ studied the effect of carbon monoxide on the reaction of methylene with trans-2-butene, and used the following additional steps to explain their results:



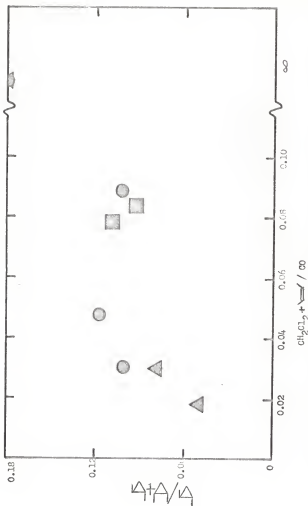


Fig. 3. Effect of adding CO to the reaction of CH_2 with CH_2Cl_2 and cis-2-butene. circles, $P_{\text{Total}} \approx 35$ mm, squares, CH_2Cl_2 :cis-2-butene varies, triangles, $P_{\text{Total}} \approx 90$ mm

the values of the various rate ratios that they measured are shown in Table 3. Also shown in Table 3 are values for the trans- to cis-1,2-dimethylcyclopropane ratio for the products of reaction 14, as measured by various workers.^{10,29,34} We found the measured ratio of $b/b+a$ of 0.18, with no added CO in this work. No corrections are needed for the geometrical or structural isomerization of the cis- or trans-1,2-dimethylcyclopropane, as the half-quenching pressures for these reactions are 2 cm and 0.2 cm, respectively, and our work was done at pressures of the order of 35 cm.¹⁰ Using the value of 2.9 for the ratio of b/a formed by $^3\text{CH}_2$ reaction measured by Montague and Rowland,²⁹ we calculate 24% $^3\text{CH}_2$ in our system. The value of 1.6¹⁰ for the ratio gives 30% triplet methylene when no carbon monoxide is added.

The intercept in Fig. 3, for no added CO, leads to another important point. The intercept is the same for both the mixed dichloromethane-cis-2-butene system and for a pure cis-2-butene reaction. This indicates that $^3k_H/{}^1k_{Cl} = ^3k_{\text{butene}}/{}^1k_{\text{butene}}$.

The effect of carbon monoxide on the mixed dichloromethane-cis-2-butene system is shown in Fig. 3 and Table 4. The circles represent runs made at a pressure of about 35 cm, and a ratio of dichloromethane to cis-2-butene of 1. These points are for direct comparison with the points in Fig. 1, at the same carbon monoxide to substrate ratios. The squares are points taken at various ratios of dichloromethane to cis-2-butene, and a constant ratio of 10 parts of CO to substrate. The significance of these points will be pointed out in the following paragraphs. The triangle represents points taken for various ratios of dichloromethane to cis-2-butene and CO to substrate, at a pressure of about 90 cm.

TABLE 3 Rate constant ratios for the reaction of ketene with carbon monoxide, dichloromethane, and cis-2-butene.

<u>Ratio</u>	<u>Value</u>	<u>References</u>
A. The photolysis of ketene.		
1 for C ₂ H ₄	0.37	31
2 for C ₂ H ₄	0.53	31
$\frac{{}^3k_{\text{CO}}}{{}^3k_{\text{CH}_2\text{CO}}}$	3.6	31
$\frac{{}^1k_{\text{CO}}}{{}^1k_{\text{CH}_2\text{CO}}}$	0.14	31
B. The reaction of ketene with cis-2-butene.		
$\frac{{}^3k_{\text{CO}}}{{}^3k_{\text{butene}}}$	1.3	31
$\frac{{}^1k_{\text{CO}}}{{}^1k_{\text{butene}}}$	0.10	31
C. Trans- to cis-1,2-dimethylcyclopropane ratio for the reaction of triplet methylene with cis-2-butene, Reaction 14.		
$\frac{W}{V}$	2.9	10
	1.6	29,34

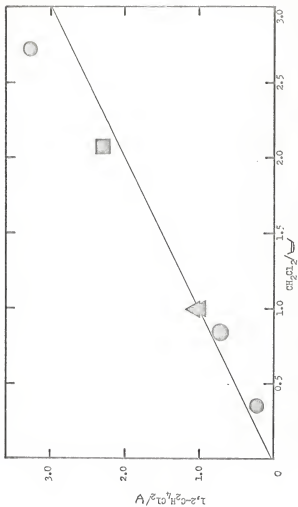


Fig 4. Relative rate of ${}^1\text{CH}_2$ reacting with CH_2Cl_2 and cis-2-butene. Circles, $P_{\text{Total}} \approx 35$ cm, CO : substrate=10; triangles, CO : substrate varies, square, $P_{\text{Total}} \approx 90$ cm

TABLE 4. The reaction of methylene with dichloromethane and *cis*-2-butene in the presence of carbon monoxide.

$\frac{\text{CH}_2\text{Cl}_2^+}{\text{CO}}$	CH_2Cl_2	$1,2\text{-C}_2\text{H}_4\text{Cl}_2$ cc x 10 ⁻²	$\text{V}^a, \text{ccx}10^{-3}$	$\text{V}^b, \text{ccx}10^{-2}$	$\text{V}^c, \text{ccx}10^{-2}$	P_{Total} cm Hg		
1.00	0.089	0.84	2.01	3.23	2.82	2.71	2.62	35.86
0.91	∞	1.04	2.24	5.60	2.52	2.33	2.17	29.94
0.91	0.030	1.00	2.04	2.37	2.11	2.03	1.96	40.93
0.84	0.047	1.00	2.96	3.88	2.94	2.81	2.70	36.31
0.46	0.083	2.72	5.20	1.72	1.67	1.61	1.56	35.27
1.21	0.078	0.34	1.22	4.42	3.64	3.49	3.36	35.52
1.50	∞	0.00	--	11.63	7.79	--	--	25.10
1.58	0.076	0.00	--	5.65	5.36	--	--	35.47
1.65	0.030	0.00	--	0.86	1.01	--	--	89.40
5.27	∞	0.00	--	17.20	7.71	--	--	79.95
0.59	0.033	2.07	1.50	0.04	0.66	0.66	0.65	89.66
1.65	0.018	0.00	--	2.48	4.59	--	--	89.76

a. Experimentally measured yields.

b. Calculated from experimental yields, using 2.9 for the V/V ratio from reaction 14.

c. Calculated from experimental yields, using 1.6 for the V/V ratio from reaction 14.

Two effects were noted when the ratio of dichloromethane to cis-2-butene was varied at a constant amount of 10 parts of CO. As can be seen from the squares in Fig. 3, the ratio of trans-1,2-dimethylcyclopropane to cis + trans-1,2-dimethylcyclopropane did not vary as the ratio of dichloromethane to cis-2-butene was varied. This means that the triplet to singlet methylene ratio that is being measured was not changed by the reactions of singlet and triplet methylene with dichloromethane and cis-2-butene.

The second effect of varying dichloromethane to cis-2-butene is the change of the ratio of 1,2-dichloroethane to cis-1,2-dimethylcyclopropane. This ratio is equal to $^1k_{Cl}/^1k_{butene}$. The slope of the line in Fig. 4 gives this ratio, and it is 1.0 ± 0.1 .

DISCUSSION

The results of the study of the reaction of methylene with dichloromethane in the presence of carbon monoxide will be analyzed in terms of first, the reactions and relative rate constants of singlet and triplet methylene with dichloromethane and CO. A steady state relation will be presented that describes the reaction system and the rate constant ratios in the relation will be fitted to reproduce the experimental curve. Then, the specificity of methylene in its reactions with various substrates is discussed in terms of the nature of singlet and triplet methylene as reactants.

A. General reactions of methylene with dichloromethane.

The curve in Fig. 1 is interpreted as having an intercept that is nearly zero when the dichloromethane to CO ratio is 0. The curves in Fig. 1 and Fig. 3 have the same shape and approximately the same values for any given substrate: CO ratio. Since Fig. 3 shows that CO removes triplet methylene, apparently singlet methylene is reacting with dichloromethane by abstracting only a chlorine atom. The triplet to singlet methylene ratio at no added CO, from the study of the reaction of methylene with cis-2-butene is about 1:2.5. Therefore, from results with no added CO, triplet methylene can only be abstracting a hydrogen atom from dichloromethane.

The first conclusion is the direct result of the near zero intercept of Fig. 1. This shows that at infinite CO, nearly all the methyl radicals are removed from the system, and only chloromethyl radicals remain. At this mythical point of infinite CO, the system is nearly a pure singlet methylene reaction system. Kistiakowsky first showed that CO removes triplet methylene 24 times as fast as singlet methylene; this ratio is based on the assumption that both states of methylene react at the same rate with ketene.³¹ This will

be shown to be somewhat reasonable in the following analysis of the $\text{CH}_2/\text{CH}_2\text{Cl}_2$, $\text{CO}/\text{CH}_2\text{CO}$ system.

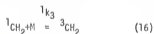
The conclusion that $^3\text{CH}_2$ only abstracts an hydrogen atom was reached by considering the intercept of Fig. 1 and 2, at no added CO. The chloroethane to 1,2-dichloroethane ratio was approximately 1:2 and the ethane to 1,2-dichloroethane ratio was approximately 1:16. If equal amounts of methyl and chloromethyl radicals were formed, these ratios would be 2:1 and 1:1, respectively. The experimental ratios indicate that twice as many chloromethyl radicals were formed as methyl radicals. The extra factor of two arises from mass balance because reaction 5 produces two chloromethyl radicals for every one methyl radical produced by reaction 4. Since the triplet to singlet methylene ratio is less than 1:2 in the system with no added CO, and since singlet methylene is producing only chloromethyl radicals, all the methyl radicals have to be formed by the reaction of triplet methylene with dichloromethane.

There are two conflicting pieces of information from the literature that must be justified before this interpretation can be assumed correct. DeGraff and Kistiakowsky³¹ found that it took only 10 parts of added CO to reduce the triplet methylene to zero in their reaction system of methylene with trans-2-butene. The problem with their system is that they used the least sensitive method of measuring the triplet to singlet methylene ratio. This is because triplet methylene reacts with both isomeric 2-butenes to form the same ratio of trans- to cis-1,2-dimethylcyclopropane of 1.6,²⁹ while singlet methylene retains the configuration of the particular 2-butene it is reacting with. This means that in the trans-2-butene system, they were

measuring *cis*-1,2-dimethylcyclopropane as their triplet methylene indicator, and this product is formed in the smaller amount. The system used in this study, *cis*-2-butene, is the most sensitive indicator of triplet methylene, since the *trans*-1,2-dimethylcyclopropane used as a triplet indicator is the isomer that is formed in the larger quantities by triplet methylene. Bamford, et. al.²⁰ found that singlet methylene abstracted chlorine at least 16.3 times faster than hydrogen, and triplet methylene abstracted hydrogen seven times faster than chlorine. However, their conclusions were based on only six parts of CO added to substrate, instead of carrying out the study to very large amounts of CO, as was done in this study. From the results of the present study, Bamford, et. al. had not added sufficient CO to remove all of the triplet CH₂; hence, they were observing the results from a mixture of singlet and triplet methylene.

B. The effect of CO on the reaction of methylene with dichloromethane.

As can be seen from Fig. 1,2 and 3, the effect of CO on the reaction of methylene with dichloromethane and *cis*-2-butene is quite dramatic. This effect can be quantitatively explained in terms of the mechanism already presented, with the addition of intersystem crossing of singlet methylene to triplet methylene:



The reactant M is just some collision partner for singlet methylene, that perturbs the system enough to permit some intersystem crossing. In this work, M is essentially CO.

The initial sharp drop in the curves as CO is added is caused by reaction 10, the rapid removal of triplet methylene by CO. As the amount

of CO is increased, reaction 16 will become important as a source of triplet methylene and the curve of $^3\text{CH}_2/{}^1\text{CH}_2$ will tend to flatten out. As will be seen in part C below, the inclusion of step 16 means that Fig. 1 will have an intercept at infinite amounts of added CO, which is related to 1k_3 .

C. Rate expressions.

By considering reactions 4,5,7,8,9, and 10, we can relate the experimentally measured ratio of chloroethane to 1,2-dichloroethane, through the steady state concentrations of the methyl and chloromethyl radicals, to the ratio of singlet and triplet methylene. We do not need to consider reactions 3 and 6, since we have already shown that they are not occurring in the system. This expression is:

$$\frac{{}^3k_H[{}^3\text{CH}_2]}{{}^1k_{Cl}[{}^1\text{CH}_2]} = 3 \frac{\left(\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}\right)^2 + \frac{2[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}}{1 + \frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}} \quad (1)$$

The ratio of methyl to chloromethyl radicals is equal to half the experimentally measured ratio of chloroethane to 1,2-dichloroethane because of the factor of 2 difference in the recombination rates. Therefore, the LHS of Eq. 2 can be calculated at various CO/CH₂Cl₂ values from the experimental data.

By considering reactions 1,2,4,5,10,11,12,13 and 16 we can derive an expression that theoretically gives the LHS of Eq. 1. This was done by using the usual steady state treatment of the concentrations of singlet and triplet methylene:

$$\frac{{}^3k_H [{}^3\text{CH}_2]}{{}^1k_{\text{Cl}} [{}^1\text{CH}_2]} = \frac{{}^3k_H}{{}^1k_{\text{Cl}}} \left(\frac{\phi_3}{\phi_1} \frac{{}^1k_{\text{CH}_2\text{CO}}}{{}^1k_{\text{CH}_2\text{CO}}} \left[\frac{\left({}^1k_{\text{CO}} + {}^1k_3 \right) [\text{CO}] + {}^1k_{\text{Cl}} + \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{Cl}_2]}}{{}^1k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{Cl}_2] + {}^1k_{\text{CH}_2\text{CO}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{Cl}_2]}} \right] \right. \\ \left. + \frac{{}^1k_3}{{}^3k_{\text{CH}_2\text{CO}} \left[\frac{{}^3k_{\text{CO}} [\text{CO}]}{{}^3k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{Cl}_2]} + \frac{{}^3k_H}{{}^3k_{\text{CH}_2\text{CO}}} + \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{Cl}_2]} \right]} \right) \quad (2)$$

The detailed derivation and the approximations are given in Appendix II.

By putting in the experimental numbers, Eq. 1 gives 0.53 as the intercept (i.e. LHS of Eq. 2) for no added CO. By setting $\text{CO}/\text{CH}_2\text{Cl}_2=0$ in Eq. 2, we can derive the following theoretical expression for the intercept at no added CO:

$$\frac{{}^3k_H [{}^3\text{CH}_2]}{{}^1k_{\text{Cl}} [{}^1\text{CH}_2]} = \frac{{}^3k_H}{{}^1k_{\text{Cl}}} \left(\frac{\phi_3}{\phi_1} \frac{{}^1k_{\text{CH}_2\text{CO}}}{{}^3k_{\text{CH}_2\text{CO}}} \left(\frac{{}^1k_{\text{Cl}}}{{}^1k_{\text{CH}_2\text{CO}}} + \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{Cl}_2]} \right) \right. \\ \left. + \frac{{}^1k_3}{{}^3k_{\text{CH}_2\text{CO}} \left(\frac{{}^3k_H}{{}^3k_{\text{CH}_2\text{CO}}} + \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{Cl}_2]} \right)} \right) \quad (3)$$

As was explained earlier, from Fig. 3, ${}^3k_H/{}^1k_{\text{Cl}} = {}^3k_{\text{butene}}/{}^1k_{\text{butene}}$. This ratio will be assumed to be 1 in this calculation, and it will be shown to be a reasonable assumption. From the rate constant ratios in Table 3,

$^3k_H/^3k_{CH_2CO} = 2.77$, and $^1k_{C1}/^1k_{CH_2CO} = 1.4$. $^1k_{C1}/^1k_{CH_2CO}$ was found by multiplying $^1k_{C1}/^1k_{butene}$ by $(^1k_{CO}/^1k_{butene})^{-1}$ and $^1k_{CO}/^1k_{CH_2CO}$, giving a value of $1.0 \times 10 \times 0.14 = 1.4$. $^3k_H/^3k_{CH_2CO}$ was found by multiplying $^3k_H/^3k_{butene}$ by $(^3k_{CO}/^3k_{butene})^{-1}$ and $^3k_{CO}/^3k_{CH_2CO}$, giving a value of $1.0 \times (1/1.3) \times 3.6 = 2.77$. Since we are assuming that $^3k_H = ^1k_{C1}$, these ratios force $^1k_{CH_2CO}/^3k_{CH_2CO} = 2.0$. The second term of Eq. 3 can be neglected, as $^1k_3/^3k_{CH_2CO} \approx 0.01$. In order to fit the intercept found from Eq. 1 for the experimental data, $\phi_3/\phi_1 = 0.5$. This value is somewhat lower than some of the results listed in Table 3, but it is consistent with the directly measured triplet to singlet CH_2 ratio measured with butene. The right hand side of Eq. 3 is essentially the quantum yield ratio, with various correction factors added to correct for the removal of singlet and triplet methylene. These factors are rather small for the CH_2Cl_2 case and the butene case. Using the rate constant ratios assumed in this study, the correction factor is $1.0 \times 2.0 \times (1.4 + 0.14) / (2.77 + 0.14)$ and is equal to 1.06. Hence, the quantum yield ratio should be very close to the measured singlet triplet ratios of 0.43 from the butene measurements and 0.5 from the dichloromethane measurements.

The attempt to fit Eq. 2 to the LHS of Eq. 1 over all values of CO/CH_2Cl_2 will now be discussed. Eq. 1 and Eq. 2 were programmed on an IBM 360/50 computer, and various values of $^3k_{CO}/^3k_{CH_2CO}$, ranging from 3.7^{31} to 20, were tried in order to fit Eq. 2 to the values calculated with Eq. 1 from the experimental data. Since $^3k_{CH_2CO} = ^3k_H/2.77$, this is equivalent to fitting $^3k_{CO}/^3k_{CH_2Cl_2}$. As can be seen from Table 5 and Fig. 5, a value between 8 and 10 fits best, if we adjust $^1k_3/^3k_{CH_2CO}$. The curves in Fig. 5 are meant to be representative of the calculated results. The best fit was obtained when $^1k_3/^3k_{CH_2CO}$ was set equal to 0.10 for $^3k_{CO}/^3k_{CH_2CO} = 10$.

This analysis gave several important rate constant ratios for methylene reaction systems. First, it has been shown to be reasonable to assume that the singlet and triplet methylene abstraction reactions from chloroalkanes and addition reactions to the 2-butenes have the same rate. Using these ratios as one, it was possible to fit the experimental curves, with reasonable values of the other rate constant ratios. Secondly, it has been shown that CO is a very good scavenger for triplet methylene, since $^1k_{CO}/^3k_{CO} = 147$, and $^3k_H/^3k_{CO} = 0.27$. This indicates that CO will scavenge 3CH_2 even in the presence of a reactant such as dichloromethane or cis-2-butene. These reactants have been estimated to have absolute rate constants for reaction with methylene on the order of the gas kinetic collision frequency.

Even though this analysis has given reasonable and useful results, there was no way of testing the results for uniqueness. At the time this work was done, there were no fitting routines available to handle such a complicated expression as Eq. 2.

TABLE 5. Values for the fitting of Eq. 1 to Eq. 2

$\frac{CO}{CH_2C_1_2}$	Eq. 1 ^d	Eq.2-1 ^a	Eq.2-2 ^b	Eq.2-3 ^c
0.000	0.532	0.533	0.533	0.533
0.100	0.403	0.446	0.422	0.401
0.179	0.318	0.396	0.364	0.336
0.236	0.273	0.367	0.331	0.301
0.338	0.193	0.325	0.286	0.255
0.762	0.169	0.223	0.185	0.158
1.283	0.166	0.165	0.133	0.111
4.229	0.129	0.077	0.060	0.048
12.094	0.105	0.045	0.034	0.027
22.250	0.088	0.036	0.027	0.022
35.657	0.056	0.032	0.024	0.019
38.019	0.052	0.032	0.024	0.019
55.053	0.032	0.030	0.022	0.018
59.018	0.027	0.029	0.022	0.018

a. ${}^3k_{CO}/{}^3k_{CH_2CO} = 6.0$, LHS of Eq. 2

b. ${}^3k_{CO}/{}^3k_{CH_2CO} = 8.0$, LHS of Eq. 2

c. ${}^3k_{CO}/{}^3k_{CH_2CO} = 10.0$, LHS of Eq. 2

d. LHS of Eq. 1, from experimental data

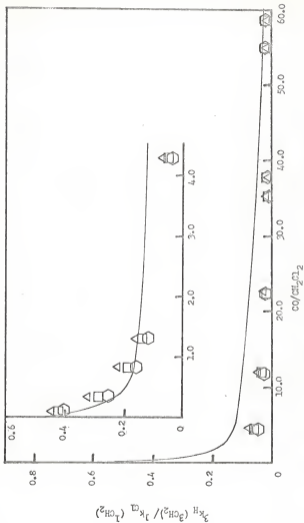


Fig 5. Examples of curves fitted by Eq 2 to Eq 1. Line, Eq 1; triangles, Eq 2-1, squares, Eq 2-2; hexagons, Eq 2-3. Insert shows the breaking region of the curve in more detail

D. Specificity of Methylene Reactions

1. Structure of Methylene

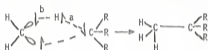
Theoretical studies indicate that triplet methylene is a linear molecule, with the two unpaired electrons in the P_x and P_y orbitals of the carbon atom.^{3,4,5} Singlet methylene is a bent molecule, with an H-C-H angle of 103° .² The paired electrons are located in orbitals that closely resemble sp^3 orbitals of carbon.^{3,4,5} These structures were confirmed by Herzberg,² in his work on the ultraviolet absorption spectra of methylene.

2. Stereospecificity of Methylene

On the basis of these structures alone, it is possible to explain the specific reactions of singlet and triplet methylene. Singlet methylene is an electrophilic reagent. It is almost in the proper configuration for forming sigma bonds of the type commonly ascribed to carbon and other group IVA elements, with sp^3 hybridization. The largest electron density for the chloroalkanes is located on the chlorine atom, while the hydrogen atoms have almost no electron density around them. Therefore, the electrophilic singlet methylene will attack the chlorine atom and pull it off the chloroalkane. A possible reason that singlet methylene wouldn't insert into the carbon-chlorine bond is that the chlorine atom is so large that it effectively shields the two carbon atoms in the transition state, so that they can't get close enough together to form a bond before the two radicals move apart. The following diagram will serve to clarify this statement.

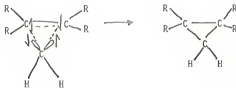


As the methylene-chlorine bond is formed, the electrons on the carbon of the methylene group, and on the carbon on the leaving group have opposite spins, as indicated by the arrows. This is a bonding state. The same arguments explain the insertion of singlet methylene into a carbon or silicon hydrogen bond in an alkane or silane. In these types of bonds most of the electron density is located near the carbon or silicon atom.



An unfilled orbital on the singlet methylene will attack at a carbon or silicon bond, leading to a three centered transition state, with a carbon-hydrogen bond, (a), being broken, while another carbon-hydrogen bond, (b), is being formed. This leads to an alkane with one more carbon. The relative rates of insertion into carbon-hydrogen and silicon-hydrogen bonds can be explained on this basis. The hydrogens in an alkane provide a close packed shield of protons around the carbon atoms, but in silanes, these protons are spread out more due to the larger silicon atom. Hence the singlet methylene can insert into a silicon hydrogen bond faster than a carbon-hydrogen bond, as observed.⁴⁷

The same explanation fits the observed results for the addition of singlet methylene to carbon-carbon double bonds.²⁶ The largest electron density is in the double bond, and since singlet methylene is almost sp^3 , it can readily add directly across the double bond to form the cyclopropane derivative, in one concerted step.

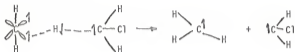


As the R groups are changed from hydrogen to methyl and ethyl groups, the electron density in the double bond increases, and the relative rates of singlet methylene addition increase, as found by Krzyzanowsky and Cvetanovic.²⁶ They studied the rates of reaction of singlet methylene and triplet methylene with a series of olefins ranging from ethene to 1,3-butadiene, relative to isobutylene. The relative rate for triplet methylene increased from 0.35 to 0.96 as the complexity of the olefin increased. The relative singlet rate is increased from 0.51 to 2.01 over the same series. The same trend was found with a known electrophilic reagent, $O(^3)$ atoms as for CH_2 . For the same series of olefins, relative to isobutylene, the rates increased from 0.038 to 4.19.⁶⁵

Triplet methylene could be described as a nucleophilic reagent having one unpaired electron in the P_x and P_y orbitals on the carbon atom. This description of triplet methylene would have to be taken rather loosely as Cvetanovic's work²⁶ showed that triplet methylene shows the same trends as singlet methylene, when reacting with olefins. At most, triplet methylene would only be described as a poor nucleophile, but it is definitely different than singlet methylene in all the reaction systems studied in this study and by the other workers.

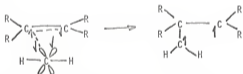
The most accessible nucleophilic sites in the chloroalkanes studies here

are the hydrogen atoms:



The triplet methylene will abstract the hydrogen atom since, as it is attacking the hydrogen, the electrons on the carbon atoms will have the same spin and the transition state will be repulsive with respect to forming a carbon-carbon bond. The same explanation holds for the attack of triplet methylene on alkanes.^{11,23,42}

The explanation of the reactivity of triplet and singlet methylene with regard to addition to double bonds proposed here agrees well with those already proposed.¹⁰ When triplet CH_2 added to a double bond, it has to form a diradical:



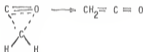
This diradical can rotate around the "olefinic" carbon-carbon bond before an electron spin inverts and forms the cyclopropyl ring.¹⁰ This formation of the diradical by triplet methylene explains why it adds to a double bond as fast as it abstracts a hydrogen atom. The transition state in both cases is nearly the same. Singlet methylene, on the other hand, adds to a double bond in one concerted step, while it inserts by a less concerted process. Hence the addition of singlet methylene is much faster than insertion.²³

3. Reactivity of Methylene toward Carbon Monoxide

As has been shown, triplet methylene reacts much faster than carbon monoxide than singlet methylene. This can be explained using the considerations of the previous sections. The transition complex for the reaction of triplet methylene with carbon monoxide is pictured as being a diradical:

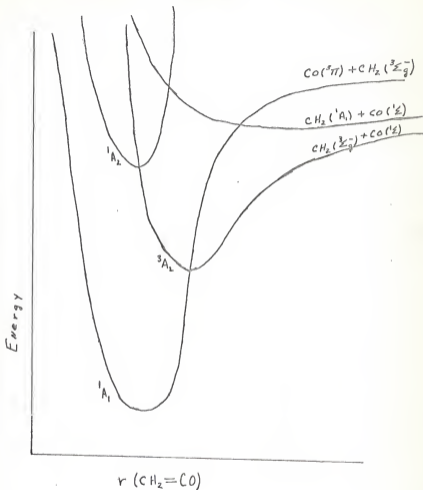


Singlet methylene should add directly across a C-O bond to form a cyclic transition state.



However, this transition complex would be very unstable and have a low probability factor for forming ketene and a higher probability factor to dissociate into carbon monoxide and singlet methylene. This is indicated in the large difference between ${}^1k_{\text{CO}}/{}^1k_{\text{CH}_2\text{CO}}$ and ${}^3k_{\text{CO}}/{}^3k_{\text{CH}_2\text{CO}}$ and the very small value of ${}^1k_3/{}^3k_{\text{CH}_2\text{CO}}$. But the diradical triplet complex could have a long enough lifetime for an electron spin to invert and form ketene.

The selectivity of carbon monoxide has been explained on the basis of the following potential energy diagram of ketene.³¹



Singlet methylene and carbon monoxide form a non-bonded state of ketene when they react. The only way for them to form stable ketene is by intersystem crossing into the 1A_2 state or the 1A_1 states of ketene, which is a slow process. Triplet methylene and carbon monoxide can react to form a bonded 3A_2 state of ketene. Therefore, triplet methylene reacts much faster than singlet methylene to form ketene, and be removed from the reaction system.

Similar transition states and complexes for the reactions of triplet methylene have been proposed by Benson, but his arguments were made before the difference in reactivity of singlet and triplet methylene was known.⁷¹ Therefore, his arguments were made for one state of methylene, but this work shows that the two low lying electronic states of methylene have quite different reactivities with respect to most substrates.

E. The reaction of methylene with chloromethane in the presence of carbon monoxide.

An attempt was made to measure the nonequilibrium kinetic isotope effect of chloroethane- d_3 formed by the reaction of methylene with chloromethane- d_3 in the presence of carbon monoxide. This reaction should have produced chloromethyl- h_2 radicals and methyl- d_3 radicals, based on the previous work discussed in this thesis, when about 10 parts of carbon monoxide was added. There was some evidence that this reaction was taking place, but methyl radicals were being removed by some unknown process, such that the collisional recombination ratios were not valid for the recombination of the radicals to form chloroethane and 1,2-dichloroethane. If the system was behaving in the expected manner, the ratio of 1,2-dichloroethane to chloroethane at infinite high pressure should have been 1/2. For the chloroethane- d_3 system studied,

this ratio was 1.7, and for the corresponding chloroethane-h₅ system, which was used as the standard, the ratio was 3.

There are a number of possible explanations for this removal of methyl radicals from the system before they could recombine with chloromethyl radicals. One possibility was that CO was reacting with methyl radicals to form an acetoxy radical, at high pressure. This possibility can be discarded, since the curves shown in Fig. 1 and 4 show no sharp drop at the points taken at high pressures. A more probable explanation is that CO diluted the radical concentrations so much that methyl radicals could be abstracting a hydrogen atom from chloromethane to form methane and a chloromethyl radical. Methyl radicals could also be abstracting a chlorine atom, but this would produce a methyl radical and chloromethane, and have no apparent effect on the system. If chloromethyl radicals were undergoing secondary abstraction, they would form methyl radicals, chloromethane, and dichloromethane. Of these four possible secondary abstraction reactions, the first one produces the observed effect of lowering the methyl radical concentration in the system, and could be the cause of the high intercepts at infinite pressure that were observed.

F. The reaction of methylene with 1,2-dichloroethane in the presence of carbon monoxide.

Preliminary studies of the reaction of singlet methylene produced by adding carbon monoxide to the photolysis of ketene with 1,2-dichloroethane were undertaken as a method of producing chemically activated 1,3-dichloropropane and 1,4-dichlorobutane. These compounds were of interest as possibilities for observing the successive unimolecular elimination of HCl. The interest in this system will be discussed later. The preliminary results indicate that the system was working and producing a reasonably clean system of chemically

activated 1,3-dichloropropane and 1,4-dichlorobutane, as expected. Secondary radical abstraction would not affect this system, since collisional recombination ratios are not needed to determine the desired rate constants. The decomposition products could be observed directly. A hydrogen abstraction product, 1-chloropropane, was formed only as a minor product, and was about a factor of 10 smaller than the desired dichloropropane and butane products. This indicated that the technique of adding CO to a methylene reaction system could be useful for producing relatively pure singlet methylene systems, if care was taken in selecting the system so that side reactions would not affect the desired results.

THE REACTION OF $\text{Hg}(6^3\text{P}_1)$ WITH CHLORO- AND DICHLOROMETHANE MIXTURESOBJECTIVE

The reaction of mercury (6^3P_1) with dichloromethane and chloromethane- h_3 and d_3 was carried out to measure the nonequilibrium kinetic isotope effect of $\text{CD}_3\text{CH}_2\text{Cl}$ relative to $\text{C}_2\text{H}_5\text{Cl}$. Although the chloroethane- h_5 rate constant has been measured several times, it was done again in order to get a better measurement of the isotope effect. Ideally, the isotope effect experiments should be done with an internal standard, but this was not possible in this system.

EXPERIMENTAL

A. Reagents

The dichloromethane was the same as used in the first part of this work. The chloromethane- h_3 was CP grade and was obtained from The Matheson Co. GC analysis on the analytical column used for this work showed it to be free of any interfering impurities. The chloromethane- d_3 was obtained from Merck, Sharpe, and Co. of Canada, Ltd. There was a small amount (-0.01%) of a high boiling impurity, but it didn't interfere with this work. Mass spectral analysis showed it to be greater than 99.9% isotopically pure, as claimed by the manufacturer. The propene used was CP grade, and was obtained from The Matheson Co. It, too, was free from any impurities.

B. Procedures

These reactions were carried out in a manner similar to that used by Setser³⁵ and Chang.^{36,37} The various reagents were measured out on the vacuum system described in the first part of this work. The usual proportions of reagents were $CH_3Cl:CH_2Cl_2:C_3H_6=2:1:0.3$, and the usual volume of gas was 3.3 cc. The samples were sealed into small quartz tubes containing a drop of mercury. Then, depending upon the tube size and sample pressure, they were photolyzed for 15 to 20 min. with a General Electric Germicidal low pressure mercury lamp (15 watt). The criterion for determining the photolysis time was that no more than 50% of the initial propene was consumed during the reaction.

C. Analysis

The samples were loaded on the GC by first transferring the contents of the reaction vessel to a packed glass trap immersed in a solid nitrogen bath

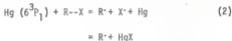
($T=63^{\circ}\text{K}$) where the noncondensable products were pumped off. The sample was then transferred to the GC inlet, using a solid nitrogen bath. Solid nitrogen baths were used to prevent loss of ethene during the transfers and pumping on the sample. The samples were analysed by the same GC used for earlier parts of this work, using a 6 feet x 1/4" Porapak S column. The column temperature was programmed twice as follows: The initial temperature was 22-25°C. After 12 min, the temperature was raised to 120°C and allowed to stabilize at 90-95°C. Twenty minutes later, the temperature was raised to 160°C and allowed to stabilize at 140-145°C. Using this temperature program, the retention times of the compounds of interest were: ethene, 7 min.; ethane, 9 min.; propene, 15.5 min.; chloromethane, 16 min.; chloroethane, 24-27 min.; and dichloromethane, 35 min. The column was purged at 150°C for at least two hours between analyses, to insure that all the high boiling compounds produced by the reaction were eluded.

The GC was calibrated using a mixture of the hydrogenated products that closely resembled the reaction products in composition and size. This calibration technique was shown to be valid for the deuterated compounds by Dees¹³ for this GC, which uses a thermal conductivity detector. To insure that the desired reaction products being observed were not overlapped by other reaction products and that they had the proper deuterium content, samples were trapped from the GC eluent and analysed on an Utek Quad 250 Residual Gas analyser. The system was complicated by very small product yields and possible nonlinearity of the GC response. These problems will be discussed later.

RESULTS

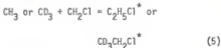
A. Mechanism

The mercury (6^3P_1) photosensitization of halomethanes has been studied previously in our laboratory,^{35,36,37} and the mechanism for production of alkyl and haloalkyl radicals has been found to be as follows:



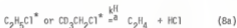
The excited mercury atoms attack the haloalkane to produce alkyl radicals and halogen atoms. The exact mechanism for the interaction of the halogen atom with mercury is not known, but during the photolysis a white deposit forms on the reaction vessel's walls that has been identified as mercurous halide.

In this particular study, the R--X in reaction 2 was a 1:2 mixture of dichloromethane and chloromethane- h_3 or chloromethane- d_3 . This particular ratio was chosen due to the differences in Hg (6^3P_1) quenching cross sections⁴⁶. This resulted in the formation of chloromethyl and methyl- h_3 or methyl- d_3 radicals, which could recombine by the following reactions:



The products of reactions 4 and 5 are highly vibrationally excited, and

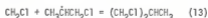
either decompose by elimination of HCl or DCl, or are collisionally stabilized. These were the reactions of interest in this system.



or



The above reactions are written for unit deactivation. Since the measurements were confined to the region below $S/D = 0.5$, this is a good approximation for these relatively efficient gases.¹³ Another reaction that has been shown to take place in these systems is the addition of the chlorine atom, formed in reaction 2 to the olefins produced by reactions 7a and 8a.³⁵ The addition reaction removes the olefin products of the reaction being studied. To prevent this loss, propene was added to the reaction system. Propene removes the chlorine atoms by the following sequence of combination reactions:



In addition, the $\text{CH}_3\text{CH}=\text{CH}_2\text{Cl}$ undergoes some disproportionation reactions which gave smaller product yields. These types of products were observed by Setser,³⁵ but were not analyzed in this study. However, numerous peaks that would correspond to such high boiling compounds were observed. It should be noted that the products of reactions 11-13 are also highly vibrationally excited and may decompose by elimination of HCl, but at much lower pressures than for chloroethane.

B. Isotopic Purity

Samples of both the chloroethane- h_5 and chloroethane- d_3 and the ethene- d_2 were analyzed by mass spectroscopy. These spectra allowed two conclusions: the chloroethane and ethene peaks observed on the GC were chemically pure compounds, and also isotopically pure.

C. Rate Constants

The apparent rate constant, k_a , for unimolecular decomposition of haloalkanes by hydrogen chloride elimination has been previously defined as $k_a = D/S$,¹²⁻¹⁸ is the collision frequency of the decomposing molecule with the surrounding bath molecules, D is the concentration of the olefinic decomposition product, and S is the concentration of the stabilized haloalkane. The data for the decomposition of the highly vibrationally excited chloroethanes are presented in Tables 6 and 7. The method of determining k_a is to plot D/S vs 1/P, where P is the total pressure and is related to the collision frequency by molecular parameters. The slope of such a plot, Fig. 6, is k_a , in units of cm of mercury pressure. The values of k_a for this study were determined by a point by point average, in order to smooth out some of the scatter in the data. Using this technique, the value of k_a^H is 30.4 ± 8.2 cm

TABLE 6 Relative Yields of Chloroethane-h₅ and ethene-h₄^a

<u>P_{Total}</u> <u>cm Hg</u>	<u>C₂H₅Cl</u>	<u>C₂H₄</u>
144.1	59	9
60.3	40	18
59.0	35	18
57.6	43	40
49.1	47	31
34.5	27	22
31.3	62	46
31.1	31	46
25.4	30	35
18.7	26	52
17.5	37	85
16.9	32	63
12.2	30	84

a. These are GC peak heights. The relative sensitivity is

$$\frac{\text{cc C}_2\text{H}_4}{\text{cc C}_2\text{H}_5\text{Cl}} = \frac{0.9 \text{ peak height C}_2\text{H}_4}{\text{peak height C}_2\text{H}_5\text{Cl}}$$

TABLE 7 Relative yields^a of 1,1,1-chloroethane-d₃ and 1,1-ethene-d₂

P _{Total} , cm Hg	CD ₃ CH ₂ Cl	CD ₂ CH ₂
30.5	88	34
25.0	73	44
18.5	42	44
17.3	47	40
13.7	62	66
9.4	19	39
9.0	23	52
5.9	31	61

a. These are GC peak heights. The relative sensitivity is

$$\frac{\text{cc CD}_2\text{CH}_2}{\text{cc CH}_3\text{CH}_2\text{Cl}} = \frac{0.9 \text{ peak height CD}_2\text{CH}_2}{\text{peak height CD}_3\text{CH}_2\text{Cl}}$$

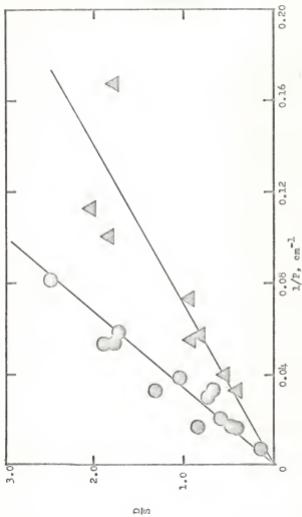


Fig 6. Unimolecular decomposition rate constants for chloroethane- d_3 and chloroethane- d_1 . Circles, d_3 points; triangles, d_1 points.

and the value for k_a^D is 14.3 ± 3.0 cm.

For this system, it is somewhat difficult to relate k_a in pressure units to the more conventional sec^{-1} units, due to the complex mixture of three bath gases. The collision frequency for the collision of a molecule A with a bath molecule B is:⁴³

$$\omega = N_B \frac{(D_A + D_B)^2}{2} \left(\frac{8\pi RT}{\mu} \right)^{1/2}$$

where N_B is the number of molecules of B per cc, D_A and D_B are the hard sphere-collision diameters of the respective molecules, R is the gas constant in ergs mole⁻¹ deg K⁻¹, T is the temperature in deg K, and μ is the reduced mass of the collision partners. To find the total collision frequency, use was made of a form of Dalton's Law of Partial Pressures:

$$\omega_T = N_T \sum_i \chi_i \frac{(D_A + D_i)^2}{2} \left(\frac{8\pi RT}{\mu} \right)^{1/2}$$

where ω_T is the total collision frequency of all the bath molecules, χ_i is the mole fraction of each component, N_T is the total number of molecules per cc (given by P/kT , where k is 1.36×10^{-20} cc cm (molecule deg K)⁻¹), and the index i denotes the various different bath species. The values for the various parameters used for the chloroethane system are shown in Table 8. Using these values and the above expression for ω_T , k_a is $3.4 \pm 0.9 \times 10^9 \text{ sec}^{-1}$ for the h_5 system and $1.6 \pm 0.3 \times 10^9 \text{ sec}^{-1}$ for the d_3 system.

TABLE 8 Molecular Collision Parameters^a

Molecule	$D, \text{\AA}^b$	_____	$M, \text{gm}(\text{mol})^{-1}$
$\text{C}_2\text{H}_5\text{Cl}$	5.41 ^c	---	64.5 ^c
CH_2Cl_2	4.748	0.293	85.0
CH_3Cl	4.151 ^c	0.616	50.5 ^c
C_3H_6	4.670	0.091	42.0

a. $R = 8.315 \times 10^7 \text{ erg mole}^{-1} \text{ deg K}^{-1}$, $T = 298$

b. The collision radii are Lennard Jones hard sphere radii from Hirshfelder, Curtiss and Bird.⁴⁴

c. The same collision radii were used for the deuterated species. $M(\text{C}_2\text{D}_3\text{H}_2\text{Cl}) = 67.5$, $M(\text{CD}_3\text{Cl}) = 53.5$

DISCUSSION

A. Comparison of Rate Constants

The chloroethane- h_5 decomposition rate constant has been measured by Hassler¹² and Dees¹³, who found values of 3×10^9 and $4.6 \times 10^9 \text{ sec}^{-1}$, respectively. The value measured in this study, $3.4 \pm 0.9 \times 10^9 \text{ sec}^{-1}$, is between these two values, but there are considerations that indicate this value may be low. The value of k_a for chloroethane- d_5 measured by Dees¹³ was $1.39 \times 10^9 \text{ sec}^{-1}$, compared to the value of $1.59 \times 10^9 \text{ sec}^{-1}$ measured for chloroethane- d_3 in this work. Again, this value may be low.

B. Comparison of Isotope Effects

Dees¹³ measured an experimental isotope effect of 3.4 for the relative rate of decomposition of chloroethane- h_5 and chloroethane- d_5 . For 1,2-dichloromethane- h_4 and 1,2-dichloromethane- d_4 , he measured an isotope effect of 3.48. Using models that will be discussed later, he calculated an isotope effect of 2.98 for the chloroethane- d_5 case. This isotope effect was partitioned into a primary effect of changing the H eliminated for a D of 1.24. This effect takes into account the difference in critical energy for the reaction, caused by deuterium substitution. On the same basis, he calculated a secondary isotope effect of 1.25 for each deuterium out of the ring. This means that an isotope effect of $(1.25)^2(1.24) = 1.94$ for CD_3CH_2Cl relative to C_2H_5Cl and $(1.25)^2 = 1.56$ relative to C_2D_5Cl would be predicted. If we take into account the difference in the experimental and calculated isotope effects, the total isotope effect for CD_3CH_2Cl relative to C_2H_5Cl should be 2.22 and 1.89 relative to C_2D_5Cl . The experimentally measured isotope effect of CD_3CH_2Cl relative to C_2H_5Cl

is 2.13, in good agreement with the expected value.

In the next section, the results of calculations performed as part of this work are given. The isotope effects were calculated, using slightly different models than Oees¹³ used. However, the results are essentially the same, giving the values of $k_a^H/k_a^{O3} = 1.82$, and $k_a^H/k_a^{D5} = 2.94$.

C. Problems with the System

There are three reasons why the values of k_a measured in this work may be low. They apply equally well to the h_5 and d_3 systems. The first possibility is that the chlorine atoms from reaction 2 may be attacking the ethene formed by reaction 8a. However, the available literature indicates that chlorine atoms attack ethene and propene with approximately equal rates.⁴⁵ Since there was about 300 times as much propene as ethene in the reaction mixture at the end of the reaction, this possibility may be ruled out. The second possibility of losing ethene may have arisen during the transfer of the sample into the GC inlet. When the sample vessel was first broken open, the contents rushed through the packed glass trap, and may not have been completely condensed, even at solid nitrogen temperature. The third possibility for causing a low value of k_a was that the amounts of products measured were near the limits of detectability of the thermal conductivity detector on the GC. The yields of products could not be increased by longer photolysis times without excessive (50%) losses of propene. Even though the calibration samples had as small a concentration of ethene and chloroethane as the reaction samples, the results they gave may not have been accurate. Previous studies by Oees with this GC indicate that the detector response was not linear in the range of sample concentrations used in this work.¹³ Some standard samples were put through the same injection procedure as the reaction samples in an

effort to determine the effect of the second possibility on the amount of ethene measured. From these samples it was found that 15% of the ethene was lost. The calibration factors listed in Tables 6 and 7 include this factor, but there was no accurate way of correcting for the nonlinearity of the detector response. But various sample sizes were tested in an effort to correct for this problem.

The above possibilities may have led to the low results of this study, but another possibility is that the work of Hassler¹² and Dees¹³ may have been liable to some serious errors, too. In their systems, ethene could not be measured directly. The rate constant was measured by comparing the amount of chloroethane measured to the amount of 1,2-dichloroethane measured. If the collision theory of radical recombinations holds, the difference between the ratio of 1,2-dichloroethane to chloroethane and 1/2 is a measure of the relative amount of ethene formed. However, the work of Dees¹³ showed that the collision recombination ratios are not entirely rigorous, but give slightly high (10%) values. The theory only pertains to ratios of the recombination rate constants, and the product ratios are given by the product of the recombination rate constants with the radical concentration ratios. If the radical concentration ratios change, the product ratios change. The relative rate constant could not be checked in this manner in the study of this thesis for two reasons. The most important is that the concentrations of chloromethyl and methyl radicals could not be assumed to be equal or even that their ratio was constant, as they were formed by two separate reactions. The second reason is that the amount of 1,2-dichloroethane could not be measured, as it was obscured by the products of reactions 11-13 in the analysis scheme used in this work.

Another problem with the mercury photosensitization system is the larger number of reactions taking place than in the ketene-chloromethane systems. Since many of these reactions have not been characterized, there is a possibility of some effects that were not considered that may effect the chloromethyl and methyl radicals or the reaction products. Radical systems in which one tries to obtain quantitative data of the yields of some of the lesser products are often troublesome.

RRKM CALCULATIONS OF UNIMOLECULAR RATE CONSTANTS

OBJECTIVE

These calculations had two objectives. The first was to examine the effect of anharmonicity on the calculated unimolecular specific rate constant and upon the nonequilibrium unimolecular kinetic isotope effect. These calculated results were compared to the experimental isotope effects measured in this study for $\text{CD}_3\text{CH}_2\text{Cl}$ and those measured by Dees,¹³ for $\text{C}_2\text{D}_5\text{Cl}$. The second objective was to calculate the specific rate constants for the unimolecular elimination of hydrogen chloride from a series of chloro- and dichloropropanes and butanes, and chloro-propenes and -butenes. These calculations were for the purpose of exploring the possibility of estimating the energy distribution of the Cl-R-CH=CH_2 product of a single hydrogen chloride elimination from a chemically activated chloroalkane. The basic idea is to measure the energy content of the Cl-R-CH=CH_2 molecule by matching the measured rate constant for HCl elimination to give $\text{CH}_2=\text{C-R-CH=CH}_2$ to a calculated rate constant. According to the modern theories of unimolecular reactions, rate constants depend only on the energy of the molecule, providing models for the reaction are known.

CALCULATIONAL PROCEDURES

A. Theoretical Rate Constants

The theoretical rate constants have been described in detail by earlier workers,^{12-18,48} and only the equations and computational procedure will be presented. In the RRKM Theory, the specific rate constant k_E at some energy E above the threshold energy E_0 for the reaction is defined as:

$$k = \frac{\sigma}{h} \frac{Z^\ddagger \sum \rho(E_{VR}^*)}{Z^* N^*(E_{VR})} \quad (4)$$

Where σ is the reaction path degeneracy, h is Plank's constant, Z^\ddagger is the product of the adiabatic partition functions of the transition complex, Z^* is the product of adiabatic partition function of the molecule. $\sum \rho(E_{VR}^*)$ is the sum of energy eigenstates of the active degrees of freedom of the complex taken over the energy interval E_0 to E_{VR} , and $N^*(E_{VR})$ is the density of energy eigenstates in an interval of energy in the active degrees of freedom around E_{VR} (the total energy of the molecule).

For the purpose of these calculations, adiabatic degrees of freedom are defined as those that cannot exchange energy with the rest of the degrees of freedom of the molecule, while active degrees of freedom are those which rapidly exchange energy.¹² In previous calculations on chloroalkanes, it was found that the rotations of the whole molecules could be treated as adiabatic and all the vibrations as active degrees of freedom.^{12,13}

A unimolecular breakdown in a chemical activation system can be represented as:



The rate equations for this reaction system $\frac{dA}{dt} = -[A^*]$ and $\frac{dD}{dt} = k[A^*]$.

If the system happens to be monoenergetic, these differential equations reduce to $k = \frac{D}{A}$, since $[A^*]$ can be considered a steady state concentration.

However, in most systems, the activated specie, A^* , has a distribution of energy, given by $f(\epsilon) d\epsilon$. The apparent rate constant, k_a , that is measured experimentally is then given by $k_a = \frac{D}{A}$, but D and A have to be averaged over energy, from the critical energy of the reaction to ∞ . Hence, k_a is given by:

$$k_a = \frac{\int_{E_{\min}}^{\infty} \frac{k_{\epsilon}}{k_{\epsilon} + \omega} f(\epsilon) d\epsilon}{\int_{E_{\min}}^{\infty} \frac{\omega}{k_{\epsilon} + \omega} f(\epsilon) d\epsilon} \quad (5)$$

The term, $\frac{k_{\epsilon}}{k_{\epsilon} + \omega}$, in the numerator is the fraction of molecules having energy ϵ that decompose, while the term, $\frac{\omega}{k_{\epsilon} + \omega}$, in the denominator is the fraction of molecules that are stabilized at energy ϵ . Equations 4 and 5 form the basis of the RRKM Theory for nonequilibrium unimolecular reactions, and the next sections will describe how k_{ϵ} and $f(\epsilon)d\epsilon$ are evaluated.

B. Molecular Models

The primary difficulty of any theory of chemical reaction rates based upon absolute rate theory is to determine the nature of the transition state (A^{\ddagger}) and to describe it in meaningful terms. It has been shown that the unimolecular elimination of hydrogen chloride from chloroalkanes is adequately described by specifying the bond order of the bonds undergoing change in the reaction.^{12,13} This model describes the activated complex as a four-centered model, with the bond orders of the four membered ring characterized by the

fractions below. For chloroethane, the complex looks thus:



With reference to the above model, the C-C, the C-Cl, the Cl-H, and the H-C bonds were assigned bond orders of 1.9, 0.9, 0.1, and 0.1, respectively. As is quite obvious, spectroscopic parameters are not available since no real molecule has this configuration. However, there are numerous empirical correlations in the literature for relating bond order, force constants and bond lengths. Many of these have been tested for describing these 4 centered, hydrogen chloride elimination complexes, and the particular correlation developed by H.S. Johnston⁴⁹ appears to be most useful.¹³

C. Moments of Inertia

The principle moments of inertia of the molecules and complexes were calculated using a computer program written by Schachtschneider.⁵⁰ This program required, as inputs the bond lengths, bond angles and dihedral angles of the individual atoms of the molecule with respect to each other. The bond lengths and bond angles used for the molecules studied in this work are listed in Table . Since the geometry of many of these molecules has not been determined, it was estimated from examination of the geometry of known molecules.

The geometry of the four-centered elimination complexes was determined in the same manner as was done in earlier work.^{12,13} The bond lengths were determined by using a correlation function developed by Pauling.⁵¹

$$D = D_0 - 0.71 \ln N$$

where D_0 is the length of a normal single bond, and D was the length of the bond of order N . The bond angles were defined by placing the out of ring HCH planes at 150° to the C-C bond and the HCH bond angle at 115° . This assignment and the bond lengths calculated above resulted in in-ring H-C-C and Cl-C-C angles of 100.37° . All complexes were treated as having the same bond order descriptions. For the hydrogen chloride elimination complex from 3-chloro-1-propene, the C=C-C bond angle was arbitrarily set at 150° . The molecular geometries used for the complexes are given in Table 9a. The values of the moments of inertia that were calculated are listed in Table 10.

D. Reaction Path Degeneracy

The reaction path degeneracy, σ^\ddagger , is the number of equivalent reaction paths for the molecule to form the activated complex. For the chloroalkanes in which the torsional mode is treated as a vibration, there are two reaction paths.^{12,13} For the chloropropene σ^\ddagger is 1 and for the chlorobutene, σ^\ddagger is 2.

E. Vibrational Frequencies

1. Molecules

The vibrational frequencies of the chloroalkanes studied in this work were recently determined and correlated by Snyder and Schachtschneider.⁵³ The same frequencies chosen by Dees¹³ were used for chloroethane- d_5 . The frequencies for chloroethane- d_3 were made up by comparison of the frequencies of chloroethane- h_5 and - d_5 . The criterion for determining the proper frequencies was that they fit the Teller-Redlich product rule within 10%.⁵⁴ The frequencies for 1,3-dichloropropane and 1,4-dichlorobutane were made up by removing the appropriate methyl group frequencies from the corresponding chloroalkane, and replacing them with the chloromethyl frequencies from the

chloroalkane. The frequencies for 3-chloro-1-propene were made up by removing the methyl group frequencies from propene and replacing them with the frequencies characteristic of a chloromethyl group. The frequencies for 4-chloro-1-butene were made up by combining the appropriate frequencies from propene and chlorobutane.

2. Complexes

Five of the ring frequencies for the four centered complexes used in this work were estimated from a special F-G Matrix computer program. This program considered the complex as a four membered ring, with each carbon atom and any out of ring groups attached to it treated as a single atom, having the same total mass as the group. The force constants were determined from the bond length and some empirical parameters. The form of the expression used is:⁵⁵

$$\log f = \frac{a-d}{b}$$

f is the force constant in units of 10^5 dynes cm^{-1} , a and b are empirical parameters which are determined from the location of atoms forming the bond in the periodic table, and d is the bond length. The particular parameters a and b used in this work were determined by Johnston.⁴⁹ For C-C bonds, $a=1.85$ and $b=0.55$; for C-Cl bonds, $a=2.06$ and $b=0.63$; for C-H bonds, $a=1.46$ and $b=0.56$; and for H-Cl bonds, $a=1.74$ and $b=0.64$. Of the five ring frequencies calculated, four are combinations of bond stretches, and the fifth corresponds to the reaction path and is usually about 30 cm^{-1} . One more frequency, the ring puckering, is needed for the four membered ring. This frequency has been treated as a semi-adjustable parameter and was adjusted to best fit the previous kinetic data for the chloro- and bromoalkanes.^{12,13,18} A value of 400 cm^{-1} was used for all the chloroalkanes studies in this work. For the

Table 9. Molecular Geometry of Molecules^a

<u>Molecule</u>	<u>C-C bond length Å</u>	<u>C-Cl bond length Å</u>	<u>C-H bond length Å</u>	<u>C-C-C bond angle deg</u>	<u>C-C-Cl bond angle deg</u>	<u>C-C-H bond angle deg</u>
C_2H_5Cl	1.54	1.79	1.09		115	109.6
$C_2D_3H_2Cl$						
C_2D_5Cl						
$1-C_3H_7Cl$	1.54	1.76	1.09	112	111	109.6
$1,3-C_3H_6Cl_2$	1.54	1.76	1.09	112	111	109.6
$1-C_4H_9Cl$	1.51	1.76	1.09	111	111	109.6
$1,4-C_4H_8Cl_2$	1.54	1.76	1.09	111	111	109.6
$3-C_3H_5Cl$	1.47, 1.35	1.82	1.09	120	109.6	109.6, 120
$4-C_4H_7Cl$	1.47, 1.35	1.76	1.09	120, 112	112.0	109.6, 120

Table 9a. Molecular Geometry of the Activated Complexes^a

Complex	C-C bond ^b length, Å	C-CI bond ^b length, Å	C-H bond ^b length, Å	C-C-C- bond angle, deg	C-C-Cl bond ^b angle, deg	C-C-H bond ^b angle, deg
C ₂ H ₅ Cl	1.34	1.82	1.80	-	100.37	100.37
C ₂ D ₃ HCl	-	-	1.09	-	-	115
C ₂ O ₅ Cl						
1-C ₃ H ₇ Cl	1.34 1.54	1.82 -	1.80 1.09	115 -	100.37 -	100.37 115,109.6
1,3-C ₃ H ₆ Cl ₂	1.34 1.54	1.82 1.79	1.80 1.09	115 -	100.37 111	100.37 115,109.6
1-C ₄ H ₉ Cl	1.34 1.51	1.82 -	1.80 1.09	115 111	100.37 -	100.37 115,109.6
1,3-C ₄ H ₉ Cl	1.34 1.51	1.82 1.76	1.80 1.09	115 111	100.37 111	100.37 115,109.6
3-ClC ₃ H ₅	1.34 1.35	1.82 -	1.80 1.09	150 -	100.37 -	100.37 115,120
4-C ₄ H ₇ Cl	1.34 1.47,1.35	1.82 -	1.80 1.09	150 120	100.37 -	100.37 115,120

a. Taken from Ref. 52 when available. Otherwise, they were determined by comparison with other

similar molecules in Ref. 52.

b. The first entry for each parameter is for the 4 membered ring. The second entry refers to the atoms adjacent to the ring. The third entry is for atoms removed from the ring by at least 1 atom, if it is different from the second entry.

chloroethane- d_3 , this frequency was set at 345 cm^{-1} . For chloroethane- d_5 , this frequency was set at 338 cm^{-1} .

The remainder of the complex frequencies were determined by comparing the complex to a similar alkene, cyclobutane, and the parent molecule.^{58,59,60,61} As an example, the chloroethane complex frequencies were determined by comparison with ethene, chloroethane, and cyclobutane.

The complex frequencies for the chloropropanes and chlorobutanes were estimated from the parent molecule, C_3 and C_4 olefins, and cyclobutane. As will be shown later, the models used for the complexes were too tight, as the Arrhenius A factors were too low. However, all that was desired in these calculations was a rough estimate of the specific rate constants for these molecules.

3. Anharmonicities

In this work, anharmonicity will be treated as a first order correction to the calculated values of the rate constants. Only the quadratic anharmonicity term will be considered, as defined by the energy eigenvalue from the Morse Potential. The vibrational dissociation energy will be used to account for this first order approximation of anharmonicity in the sum of states for the complex and the density of states for the molecule.

The vibrational spectra of all of the molecules have not been studied well enough to know the anharmonicity factors, α , or the harmonic frequencies, ω . However, chloromethane,⁵⁶ ethane,⁵⁷ and ethene,⁵⁸ and their totally deuterated counterparts have been analysed in enough detail to know these parameters. Hence the anharmonicities for the chloroalkanes and their activated complexes studied in this work were estimated from the anharmonicities of the normal modes of the known molecules.

Table 10 lists the fundamental and harmonic frequencies used for the molecules and activated complexes studied in this work. The frequencies were not grouped, as each normal mode has a different . Therefore, they are listed individually in most Tables. The four ring frequencies were treated as stretches and were assigned harmonic frequencies that were 10-20 wave numbers larger than the fundamental frequencies that were calculated.

F. Sum and Density of States

The sum and density of vibrational states were calculated, using expressions developed by Haarhoff,⁶² or a direct counting procedure for energies less than 15 kcal above the ground state. When the energy is high enough above the ground vibrational state, the vibrational states become so numerous and close together than they may be treated as continuous. The vibrational partition function, Q , becomes

$$Q = \int_{\epsilon=0}^{\infty} \rho(\epsilon) \prod_i \sum_s \exp(-hs\nu_i/kT) d\epsilon$$

The product over i is over all the vibrational modes of the molecule, having frequencies, ν_i . $\rho(\epsilon)$ is the vibrational degeneracy around an energy ϵ , but since there are so many states, it is a continuous variable and becomes the density of states. The sum is over all the s populated vibrational levels of each vibrational mode. Since the normally discrete variables in the partition function have become continuous, the vibrational partition function is put in the form of a Laplace transform of $\rho(\epsilon)$. After expanding the sum over s and reducing it to a sinh function, it is possible to invert Q and have an expression for $\rho(\epsilon)$. In order for this inverted expression to give a reasonable answer, the total energy of the vibrational states being considered must be

TABLE 10 Molecular Models of Molecules and Complexes^aA. Chloroethane Molecule¹³

2983	(2)	3133
2946	(1)	3006
2890	(1)	2950
1452	(3)	1532
1383	(1)	1453
1287	(1)	1337
1080	(1)	1120
972	(1)	992
676	(1)	681
336	(1)	386
3012	(1)	3202
1244	(1)	1304
972	(1)	972
785	(1)	785
251	(1)	283

16.02, 98.45, 103.15

B. Chloroethane Complex, Model 1^{b,13}

3050	(4)	3250
1393	(2)	1450
987	(2)	987
987	(2)	1000
890	(2)	900
400	(1)	450
FG Matrix for the complex		
1398	(1)	1430
629	(1)	650
861	(1)	920
650	(1)	700
(35)		

Chloroethane Complex, Model 2

3050	(4)	3200
1393	(2)	1483
987	(2)	987
987	(2)	1000
890	(2)	910
400	(1)	450
FG Matrix for the complex		
1398	(1)	1430
629	(1)	650
861	(1)	920
650	(1)	700

17.82, 76.42, 8839

- a. These tables are lists of the fundamental frequencies, degeneracies, and harmonic frequencies in this order. The frequencies are in cm^{-1} . The three numbers at the end of each column are the moments of inertia in $\text{AMU} \text{ \AA}^2$. The frequency in parenthesis is the reaction path.

TABLE 10 cont.

C. Chloroethane-d₃ molecule^{b,13}

2940 (2) 3140
 2160 (3) 2250
 1376 (2) 1456
 1236 (1) 1300
 1050 (3) 1105
 880 (3) 900
 640 (2) 640
 300 (1) 350
 184 (1) 200

19.49, 107.44, 117.43

D. Chloroethane-d₃ complex^{b,13}

3050 (2) 3250
 2270 (2) 2420
 1393 (1) 1443
 1000 (1) 1080
 987 (2) 1037
 890 (1) 940
 690 (2) 760
 632 (1) 632
 345 (1) 400

FG Matrix Frequencies

1382 (1) 1410
 633 (1) 650
 614 (1) 630
 471 (1) 500
 (33)

22.57, 38.42, 102.20

TABLE 10 cont.

E. Chloroethane-d₅ molecule^{b,13}

2160	(5)	2250
1059	(4)	1100
865	(5)	905
599	(2)	599
300	(1)	350
184	(1)	214

24.52, 109.64, 121.50

F. Chloroethane-d₅ complex^{b,13}

2270	(4)	2400
1040	(2)	1100
739	(4)	790
632	(2)	632
338	(1)	390
FG Matrix Frequencies		
1308	(1)	1450
598	(1)	610
620	(1)	660
471	(1)	520
(30)		

27.82, 89.59, 105.69

- b. Some of these frequencies have been grouped, by taking the geometric mean of the frequencies that are within a few hundred wave numbers of each other.
- c. Model 2 is identical to model 1, except that some of the harmonic frequencies have been changed for the complex.

TABLE 10 cont.

G. 1-chloropropane molecule⁵³

2965	(2)	3165
2960	(1)	3160
2877	(1)	3077
2856	(1)	3080
1470	(1)	1550
1452	(2)	1530
1437	(1)	1487
1373	(1)	1443
1335	(1)	1385
1270	(1)	1320
1100	(1)	1140
1032	(1)	1052
898	(1)	950
720	(1)	730
362	(1)	400
242	(1)	360
3002	(1)	3200
2916	(1)	3120
1227	(1)	1270
1291	(1)	1350
1070	(1)	1150
864	(1)	930
739	(1)	800
210	(1)	250
94	(1)	140

16.96, 211.20, 218.67

H. 1-chloropropane complex

3000	(3)	3200
1419	(1)	1500
1300	(1)	1390
990	(1)	1080
2933	(2)	3133
2870	(1)	3070
1474	(1)	1525
1443	(1)	1495
174	(1)	220
1045	(1)	1100
1378	(1)	1390
1172	(1)	1220
920	(1)	930
450	(1)	500
912	(1)	990
1229	(1)	1100
1200	(1)	1300
400	(1)	450
FG Matrix Frequencies		
1262	(1)	1370
627	(1)	650
861	(1)	950
641	(1)	720
(30)		

These frequencies were estimated by comparison with propene⁵⁹ and 1-chloropropene.⁵³

30.98, 171.13, 180.54.

TABLE 10 cont.

I. 1,3-dichloropropane Molecule

2960	(2)	3160
2856	(1)	3077
1470	(1)	1550
1437	(1)	1487
1373	(1)	1443
1270	(2)	1320
1100	(1)	1140
1032	(1)	1050
898	(1)	950
720	(2)	730
362	(2)	400
242	(1)	360
3002	(2)	3200
2919	(1)	3120
1291	(1)	1350
1227	(1)	1270
1070	(1)	1150
864	(1)	930
739	(1)	800
94	(2)	140

Frequencies were estimated
from 1-propane.⁵³

30.68, 575.91, 397.10

J. 1,3-dichloropropane Complex

3000	(4)	3200
1300	(1)	1360
990	(1)	1050
920	(1)	930
912	(1)	950
1229	(1)	1280
1100	(2)	1170
1437	(1)	1500
2960	(1)	3160
1270	(1)	1320
450	(1)	500
720	(1)	770
1227	(1)	1370
1070	(1)	1130
100	(1)	150
850	(1)	900
730	(1)	800
400	(1)	450

FG Matrix Frequencies

1198	(1)	1250
624	(1)	685
861	(1)	910
634	(1)	695
(25)		

Frequencies were estimated from
propene⁵⁹ and 1-propene.⁵³

49.54, 475.79, 504.89

TABLE 10 cont.

K. 3-chloro-1-propene Molecule^a

3090	(1)	3290
3017	(2)	3200
2992	(1)	3200
1652	(1)	1750
1419	(1)	1500
1298	(1)	1370
428	(1)	500
991	(1)	1000
578	(1)	590
912	(1)	1000
1229	(1)	1300
2960	(1)	3160
1437	(1)	1500
1270	(1)	1350
720	(1)	730
3002	(1)	3200
1227	(1)	1290
1070	(1)	1130
94	(1)	120
864	(1)	950

Frequencies estimated
from propene⁵⁹ and 1-
chloropropane.⁵³

35.63, 117.09, 149.56

L. 3-chloro-1-propene Complex

2996	(1)	3200
1440	(1)	1520
3005	(1)	3200
1957	(1)	2000
1398	(1)	1500
3085	(1)	3285
1015	(1)	1085
842	(1)	860
354	(1)	420
865	(1)	940
3090	(1)	3290
2992	(1)	3200
1419	(1)	1490
1298	(1)	1300
400	(1)	450
FG Matrix Frequencies		
1253	(1)	1453
627	(1)	640
860	(1)	880
640	(1)	650
(30)		

Frequencies estimated
from allene⁶¹ and 1-chloropropane.⁵³

41.05, 112.38, 149.61

- a. A recent determination of the vibration spectra of this molecule was found after these calculations were finished: R. D. McLachlan and R. A. Nyquist, *Spect. Chim. Acta.*, 24, 103 (1968).

TABLE 10cont.

M. 1-chlorobutane Molecule⁵³

2965	(2)	3200
2961	(1)	3200
2877	(1)	3100
1461	(4)	1551
1437	(1)	1517
1366	(2)	1416
1301	(2)	1360
1251	(1)	1300
1108	(1)	1130
1058	(1)	1070
1016	(1)	1025
894	(1)	910
721	(1)	730
405	(1)	420
331	(1)	370
160	(1)	210
3002	(1)	3200
2924	(1)	3125
2915	(1)	3115
1280	(1)	1370
1211	(1)	1300
1079	(1)	1150
918	(1)	1100
786	(1)	880
728	(1)	800
212	(1)	270
105	(1)	170
81	(1)	150

29.49, 371.96, 388.80

N. 1-chlorobutane Complex

3000	(3)	3200
1419	(1)	1500
1300	(1)	1370
990	(1)	1010
1229	(1)	1300
912	(1)	980
1100	(2)	1200
2965	(2)	3165
3877	(1)	3077
3856	(2)	3056
1461	(1)	1531
1372	(1)	1450
1300	(1)	1380
1250	(1)	1330
331	(1)	350
1108	(1)	1200
1058	(1)	1150
894	(1)	950
405	(1)	470
160	(1)	200
2924	(1)	3125
2915	(1)	3115
1079	(1)	1180
212	(1)	250
81	(1)	100
400	(1)	450
FG Matrix Frequencies		
1168	(1)	1180
625	(1)	645
861	(1)	880
636	(1)	650
(27)		

Estimated from propene⁵⁹ and 1-chlorobutane.⁵³

55.99, 246.29, 261.35

TABLE 10 cont.

0. 1,4-dichlorobutane Molecule

2961	(2)	3200
2865	(2)	3200
1461	(4)	1551
1366	(2)	1516
1301	(1)	1360
1251	(1)	1300
1108	(1)	1130
1058	(1)	1070
1016	(1)	1025
894	(1)	910
721	(2)	730
405	(1)	420
331	(1)	370
160	(1)	210
3002	(1)	3200
2924	(1)	3125
2915	(1)	3015
1280	(1)	1300
1211	(1)	1370
1079	(1)	1150
918	(2)	1110
786	(1)	880
728	(2)	800
81	(2)	150

Estimated from 1-chlorobutane.⁵³

31.51, 911.67, 930.53

P. 1,4-dichlorobutane Complex

2961	(1)	3160
2856	(1)	3060
1461	(2)	1540
1437	(1)	1500
1366	(1)	1450
1301	(1)	1380
1251	(1)	1320
1108	(1)	1160
1016	(1)	1070
906	(3)	970
721	(1)	750
3000	(2)	3200
1419	(1)	1490
1300	(1)	1380
990	(1)	1000
1229	(1)	1300
1100	(2)	1150
81	(1)	120
105	(1)	170
786	(1)	796
1079	(1)	1090
1211	(1)	1300
2924	(1)	3125
405	(1)	450
331	(1)	380
400	(1)	450
FG Matrix Frequencies		
1101	(1)	1300
624	(1)	644
861	(1)	881
633	(1)	653
(24)		

Estimated from propene⁵⁹ and
1-chlorobutane.⁵³

57.52, 779.17, 795.12

TABLE 10 cont.

Q. 4-chloro-1-butene Molecule

3090	(1)	3200
3010	(1)	3210
2992	(1)	3200
1652	(1)	1750
1419	(1)	1490
1298	(1)	1370
428	(1)	440
991	(1)	1050
578	(1)	590
912	(1)	980
1229	(1)	1300
2961	(1)	3261
2865	(2)	3056
1461	(2)	1540
1437	(1)	1540
1301	(2)	1380
81	(1)	1380
728	(1)	740
918	(1)	1000
331	(1)	400
160	(1)	220
1016	(1)	1030
1058	(1)	1100
1251	(1)	1320
3002	(1)	3200
2924	(1)	3125
2914	(1)	3115

Estimated from propene⁵⁹
and 1-chlorobutane⁵³.

23.09, 356.99, 373.65

R. 4-chloro-1-butene Complex

3082	(1)	3282
3002	(1)	3282
2992	(1)	3200
1630	(1)	1830
1438	(1)	1500
1280	(1)	1350
1196	(1)	1250
894	(1)	950
572	(1)	585
162	(1)	210
912	(1)	1000
3101	(1)	3301
2984	(1)	3185
1381	(1)	1450
990	(1)	1050
976	(1)	1030
3055	(1)	3255
1294	(1)	1370
301	(1)	350
1100	(2)	1170
400	(1)	450
FG Matrix Frequencies		
1179	(1)	1379
626	(1)	640
861	(1)	880
636	(1)	650
(28)		

Estimated from 1,3-butadiene⁶⁰
and 1-chlorobutane⁵³.

42.56, 236.36, 241.75

about 15 kcal. above the ground vibrational levels. The sum of states is simply the integral of the density of states over the range of 0 to energy. A closed form expression for this quantity may also be derived from the partition function, Q . The total expression derived by Haarhoff⁶² is:

$$I_m = \left[\left(\frac{2}{\pi n} \right)^{1/2} \left(\frac{n}{n+m} \right)^{n+m-1/2} \left(1 - \frac{1}{12(n+m)} \frac{\lambda (h\nu)^{m-1}}{(1+\eta)} \right) \right. \\ \left. \left[\left(1 + \frac{\eta}{2} \right) \left(1 + \frac{2}{\eta} \right) \right]^{\eta/2^{n+m}} \left[1 - \frac{1}{(1+\eta)^2} \right]^{\beta_m} \right]$$

m is an index governing the number of times the density of state is integrated over energy. For the density of states, m is 0 and for the sum of states, it is 1. n is the number of vibrational modes, ν is the arithmetic average of the n vibrational frequencies, λ is defined as

$\frac{1}{\lambda} = \prod_i \left(\frac{\nu_i}{\bar{\nu}} \right)$ $\eta = \frac{\epsilon}{\epsilon_z^0}$, where ϵ is the energy being summed to, and ϵ_z^0 is the zero point energy, and

$$\beta_m = (n+m-1)(n+m-2)\alpha_2 - n(n+m)3/6n, \text{ with } \alpha_2 = \frac{\bar{\nu}^2}{(\bar{\nu})^2}$$

Haarhoff⁶² also developed a method of correcting these expressions for anharmonicity. He treated each vibrational mode as a Morse oscillator with a harmonic frequency, ω_i , and anharmonicity, χ_i . The dissociation energy for a Morse oscillator is defined as $D_i = \frac{\omega_i}{2\chi_i}$. The expression he derived is:

$$\frac{I_m}{I_m(D\bar{E}=\omega)} = \left[\left(1 + \frac{2}{\eta} \right) \left(\eta/2 \right) \left(1 + \eta/2 \right) \exp \left(\frac{-\alpha_2 - 1}{3(1+\eta)} \right) \right] n \epsilon_z^0 / (n+m) D\bar{E} \\ \exp \left[M_2 (1+\eta)^2 \left(\frac{\epsilon_z^0}{D\bar{E}} \right)^2 + M_3 (1+\eta)^3 \left(\frac{\epsilon_z^0}{D\bar{E}} \right)^3 \right]$$

Where $M_2 = n(4n+5m)/8(n+m)^2(n+m+1)$,

$$M_3 = n(24n^2+59nm+37m^2)/24(n+m)^3(n+m+1)(n+m+2),$$

DE is the arithmetic average of the dissociation energies, D_i , and the other symbols were defined above. In the computational procedure; an average dissociation energy is used. This average is formed by weighting each value of D by its degeneracy and dividing by the total number of vibrational modes.

6. Distribution Function for k_a

In order to calculate the apparent rate constants, k_a , we need the distribution function for the energy of the reacting molecules. This distribution function, $f(\epsilon_{VR})d\epsilon_{VR}$, was calculated from consideration of the recombination of radicals to form the excited molecule. $f(\epsilon_{VR})d\epsilon_{VR}$ has the form:

$$f(\epsilon_{VR})d\epsilon_{VR} = \frac{k'_\epsilon K(\epsilon_{VR})d\epsilon_{VR}}{\int_{\epsilon_0}^{\infty} k'_\epsilon K(\epsilon_{VR})d\epsilon_{VR}} \quad (6)$$

k' is the specific rate constant at an energy ϵ for the excited molecules decomposing into the radicals that form it. $K(\epsilon_{VR})$ is the thermal, quantum Boltzmann distribution at the temperature of formation of the excited molecule. The integral in the denominator is to normalize the distribution function.

In order to calculate k'_ϵ , we need a model for the association of radicals to form the excited molecule. The chloroethane molecules studied in this work were formed from the appropriate methyl and chloromethyl radicals. The frequencies for these radicals were the same as used by Dees,¹² with the exception of the ν_2 , out of plane bending mode of the methyl and methyl- d_3 radical. For these frequencies, the more recent values of Milligan and Jacox were used.⁶³

The formation of the C-C bond was described by four low frequency bonds, and a free rotor. The remaining frequency (the C-C stretch) was the reaction path. The frequencies for the association complexes considered are listed in Table II. There is no need to consider the effect of anharmonicity upon the distribution junction, as the partition functions in it are very insensitive to small changes in the vibrational frequencies.

II. Thermochemistry

In order to calculate k , we need to know the critical energy, E_0 , for the reaction. This energy differs from the conventional thermal activation energy, E_{act} , by a small amount and can be calculated by standard equations. The equilibrium thermal absolute rate theory expression for a unimolecular reaction rate constant is:

$$k = \frac{\sigma \kappa kT}{h} \frac{Q^\ddagger}{Q^*} \exp(-E_0/RT) = \int_0^\infty k_e^\ddagger K(\epsilon) d\epsilon \quad (7)$$

is the reaction path degeneracy, Q and Q^* are the partition functions for the active degrees of freedom of the activated complex and the molecule, respectively, and $K(\epsilon)$ is the thermal Boltzmann distribution. The other symbols have their standard significance. In terms of the Arrhenius theory of chemical reactions, Eq. 7 has the form:

$$k = A \exp(-E_{act}/RT) = \frac{\sigma \kappa kT}{h} e^{AS/R} e^{-(E_{act}/RT)} \quad (8)$$

The models for the molecule and activated complex were adjusted to give the known A factor, for some estimate of E_0 . At the same time, E_{act} was calculated from the entropy change of the reaction. The difference between E_{act} calculated, and the estimated E_0 used in the calculation is an estimate of the amount that the thermal E_{act} must be lowered to get E_0 .

Thermal pyrolysis data are not available for the dichloroalkanes and chloroalkenes. For these molecules, E_0 was estimated from known values for similar compounds, and various different values of k were calculated for a range of values of E_0 . From the thermal data presented in a review article by Macoll,⁶⁴ E_0 for 1-chloropropane and 1-chlorobutane is 53.8 and 54.0 kcal, respectively. E_0 for 1,3-dichloropropane and 1,4-dichlorobutane were estimated to be 56 and 58.8 kcal, by comparison with the values estimated for 1,3-dichloroethane¹³ and 1,2-difluoroethane.³⁶ Macoll listed values of E_{act} of 45-50 kcal for compounds such as 3-chloro-1-butene, which have an allylic chlorine atom. From these compounds, E_0 for 3-chloro-1-propene was estimated to be 47 ± 2 kcal. There has been no thermal pyrolysis studies of a chloroalkene with the chlorine atom removed from the double bond by two carbon atoms. Therefore, E_0 for 4-chloro-1-butene was arbitrarily set at 55 ± 2 kcal. The values of E_0 for chloroethane and chloroethane- d_5 used in this study were the same values Dees used in his earlier work.¹³ The value of E_0 for chloroethane- d_3 was calculated from the E_0 for chloroethane by correcting for the difference in zero point energies.

For the calculation of k_a the minimum energy in the activated molecule must be known. This energy, E_{min} , is simply the bond energy of the C-C bond at 0°K, plus any activation energy for the radical recombination reaction that is formed by the combination of radicals in the system. This is the energy where the distribution function, $f(\epsilon_{VR})d\epsilon_{VR}$, starts. For this study, the values used by Dees were used for chloroethane and chloroethane- d_5 . E_{min} for chloroethane- d_3 was estimated by the difference in zero point energies between chloroethane and chloroethane- d_3 .¹³

The values of E_0 and E_{min} used in this study are listed in Table 12. A representative value is listed for the dichloroalkanes and chloroalkenes.

Table 11 Association Complex Frequencies^{a, e}

C_2H_5Cl	$C_2D_3H_2Cl$	C_2D_5Cl
<u>Frequency^b</u>	<u>Frequency</u>	<u>Frequency^b</u>
3000 (6)	3000 (3)	2230 (5)
1400 (4)	2230 (3)	980 (3)
732 (1)	1400 (2)	800 (1)
615 (1) ^c	847 (3)	615 (1)
230 (2)	473 (1) ^c	449 (2) ^d
150 (2)	209 (2)	190 (2)
	145 (2)	140 (2)

a. Frequencies in cm^{-1} . The frequencies have been grouped to save time on the computer. The degeneracies are in parenthesis after each frequency.

b. Ref. 13, unless otherwise stated.

c. Ref. 63

d. Contains the γ_2 out of plane bond from Ref. 63

e. The C-C stretch is the reaction coordinate.

Table 12 Thermochemistry

Molecule	E_{02}^{\ddagger} , kcal mol ⁻¹	E_{mid}^{\ddagger} , kcal mol ⁻¹	E_{act}^{\ddagger} , kcal mol ⁻¹	log A calc.	log A exp't
C ₂ H ₅ Cl ^a	55.0	88.4	56.7	13.78	13.46
C ₂ D ₃ H ₂ Cl ^a	56.2	89.4	58.5	13.89	13.77
C ₂ D ₅ Cl ^d	56.4	89.4	58.7	13.86	13.78
1-C ₃ H ₇ Cl ^b	53.8	---	55	13.13	13.45
1,3-C ₃ H ₆ Cl ₂ ^c	56.0	---	---	12.95	---
3-C ₃ H ₅ Cl ^c	47.0	---	---	13.00	---
1-C ₄ H ₉ Cl ^b	54.0	---	55.1	13.40	13.50
1,4-C ₄ H ₈ Cl ₂ ^c	58.8	---	---	14.20	---
4-C ₄ H ₇ Cl ^c	55	---	---	12.85	---

a. Ref. 72

b. Estimated from thermal data in Ref. 64

c. Estimated from other compounds in Ref. 64 (thermal data)

d. Ref. 13

e. At 800°K. These are the calculated Arrhenius A factors, calculated from the entropy of activation.

RESULTS

A. The effect of anharmonicity on the specific rate constant

The calculated specific rate constants for both the harmonic and anharmonic models for the three isotopic chloroethanes are listed in Table 13 along with the corresponding values of the sum and density of vibrational states. The overall effect of including anharmonicity is to lower the specific rate constants, relative to the value calculated for a harmonic model. Anharmonicity corrections increased the values of the sum and density of states, since anharmonicity makes the vibrational levels of each mode closer spaced. The net effect of lowering the specific rate constant was caused by anharmonicity having a larger effect on the density of states of the molecule than on the sum of states of the complex. This effect is shown in Fig. 7, for chloroethane- h_5 , chloroethane- d_5 and 1-chloropropane. The reason for the large effect for the molecule is due to the fact that the energy of the molecule is much larger than for the complex, about 50-60 kcal. The curve for chloroethane- d_3 has the same shape and the same values as that for chloroethane- d_5 and was not shown.

B. The effect of anharmonicity on the specific isotope effect.

The specific isotope effect, k_e^H/k_e^D is shown in Fig. 8. The effect of anharmonicity was to increase the specific isotope effect. Anharmonicity had a larger effect on the deuterated compounds because their overall vibrational frequencies are lower than the vibrational frequencies of the hydrogenated chloroethane. The correction factor for anharmonicity depends inversely on the square of the harmonic frequency of the vibrational modes, hence if the vibrational frequencies are lower, the anharmonicity correction is larger.

• The values of the average molecular dissociation energy are given in Table 13

for the chloroethanes, and Table 14 for the chloropropanes and butanes. Since the dissociation energy enters the Haarhoff equations as its inverse, molecules having overall lower vibrational frequencies will have a larger anharmonicity correction.

It should be noted here that the calculated values of DE from the Morse potential are much lower for the deuterated chloroethanes than for chloroethane- h_5 . This effect is the result of the crude way in which the dissociation energy is determined for the models of anharmonicity used in this work. What has happened is that the definition of DE in this work is requiring a different potential function for every molecule, even though this is physically wrong. The three isotopically substituted chloroethanes should all have the same potential function and similar values of DE.

C. The effect of anharmonicity on a series of chloroalkanes.

The specific rate constants for chloroethane, chloropropane and chlorobutane were calculated for a fixed value of the average dissociation energy, DE, of 15000 cm^{-1} , for the values of E_0 shown in Table 12. The results of this calculation are shown in Fig. 9. There are two effects to be noticed from this figure. As a methyl group is added to the molecule, the values of the specific rate constant as a function of energy are decreased by approximately a factor of 10^3 . The values of the specific rate constant were calculated for the same value of DE for both the molecule and the complex. From Fig. 9, k_e (harmonic)/ k_e (anharmonic) is 2.8 for chloroethane, 2.73 for 1-chloropropane, and 2.54 for 1-chlorobutane, at 90 kcal of energy in the molecule for a constant value of DE. The corresponding numbers from Fig. 7 and Fig. 11 are 1.65 for chloroethane, 2.3 for 1-chloropropane, and 1.67 for 1-chlorobutane for the values of DE calculated from the estimated

harmonic frequencies. Fig. 9 shows that the smallest difference in DE between the molecule and complex gives the largest difference between the harmonic and anharmonic models for the reaction, when compared to the effects of anharmonicity on the specific rate constant shown in Fig. 7. Thus increasing the number of degrees of freedom doesn't alter the effect of anharmonicity on the specific rate constant as is seen from Fig. 9.

D. The specific rate constants for chloropropanes and chlorobutanes.

The specific rate constants were calculated for the unimolecular elimination HCl from 1-chloropropane, 1,3-dichloropropane, 3-chloro-1-propene, 1-chlorobutane, 1,4-dichlorobutane, and 4-chloro-1-butene, and are shown in Fig. 10 and 11. These curves are just estimates of the rate constants because this is the first attempt to define the models and several pieces of experimental data normally used to refine the models are not available. The vibrational frequencies and thermochemistry were available for 1-chloropropane, and 1-chlorobutane, hence these models have the best chance of being correct. These quantities had to be estimated for the other molecules.

The only test that could be applied to the models for these reactions was to calculate the Arrhenius A factors for each reaction. The calculated values are listed in Table 13. For most of the reactions, the A factor is low by a factor of approximately two, compared to the usual experimental A factors found by thermal experiments.⁶⁴ However, the rate constants show the proper trends: decreasing as the number of chlorine atoms increases, and increasing as the number of vibrational modes decreases.

TABLE 13 Specific Rate Constants for the Isotopic Chloroethanes.

A. Chloroethane, Model 1. $OE(\text{Molecule})=26287 \text{ cm}^{-1}$, $OE(\text{Complex})=23769 \text{ cm}^{-1}$									
E_a , kcal/Molecule	$\sum f(\epsilon_{\text{vib}})$ harmonic	$N^*(\epsilon)$ harmonic	k_e harmonic	$\sum \rho(\epsilon)$ anharmonic	$N^*(\epsilon_{\text{vib}})$ anharmonic	k_e anharmonic			
70.09	2.03×10^4	2.43×10^7	4.45×10^7	3.09×10^4	5.43×10^7	2.63×10^7			
75.09	1.59×10^5	5.37×10^7	1.58×10^8	2.05×10^5	1.15×10^8	9.45×10^7			
80.09	9.52×10^6	1.14×10^8	4.44×10^8	1.29×10^6	2.57×10^8	2.67×10^8			
85.09	4.65×10^6	2.36×10^8	1.05×10^9	6.62×10^6	5.54×10^9	6.37×10^9			
90.09	1.94×10^7	4.71×10^8	2.20×10^9	2.91×10^7	1.16×10^9	1.34×10^9			
94.57	6.33×10^7	8.56×10^8	3.94×10^9	9.89×10^7	2.19×10^9	2.40×10^9			
B. Chloroethane, Model 2. $OE(\text{Molecule})=26287 \text{ cm}^{-1}$, $OE(\text{Complex})=25000 \text{ cm}^{-1}$									
70.09	Same as above values for Model 1.								
75.09	harmonic case.								
80.09				1.27×10^6	1.15×10^8	9.32×10^7			
85.09				6.50×10^6	2.57×10^8	2.63×10^8			
90.09				2.85×10^7	5.54×10^9	6.25×10^9			
94.59				9.65×10^7	1.16×10^9	1.31×10^9			
					2.19×10^9	2.35×10^9			
C. Chloroethane- d_3 . $OE(\text{Molecule})=17077 \text{ cm}^{-1}$, $OE(\text{Complex})=13977 \text{ cm}^{-1}$									
70.00	4.40×10^4	2.01×10^8	1.19×10^7	5.99×10^4	6.26×10^8	5.22×10^6			
75.00	4.37×10^5	4.61×10^8	5.18×10^8	6.57×10^6	1.54×10^9	2.32×10^7			
80.00	3.12×10^7	1.01×10^9	1.68×10^8	5.14×10^6	3.66×10^9	7.66×10^8			
85.00	1.76×10^7	2.15×10^9	4.46×10^9	3.16×10^7	8.37×10^9	2.06×10^8			
90.00	8.26×10^8	4.41×10^9	1.02×10^9	1.62×10^8	1.85×10^9	4.77×10^8			
95.00	3.35×10^8	8.78×10^9	2.08×10^9	7.18×10^8	3.99×10^9	9.82×10^8			
D. Chloroethane- d_5 . $OE(\text{Molecule})=15902 \text{ cm}^{-1}$, $OE(\text{Complex})=11055 \text{ cm}^{-1}$									
70.00	6.05×10^4	6.82×10^8	4.72×10^7	8.97×10^6	2.27×10^9	2.11×10^6			
75.00	6.93×10^5	1.61×10^9	2.30×10^7	1.16×10^6	5.80×10^9	1.07×10^7			
80.00	5.53×10^7	3.62×10^9	8.13×10^8	1.04×10^7	1.42×10^{10}	3.91×10^8			
85.00	3.41×10^7	7.87×10^9	2.31×10^8	7.18×10^8	3.34×10^{10}	1.15×10^8			
90.00	1.75×10^8	1.65×10^{10}	5.59×10^8	4.08×10^8	7.62×10^{10}	2.85×10^8			
95.00	7.52×10^8	3.36×10^{10}	1.20×10^9	1.99×10^9	1.68×10^{11}	6.27×10^8			

TABLE 14. Calculated apparent rate constants and values of the average molecular dissociation energy.

A. Apparent rate constants

Molecule	k_a , harmonic, sec^{-1}	k_a , anharmonic, sec^{-1}
$\text{C}_2\text{H}_5\text{Cl}$	2.39×10^9	1.45×10^9
$\text{C}_2\text{D}_3\text{H}_2\text{Cl}$	1.32×10^9	6.53×10^8
$\text{C}_2\text{D}_5\text{Cl}$	8.11×10^8	4.20×10^8

B. Average molecular dissociation energies

Molecule	DE, molecule, cm^{-1}	DE, complex, cm^{-1}
1- $\text{C}_3\text{H}_7\text{Cl}$	15848	14131
1,3- $\text{C}_3\text{H}_6\text{Cl}_2$	15475	13627
3- Cl -1- C_3H_5	17806	17338
1- $\text{C}_4\text{H}_9\text{Cl}$	17942	14132
1,3- $\text{C}_4\text{H}_8\text{Cl}_2$	15950	15023
4- Cl -1- C_4H_7	16405	13029

Fig 7. 1-chloropropene, Model 1, DE was fixed at 15000 cm^{-1} for both the molecule and complex, Model 2, $DE=15848\text{ cm}^{-1}$ for the molecule and 14131 cm^{-1} for the complex. Chloroethane- h_5 , Model 1, $DE=26286\text{ cm}^{-1}$ for the molecule and 23769 cm^{-1} for the complex. Model 2 (lower line, not labeled) $DE=26286\text{ cm}^{-1}$ for the molecule and 25000 cm^{-1} for the complex.

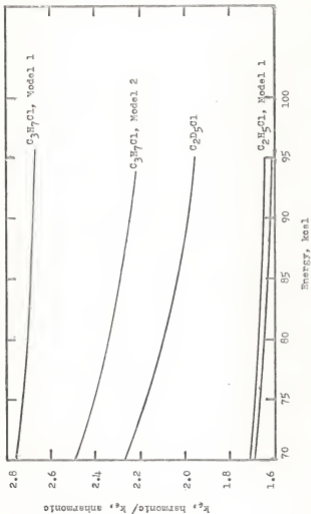


Fig 7 Effect of anharmonicity on the specific rate constant. See facing page for explanation of models.

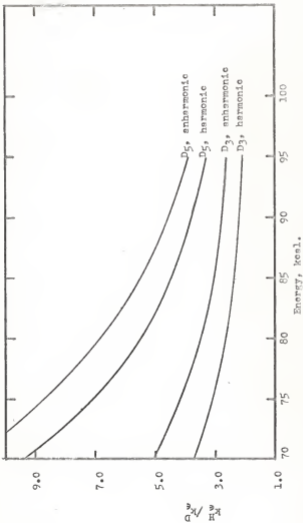


Fig. 8 Effect of anharmonicity on the specific isotope effect for chloroethane-d₃ and chloroethane-d₅, relative to chloroethane-h₅.

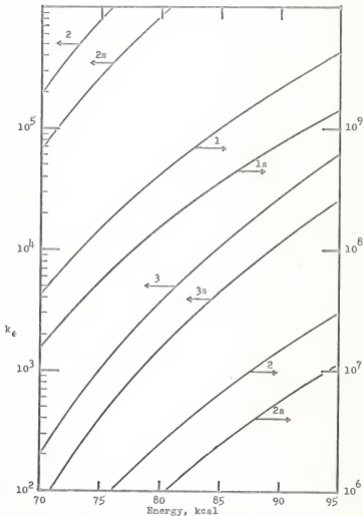


Fig 9 k_e for constant DE of 15000 cm^{-1} . (1) chloroethane, (2) 1-chloropropane, (3) 1-chlorobutane. The curves marked (a) are corrected for anharmonicity.

- Fig 10. (1) 1-chloropropane, harmonic, $E_0 = 53.8$ kcal.
(2) 1-chloropropane, anharmonic, $E_0 = 53.9$ kcal.
(3) 3-chloro-1-propene, harmonic, $E_0 = 47$ kcal.
(3a) 3-chloro-1-propene, harmonic, $E_0 = 49$ kcal.
(3b) 3-chloro-1-propene, harmonic, $E_0 = 44.7$ kcal.
(4) 3-chloro-1-propene, anharmonic, $E_0 = 47$ kcal.

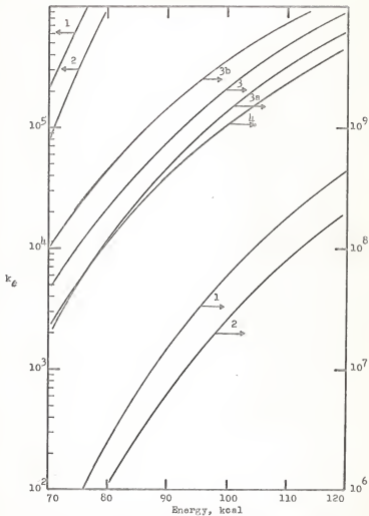


Fig 10 Specific rate constants for 1-chloropropane and 3-chloro-1-propane. See facing page for explanation of curves.

- Fig 10a. (1) 1,3-dichloropropane, harmonic, $E_0=54.1$ kcal.
(1a) 1,3-dichloropropane, harmonic, $E_0=58.0$ kcal.
(1b) 1,3-dichloropropane, harmonic, $E_0=56.2$ kcal.
(2) 1,3-dichloropropane, anharmonic, $E_0=54.1$ kcal.

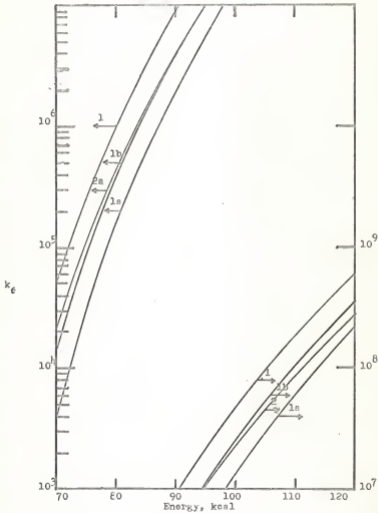


Fig 10e Specific rate constants for 1,3-dichloropropene. See facing page for explanation of curves.

- Fig 11. (1) 1-chlorobutane, harmonic, $E_0=54.0$ kcal.
(2) 1-chlorobutane, harmonic, $E_0=54.0$ kcal.
(3) 1,4-dichlorobutane, harmonic, $E_0=54.0$ kcal.
(3a) 1,4-dichlorobutane, harmonic, $E_0=57.0$ kcal.
(3b) 1,4-dichlorobutane, harmonic, $E_0=55.7$ kcal.
(4) 1,4-dichlorobutane, anharmonic, $E_0=57.0$ kcal.

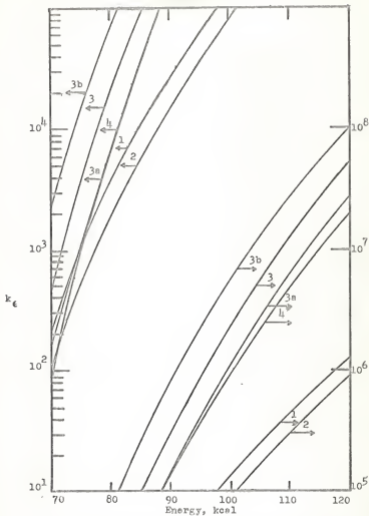


Fig 11 Specific Rate constants for 1-chlorobutane and 1,4-dichlorobutane. See facing page for explanation of the curves.

- Fig 11a. (1) 4-chloro-1-butene, harmonic, $E_0=54.9$ kcal.
(1a) 4-chloro-1-butene, harmonic, $E_0=57.0$ kcal.
(1b) 4-chloro-1-butene, harmonic, $E_0=52.9$ kcal.
(2) 4-chloro-1-butene, anharmonic, $E_0=54.9$ kcal.

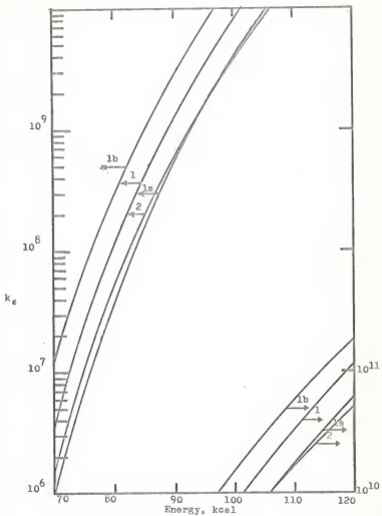


Fig 11a Specific rate constants for 4-chloro-1-butene.
See facing page for explanation of curves.

DISCUSSION

A. The nonequilibrium kinetic isotope effect for chloroethane-d₃

The calculated value of the nonequilibrium kinetic isotope for chloroethane-d₃, from the apparent rate constant for the harmonic case, was 1.81. This total isotope effect may be partitioned into a primary effect and a secondary effect, by considering the value of the isotope effect for chloroethane-d₅ of 2.95. The ratio of the isotope effect for chloroethane-d₅ to the isotope effect for chloroethane-d₃ is the square of the secondary isotope effect, hence the secondary isotope effect is $(2.95/1.81)^{1/2}$, or 1.28. The primary isotope effect is given by the ratio of the calculated total isotope effect to the square of the secondary isotope effect, or $1.81/(1.28)^2=1.11$. These primary and secondary effects should be compared to those calculated by Dees¹³, 1.24 and 1.25, respectively. The experimental secondary isotope effect is $(3.4/2.1)^{1/2} = 1.27$, and the experimental primary effect is $2.1/(1.27)^2=1.30$.

When calculating the isotope effects, there are two related factors that must be considered. They are the difference in E_0 between the hydrogenated and deuterated species, and the low bending frequency associated with the ring in the complex. Small variations in the critical energy for reaction, E_0 have very large effects on the sum of states of the complex.¹³ For this study, the difference in E_0 for the hydrogenated reaction and the deuterated reaction was made as large as possible, in order to fit the isotope effect. However, the same effect could have been achieved by lowering the ring bending frequency.¹⁷ This makes selection of a proper model very difficult. Thermal data on the isotope effects in chloroethanes favors a large difference in E_0 ,⁷² and for this reason, the difference in E_0 was made as large as possible while still keeping the models consistent with the Teller-Redlich product

rule. In maximizing the difference between E_0 for the deuterated reaction and the hydrogenated reaction, the product rule for the molecule was extended to give a result about 12% low from the frequency product, relative to the mass product, and the complex was extended to give a frequency product that was 10% high relative to the mass product.

Even after extending the product rule to the acceptable limit, the isotope effect was too low. In order to raise it, the models for all three chloroethanes would need to be optimized with respect to each other.

B. Accuracy of the method of correcting for anharmonicity

In these calculations an arithmetic average was taken of the hypothetical Morse dissociation energy associated with each normal mode. This tends to weigh the higher frequencies more than the lower frequencies. The problem with this inherent weighting of the high frequencies is that the important quantities for this type of calculation, the sum and density of vibrational states, depend most on the low frequencies of the molecule and complex, since the low frequency vibrational modes have the higher populations at any given energy. Another problem is that the low frequency vibrational modes are usually bending, wagging or torsional normal modes. These types of motion are described very poorly by the Morse potential, while the high frequency stretching normal modes are described quite well by the Morse potential. The anharmonicity of bending, wagging and torsional modes is probably described better by a quartic potential function than by the Morse potential. Torsional modes could also be described by hindered rotors. These types of potential functions would have the effect of decreasing the density of states of the molecule. Therefore, this method of weighting the high frequency vibrations and ignoring the low frequency vibrations may be

qualitatively correct for this treatment of anharmonicity.

However, the treatment of anharmonicity used in this work shows that an accurate evaluation of anharmonic sums and densities of vibrational states is needed. The most accurate treatment of anharmonicity should consider each normal mode with its own particular potential function, and should include as high order anharmonicities as are available, particularly for the low frequency normal modes, which are highly populated at the usual energies considered in chemical kinetics.

C. Sensitivity of the anharmonic correction factor.

There are three quantities that have to be considered when examining the effect of anharmonicity on the specific rate constant. They are the magnitude of DE , the difference between DE for the molecule and the complex, and the number of normal modes of the molecule. The problem with attempting to separate these effects is that the anharmonic correction factor for the specific rate constant did not vary very much as these quantities were changed. It was between 1.6 and 3 for all the models examined in this study.

From Fig. 9, where the number of normal modes was increased in a systematic manner, the anharmonicity correction only decreased slightly for a constant value of DE and a constant DE difference between the molecule and complex. This shows that the anharmonicity correction does not have any marked dependence on the number of normal modes of the molecule and complex.

The anharmonic correction was calculated for chloroethane for different values of the difference between DE for the molecule and complex, but at a constant value of DE for the molecule. This comparison is shown in Fig. 7, where the ratio of the specific rate constant for the harmonic model to the anharmonic model is plotted against energy. As the difference in DE was

increased by a factor of two, the anharmonic correction for the specific rate constant increased only slightly. This shows that the anharmonic correction is only slightly dependent on the difference between the correction factors for relatively high values of DE.

By comparing the anharmonic corrected density of states for chloroethane and 1-chloropropane, the effect of the magnitude of DE on the anharmonic correction can be examined. The difference in DE for these two molecules is about $10,000 \text{ cm}^{-1}$, and the anharmonic correction factors differ by a factor of about 1.6 at 70 kcal of energy in the molecule and a factor of about 2.2 at 95 kcal of energy in the molecule. This change is reasonable, because as the value of DE increases, the amount of anharmonicity is decreasing. The harmonic case corresponds to DE equal to infinity.

D. Effect of energy on the anharmonic correction factor.

As the energy of the reaction system increases, the anharmonic correction factor decreases, for both the sum of states of the complex and the density of states of the molecule, as is seen from Table 13, and Fig. 7. This is because as the energy increases, the rate of change of the sum and density of states with respect to energy decreases. As an example, consider chloroethane- η_5 . Changing the energy of the molecule by 5 kcal at 70 kcal of energy produces a 78% change in the sum of states and a 22% change in the density of states. A five kcal change in energy at 85 kcal of energy in the molecule changes the sum of states by 42% and the density of states by 21%. The density changes are much smaller than the sum changes because the molecule is at much higher energy than the complex. Putting anharmonicity into the model of the reaction increases the sum and density of states, and therefore decreases the relative change with energy. Hence, the anharmonic correction factor decreases with energy.

For molecules having low values of DE, this effect is greater than for molecules having a large value of DE. This is a result of the rate of change of the sum and density of states with energy. A low value of DE means that the molecule has a high anharmonicity, and the continuum of states is reached at a lower energy, relative to the bottom of the potential well.

E. Effect of increasing molecular size on the specific rate constant.

As the size of the reacting molecule or the number of vibrational modes increases, the value of the specific rate constant decrease, as is illustrated in Fig. 9, for chloroethane, 1-chloropropane, and 1-chlorobutane. This effect is the result of the larger increase in the density of states with a large number of normal modes. The sum of states is also increased, but it still starts at one at the energy E_0 .

As the size of the molecule is increased, the value of DE should decrease slightly. This is because as the size of the molecule is increased, the number of low frequency bends and torsions increases. In the treatment of anharmonicity being used in this work, these frequencies have small anharmonicities, and small dissociation energies. However this effect should be very small, and may be overpowered by the increase in the number of high frequency stretches, which have large anharmonicities. This appears to be the case for the molecules used in this study, as there was no uniform trend in the value of DE as the size of the molecule was increased.

F. Consecutive unimolecular eliminations from chloroalkanes.

One of the objectives of these calculations was to examine the possibility of using the second elimination of HCl from a dichloroalkane as a means of determining the energy distribution of the products of the first elimination of HCl from the dichloroalkane. The procedure would be to measure the rate

constant for both eliminations, and match the measured rate constants to the corresponding calculated rate constants. As an example of this procedure, assume that the 1,3-dichloropropane--3-chloro-1-propene system is being used, and that the 1,3-dichloropropane initially has 90 kcal of energy. The specific rate constant for 1,3-dichloropropane at 90 kcal of energy is about 10^7 sec^{-1} , which corresponds to a half quenching pressure of about 0.1 cm. The rate constant was converted from sec^{-1} to cm in the same way that it was converted to sec^{-1} from cm in the Results section in the second part of this thesis. The rate constant for 3-chloro-1-propene is about 10^7 sec^{-1} at 70 kcal of energy in the molecule. This corresponds to a half quenching pressure of about 0.1 cm. Since 70 kcal is an upper limit on the amount of energy that might be in the olefin after the first HCl elimination, low pressure experiments would be required. The actual energy would probably be between 50 and 70 kcal. There are two factors that make the energy left in the olefin lower than that initially in the dichloroalkane. The first is that the reaction is endothermic by about 20 kcal. The second is that Pimentel has shown that the HF eliminated from 1,1,1-trifluoroethane contains about 10-20 kcal of vibrational energy.⁶⁷ For the lower limit, the olefin would have only about 50 kcal of energy, since E_0 was estimated to be about 47 kcal for 3-chloro-1-propene. The excess energy would only be 2-3 kcal and the rate constant would be less than 10^2 sec^{-1} . This corresponds to a half quenching pressure of less than 0.01 microns. These experiments would be impossible to carry out, unless the energies happened to be toward the upper limits.

Since that rate constants for 1,4-dichlorobutane and 4-chloro-1-butene are even lower at the same energies than the corresponding propyl compounds, it would be almost impossible to do this experiment with these compounds.

6. Comparison of anharmonic corrections.

There have been a number of attempts to correct the sums and densities of states for anharmonicity in the literature.^{57,68,69,70} Wilde considered a direct counting procedure, using the Morse potential to describe anharmonicity.⁶⁸ His procedure gave results for the sum of states for cyclopropane that were about a factor of three higher than the harmonic sum of states at energies of about 100 kcal. His correction for anharmonicity was not considered in this work for two reasons. A direct counting procedure takes a large amount of time on a computer, the computing time increasing exponentially with energy. At the energies of interest in this study, the Haarhoff expressions are as good as direct counting for the sums and densities of states. Wilde's expression also depends upon an empirical factor, in addition to using the relatively empirical Morse potential, and one objective of this study was to minimize the number of empirical parameters used. It seemed reasonable to assume that Wilde's expression wouldn't give any different results than the Haarhoff expression, since they both were derived from the same potential function.

Forst^{57,69} used the same formulation of anharmonic corrections as used in this work in his theoretical studies of the thermal decomposition of chloromethane and the electron impact decomposition of ethane. He found essentially the same magnitude for the anharmonicity corrections as found here. This indicated that the correction factors calculated in this work were calculated correctly, but Forst's work doesn't add anything to the methodology for treating anharmonicity. He arrives at the same results found in this work, using the same methods, for different molecules.

Rabinovitch⁷⁰ attempted to correct for anharmonicity in the thermal isomerization reaction of methyl isocyanide. His correction factor was based

on a direct counting procedure using the Morse potential, but he used a slightly different approach than Wilde in changing the energy levels from the harmonic model to the anharmonic model. His conclusions were the same as found in this work, that corrections for anharmonicity using a Morse potential function are hardly better than empirical corrections. However, he found that putting in anharmonicity corrections helped to fit the theory to experimental results in the low pressure fall off region of the unimolecular isomerization of methyl isocyanide. Rabinovitch's anharmonicity correction amounted to an increase of 25-50% at an energy of 40 kcal in the molecule for the density of states of the molecule, relative to the harmonic model. His correction factor varied according to the anharmonic model he used.

H. Comparison of calculated to experimental results.

There are two effects of anharmonicity on the calculated results, relative to the experimental results found in this work, the effect on the magnitude of the rate constant, and the effect on the unimolecular, non-equilibrium isotope effect.

Anharmonicity had the effect of increasing the calculated unimolecular isotope effect which gives better agreement with the experimental results. This arises because anharmonicity had a larger effect on the deuterated molecules, due to the lower apparent value of DE with respect to the hydrogenated molecule. Anharmonicity raised the calculated result for the d_5 isotope effect from 2.95 to 3.45; this compares well with the experimental effect of 3.4.¹³ The isotope effect for the d_3 case was raised from 1.82 to 2.2, in comparison with the experimental effect of 2.1.

The lowering of the calculated apparent rate constant when anharmonicity is included is the expected result, as discussed earlier. If it is assumed that the anharmonicity corrections applied in this work are valid, then a conflict arises between the calculated and experimentally measured rate constant. This conflict can be resolved, in general terms, by three approaches: (1) considering that the RRKM formulation is inadequate in some of the finer details. (2) Considering that the anharmonicity corrections were overestimates, and (3) considering the experimental values to be in error, and particularly questioning the magnitude of the collision cross sections used to define the collisional deactivation frequency. It is possible that the collision cross sections used to convert the experimental rate constants in pressure units to sec^{-1} units should be lower than the Lennard-Jones hard sphere cross sections normally used. If the cross sections used were lowered by some constant factor, the experiments would be brought into agreement with the calculated results and still fit the isotope effects calculated. However, fitting the absolute value of the rate constants is not a very good way of testing the theory, since several features of the model can be varied to give the desired value of the rate constant. Clearly a better test of the theory is needed, and it was hoped that isotope effects would provide this test, but they don't seem to be sufficiently sensitive to serve this purpose.

Another possibility for fitting the theoretical rate constants to the experimental rate constants would be to put in a special anharmonicity for the activated complex. This would raise the sum of states and the rate constant, and it may be justifiable to put in enough special anharmonicity to get exact agreement between theory and experiment. However, such special

anharmonicity has no physical basis and would amount to just another fitting parameter. It must be noted that any physically real treatment of anharmonicity must lower the calculated values of the rate constants, since anharmonicity increases the number of available vibrational states.

This work does not have any firm evidence to offer on these points, as the anharmonic corrections were too crude to be considered as final answers. All that can be said about the anharmonicity corrections used in this work is that they show the correct trends and are an effort to point the theory in the right direction.

APPENDIX 1. Relative output of the AH-6 lamp for photolyzing ketene.

Table A1-1 lists the values of the lamp output intensity,³⁸ Pyrex transmission coefficients,³⁹ ketene molar absorptancy⁴⁰ and quantum yields,⁴¹ as taken from various published sources. The last three quantities are only approximate values, as they were taken from graphs published in the appropriate sources. The values of the ketene quantum yields were available for only three wavelengths, and therefore, it was assumed that they were constant over the wavelength bands as indicated in Table A1-1.

Using the Beer-Lambert law, we can calculate the fraction of incident radiation absorbed by a representative sample of ketene: $\frac{I}{I_0} = e^{-\epsilon cl}$, where I_0 is the light intensity incident on the sample, I is the light intensity emerging from the sample, ϵ is the molar absorptancy of ketene, c is the concentration of ketene (1.88×10^{-2} mole l^{-1} for this calculation), and l is the path length (1 cm for this calculation). The fraction of the light absorbed is then $\frac{I_0 - I}{I_0}$. From Table A1-1, we can calculate the initial intensity by multiplying the lamp output by the Pyrex transmittancy, and assume that the reaction vessel is 1 cm. from the lamp. The amount of ketene reacted by photons from each wavelength band, R_i , is found by the expression:

$$R_i = I_0 \frac{(I_0 - I)}{I_0} \phi_{co}$$

Then the fraction of ketene photolyzed by each wavelength band, f_i , is given by:

$$f_i = \frac{R_i}{\sum_i R_i}$$

Table A1-1 Lamp output intensity and ketene photolysis parameters

$\lambda/\text{\AA}$	$I, \frac{\text{watts}^a}{\text{steradian}}$	$I, \frac{\text{photons}^b}{\text{cm}^2 \text{sec}} \times 10^{17}$	Pyrex transmission coefficient	ϕ_{C_0} for ketene ^c	$\epsilon, \text{l m}^{-1} \text{cm}^{-1}$ for ketene
2973	0.031	0.463	0.30	0.455	8.9
3024	0.068	1.04	0.40	0.455	10.0
3078	0.077	1.19	0.65	0.455	11.2
3130	0.315	4.96	0.70	0.455	12.5
3195	0.291	4.68	0.73	0.455	14.1
3259	0.265	4.35	0.79	0.455	12.5
3326	0.445	7.45	0.85	0.285	11.2
3397	0.365	6.25	0.90	0.285	10.0
3474	0.352	6.15	0.93	0.285	8.9
3558	0.368	6.59	0.95	0.00285	7.1
3649	2.51	46.2	0.95	0.00285	2.0
3747	1.50	28.3	0.95	0.00285	1.4
3855	0.87	1.69	0.95	0.00285	0.32

a. Pyrex jacket on the lamp, total lamp output.

b. I_0 ($\frac{\text{photons}}{\text{cm}^2 \text{sec}}$ at 1 cm) = I_0 watts $\times 10^{-4}$ $\frac{\text{watts}}{\text{cm}^2}$ at 1 m from the lamp $\times 10^4$ $\frac{\text{cm}^2}{\text{m}^2} \times 10^7$ $\frac{\text{erg/cm}^2 \text{sec}}{\text{watts/cm}}$

$\frac{\text{photons}}{\text{hc erg}}$

c. Values were available for only the 3130, 3340 and 3660 bands. These values were assumed constant over the wavelengths indicated.

Table A1-2 Calculated amount of ketene reaction

$\lambda, \text{\AA}$	$\frac{I_a}{I_0}$	$\frac{I_0 - I}{I_0}$	$I_0 \times 10^{17b}$	$R_t \times 10^{17c}$	f_t
2973	0.846	0.154	0.139	0.00974	0.00378
3024	0.829	0.171	0.416	0.0324	0.0126
3078	0.812	0.188	0.774	0.0662	0.0257
3130	0.791	0.209	3.47	0.330	0.128
3195	0.768	0.232	3.41	0.360	0.140
3259	0.791	0.209	3.43	0.326	0.127
3326	0.811	0.189	6.33	0.309	0.120
3397	0.829	0.171	5.63	0.248	0.0965
3474	0.846	0.154	5.72	0.881	0.342
3558	0.875	0.125	6.25	0.00251	0.00975
3649	0.963	0.077	43.8	0.00961	0.00374
3747	0.974	0.026	26.9	0.00199	0.000774
3855	0.999	0.001	1.68	4.78×10^{-5}	1.86×10^{-5}

a. calculated from the Beer-Lambert law, $\frac{I}{I_0} = e^{-\epsilon c l}$, with $c = 1.88 \times 10^{-2} \text{ m. l}^{-1}$ and $l = 1 \text{ cm}$.

b. calculated from I (Table A1-1) x Pyrex transmission coefficient

c. $\sum R_t = 2.577 \times 10^{17}$ molecules/cm² sec

Appendix II. Deviation of Equation 1 and 2.

A. Eq. 1

The steady state for methyl and chloromethyl radicals are:

$$\frac{d[\text{CH}_3]}{dt} = 3k_H [{}^3\text{CH}_2][\text{CH}_2\text{Cl}_2] - k_8[\text{CH}_3][\text{CH}_2\text{Cl}] - k_9[\text{CH}_3]^2 - k_{8a}[\text{CH}_3][\text{CHCl}_2] = 0 \quad (\text{A2-1})$$

$$\frac{d[\text{CH}_2\text{Cl}]}{dt} = 2^1 k_{C1} [{}^1\text{CH}_2][\text{CH}_2\text{Cl}_2] - k_7[\text{CH}_2\text{Cl}]^2 - k_8[\text{CH}_3][\text{CH}_2\text{Cl}] - k_{8a}[\text{CHCl}_2][\text{CH}_2\text{Cl}] = 0 \quad (\text{A2-2})$$

It is reasonable to assume that $[\text{CH}_3] = [\text{CHCl}_2]$, as these two radicals are related by mass balance providing they have similar removal rates. If the collision theory of radical recombination holds as has been shown for several cases,⁶⁵ then $k_8 = 2k_9$, $k_8 = k_{8a}$, $k_9 = k_7$. This reduces Eq. A2-1 and A2-2 to

$$3(\text{CH}_3)^2 + 2[\text{CH}_2\text{Cl}][\text{CH}_3] - \frac{3k_H[{}^3\text{CH}_2][\text{CH}_2\text{Cl}_2]}{k_9} = 0 \quad (\text{A2-3})$$

$$[\text{CH}_2\text{Cl}]^2 + 4[\text{CH}_3][\text{CH}_2\text{Cl}] - \frac{2^1 k_{C1} [{}^1\text{CH}_2][\text{CH}_2\text{Cl}_2]}{k_7} = 0 \quad (\text{A2-4})$$

Dividing Eq. A2-3 and A2-4 by $[\text{CH}_2\text{Cl}]^2$, we obtain:

$$3 \frac{[\text{CH}_3]^2}{[\text{CH}_2\text{Cl}]^2} + 2 \frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]} - \frac{3k_H [{}^3\text{CH}_2][\text{CH}_2\text{Cl}_2]}{k_9 [\text{CH}_2\text{Cl}]^2} = 0 \quad (\text{A2-5})$$

$$1 + 4 \frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]} - \frac{2^1 k_{C1} [{}^1\text{CH}_2][\text{CH}_2\text{Cl}_2]}{k_7 [\text{CH}_2\text{Cl}]^2} = 0 \quad (\text{A2-6})$$

Solving Eq. A2-6 for $[\text{CH}_2\text{Cl}]^2$:

$$[\text{CH}_2\text{Cl}]^2 = \frac{2^1 k_{C1} [{}^1\text{CH}_2][\text{CH}_2\text{Cl}_2]}{\frac{(1+4[\text{CH}_3])}{[\text{CH}_2\text{Cl}]} k_7} \quad (\text{A2-7})$$

Now substituting into Eq. A2-5, treating $\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}$ and $[\text{CH}_2\text{Cl}]^2$ as separate

variables:

$$3\left(\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}\right)^2 + 2\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]} - \frac{3k_H[{}^3\text{CH}_2][\text{CH}_2\text{Cl}]_2(1+4\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]})k_7}{k_9(2k_{C1}[{}^1\text{CH}_2][\text{CH}_2\text{Cl}]_2)} = 0 \quad (\text{A2-8})$$

Rearrangement of this expression gives Eq. 1:

$$\frac{3k_H[{}^3\text{CH}_2]}{k_{C1}[{}^1\text{CH}_2]} = \frac{3\left(\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}\right)^2 + 2\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}}{1+4\frac{[\text{CH}_3]}{[\text{CH}_2\text{Cl}]}}$$

B. Eq. 2

The steady state equations for ${}^1\text{CH}_2$ and ${}^3\text{CH}_2$ are:

$$\frac{d[{}^1\text{CH}_2]}{dt} = \phi_1 [\text{CH}_2\text{CO}] - {}^1k_{c1} [{}^1\text{CH}_2][\text{CH}_2\text{C}_1\text{I}_2] - ({}^1k_{c0} + {}^1k_3) [\text{CO}][{}^1\text{CH}_2] - {}^1k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{CO}][{}^1\text{CH}_2] = 0 \quad (\text{A2-9})$$

$$\frac{d[{}^3\text{CH}_2]}{dt} = \phi_3 [\text{CH}_2\text{CO}] - {}^3k_{c1} [{}^3\text{CH}_2][\text{CH}_2\text{C}_1\text{I}_2] - {}^3k_{c0} [\text{CO}][{}^3\text{CH}_2] - {}^3k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{CO}][{}^3\text{CH}_2] + {}^1k_3 [{}^1\text{CH}_2][\text{CO}] = 0 \quad (\text{A2-10})$$

Solving these eq. for $[{}^1\text{CH}_2]$ and $[{}^3\text{CH}_2]$, we have:

$$[{}^1\text{CH}_2] = \frac{\phi_1 [\text{CH}_2\text{CO}]}{{}^1k_{c1} [\text{CH}_2\text{C}_1\text{I}_2] + ({}^1k_{c0} + {}^1k_3) [\text{CO}] + {}^1k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{CO}]} \quad (\text{A2-11})$$

$$[{}^3\text{CH}_2] = \frac{\phi_3 [\text{CH}_2\text{CO}] + {}^1k_3 [{}^1\text{CH}_2][\text{CO}]}{{}^3k_{c1} [\text{CH}_2\text{C}_1\text{I}_2] + {}^3k_{c0} [\text{CO}] + {}^3k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{CO}]} \quad (\text{A2-12})$$

To put these expressions into useful form, containing known rate constant and reactant ratios, we multiply the denominator of Eq. A2-11 by ${}^1k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{C}_1\text{I}_2] / {}^1k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{C}_1\text{I}_2]$ and the denominator of

Eq. A2-12 by ${}^3k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{C}_1\text{I}_2] / {}^3k_{\text{CH}_2\text{CO}} [\text{CH}_2\text{C}_1\text{I}_2]$.

This gives us:

$$[{}^1\text{CH}_2] = \frac{\phi_1}{1 + \frac{1}{k_{\text{CH}_2\text{CO}}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \quad (\text{A2-13})$$

$$\left[\frac{1}{k_{\text{CH}_2\text{CO}}} + \frac{1}{k_3} \frac{[\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \right]$$

$$+ \frac{\phi_3}{3} \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{1}{3} \frac{k_3 [\text{CO}][\text{CH}_2]}{k_{\text{CH}_2\text{CO}}[\text{CH}_2\text{C}1_2]} \quad (\text{A2-14})$$

$$\left[\frac{3}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{3}{3} \frac{k_{\text{H}}}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \right]$$

Now substitute Eq. A2-13 into A2-14 and divide by A2-13:

$$\frac{3}{1} \frac{k_{\text{CH}_2}}{\text{CH}_2} = \frac{\phi_3}{\phi_1} \frac{1}{k_{\text{CH}_2\text{CO}}} + \left(\frac{1}{3} \frac{k_3}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{\phi_1}{k_{\text{CH}_2\text{CO}}} \right) \left(\frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{1}{k_{\text{CH}_2\text{CO}}} \right) + \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \quad (\text{A2-15})$$

$$\left[\frac{3}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{3}{3} \frac{k_{\text{H}}}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \right] \left[\frac{\phi_1}{\phi_1} \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \right] \left[\frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \right] + \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} + \frac{1}{k_{\text{CH}_2\text{CO}}} \frac{[\text{CH}_2\text{CO}]}{[\text{CH}_2\text{C}1_2]} \quad (\text{A2-15})$$

Cancelling out like terms, and multiplying both sides by $\frac{{}^3k_H}{{}^1k_{Cl}}$ gives us Eq. 2.

$$\frac{{}^3k_H [{}^2CH_2]}{{}^1k_{Cl} [{}^1CH_2]} = \frac{{}^3k_H}{{}^1k_{Cl}} \left[\frac{{}^1k_{CO} + {}^1k_3}{{}^1k_{CH_2CO}} \frac{CO}{CH_2Cl_2} + \frac{{}^1k_{Cl}}{{}^1k_{CH_2CO}} + \frac{{}^1k_{Cl}}{{}^1k_{CH_2CO}} \frac{[CH_2CO]}{[CH_2Cl_2]} \right] + \frac{\left(\frac{{}^3k_{CO}}{{}^3k_{CH_2CO}} \frac{[CO]}{[CH_2Cl_2]} + \frac{{}^3k_H}{{}^3k_{CH_2CO}} + \frac{[CH_2CO]}{[CH_2Cl_2]} \right)}{{}^1k_3}$$

$$\frac{{}^3k_{CH_2CO}}{{}^3k_{CH_2CO}} \left[\frac{{}^3k_{CO}}{{}^3k_{CH_2CO}} \frac{[CO]}{[CH_2Cl_2]} + \frac{{}^3k_H}{{}^3k_{CH_2CO}} + \frac{[CH_2CO]}{[CH_2Cl_2]} \right] \quad (2)$$

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STUDIES OF UNIMOLECULAR REACTIONS OF CHEMICALLY ACTIVATED
CHLOROALKANES AND IDENTIFICATION OF REACTIONS OF
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ABSTRACT

Methylene reacts with chloromethanes by an abstraction mechanism. Both a hydrogen and a chlorine atom are abstracted. In order to differentiate between the reactions of the two low energy electronic states of methylene, the reaction of methylene with dichloromethane in the presence of various amounts of added carbon monoxide was studied. Carbon monoxide is known to be a scavenger for the ground, triplet state of methylene. The singlet methylene produced by this technique was found to react with dichloromethane by abstracting a chlorine atom. From consideration of the radical recombination reactions taking place in the system, it was deduced that triplet methylene reacts with dichloromethane only by abstracting a hydrogen atom. A study of the relative rates of reaction of singlet methylene with dichloromethane and *cis*-2-butene showed that singlet methylene abstracts a chlorine atom from dichloromethane as fast as it adds to the double bond of *cis*-2-butene. Analysis of the relative product yields as a function of carbon monoxide added to the reaction of methylene with dichloromethane indicates that singlet and triplet methylene react with CH_2Cl_2 with approximately equal rate constants.

As an extension of the earlier work of Dees, and in an effort to further refine the models used to describe the nonequilibrium, unimolecular elimination of hydrogen chloride from highly vibrationally excited chloroalkanes, the nonequilibrium kinetic isotope effect of 1,1,1-trideuteriochloroethane relative to chloroethane- h_5 was studied. The appropriate radicals were generated by the mercury (6^3P_1) photosensitization of a mixture of chloromethane- d_3 or chloromethane- h_3 and dichloromethane. An isotope effect of 2.1 was found which is in agreement with the models developed for chloroethane- h_5 and chloroethane- d_5 reactions.

The effect of anharmonicity on the specific rate constants and upon the nonequilibrium isotope effect for the unimolecular elimination of hydrogen chloride from chloroethane- h_5 , $-\text{d}_3$, and $-\text{d}_5$ was studied, using the RRKM (Rice-Ramsperger-Kassel-Marcus) theory of unimolecular reactions. Anharmonicity was introduced into this formulation through the density of vibrational states of the molecule and the sum of vibrational state of the activated complex. The general formulation of anharmonicity was to treat each vibrational mode of the molecule and complex as a Morse oscillator, with a dissociation energy related to the anharmonicity of the vibrational mode. This allowed a correction factor for the sum and density of vibrational states to be calculated, using the Haarhoff approximation.

The specific rate constant for the unimolecular elimination of hydrogen chloride from 1-chloropropane, 1,3-dichloropropane, 1-chlorobutane, 1,3-dichlorobutane, 3-chloro-1-propene, and 4-chloro-1-butene were calculated. These calculations were done in order to investigate the possibility of these systems serving as models for observing the successive elimination of hydrogen chloride from 1,3-dichloropropane and 1,4-dichlorobutane. The purpose of such an observation is to determine the energy distribution of the products of the first elimination of hydrogen chloride by matching the rate constant of the second reaction to the calculated rate at an appropriate energy.