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Infrared laser multiple-photon dissociation of $CDCl_3$ in a molecular beam[a]

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Pulsed CO_2 laser multiple-photon dissociation of $CDCl_3$ was examined in a molecular beam using 11 μ radiation. The only observed dissociation channel was hydrogen chloride elimination ($> 99.1\%$), with no evidence of simple chlorine atom cleavage ($< 0.9\%$). Implications for isotope separation are discussed.

I. INTRODUCTION

The determination of the primary dissociation steps in the classical pyrolysis and bulb infrared multiple-photon dissociation (MPD) of molecules is sometimes complicated by subsequent homogeneous and heterogeneous chemistry. Pulsed infrared laser MPD in a molecular beam has been used to clarify the ground electronic state decomposition pathways in some systems, taking advantage of the collisionless environment to detect directly the primary products. This technique is used here to elucidate the unimolecular reaction mechanism of deuterated chloroform.

A molecular beam study of the MPD of chloroform ($CDCl_3$) is of interest because past studies[1-5] have failed to determine unambiguously whether hydrogen chloride or chlorine atom elimination is the dominant initial step in thermal decomposition:

$$CDCl_3 \rightarrow :CCl_2 + DCl \qquad (1)$$

$$\rightarrow \cdot CDCl_2 + Cl\ . \qquad (2)$$

Furthermore, recent studies have shown that MPD of $CTCl_3/CDCl_3$ gas mixtures with $12\,\mu$ photons is highly isotopically selective in decomposing tritiated chloroform.[6,7] Since this T/D selective MPD method can efficently remove tritium from contaminated heavy water fission reactor D_2O inventories, knowledge of the unimolecular decay pathway of chloroform is particularly important. The MPD of the deuterated version of chloroform is examined here for convenience because the ν_4 mode of $CDCl_3$ is resonant with several lines from a CO_2 laser oscillating near $11\,\mu$.

Several investigations of the thermal decomposition of chloroform have been conducted. In an early, detailed study, Semeluk and Bernstein[1] pyrolyzed $CHCl_3$ and $CDCl_3$ in both static and flow systems and concluded that the nascent step is chlorine atom elimination, which (for $CDCl_3$) is followed by the steps:

$$Cl + CDCl_3 \rightleftharpoons DCl + \cdot CCl_3\ , \qquad (3)$$

$$\cdot CCl_3 + Cl + M \rightarrow CCl_4 + M\ , \qquad (4)$$

$$\cdot CCl_3 \rightarrow :CCl_2 + Cl\ , \qquad (5)$$

$$:CCl_2 + CDCl_3 \rightarrow C_2Cl_4 + DCl\ , \qquad (6)$$

and a number of other radical reactions. DCl and C_2Cl_4 were formed as the major products and several chlorinated methanes and ethanes as minor products. They estimated an upper limit for the activation energy of reaction (2) of 72 kcal/mol.

In those chloroform pyrolysis studies in which hydrogen chloride elimination is deduced to be the nascent step, the proposed reaction mechanism consists of reaction (1) followed by reaction (6) and

$$:CCl_2 + :CCl_2 + M \rightarrow C_2Cl_4 + M \qquad (7)$$

Shilov and Sabirova[2] pyrolyzed separate samples of $CHCl_3$ and $CDCl_3$, either neat or with added light hydrogenated toluene in a flow reactor. Since no HCl was observed when $CDCl_3$/toluene mixtures were pyrolyzed, they deduced that there were no free chlorine atoms, and that hydrogen chloride elimination is the nascent step with a measured 47 kcal/mol activation energy. Engelsma[3] arrived at a similar conclusion by examining the thermal decomposition of chloroform in the presence of one of several different olefins in a flow reactor. In each case he observed the dichlorocyclopropane product expected from the addition of dichlorocarbene [from reaction (1)] to the respective olefin. However, in no case did he observe products due to olefin plus Cl or $\cdot CCl_3$ [from step (3)] reactions. Murgulescu and Weissmann[4] added CH_4 to $CHCl_3$ in a flow reactor and deduced that reaction (1) was the dominant route because the observed products apparently resulted from the competitive formation and subsequent decomposition of ($:CCl_2 + CHCl_3 \rightarrow$) pentachloroethane and ($:CCl_2 + CH_4 \rightarrow$)1, 1 dichloroethane.

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Wall reactions may have distorted the observations in these static and flow reactor studies. Yano[5] investigated the expectedly cleaner, shock-tube decomposition of $CHCl_3$ and of $CDCl_3$, with added D_2, CH_4, or CD_4 and concluded that Cl elimination is the first step in chloroform dissociation on the basis of the hydrogen isotope distribution in the products.

Two other studies reported in the literature were concerned with determining the activation energy of the initial step in chloroform thermal decomposition, which in both cases was presumed to be step (1). In a very low pressure pyrolysis reactor, Benson and Spokes[8] obtained a lower limit of 53 kcal/mol for the activation energy. Schug *et al.*[9] measured the appearance of C_2Cl_4 by ultraviolet absorption after a shock tube pulse, giving a 54.5 kcal/mol activation energy (1200 K). Subsequent analysis[10] yielded a 51.6 kcal/mol barrier height for this reaction.

Magnotta, Herman, and Aldridge[6,7] recently observed highly isotopically selective 12μ MPD of dilute $CTCl_3/CDCl_3$ mixtures. Their measurement of extremely high single step T/D enrichment factors ($\beta \gg 1000$), implies that if reaction (2) does occur to a significant degree, any chain mechanism occurring after the initiation MPD step must be very short. In bulk MPD of $CDCl_3$ using resonant $10.9-11.1\mu$ CO_2 radiation,[11] C_2Cl_4 was again found to be the major observed carbon-bearing product. Much C_2Cl_2 was also detected, which is presumably formed by the decomposition of the hot C_2Cl_4 formed by steps (6) and (7). However, even after heterogeneous effects were removed, CCl_4 was still observed; this is not easily reconciled in a mechanism assuming only hydrogen chloride elimination from chloroform unless CCl_4 is formed as the result of the decay of hot C_2Cl_4.

The relative importance of the two channels in the overall unimolecular decomposition is dependent on the level of excitation. A pyrolysis experiment tends to favor the channel with the lowest barrier and most decomposition occurs just above threshold. Shock tube excitation may generate a much hotter molecule and the observed branching ratio can be quite different from the pyrolysis experiment, though the apparent discrepancies in the chloroform decomposition experiments do not appear to be due to this. The level of excitation reached in multiple-photon excitation is fluence and intensity dependent, and therefore it is important to investigate the dissociation behavior with laser excitation if this method is to be used for isotope separation.

II. EXPERIMENTAL ARRANGEMENT

A supersonic molecular beam of $CDCl_3$ crossed the focused beam of a pulsed TEA CO_2 laser in a liquid nitrogen cooled chamber maintained near 5×10^{-7} Torr. Dissociation products were detected in the plane defined by the laser and the molecular beam by a rotatable mass spectrometer consisting of an electron bombardment ionizer, quadrupole mass filter and ion counter. Details of this apparatus have been provided previously.[12]

The molecular beam was formed by expanding 170 Torr of neat $CDCl_3$ in a supersonic nozzle maintained at 340 °C. The molecular beam was characterized by a 6.6×10^4 cm/s peak velocity with a FWHM velocity spread of 20% as determined by time of flight (TOF) measurements.

The Lumonics 103 CO_2 laser passed through a 50 cm focal length lens and then was focused to an $\sim 2\times 3$ mm area on the molecular beam. It was then retroreflected and refocused to the same place on the $CDCl_3$ beam with the same area, by a 40 cm radius of curvature mirror placed 40 cm beyond the beam. The laser provided ~ 1.5 J at the $P(50)$, 10.94μ (914.4 cm^{-1}) line used, which is resonant with the peak of $\nu_4 \leftarrow 0$ transition in room temperature $^{12}CD^{35}Cl_3$ (914 cm^{-1}). The maximum net fluence incident on the $CDCl_3$ beam is estimated to be ~ 35 J/cm^2, which exceeds the ~ 25 J/cm^2 needed [at $P(48), 10.9\mu$] to saturate the MPD of $CDCl_3$ in room temperature, bulb experiments.[7]

Further details regarding experimental technique may be found in Ref. 13.

III. EXPERIMENTAL RESULTS AND ANALYSIS

The contribution of hydrogen chloride elimination [step (1)] was determined by the $:CCl_2$ chlorine isotope peaks at masses 82, 84, and 86 and the $\vdots CCl$ fractionation products at masses 47 and 49. Reaction (2) was analyzed by the chlorine atom elimination product $\cdot CDCl_2$ at masses 84, 86, and 88 and at masses 49 and 51 for the $:CDCl$ fragmentation product. In analogy with the fragmentation pattern of $CDCl_3$, it is assumed that in the ionizer the main fragments of $:CCl_2$ and $\cdot CDCl_2$ are $:CCl^+ + Cl$ and $\cdot CDCl^+ + Cl$, respectively, which are formed with equal cross section. Since $\nu_4 \leftarrow 0$ in all the $^{12}CDCl_3$ chlorine isotopes are very close in frequency (the isotope shift in $^{12}CD^{37}Cl_3$ relative to $^{12}CD^{35}Cl_3$ is only 0.4 cm^{-1}),[14] no significant chlorine isotope enrichment is anticipated in the products. Consequently, the natural $^{35}Cl:{}^{37}Cl$, 3:1 ratio is used to determine reaction branching to routes 1 and 2. Furthermore, product from the two channels is expected to exhibit different angular and velocity distributions because the three-center DCl elimination probably has an exit barrier (~7 kcal/mol)[15] which will channel energy into translation, while the simple C–Cl bond cleavage without such a barrier will have low product translational energy and hence a narrow angular distribution.

The mass peak amplitudes at 82, 84, and 86 and at 47 and 49 were in the expected isotopic ratios for $:CCl_2$ and $\vdots CCl$. The $\vdots CCl$ peaks were typically three to four times larger than those for $:CCl_2$. No significant signal was observed at either 88 or 51 corresponding to $\cdot CD^{37}Cl_2$ and $:CD^{37}Cl$. There were 12.91 ± 0.27 counts per pulse at mass 47 and -0.090 ± 0.065 counts per pulse at mass 51 at 8° with maximum fluence (~35 J/cm^2) irradiating the $CDCl_3$ beam. Using the expected ratio of $:CCl_2/\cdot CDCl_2$ signal at 8° if the reaction rates for steps (1) and (2) were equal (0.62 ± 0.20), which accounts for kinematic differences, and the expected chlorine isotope factor for mass 47/mass 51 (3.09), the chlorine reaction contribution is <0.9% (for two standard

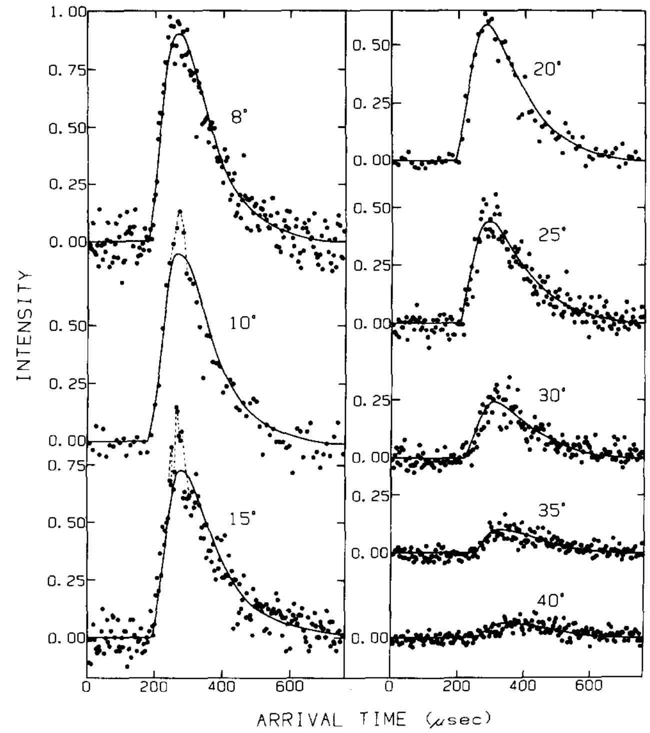

FIG. 1. Time of flight data at several laboratory angles for the mass 47 fragment from $:CCl_2$, with best product translational energy distribution fits.

deviations). Under these reaction conditions, the only major dissociation channel is the molecular elimination of DCl (>99.1%).

Time of flight data for the mass 47 fragment from $:CCl_2$ is shown in Fig. 1 for various laboratory detection angles. In Fig. 2, the integrated signal is plotted vs angle. Error bars signify two standard deviations statistical error.

The product translational energy distribution [$P(E)$] was obtained from the angular and TOF data by the direct convolution of an assumed $P(E)$ and center-of-mass angular function with the known velocity spread of the $CDCl_3$ beam. The product was assumed to be isotropically distributed in cm angle and a flexible functional form for the $P(E)$ was varied to obtain best fit to the data. The resulting $P(E)$, shown in Fig. 3, gives the best fit curves shown as solid lines in Figs. 1 and 2. Also shown in Fig. 2 (dashed curve) is the expected angular distribution of the $\cdot CDCl_2$ product from Cl atom elimination assuming a statistical $P(E)$.

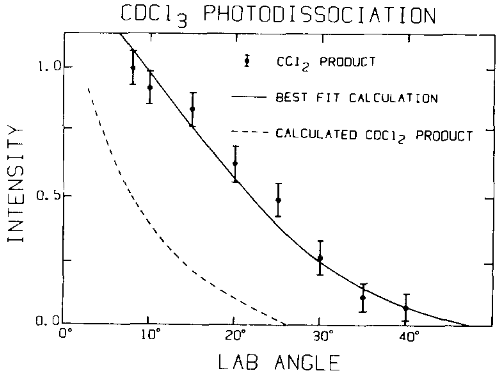

FIG. 2. Total mass 47 signal vs laboratory angle with best translation energy distribution fit for the $:CCl_2$ product (unbroken line). Calculated $\cdot CDCl_2$ product vs angle fit also shown (dashed line).

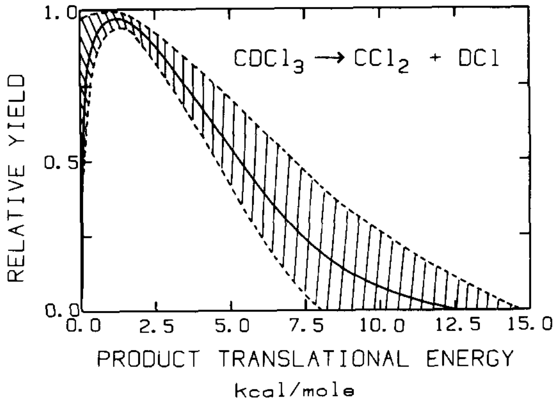

FIG. 3. Calculated product translational energy distribution fit to data in Figs. 1 and 2.

As seen in Fig. 3, the average energy in product translation is 2.8 kcal/mol, while the fastest product has kinetic energy about $12.5\pm^{1.5}_{4.5}$ kcal/mol.

IV. DISCUSSION

The reaction mechanism for the unimolecular decay of a moleculelike chloroform depends on the relative barrier heights for the possible processes and their statistical factors. A simple bond cleavage, as in reaction (2), will typically have a loose critical configuration and will be favored statistically over a three center elimination with a tight complex [reaction (1)]. However, the barrier heights of the complex elimination may be significantly lower than that of the simple bond cleavage, overcoming the statistical disadvantage at lower levels of excitation. This is certainly the case in the present study in which the DCl elimination is found to be the only product channel.

The endoergicities of reactions (1) and (2) may be obtained from the measured enthalpies of the protonated species of interest (Table I). For reaction (1), ΔH is 56±3 kcal/mol, with the dichlorocarbene heat of formation the major uncertainty. Evidently, Ref. 18 gives the most precise value, 53.4±2.5 kcal/mol; earlier measurements ranged from 46–57 kcal/mol.[19,20] The reverse reaction barrier is expected to equal roughly the 7 kcal/mol barrier for $CF_2HCl \rightarrow :CF_2 + HCl$[15] since both reactions are $\alpha-\alpha$ HCl eliminations from halomethanes. The barrier height for DCl elimination from $CDCl_3$ should then be $E_0 \sim 63$ kcal/mol. This is much higher than the barrier height determined by Schug *et al.*(51.6 kcal/mol)[9,10] by shock-tube pyrolysis of $CDCl_3$.

Using Table I, ΔH for chlorine atom elimination [reaction (2)] is 79 kcal/mol. This is significantly

TABLE I. Enthalpies of reactants and products (kcal/mol).[a]

$CHCl_3$	-24.6^b
$\cdot CHCl_2$	25.7^b
$:CCl_2$	53.4 ± 2.5^c
HCl	-22.0^b
Cl	28.9^b

[a] These cited enthalpies, as well as the reaction endoergicities and the barrier heights determined in this study, are at 300 K. Correction to 0 K, as is sometimes done for RRKM analysis, lowers the endoergicities of reactions (1) and (2) by ~0.6 and ~1.3 kcal/mol, respectively. This change in the relative energy of the two reaction channels (0.7 kcal/mol) is small compared to the uncertainty of ΔH for $:CCl_2$.

[b] References 16 and 17.

[c] Reference 18.

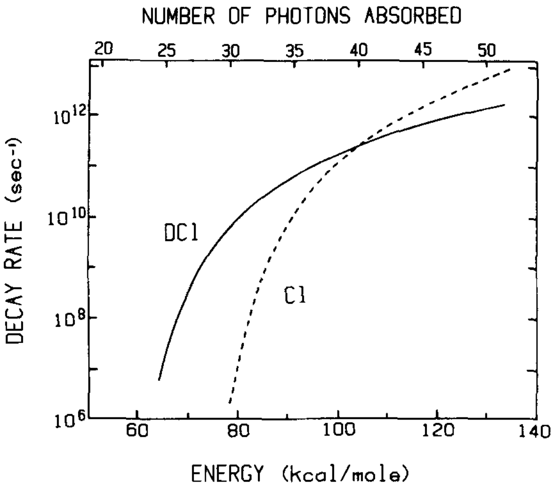

FIG. 4. Calculated RRKM reaction rates vs molecular energy or equivalent 11μ photons for DCl and Cl elimination. For DCl elimination (62 kcal/mol barrier, $\log A = 14.3$), the model included five adjustable activated complex frequencies, while for Cl bond cleavage (79 kcal/mol barrier, $\log A = 15.8$) there were two adjustable modes.

higher than for Cl removal from CCl_4 (70 kcal/mol),[17] but comparable to other similar molecules such as CF_2Cl_2 (80 kcal/mol).[13] Since simple atom fissions have quite small reverse barriers, the barrier height for reaction (2) should also be 79 kcal/mol.

RRKM calculations were performed to determine the statistical unimolecular decay rates of reactions (1) and (2). Intramolecular relaxation is assumed to be complete before reaction, and rotational effects have not been included. The chloroform molecular frequencies used for these calculations are listed in Table II. For DCl elimination, three $CDCl_3$ activated complex frequencies were fixed at ν_1, ν_2, and ν_6, and the other five were assumed degenerate, and were varied to obtain the desired Arrhenius preexponential factor, A. For the Cl elimination transition state complex, the molecular ν_3 mode, and one each of the doubly degenerate ν_5 and ν_6 modes (all involving CCl stretch or CCl_3 rocking) were transferred to two degenerate complex frequencies and the reaction coordinate translation. Again, the variable complex frequencies were adjusted to obtain the desired A factor. A tight complex was assumed for step (1) with $\log_{10}A = 14.3$, as measured in shock tube pyrolysis of $CHCl_3$,[9] used as the most representative value while for step (2), $\log_{10}A$ of the assumed loose complex should be significantly larger and was chosen to be 15.8. The exact number of varied frequencies in the model of the complex, did not significantly affect the results. For instance, the DCl elimination complex model with five adjustable frequencies was modified to one with two varying frequencies, in which one each ν_4, ν_5, and ν_6 molecular mode was removed. The unimolecular lifetime at 70.5 kcal/mol then only decreased from 2.74 to 2.32 ns.

Typical results are shown in Fig. 4. For DCl elimination the base case barrier height is 62 kcal/mol, while for Cl bond fission it is 79 kcal/mol. Plots similar to those presented here, with the route 1 critical energy varying but that of route 2 fixed, can be used to obtain an upper limit for the barrier height, using the experimental observation that the branching ratio to route 2 is $<1\%$. If the average decomposing molecule has a ~1 ns lifetime, due to the dynamics of laser pumping and the dissociation rates, then the DCl route barrier height must be ≤ 66 kcal/mol. The reverse reaction barrier for reaction (1) must then be <10 kcal/mol for $\Delta H = 56$ kcal/mol. For smaller A values, the barrier height decreases; with $\log A = 13.8$ the forward barrier must then be <62 kcal/mol.

If products with maximum translational energy are rotationally and vibrationally cold, then this maximum kinetic energy equals the sum of the excess energy absorbed above the barrier and the reverse reaction barrier. With a maximum translational energy of 12.5 kcal/mol (Fig. 3), RRKM calculations ($\log A = 14.3$; DCl elimination) support a reverse barrier of 2.8–6.5 kcal/mol for decay times ranging from 1–10 ns, as expected in MPD. The uncertainty in the maximum translational energy in Fig. 3 (8–14 kcal/mol) leads to

TABLE II. Chloroform molecular frequencies (cm^{-1}).

	$CHCl_3^a$	$CDCl_3^a$	$CTCl_3^b$
ν_1	3033	2265	1932
ν_2	675	658	633
ν_3	367	364	361
ν_4	1220	914	835
ν_5	774	747	673
ν_6	260	259	259

[a] Reference 14.

[b] ν_5 was measured in Ref. 6. Other values were calculated in Ref. 21.

a range in reverse barrier energies of 2.8–7.6 kcal/mol for 10 ns decay. In this regime, a differential change in $\log A$ of +0.1, increases the expected barrier by +0.35 kcal/mol. The 5 ± 2 kcal/mol reverse barrier height suggested here for $CDCl_3$ dissociation is consistent with the 7 kcal/mol height measured for $CF_2HCl \rightarrow :CF_2 + HCl$.[15] The maximum reactant energy is ~68.5 ± 3 kcal/mol, assuming that the maximum product translational energy equals the total product energy; this has not been firmly established for three-center reactions. If this is not the case, the $CDCl_3$ is even more highly excited before it decomposes.

The branching ratios to routes 1 and 2 for the reported studies of chloroform pyrolysis can be calculated by convoluting the respective RRKM reaction rates plotted in Fig. 4 [for the $CDCl_3$ base case of 62 kcal/mol barrier and $\log A = 14.3$ for reaction (1), and 79 kcal/mol barrier and $\log A = 15.8$ for reaction (2)] with the population distribution. Assuming that collisions always maintain thermal equilibrium, the number of molecules with total vibrational energy E is given by[22]

$$N(E) \propto \frac{\left(\dfrac{E}{h\nu}\right)^{s-1}}{(s-1)!}\, e^{-E/kT}\,, \tag{8}$$

where s is the number of modes and $h\nu$ is the geometrical mean of the vibrational eigenfrequencies. For $CDCl_3$ $s = 9$ and $h\nu = 635\ \mathrm{cm}^{-1}$. At 800 K, typical of the reported flow tube studies, only an 8.7×10^{-4} fraction of reacting molecules should decompose via reaction (2). In the shock tube study of Yano[5] the temperature was varied from 1000–1200 K, for which the chlorine atom fractional contribution ranges from 6.9×10^{-3}–2.7×10^{-2}. The highest temperature in the shock tube investigation by Schug *et al.* [9] was 1380 K, with an expected branching fraction of 6.6×10^{-2} to route 2. (These branching fractions are smaller in $CHCl_3$ than in $CDCl_3$ by 5%–10%, as shown using the $CHCl_3$ RRKM rates obtained below.) Therefore, chlorine atom cleavage can dominate the observed kinetics of chloroform pyrolysis only if Cl atoms start very long chain reactions (length ≫ 100) via reaction (3), or if there are significant heterogeneous reactions.

RRKM unimolecular reaction rate constants were also determined for $CHCl_3$ and $CTCl_3$ using the activated complex model described above. The absolute isotope effects for reactions (1) and (2), as well as the isotope effects on the branching ratios, were examined. For $CDCl_3$, the critical energy and $\log A$ were fixed at 62 kcal/mol and 14.3, respectively for DCl elimination, and 79 kcal/mol and 15.8 for Cl fission. $CHCl_3$ and $CTCl_3$ vibrational frequencies are presented in Table II. The complex frequencies were adjusted either to obey the Teller–Redlich isotope product frequency rule[23] for the asymmetric activated complex or to maintain the same pre-exponential factor for each isotope. Since part of a C–H/D/T vibrational mode is converted to translation along the reaction coordinate, for hydrogen chloride elimination use of the Teller–Redlich rule for the reaction (1) transition state may overestimate the isotope shifts. However, both the complex frequencies obtained and resulting A factors for each model are very nearly equal, and indeed the calculated reaction rates are found to be within 5% of each other. For both $CHCl_3$ and $CTCl_3$ the critical reaction energies were shifted from the $CDCl_3$ value by the isotopic change in the molecule and complex zero-point energy difference. Both the adjustable two and five frequency models were tested for HCl/DCl/TCl elimination, for which the zero-point energy correction was quite important. The isotopic ratios of rate constants were virtually identical for both models; above one quantum over the critical energy, the ratios were within 5% of each other.

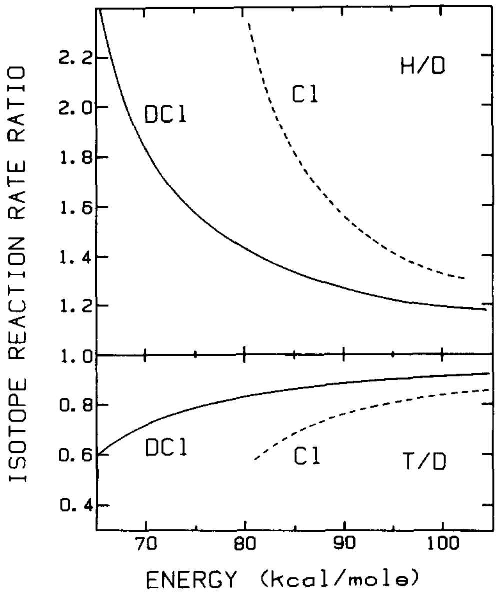

FIG. 5. Ratio of calculated RRKM reaction rates of chloroform for the H/D and T/D isotope pairs vs energy for both reaction (1)/molecular elimination and reaction (2)/Cl elimination. The top half curve labeled "DCl" is the HCl/DCl ratio from reaction (1), while that labeled "Cl" is the atom ratio from $CHCl_3$ vs $CDCl_3$. The bottom half shows similar ratios for $CTCl_3/CDCl_3$ photolysis. The base case for $CDCl_3$ is reaction (1): 62 kcal/mol barrier, $\log A = 14.3$; reaction (2): 79 kcal/mol barrier, $\log A = 15.8$. Five (two) complex frequencies were adjusted for route 1(2), using either the Teller–Redlich product rule or an isotope-independent $\log A$. Plotted results show an average of the two methods, and include zero-point energy effects.

As expected, the reaction rate ratios for isotopes were largest just above the critical energy and monotonically approached unity at higher energies. For $CHCl_3 \rightarrow :CCl_2 + HCl$ the zero-point energy change and the statistical weight effect equally influence the primary isotope effect. However, for $CTCl_3$ [reactions (1) and (2)] and $CHCl_3$ [reaction (2)] the statistical weight effect dominates.

The ratios of the unimolecular reaction rates for isotope pairs are plotted in Fig. 5. In $CDCl_3$ the lifetime is ~3 ns (and thus typical of MPD decomposition) for an energy of 70.5 kcal/mol, corresponding to the absorption of 27 11μ equivalent energy photons; this amounts to ~3 quanta above the barrier. At this energy for route 1, the TCl/DCl ratio is ~0.73, while for HCl/DCl it is 1.74–1.87 (depending on the complex frequency model used). Increasing the energy to 83.5 kcal/mol

(32 quanta) route 1 still dominates and the branching ratio [reaction (1)/reaction (2)] decreases to 60. At this energy this branching ratio is larger in $CTCl_3$ by a factor of 1.29 and smaller in $CHCl_3$ by a 0.70 factor. As expected, this branching ratio is always relatively larger in $CTCl_3$ than in $CDCl_3$ and smaller in $CHCl_3$, and at higher energies both the isotopic branching ratio factors approach unity. These calculations suggest that the very large DCl/Cl elimination branching ratio observed here will be even larger for MPD of $CTCl_3$, assuming similar photon absorption dynamics. Consequently, under typical experimental conditions only TCl elimination is expected from infrared laser photolysis of $CTCl_3$. This has quite favorable implications for tritium-from-deuterium isotope separation by MPD of chloroform.

Physical separation of the isotope-enriched product can be complicated in photochemical isotope separation schemes with two (or more) accessible reaction channels because of the isotopic enrichment of more than one product. For T/D recovery by MPD of chloroform, the expected enriched products are TCl and tritiated alkanes (such as $CDTCl_2$) for reactions (1) and (2), respectively. Ideally, experimental conditions should be adjusted so only one reaction channel is accessed. In chloroform, Cl atom elimination (reaction 2) can lead to nonselective, chain reactions (reaction 3)—which can seriously degrade the overall T/D enrichment in the products, though they may not decrease the yield of tritiated products. With TCl elimination, the only possible source of deuterium product formation, other than isotopic scrambling of products, is reaction (6); for the dilute T/D mixtures of practical interest,[6] this does not noticeably degrade performance. Therefore, for isotope separation using chloroform reaction (1) is preferred to reaction (2). This study shows that for (otherwise) desirable operating conditions, TCl elimination will totally dominate MPD, as is desired in T/D separation. The laser fluence and intensity must be chosen to limit excitation to levels where the Cl channel is still not competitive. From Figs. 4 and 5 it can be seen that the chloroform molecule must not be pumped to levels much higher than about 30 photons (corresponding to 11 μ), at which the Cl atom yield is still negligible. The lifetime of $CTCl_3$ must be greater than ~0.1 ns if reaction (2) is to remain insignificant.

In principle, the fluence and intensity limitations imposed by the competitive Cl reaction could impose a maximum pressure limitation for MPD of chloroform by reaction (1) alone, in a gas cell. In molecules with only one accessible reaction channel, such as SF_6, a high collision rate can be compensated by increasing the laser fluence or intensity thereby pumping the molecule higher and shortening its lifetime. This is not feasible for chloroform because of competition with reaction (2). However, in cases of interest, the laser pulse width (2–100 ns FWHM) is much longer than the shortest attainable reaction (1) unimolecular lifetime with no contribution from reaction (2) (0.1 ns). Consequently, high pressure operation is limited by collisions occurring both during laser excitation and after excitation (only for the molecules weakly excited above the barrier), and not by the fluence and intensity limitations on the highest excited reacting level.

V. CONCLUDING REMARKS

The primary unimolecular decay process of $CDCl_3$, excited by multiple 11 μ photon absorption, was found to be the molecular elimination of DCl. Angular and velocity distributions of the product are consistent with the existence of a small barrier (~7 kcal/mol) for the reverse reaction. More detailed knowledge of exit channel features should come from studies of the reverse reaction.

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