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LASER-INDUCED DECOMPOSITION OF SOME ALLYL HALIDES

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20. Abstract (Cont'd).

Kinetic studies of allyl bromide and chloride were also performed. The bromide and chloride were determined to follow a first and three-halves overall reaction order, respectively.

Most of the products observed from laser-induced decomposition are also formed in pyrolysis; however, differences in concentrations were also observed. Formations of polymeric deposits were found to be small. Benzene was one of the main products in all of the allyl halide decompositions.

Chlorobenzene and toluene were produced from the laser-induced decomposition of 2,3-dichloropropene and 2-methyl-3-chloropropene, respectively.

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## I. INTRODUCTION

The development of chemical processes that are cleaner with higher yield and less costly, are highly desirable. Using lasers to drive some chemical reactions has provided these results [1-5]. The recent widespread availability of tunable lasers has enhanced the interest in photochemical processes. The output of a carbon dioxide (CO<sub>2</sub>) infrared laser is resonant with the vibrational frequencies of a wide range of organic molecules; therefore, this type of gas laser has become the most popular for studies of infrared laser-induced chemical processes [1,2]. The absorption of the laser radiation by the molecules promotes the molecules into excited vibrational states, thus causing the molecules to become very reactive.

In principle, the laser energy can be deposited into a single vibrational mode and the vibration excited to the point of dissociation [3,4]. The resulting reactive species would be expected to react further. However, energy relaxation within a given vibrational mode generally occurs on a time scale of picoseconds [5]. For complex molecules there is also a redistribution of energy among different vibrational modes and rotational and translational levels. Furthermore, at pressures of a few torr and higher, intermolecular redistribution accompanies collisions. Consequently it has been concluded that only a few microseconds [5] are required for a molecule (which has been excited by an infrared laser) to reach a thermal equilibrium. Once the laser energy has been distributed throughout the molecule, any reaction which proceeds would very likely be similar to an ordinary pyrolysis reaction. Even if the reactions are governed by thermal processes, the laser-induced reactions will generally differ from ordinary pyrolytic thermal reactions because wall reactions are essentially eliminated from the former. In that case, it should be possible to compare the results of laser-induced "thermal" reactions with those carried out in shock tubes.

Elimination reactions have been extensively investigated in polyatomic molecules exposed to an intense infrared laser field [5]. The results obtained with organic halides have been the elimination of hydrogen halide and the formation of an alkene or alkyne compound. Some fragmentation of the parent molecule is also observed depending on the molecular size and laser fluence. However, recombination of radicals or thermally excited parent molecules to form larger molecules is usually not observed.

Pyrolysis of organic halides is found to follow several reaction paths, including unimolecular, radical chain, and bimolecular reactions [6,7]. These reactions can produce simple and complex molecules by decomposition and radical addition.

The allyl-type halides comprise a group of compounds with enhanced reactivity which is utilized in many hydrocarbon synthesis. The allyl halides exhibit a series of very strong absorption bands in the 900 - 1000 cm<sup>-1</sup> region which are resonant with the output of the CO<sub>2</sub> laser. This afforded an opportunity for comparison of products produced from laser-induced reactions to pyrolysis experiments.

## II. EXPERIMENTAL

Samples of allyl chloride, 2-methyl-3-chloropropene, and 2,3 dichloropropene were obtained commercially. Their stated purities ranged between 95 percent and 99 percent, and each was used without further purification. Samples of allyl bromide and allyl fluoride were obtained from the Chemistry Department of the University of South Carolina. All sample transfers were performed using standard vacuum techniques.

The reactions were carried out in stainless steel cells (5 x 10 cm) equipped with O-ring seals for securing the windows (5 cm diameter) onto the cells. The infrared beam entered through ZnSe windows at either end of the cell (traversing a 10 cm path) and the infrared spectra of the cell contents were measured through KCl or ZnSe windows mounted perpendicular to the ZnSe windows (5 cm path).

Infrared laser excitation in the range of 10.4 or 9.4  $\mu\text{m}$  was provided by a Coherent Radiation Laboratories model 41 continuous-wave (cw)  $\text{CO}_2$  laser. The exact laser frequencies were verified using an Optical Engineering  $\text{CO}_2$  Spectrum Analyzer. In single-line operation, output powers up to 150 W could be obtained by varying the current and the ( $\text{CO}_2\text{-N}_2\text{-He}$ ) gas mixture in the laser tube.

Infrared spectra were collected on a Digilab FTS-20 interferometer equipped with a KBr/Ge beamsplitter and a triglycine sulfate (TGS) detector. Interferograms were transformed after applying a trapezoidal apodization function with an effective spectral resolution of  $1.0\text{ cm}^{-1}$ . This resolution was sufficient to allow unequivocal identification of products (and starting materials) to be made from the infrared frequencies.

## III. RESULTS

### A. Allyl Chloride (3-Chloropropene)

Allyl chloride exhibits infrared absorptions between 1010 and 880  $\text{cm}^{-1}$ , while the most intense bands are between 940 and 920  $\text{cm}^{-1}$ . The P(26) [00 $^{\circ}$ 1 - 10 $^{\circ}$ 0] line of the  $\text{CO}_2$  laser at 938.69  $\text{cm}^{-1}$  is resonant with the wing of the bands assigned to the C-C stretch and the  $\text{CH}_2$  wag. This excitation frequency was used for most of the studies of allyl chloride [8].

Sample pressures were varied between 10 and 100 torr and laser powers were between 25 and 150 W, with irradiation times from .2 to 60 seconds. At low pressures (10 torr) and relatively low powers (50 W), no reaction of the allyl chloride was observed. At high pressures (50 - 100 torr) a reaction could be initiated using the range of laser powers given above. A luminescence was also observed during irradiation. The luminescence lasted approximately 3-4 seconds and the intensity was pressure-dependent.

The spectra in Figure 1 indicate typical results for the laser-induced reaction of allyl chloride. The absorbance spectrum of the products is shown at the bottom of the figure and indicates the existence of propene [9], propyne [10], 1,3 cyclohexadiene [11] (trace), benzene [12], acetylene [12], allene [13], ethene [12], and butadiene [14]. Large amounts of hydrogen chloride were also noted. The vibrational frequencies

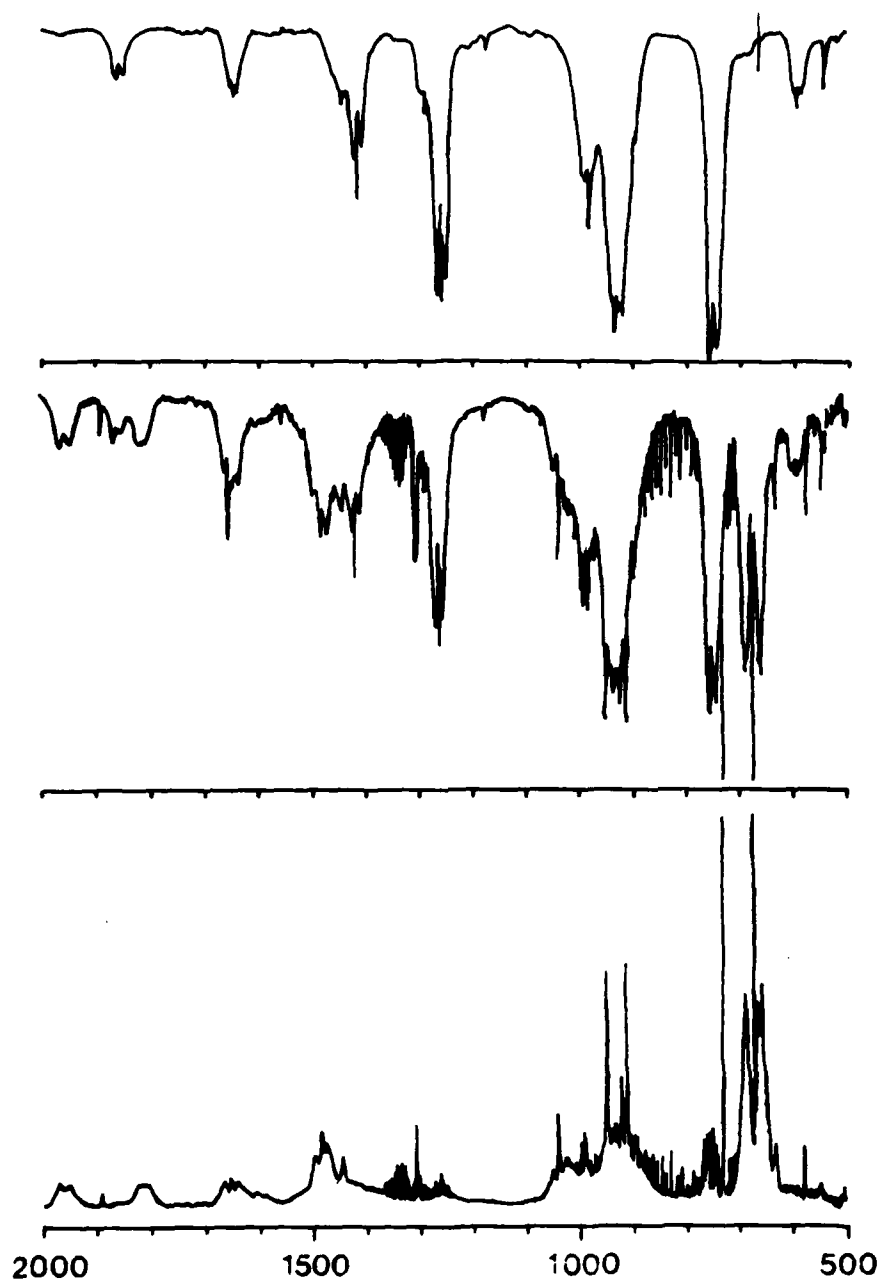
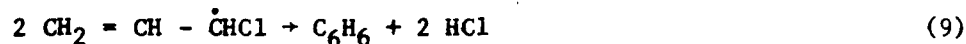
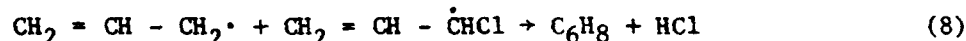
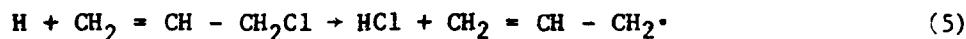
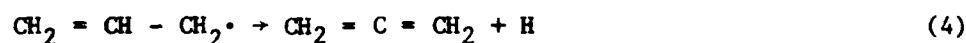
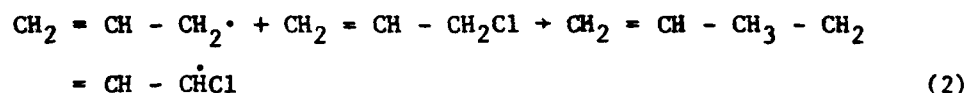
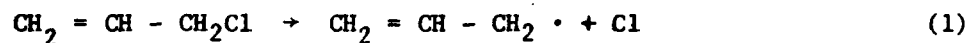


Figure 1. Infrared spectra of (A) allyl chloride; (B) the mixture of allyl chloride and the products of the laser-induced reaction, 2 sec, 100 W, P(26); and (C) the absorbance spectrum of the products after subtracting the allyl chloride spectrum from the mixture.

used to identify these compounds are summarized in Table 1. These products differ from the reported pyrolysis products only in the absence of diallyl and butene.

Figure 2 is a plot of allyl chloride pressures versus benzene absorbances at 50 and 100 W for 30 and 15 seconds, respectively. A laser fluence of 1500 J was arbitrarily chosen. The plot indicates that a threshold pressure of allyl chloride is needed for benzene production with the percent yield of benzene determined to reach a steady state above 60 torr. A laser power dependence was also indicated from this figure as can be seen in Figure 3. It was observed that a threshold of laser power is required for a reaction to occur. The yield of benzene increased rapidly with laser power and then leveled off. When laser irradiation time was varied at constant laser power and allyl chloride pressure (Figure 4), an optimum laser energy was indicated.

The pyrolysis of allyl chloride is reported to be a combination of radical non-chain and chain heterogeneous first-order reactions [15, 16]. The main reactions in the proposed mechanism for the gas phase pyrolysis of allyl chloride are:



At first it was believed that this mechanism could explain most of the products observed in the LIR experiments. However, when the ethene concentration was determined, it was found to be greater than propene. This mechanism only considers ethene to be a minor side product. New reactions must therefore be added to explain ethene as a main reaction product.

In the decomposition of a molecule there can be several reaction paths with the preferred path normally being the one with the lowest activation energy [16]. If the energy requirements for two reactions differ by a small amount, a higher temperature may allow the higher energy reaction to become competitive. This is believed to happen in the case of allyl chloride. Energy to break the C-C bond is not much greater than the energy of the C-Cl bond. In the initial laser irradiation a large temperature gradient is

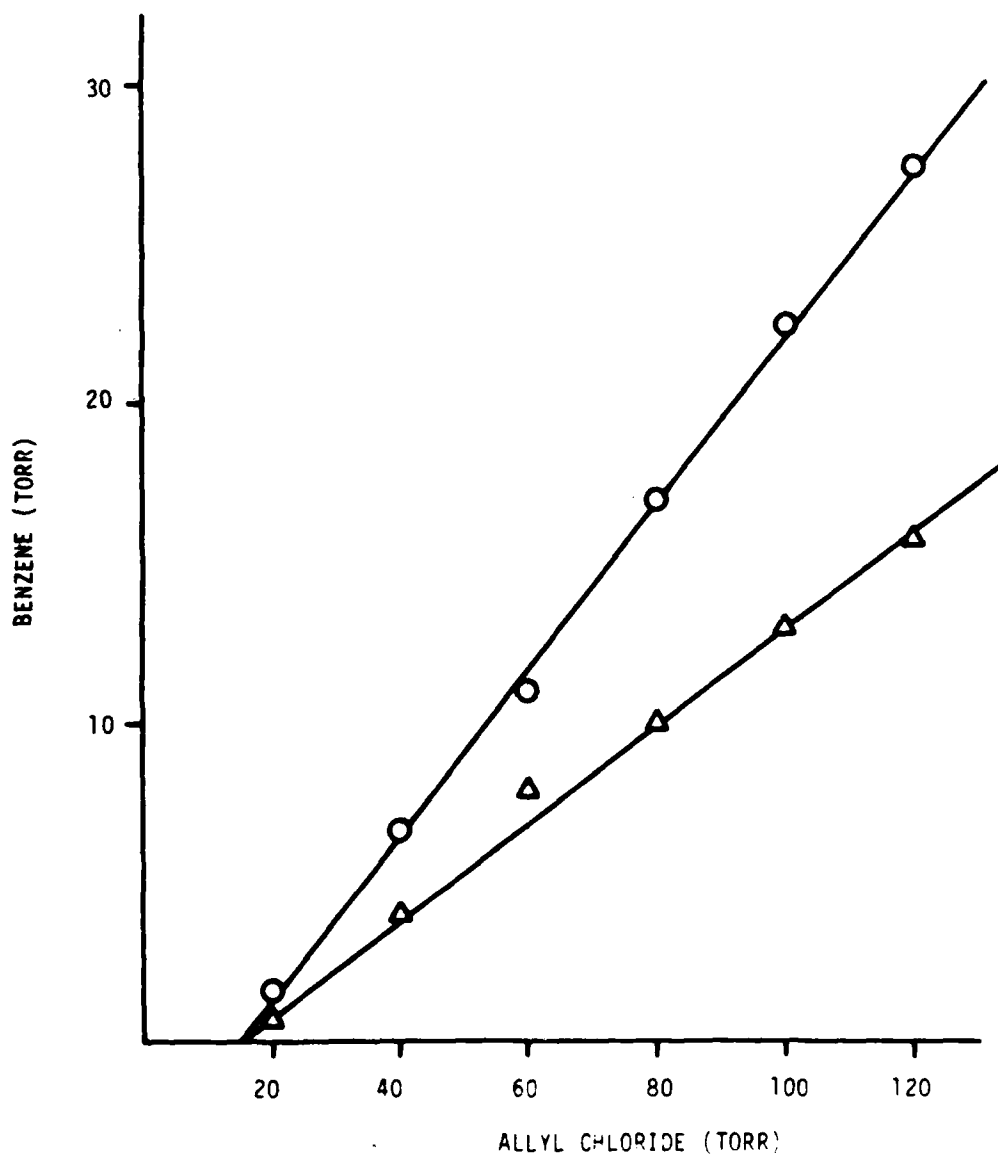


Figure 2. Benzene yield as a function of allyl chloride at a constant 1500J laser irradiation. ○: 100 watts/cm<sup>2</sup>; △: 50 watts/cm<sup>2</sup>.

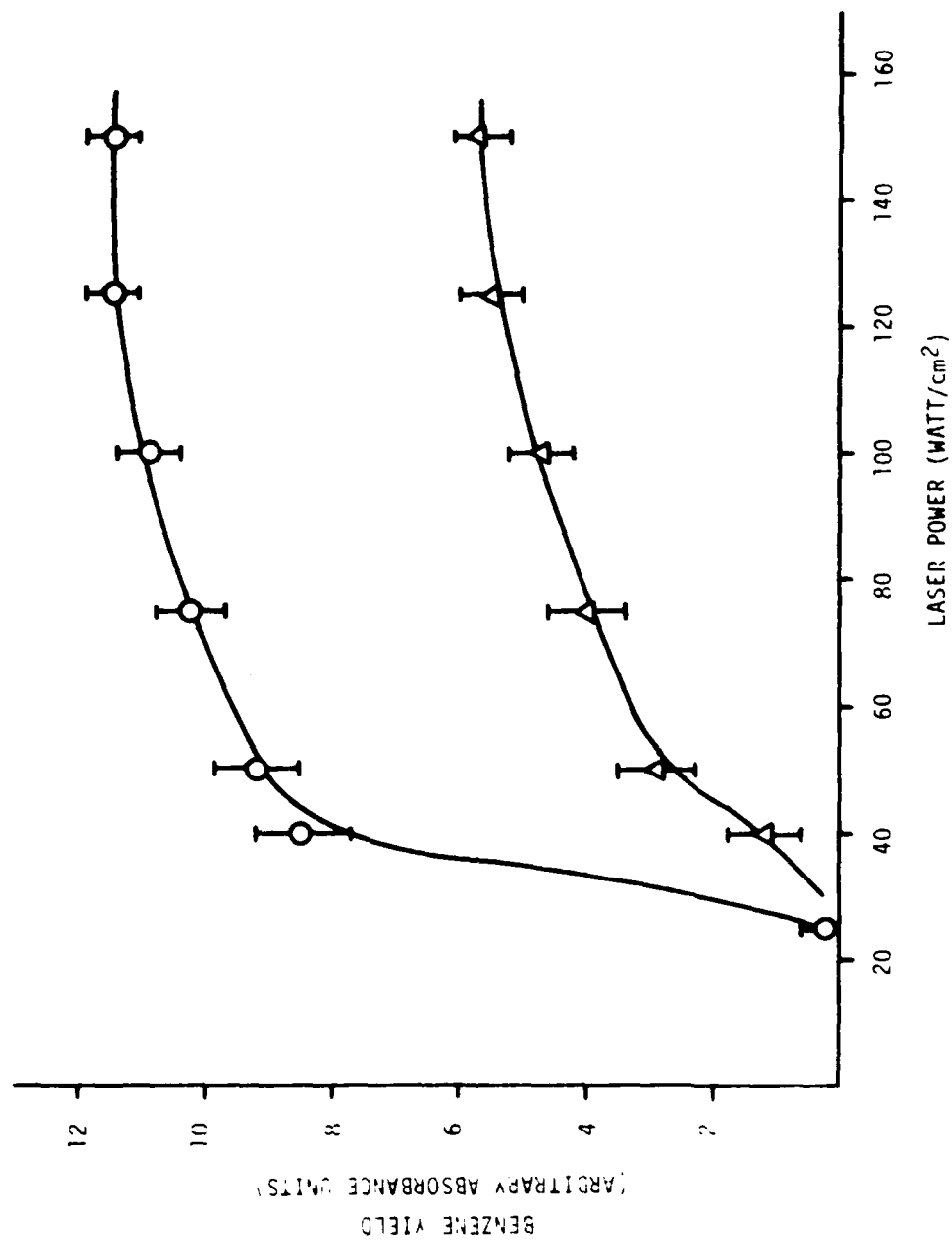


Figure 3. Benzene yield as a function of laser power at constant 1500J irradiation. ○ : 80 torr allyl chloride; △ : 40 torr allyl chloride.

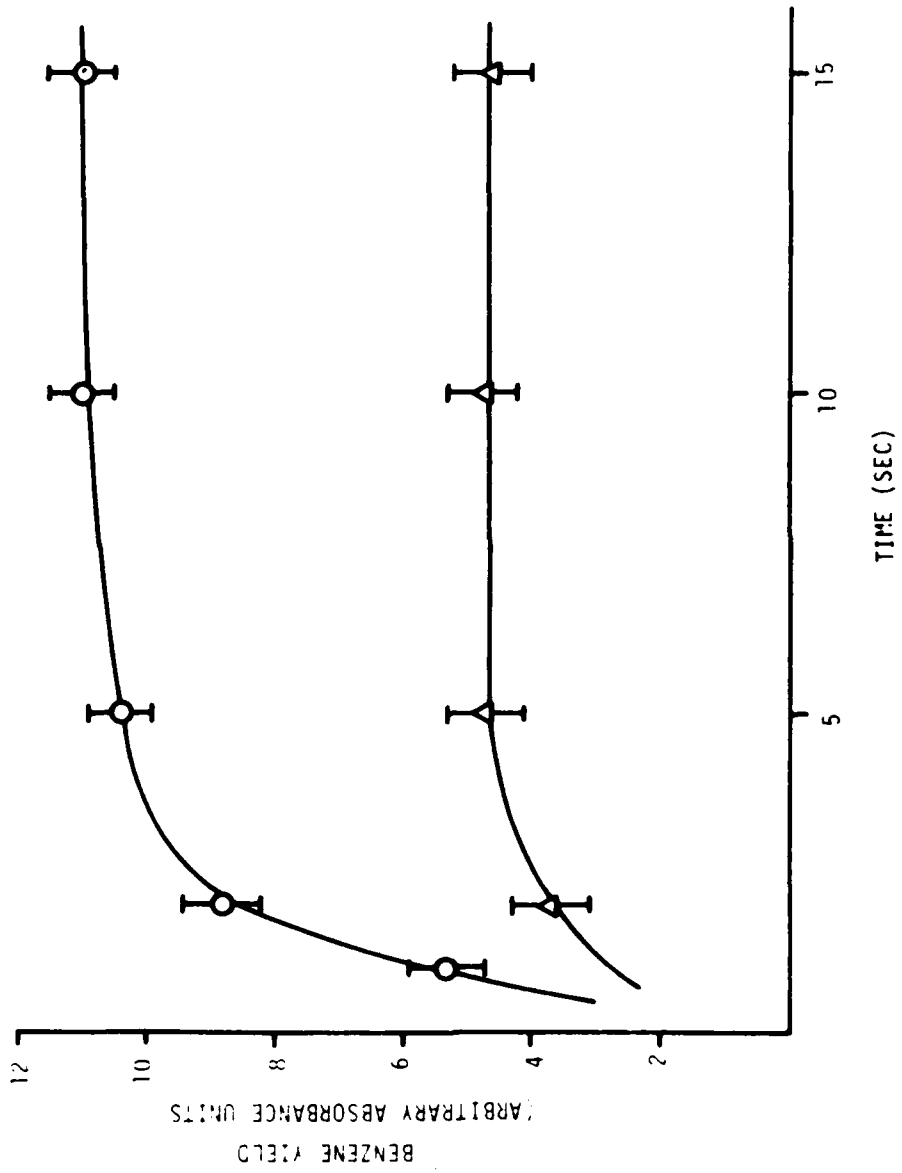
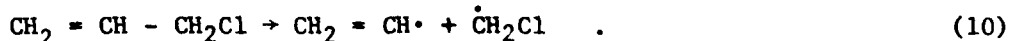


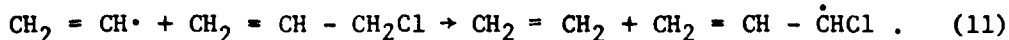
Figure 4. Benzene yield as a function of laser power at 100 watt/cm<sup>2</sup> laser power. ○: 80 torr allyl chloride; △: 40 torr allyl chloride.

established in a small volume along the laser path. The temperature in this volume could easily exceed 1000°C. At these higher temperatures, the C-C bond, as well as the C-Cl bond can easily be broken.

Two initial steps are then possible. Reaction (1) and the reaction



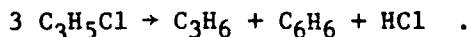
The ethene radical could react further with allyl chloride by the reaction



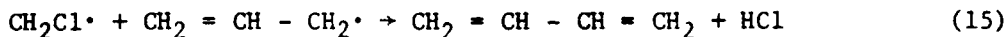
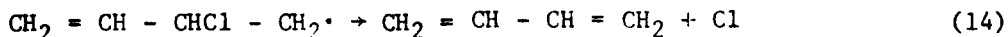
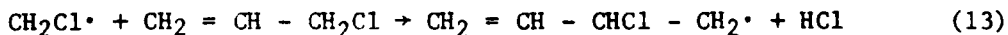
This reaction would explain the large yield of ethene observed. The ethene radical could also give up a hydrogen atom



Considering only Reactions (1), (2), (3) and (9), the stoichiometry is represented by



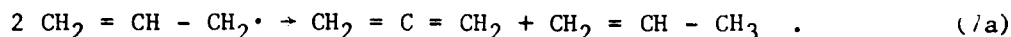
A one-to-one ratio of propene to benzene should be produced. If the yield of propene is subtracted from the yield of benzene, the ratio of ethene to remaining benzene is approximately 1.6:1. Reaction (11) produces one ethene molecule and one-half of the radical responsible for benzene. The postulated mechanism for the chloromethyl radical should not indicate the chloroallyl radical as a major product. With this restriction in mind, the following mechanism is postulated:



Chloroethane or chloroethene are not observed as products; therefore, if Reaction (16) occurs, Reaction (18) would have to be the end result. The high temperature of the decomposition makes this possible. The reverse of Reaction (19) could also explain the small amount of butadiene observed.

The mechanism explains the appearance of most of the observed products. Propyne (methyl acetylene) is the result of thermal isomerization of allene [17]. This was shown to be true by laser-irradiating a sample of allene. Propyne was observed as a product in good yield.

Instead of Reaction (7) forming diallyl, a disproportionation could also occur



The allyl radicals should be highly energetic and Reaction (7) would require a third body to occur while Reaction (7a) would not. The vibrational frequency of propene and diallyl overlaps at the strongest absorbance of diallyl [18]. It is possible that trace quantities of diallyl were present. Methane is probably the result of some product decomposition into a methyl radical with subsequent hydrogen abstraction.

The LIR of allyl chloride was a reasonably slow reaction; therefore, a series of kinetic experiments were performed. A graphite shutter adjustable to .1 sec was used to control laser irradiation time. Samples of allyl chloride were irradiated from .1 to 1.9 sec at 75 and 100 W of laser power. The concentrations of allyl chloride, benzene, allene, hydrochloric acid, ethylene and propene were determined from their infrared spectra. A plot of concentration of ethene, propene, benzene and allene versus irradiation time is shown in Figure 5 for one of the kinetic runs. A steady rise in concentration of ethene, propene, and benzene was observed while a leveling-off of allene was noted. The concentrations of methane and acetylene also continued to increase with irradiation time.

Various functional plots of allyl chloride concentrations versus time indicated that the best straight line plot was obtained for a three-halves reaction order. For confirmation of this result, initial rates at two different concentrations were obtained.

Since various pressures of allyl chloride absorb different amounts of laser fluence, the effective temperature of the reaction would be different and therefore the rate constant. To minimize this problem, laser lines were chosen so that the amount of absorbance would be approximately equal. The P(8),  $954.55 \text{ cm}^{-1}$ , and P(26),  $938.69 \text{ cm}^{-1}$   $\text{CO}_2$  laser lines were used for 80 and 40 torr of allyl chloride, respectively. The results of these kinetic experiments are given in Table II. The ratio of the initial rates again indicated an overall three-halves reaction order.

This result confirmed that the LIR of allyl chloride follows a three-halves reaction order. This order disagreed with the first-order rate reported in the pyrolysis experiments [15]. The three-halves order could be the result of a low pressure, high temperature mechanism or represent overall order of competing mechanisms. A 3/2 order is not unexpected since the overall order in the pyrolysis of propene is 3/2 order [27].

An induction period was indicated in the kinetic runs. A slower reaction rate was observed in the first .2 sec of irradiation than in longer irradiation times.

#### B. Allyl Bromide (3-bromopropene)

The infrared absorption of allyl bromide has the same fundamental vibrations in the  $900 - 1000 \text{ cm}^{-1}$  region as allyl chloride with only slight shifts in the absorbance maximum [8]. LIR of allyl bromide should be similar to that observed for allyl chloride.

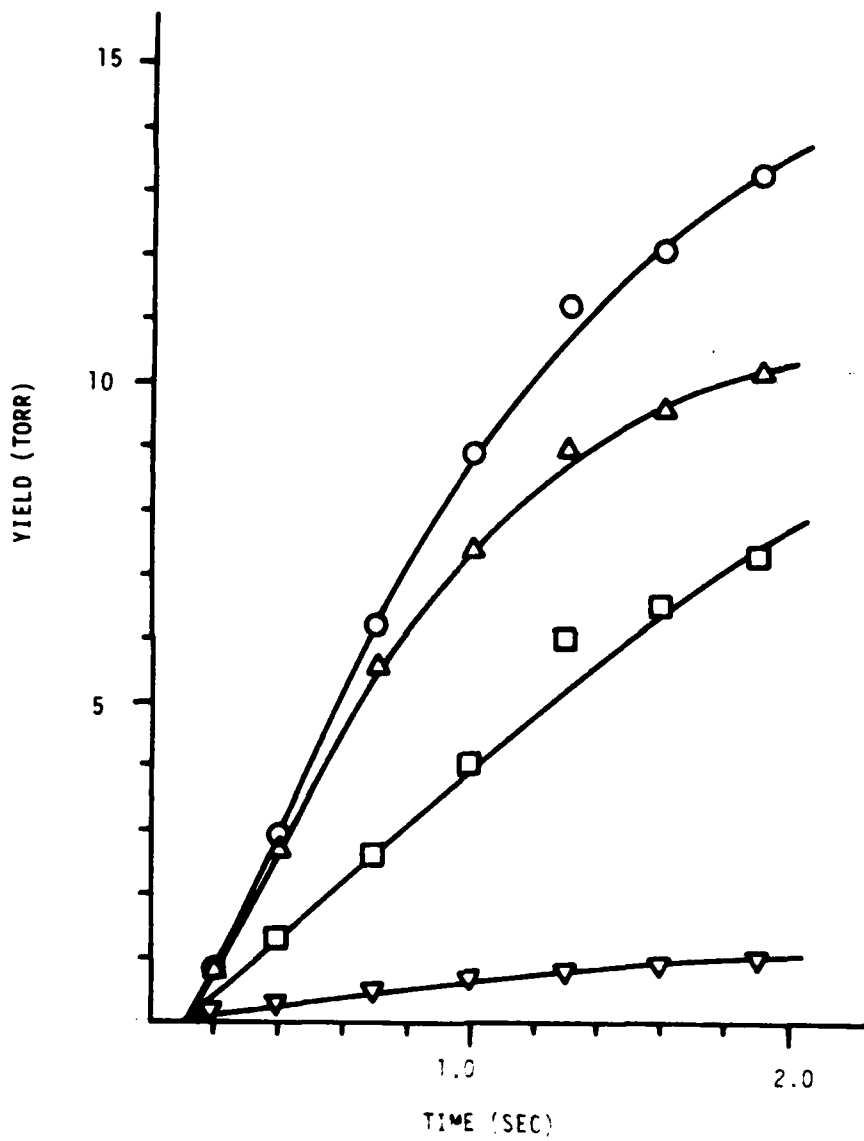


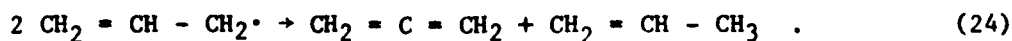
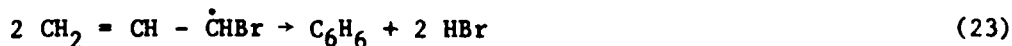
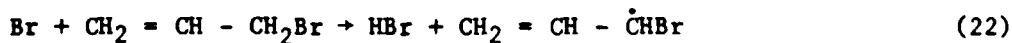
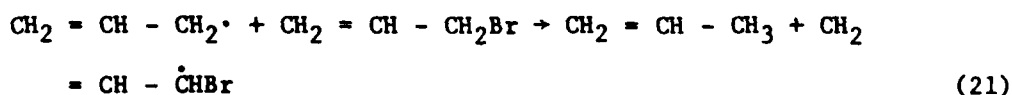
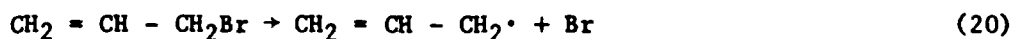
Figure 5. Product yields as a function of irradiation time. ○ : benzene; △ : ethene; □ : propene, ▽ : allene.

The P(36), 929.02  $\text{cm}^{-1}$  line of the  $\text{CO}_2$  laser was used for most of the investigations. As expected, laser irradiation of allyl bromide produces essentially the same compounds as allyl chloride (Figure 6). Hydrogen bromide, benzene, propene, ethylene, acetylene and methane were the most abundant products (Table I). Only trace quantities of allene and propyne and no detectable cyclohexadiene were observed. A pressure-dependent weak glow was observed along the laser path during irradiation and a carbon deposit was also observed on the cell walls and windows.

A reactant/product concentration as a function of laser power was determined at an arbitrary 1000 J laser fluence (Figure 7). A laser power threshold was not indicated for the bromide. Above 100 W, the reaction appears to be independent of laser power. However, the optimum laser power for the percent yield of benzene and propene production is 50 - 80 W. Higher powers tend to produce more of the side products and solid deposits. The approximate 31 percent yield of benzene for allyl bromide consumed compares very favorably to a theoretical 33 percent yield.

A reaction order for allyl bromide was also determined using 25 and 50 torr. P(36), 929.02  $\text{cm}^{-1}$ , and P(22), 942.38  $\text{cm}^{-1}$   $\text{CO}_2$  laser lines were utilized on the 25 and 50 torr, respectively. The ratio of the initial rates indicated that allyl bromide followed an overall first order reaction. This order agreed with the results obtained from pyrolysis experiments. It was noted in the 25 torr kinetic run as the concentration decreased the overall reaction order tended to second order. The allyl bromide concentration becomes sufficiently low that a bimolecular initiation reaction is required.

The overall mechanism is essentially the same as obtained in pyrolysis and may be represented by [19]



Ethene and methane are probably results of a side reaction involving the decomposition of propene and subsequent hydrogen abstraction.

Using the Arrhenius equation determined by Maccoll for allyl bromide and the LIR determined rate constant, an effective temperature of 790K can be obtained. The long extrapolation of the Arrhenius equation gives only an approximate temperature but it does indicate the magnitude of heat that is available during laser irradiation. Unlike allyl chloride, no apparent induction period is observed in allyl bromide.

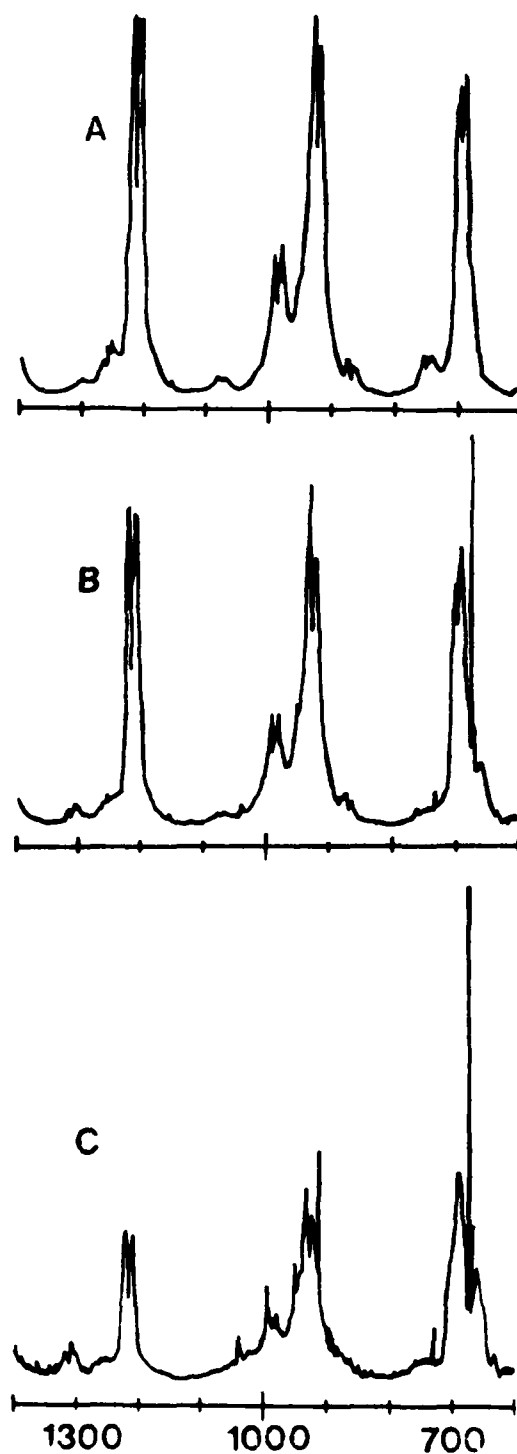


Figure 6. Infrared spectra of (A) allyl bromide; (B) the mixture of allyl bromide and the laser-induced reaction, 0.5 sec, 75 W, P(36); and (C) the mixture after a total of 1.5 sec, 75 W, P(36).

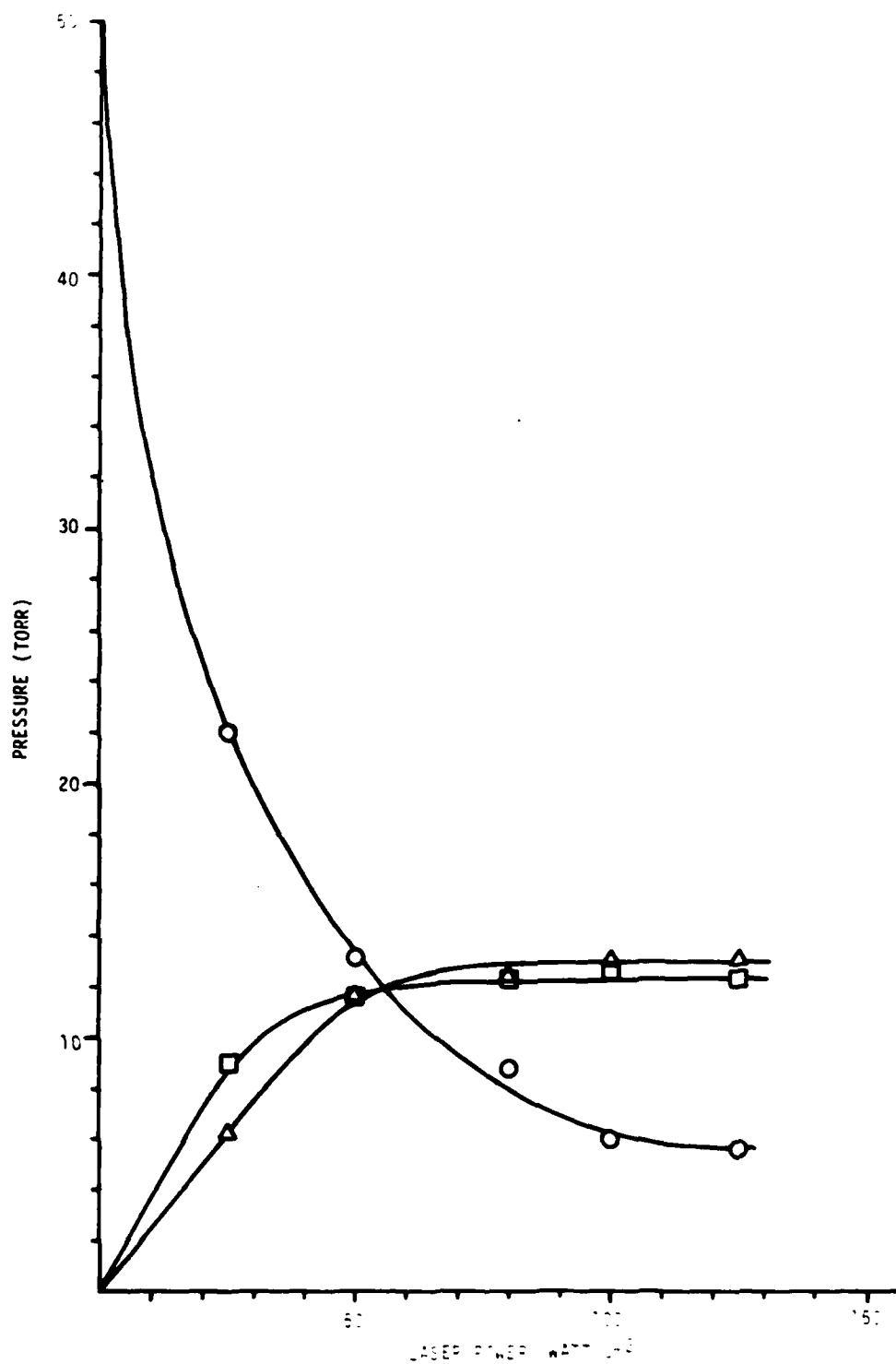


Figure 7. Dependence of decomposition of allyl bromide to laser power at constant 1000J laser energy ○: allyl bromide; □: propene; △: benzene.

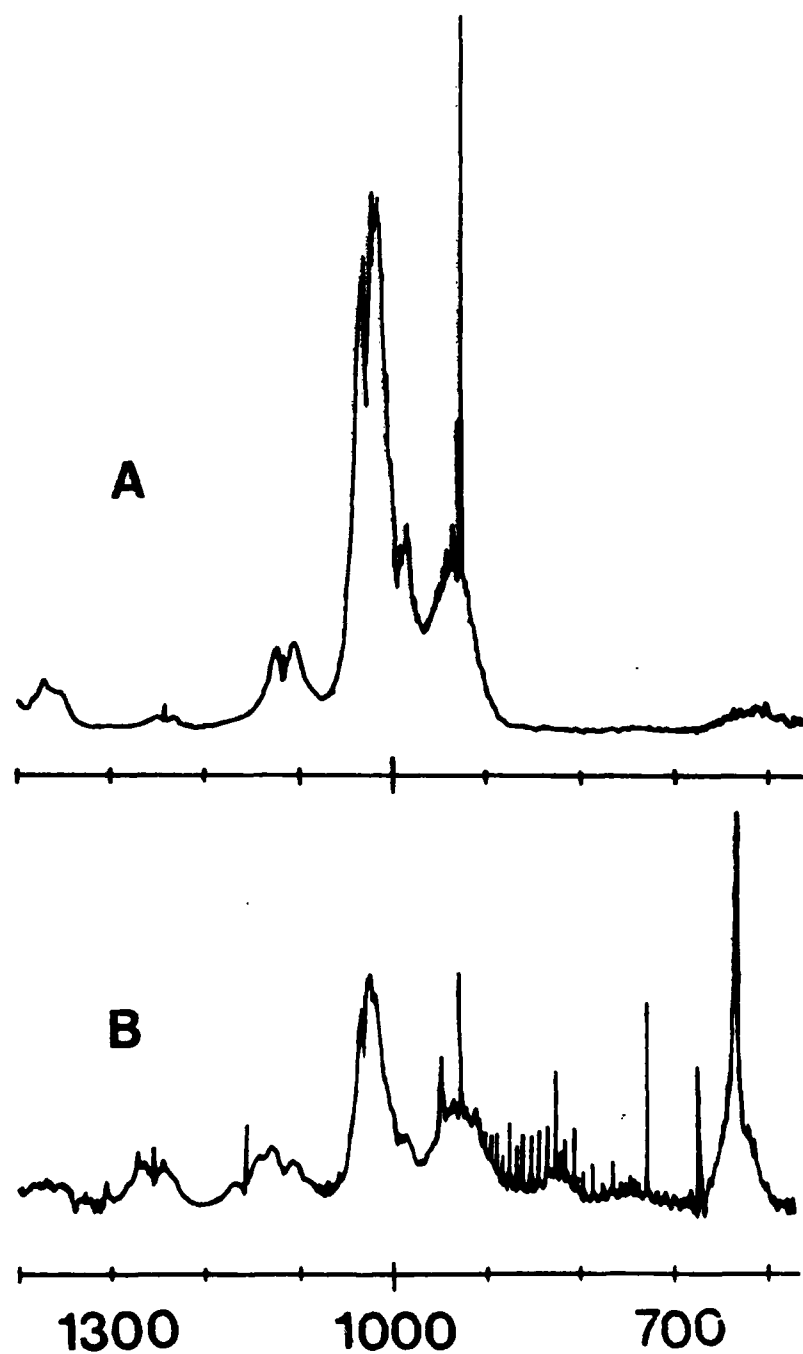


Figure 8. Infrared spectra of (A) allyl fluoride; and (B) the mixture of allyl fluoride and the products of the laser-induced reaction, 10 sec, 100 W, P(32).

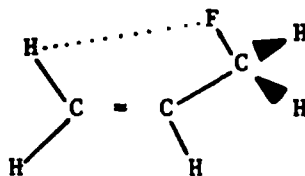
### C. Allyl Fluoride (3-fluoropropene)

Allyl fluoride exhibits infrared absorptions between 1050 and 900  $\text{cm}^{-1}$ , and the most intense maxima are near 1020 and 930  $\text{cm}^{-1}$  (Figure 8). The P(32), 931.00  $\text{cm}^{-1}$  and the P(32) [00°1 - 02°0; 1035.41  $\text{cm}^{-1}$ ] lines of the  $\text{CO}_2$  laser are resonant with the bands of allyl fluoride and were used as the excitation frequencies.

The spectrum in Figure 8.B. is representative of the mixture of products which form when allyl fluoride gas is exposed to the  $\text{CO}_2$  laser. The principal products are propyne, allene, and hydrogen fluoride. Smaller relative amounts of acetylene and ethylene were formed, and trace amounts of benzene, propene, methyl fluoride [12], and vinyl fluoride [20] were identified in the infrared spectrum (Table I). There have been no pyrolysis studies of allyl fluoride reported in the literature. In contrast to the other allyl halides, allyl fluoride appears to decompose more by a unimolecular reaction as opposed to the radical non-chain reaction. This is not surprising in view of the fact that C-F bond dissociation energies are relatively large (larger than for other C-halogen bonds and some C-C bonds as well).

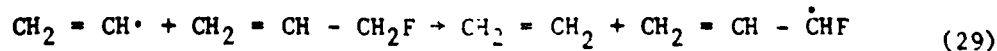
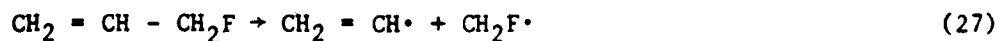
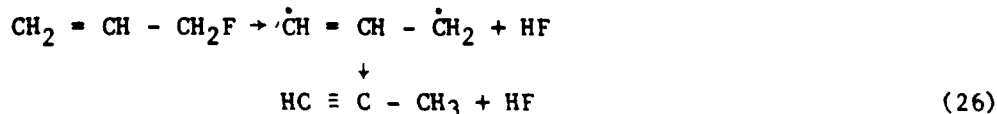
Instead of allene isomerizing to propyne, another possibility exists for allyl fluoride. The amount of cis-isomer varies from 4 percent in allyl bromide to 45 percent in allyl fluoride [21].

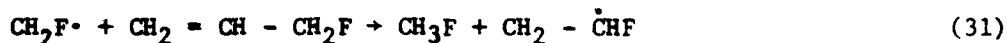
In the cis-conformer, an interaction between the fluorine and  $\gamma$  hydrogen atoms is possible:



On excitation, this conformer could eliminate HF and form a biradical which could rearrange to propyne.

From the observed products, an overall mechanism for allyl fluoride is represented by





The smaller yields of radical products are an indication that Reactions (25) and (26) are the preferred initial reaction paths.

The sample of allyl fluoride was insufficient to perform any kinetic experiments.

#### D. 2,3-dichloropropene and 2-methyl-3-chloropropene

To determine if substituted benzenes could also be produced by laser-induced reactions, experiments with 2,3-dichloropropene and 2-methyl-3-chloropropene were performed. If these compounds follow similar mechanisms as allyl chloride, the mono- and di-substituted benzenes should be observed. When 2,3-chloropropene was irradiated, HCl, propargyl chloride ( $\text{H} - \text{C}\equiv\text{C} - \text{CH}_2\text{Cl}$ ) [22], benzene, chlorobenzene [23], allene, ethylene, chloroallene [24], and acetylene were the only products observed (Table III).

Irradiation of 2-methyl-3-chloropropene produces HCl, propyne, benzene, toluene, allene, isobutene [25], ethene, acetylene and methane. Again, the di-substituted benzene (xylene) was not observed.

Although some of the reaction products are the same for these two compounds as for allyl chloride, different radicals and reaction paths must be operative. A highly reactive  $\beta$  carbon is also indicated by the formation of benzene and only the mono-substituted benzene. These reactions show that substituted benzenes can be formed by laser irradiation.

#### IV. CONCLUSIONS

The allyl halides constitute a very interesting family of compounds. The results obtained from the laser-induced reactions show that the fluoride, chloride and bromide all decompose by slightly different mechanisms. This can be directly related to the strength of the C-X bond and the halide reactivity.

In allyl bromide, breaking the C-Br bond is the lowest energy path for decomposition. Unimolecular and other bond-breaking reactions appear to be sufficiently different in energy to occur. As in pyrolysis, LIR proceeds by a radical non-chain mechanism.

The C-Cl bond is also the weakest in allyl chloride. Pyrolysis can best be explained as the initial breaking of this bond. It is also observed in pyrolysis at  $\geq 1000^\circ\text{C}$  larger quantities of  $\text{C}_2$  compounds are produced. Diallyl decomposition was suggested as the main source of these  $\text{C}_2$  and  $\text{C}_4$  compounds although the yield of  $\text{C}_4$  compounds did not increase in proportion to the  $\text{C}_2$  compounds. The amount of  $\text{C}_2$  compounds was even greater in the present experiments. Other explanations for the greater amounts of  $\text{C}_2$  compounds exist. Raising the temperature could cause decomposition of products such as propene or allow alternate reaction paths such as breaking the C-C bond in allyl chloride to occur. The latter is believed to occur

in the LIR experiments and to some degree in pyrolysis.

Although initially the photon concentration is too low for mode-selective decomposition, over the length of irradiation time a sufficient number of photons are present for multiphoton absorption and decomposition. Since the CO<sub>2</sub> laser absorption is in the CH<sub>2</sub> wag and C-C stretching modes, all of the absorbed energy must be redistributed to the C-Cl bond for its dissociation. The C-C and C-Cl bond energies are not widely separated in energy and some of the higher energy paths would be expected at higher temperatures. This is apparently observed in pyrolysis. If a weak coupling exists between the C-C stretch and the C-Cl stretch, a non-randomization of energy could occur, leading to a non-statistical dissociation along the higher energy path [26]. This is believed to occur for the laser-induced reaction.

The observation of many products points out the complexity of the allyl chloride reaction mechanism compared to allyl bromide. The observed induction period and deviation from first-order kinetics are indicative of a radical chain mechanism [7]. As in pyrolysis, some radical non-chain reactions are also present.

In allyl fluoride the C-F bond is approximately of equal bond strength with the C-C bond and the C-H carbon bond. Unlike the other halides, fluorine atoms are much more reactive and would not be expected on decomposition of fluoro-compounds. The presence of large quantities of allene and propyne indicates, as expected, a different initial reaction in allyl fluoride. The decomposition primarily follows a unimolecular reaction with the loss of HF. Some C-C bond dissociation is also indicated from the observed products; therefore, a radical chain mechanism is also partially operative.

TABLE I. INFRARED BANDS ( $\text{cm}^{-1}$ ) OF PRODUCTS OF THE LASER-INDUCED DECOMPOSITION REACTIONS OF ALLYL HALIDES <sup>a</sup>

<u>Allyl Fluoride</u>	<u>Allyl Chloride</u>	<u>Allyl Bromide</u>	<u>Identify</u>
633	633	633(trace)	propyne ( $\text{C}_3\text{H}_4$ )
	658		1,3-cyclohexadiene ( $\text{C}_6\text{H}_8$ )
	664		unidentified
674	674	674	benzene ( $\text{C}_6\text{H}_6$ )
729	729	729	acetylene ( $\text{C}_2\text{H}_2$ )
800-900	800-900	800-900(trace)	allene ( $\text{C}_3\text{H}_4$ ) <sup>b</sup>
830			unidentified
912(trace)	912	912	propene ( $\text{C}_3\text{H}_6$ )
929			vinyl fluoride ( $\text{C}_2\text{H}_3\text{F}$ )
949	949	949	ethylene ( $\text{C}_2\text{H}_4$ )
990(trace)	990	990	propene
	1038	1038	benzene
1048			methylfluoride ( $\text{CH}_3\text{F}$ )
1156			vinyl fluoride
1249			propyne
1275			unidentified
1306	1306		methane ( $\text{CH}_4$ )
		2400-2700	hydrogen bromide ( $\text{HBr}$ ) <sup>c</sup>
	2700-3000		hydrogen chloride ( $\text{HCl}$ ) <sup>c</sup>
3334			propyne
3700-4000			hydrogen fluoride ( $\text{HF}$ ) <sup>c</sup>

<sup>a</sup> Only the major bands for a given compound are listed.

<sup>b</sup> Allene exhibits a perpendicular band whose Q branches are at 808, 818, 827, 836, 845, 854, 862, 869, and 876  $\text{cm}^{-1}$ .

<sup>c</sup> The hydrogen halides exhibit parallel bands whose P and R branches cover these respective regions.

TABLE II. Concentration of Remaining Allyl Chloride After Irradiation and Calculated Reaction Order.

Irradiation Time	40 Torr Allyl Chloride (Torr)	80 Torr Allyl Chloride (Torr)	Reaction Order*
0.1	39.3		
0.2	38.7	74.5	2.08
0.4	35.5	67.2	1.51
0.7	32.8	56.3	1.72
1.0	29.5	48.5	1.58
1.3	27.4	42.0	1.59
1.6	24.4	37.5	1.45
1.9	22.5	33.5	1.41

\*Reaction order =  $\frac{\ln (\text{Rate 2/Rate 1})}{\ln 2}$

TABLE III. Infrared Bands ( $\text{cm}^{-1}$ ) of Products of the Laser-induced Decomposition Reactions of 2-Methyl-3-Chloropropene (MCP) and 2,3-Dichloropropene (DCP)

<u>MCP</u>	<u>DCP</u>	<u>Identity</u>
633		propyne
	638	
	646	propargyl chloride
	654	
674	674	benzene
	685	chlorobenzene
694		toluene
730	730	acetylene & toluene
	742	chlorobenzene
	760 P	
	768 Q	chloroallene
	774R	
900-800	900-800	allene <sup>a</sup>
889		isobutylene
950	950	$\text{C}_2\text{H}_4$
	960	chloroallene
	1095	chloroallene
1307		$\text{CH}_4$

<sup>a</sup>see Table I.

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