

PULSED INFRARED LASER-INDUCED CHLORINATION REACTIONS

by

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I. INTRODUCTION

The unique characteristics of a laser in providing a coherent and highly monochromatic light source have found applications in many areas of science as well as in communication, medicine, and military roles. Being able to tune the laser to a specific wavelength of light has allowed selective excitation in photochemistry and has made conventional light sources obsolete in some respects. Lasers have been developed with a wide range of wavelength bands from the ultraviolet to far infrared. A number of lasers are now available commercially which operate in either the pulsed or continuous wave modes.

The most efficient and widely used laser to date is the infrared laser which offers a totally new approach to photochemistry. Ultraviolet and visible lasers continue to find uses but many aspects of their applications are similar to conventional light sources. On the other hand, intense infrared lasers have opened a new area in which vibrational excitation can be achieved by multiphoton excitation rather than by conventional thermal processes.

Selective excitation by infrared laser has been employed in isotope separation,^{1,2} non-thermal unimolecular reaction,³⁻⁵ and inducement of specific reaction pathways which could not be achieved by ordinary means. The first two examples of the application in infrared lasers mentioned above have received the bulk of research effort in infrared laser photochemistry. A number of successful attempts have

been reported in isotope separation.¹ Isotopic compounds have slightly different infrared absorption bands which permit some selectivity in exciting one of the isotopic compounds to react chemically. Thus, through some separation technique, the less abundant isotope can be enriched.

Unimolecular reactions have also drawn a lot of research interest with much addressed at the multiphoton absorption phenomenon itself. Being able to break a bond with infrared photons in the absence of collisions was unanticipated and a number of papers have investigated the process and factors that affect it, such as laser power, laser intensity, pressure of reactant, effect of bath gas, etc.⁴⁻⁷

Laser-induced syntheses have not been extensively studied. To date, only a few attempts have been reported where infrared lasers have been used to drive chemical reactions to produce compounds of synthetic importance. A number of bimolecular reactions have been reported⁶⁻⁸ but most of these reports just attempted to employ infrared laser in driving the reaction and most results show no advantages over conventional methods.

A group of workers at the Los Alamos Scientific Laboratory reported⁹ the synthesis of difluoroamino sulfur pentafluoride, SF_5NF_2 , by infrared laser excitation. The standard procedure for the preparation of this compound involved heating relatively high pressures of S_2F_{10} and N_2F_4 to 425° K in a sealed reactor for 10-20 hours.¹⁰ The authors

employed a CO_2 pulsed infrared laser and irradiated a low pressure mixture of the two reactants and obtained a substantial amount of SF_5NF_2 in a single pulse. A radical-radical combination was postulated as the reaction mechanism where the infrared laser photons were used to homolytically break the symmetrical reactants into radicals. Even though this example offers no significant advantage over the thermal method, it was suggested⁹ this technique might possibly be used to prepare previously unsynthesized compounds such as SF_5COCl and SF_5NO_2 through the radical-radical combination.

Infrared lasers have also been applied to the reaction of boron compounds. One example that shows synthetic utility of infrared lasers is the reaction of diborane with hydrogen sulfide.¹¹ Irradiation of the two-gas mixture with a continuous wave infrared laser produced a few new boron-sulfur compounds, notably $(\text{HS})_2\text{BH}$ and $\mu\text{-HSB}_2\text{H}_5$ in isolatable amounts which could not be obtained under normal thermal conditions.

In our research laboratory, it has been demonstrated¹² that an organic compound which is thermally more reactive than its precursor can be synthesized by a pulsed infrared laser under appropriate conditions. Pulsed irradiation of cyclobutyl acetate ($E_a \sim 47$ kcal/mole) at low laser fluences produced only cyclobutene and acetic acid even though cyclobutene can undergo a facile ($E_a = 32.9$ kcal/mole) ring-opening to form 1,3-butadiene. At higher fluence or higher pressure of cyclobutyl acetate, a significant secondary

reaction of cyclobutene to form 1,3-butadiene became important. However, with appropriate selection of laser fluence and CF_4 bath gas pressure, it was possible to increase the cyclobutene yield and reduce the amount of secondary reaction product. This demonstrated the ability of the pulsed infrared laser to generate highly vibrationally excited reactant molecules but to restrict the reaction time to a few microseconds in order to produce a product that is thermally more reactive than its precursor.

There are a few limitations in employing infrared lasers to drive chemical reactions. One obvious drawback is the short range of frequencies that can be obtained from a specific laser. A compound to be irradiated might not have any absorption or the absorption cross-section of the compound at the particular band is too small to effect any chemical reaction. Still, chemical reactions can be induced by the infrared laser with the addition of a chemical sensitizer. There is a number of reactions that has been reported in which an inert absorber molecule has been used to induce infrared laser reactions. Ideally, a sensitizer molecule should be chemically inert, absorb strongly at a suitable frequency and be efficient at V-V, T/R energy transfer. These requirements proved to be important and a number of molecules such as SiF_4 ¹³, SF_6 ¹⁴, and CH_3F ¹⁵ were used as sensitizers. Both SiF_4 and SF_6 have strong absorption bands in the infrared region of the CO_2 laser but SiF_4 is more inert and is the preferred choice in the more recent reports.

It should be expected that any selectivity is removed with the use of a sensitizer. A compound in a mixture cannot be selectively activated without exciting the rest of the mixture. Most sensitized reactions involved unimolecular isomerization^{14,16} and retro-Diels-Alder reactions.¹⁷ Infrared laser sensitized reactions can be compared to pyrolysis reactions but possess advantages over conventional pyrolysis reactions in that hot wall effects are avoided and the short pulse excitation and fast cooling rate produce "instantaneous" excitation and rapid quenching.

Of direct relevance to the present work, to date, only one paper in the literature has reported in detail on infrared laser-induced chlorination and bromination reaction.¹⁸ Single-pulse infrared irradiation of CHClF_2 with bromine or chlorine produced relatively high yield of products. In the case of the bromination reaction, up to 64% reaction was observed by a single pulse irradiation to produce an industrially important compound, bromochlorodifluoromethane (CBrClF_2), a useful fire retardant, together with CBr_2F_2 and $\text{C}_2\text{Br}_2\text{F}_4$ as byproducts. Chlorination of CHClF_2 with single-pulse infrared irradiation produced mainly dichlorodifluoromethane in up to 98% yield. The bromination and chlorination of CHClF_2 involve a chain reaction and, thus, not surprisingly, produced large conversion with just a single pulse of infrared laser irradiation.

Nesbitt and Leone¹⁹ studied laser-initiated chemical chain reactions in an effort to understand similar

processes that occur in internal combustion engines. Three systems were studied, namely $\text{Cl}_2/\text{H}_2\text{S}$, Cl_2/H_2 , and $\text{Cl}_2/\text{CH}_3\text{SH}$. Real time evolution of the chain reactions was followed by direct detection of infrared chemiluminescence from vibrationally excited HCl produced by one of the propagation reactions in the chain. A frequency-doubled dye laser was employed to dissociate some of the chlorine molecules to initiate the chain reaction. Detailed rate constants for the fundamental chain propagation steps were reported for these reacting systems. This pulsed laser-initiation technique was reported to exhibit distinctly different chainlengths, rates, and termination behaviors for each of these systems.

The present research project involved the study of infrared laser-induced chlorination of cyclopropane and n-butane. Chlorination of hydrocarbons such as cyclopropane and n-butane was extensively studied with reaction induced either photochemically or thermally and it is well known that these reactions involve a free radical chain mechanism.²⁰ Our primary objective was to characterize the main features of megawatt infrared laser-induced chlorination reactions with particular emphasis on the effective temperature of the reaction and chainlength. Of synthetic interest, we were able to produce chlorocyclopropane in high yield and essentially free of impurities by inducing the chlorination in the presence of a small amount of di-*t*-butyl peroxide by means of SiF_4 sensitized laser

excitation. This laser synthesis is significant in that cyclopropane has not been obtained in satisfactory yield previously by conventional means.

The effects of several variables on the effective temperature, reaction time, and chain-length of the pulsed infrared laser reactions were determined. Calculations of the effective temperature, reaction time, and chainlength were made for the laser-induced chlorination of cyclopropane. These methods were then extended to the laser-induced chlorination of n-butane so that a comparison between the two similar reactions could be made. The effective temperature was calculated from the energy absorbed by the reaction system and the heat capacity of the gas mixture present in the irradiated volume. In the case of n-butane, another method which employed the known Arrhenius parameters and the ratio of the two products formed, i.e., 1-chlorobutane and 2-chlorobutane, was also used to calculate the effective temperature. The chainlengths for both reactions were found to be relatively short, between 8 and 120, depending on the particular experimental conditions. The reaction times for the decomposition of di-*t*-butyl peroxide were in the order of milliseconds to several microseconds.

II. EXPERIMENTAL

1. Chemicals

All gases were research grade purity. Chlorine, n-butane and silicon tetrafluoride were from Matheson Company, and cyclopropane was from Union Carbide Company or Eastman Kodak Chemical Company. Di-t-butyl peroxide was distilled and the fraction boiling at 50-52° C under 90 torr pressure was collected. Since all experiments were done in the gaseous phase, all chemicals were stored in closed containers and degassed by several freeze-pump-thaw cycles to remove air and to obtain true partial pressures of these gases.

2. Procedure

All experiments were conducted in Pyrex reaction cells 10 cm long by 2 cm inside diameter fitted with polished sodium chloride windows. A cold finger on the cell which could be isolated from the reaction chamber by means of a Teflon-Viton-O-ring seal was employed to obtain accurate partial pressure of each gas. The cell was wrapped with black electrical tape to avoid any reaction induced by room light.

Infrared laser irradiation was obtained from a Lumonics TEA Model 103-2 pulsed carbon dioxide laser. A standard lasing mixture included carbon dioxide at a flow rate of 2.0 ft³/hr (10 psi regulator pressure), nitrogen at 0.8 ft³/hr (10 psi), and helium at 8.0 ft³/hr (10 psi). The laser beam was directed through a 15 mm diameter plexiglass iris in order to obtain a uniform energy density. The energy

from the laser was measured using a Scientech, Model 380102 volume absorbing disc calorimeter. Most experiments were conducted utilizing the P(42) laser line (1025 cm^{-1}). The duration between each laser pulse was about 9 seconds.

Photochemical experiments employed the same reaction cell and a 275 watt sun-lamp placed 60-80 cm away from the cell to avoid heating of reaction mixture.

3. Chlorination of Cyclopropane

In the laser induced chlorination of cyclopropane, 10.0 torr of the substrate was used in most experiments. Standard vacuum line techniques were employed to introduce gases into the reaction cell and the partial pressure of each gas was measured by a MKS Baratron, Model PDR-3 pressure gauge. All gases except chlorine were trapped in the cold finger and only allowed to mix just before laser irradiation to minimize any non-laser induced reaction.

The reaction mixture was analyzed by gas-liquid phase chromatography (glpc) with a Hewlett Packard Model 700 with a flame ionization detector so that only carbon containing compounds were detected. The reacted gas mixture was injected into the separating column via a glass gas injection system. In most analysis, a 20' by $\frac{1}{4}$ " DEGS column was used with temperature programming at 1° C/min . The helium flow rate was kept constant at 20 ml/min and the hydrogen and air mixture for the ionization flame was calibrated to give the maximum response. Each product was identified by retention time and the major products, chlorocyclopropane

and 1,1-dichlorocyclopropane, were confirmed by infrared spectroscopy. Under the standard glc conditions, cyclopropane exhibited a retention time of ~ 8 minutes, chlorocyclopropane ~ 18 minutes, and 1,1-dichlorocyclopropane ~ 28 minutes; two other unidentified products eluted after ~ 40 and ~ 46 minutes, and 1,3-dichloropropane came after 65 minutes. In most experiments the "other products" were very minor constituents of the mixture and a much higher sensitivity was required in order to see these peaks. Quantitative data were based on the peak areas of the chromatograms, measured by a planimeter. Calibration for the flame ionization detector response for each of these compounds was obtained by injecting known amounts of cyclopropane, 3-chloropropene and 1,3-dichloropropane. Since chlorocyclopropane is not available commercially and not readily synthesized by conventional means, 3-chloropropene, which has a similar retention time and identical molecular formula as chlorocyclopropane, was used for its calibration. Dark reactions for each chlorine to cyclopropane ratio were also carried out and the resulting products were subtracted from the respective compounds produced in the infrared laser-induced reactions. The yield of each product was then calculated in terms of the irradiated volume which was 17.7 cm^3 , assuming all the reaction had occurred in the active volume of the reaction cell. Percent yield of chlorocyclopropane reported in Tables 2-7 were based on the limiting reagent which was usually chlorine.

Photochlorination of cyclopropane involved reacting cyclopropane and chlorine only. No effect was observed in the photochemical reaction when either di-*t*-butyl peroxide or SiF₄ was added to the mixture. The products were analyzed using the same procedure mentioned above.

4. Chlorination of *n*-Butane.

Since *n*-butane reacts readily with chlorine, laser-induced experiments were carried out in total darkness until the sample was injected into the gas-chromatograph. The time taken to complete the experiments was as short as possible and usually between 3-5 minutes. We were able to react only up to 1.0 torr of chlorine with 10.0 torr of *n*-butane before the dark reaction became significant. Even then, the extent of dark reaction was determined at various times and the laser reactions were corrected for the amounts of product formed during the dark reaction. The laser-induced chlorination produced 1- and 2-chlorobutane which were identified by retention times of the GC peaks. A 13' x $\frac{1}{4}$ " porapak Q column was used to separate the two isomers which, at 200° C oven temperature and 15 ml/min helium flow rate can be easily separated and exhibited retention times of 55 and 65 minutes, respectively for 2-chloro and 1-chlorobutane. Similar quantitative treatment of the products as that for cyclopropane mentioned above, was applied.

5. Spectra

Figures 1-5 show the spectra of various neat gases and mixtures used in the experiments at their experimental

pressure taken with a Perkin-Elmer Model 180 infrared spectroscopy using the same cell used in the laser-induced reactions. Figure 1 is the spectrum of neat SiF_4 at 1.0 torr pressure. The maximum absorption band is at 1028 cm^{-1} but maximum infrared photon absorption was found to be at 1025 cm^{-1} (P(42) line of the $9\text{ }\mu\text{m}$ band).¹³ Figure 2 is the spectrum of cyclopropane at 10.0 torr pressure and 10 cm pathlength cell. Attempts to irradiate at lines P(38) and P(42) which are near the maximum 1030 cm^{-1} absorption peak failed to yield any significant reaction in the presence of chlorine and di-*t*-butyl peroxide. Figure 3 shows the spectrum of a mixture of 10.0 torr cyclopropane, 1.0 torr SiF_4 , and 2.0 torr chlorine. It can be noted that the absorption peak for SiF_4 overlaps somewhat with part of the cyclopropane band near 1028 cm^{-1} and the absorption coefficient of SiF_4 can be easily seen to be much higher than cyclopropane at that region. Chlorine does not absorb at these regions. The last two spectra are of pure n-butane at 10.0 torr pressure and a mixture of 10.0 torr n-butane, 1.0 torr SiF_4 , and 1.0 torr chlorine respectively. From the two spectra, it is obvious that a sensitizier is required to induce the laser chlorination reaction of n-butane.

Figure 1. Infrared Spectrum of 1.0 torr
 SiF_4 in 10.0 cm pathlength cell.

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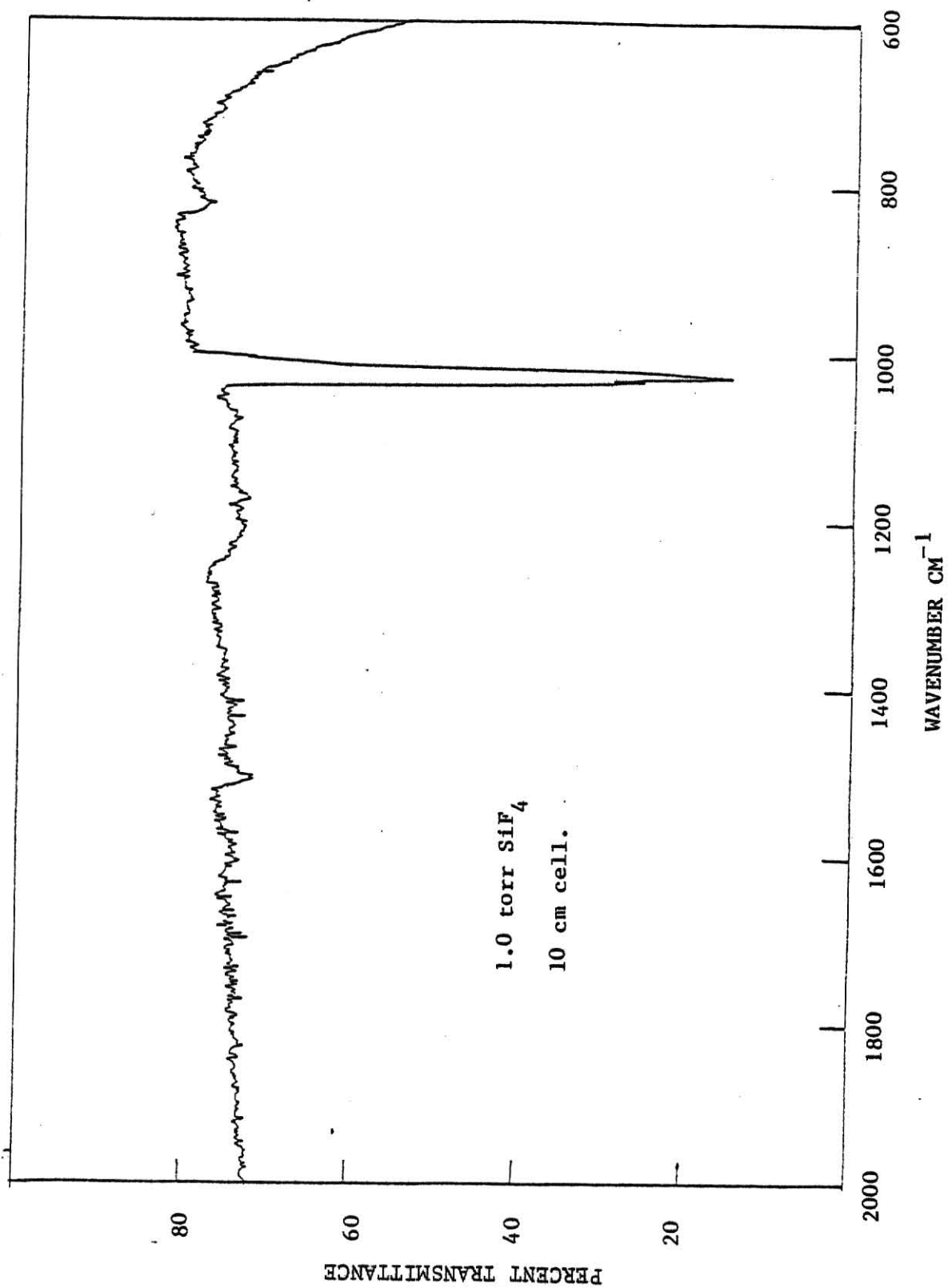


Figure 2. Infrared spectrum of 10.0 torr
cyclopropane in 10.0 cm pathlength
cell.

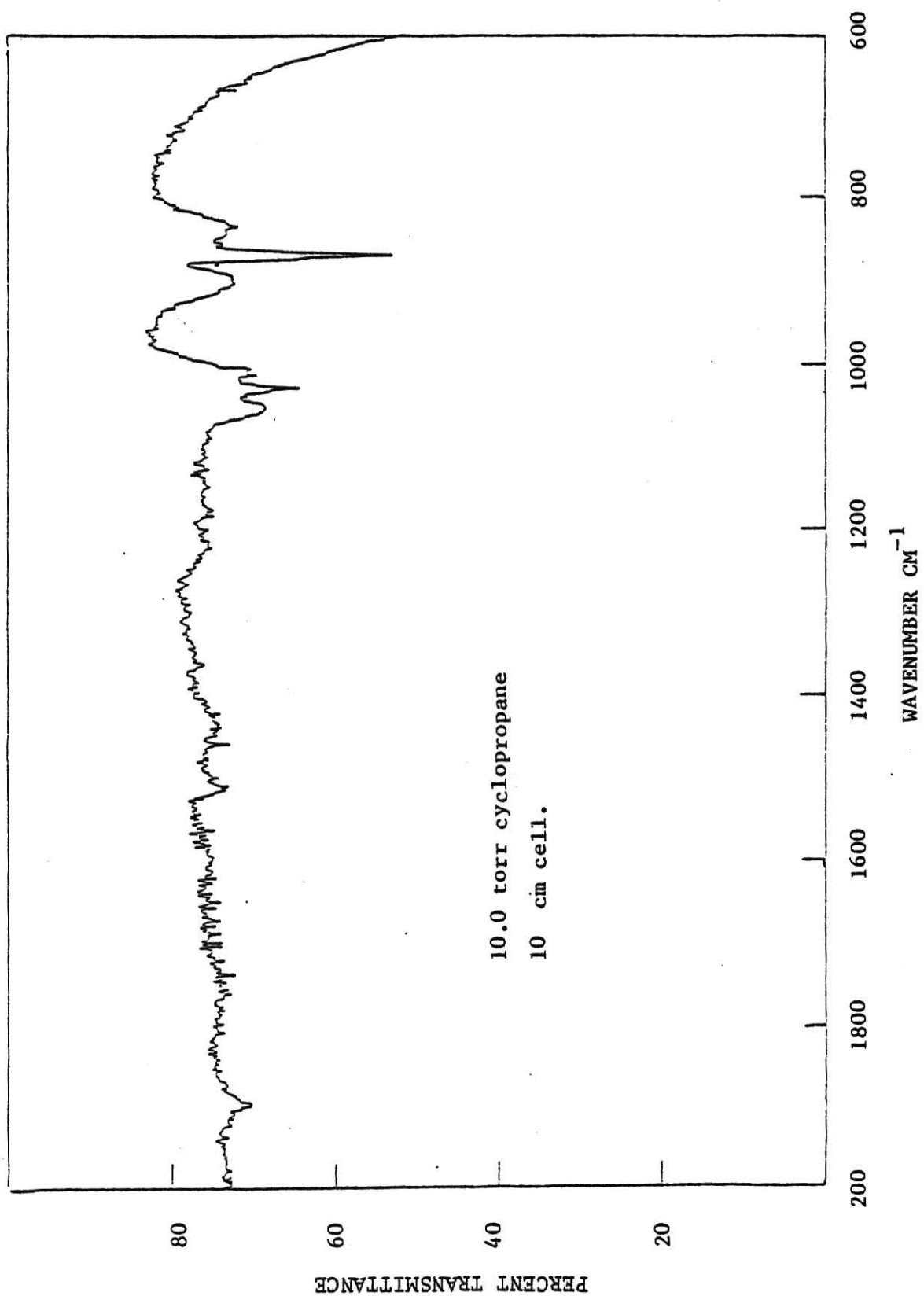


Figure 3. Infrared spectrum of 10.0 torr cyclopropane, 1.0 torr SiF_4 , and 2.0 torr Cl_2 in 10.0 cm pathlength cell.

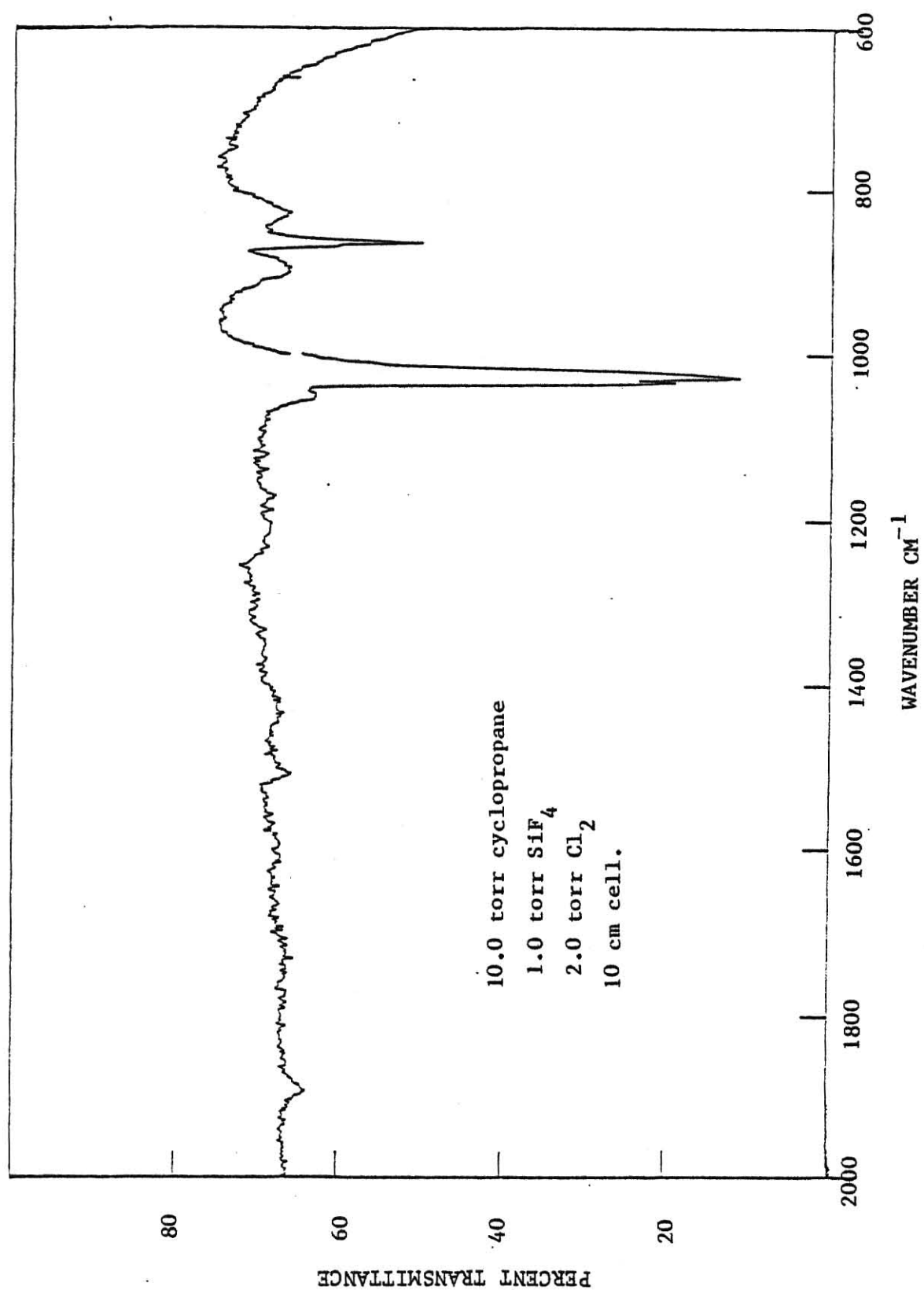


Figure 4. Infrared spectrum of 10.0 torr
n-butane in 10.0 cm pathlength
cell.

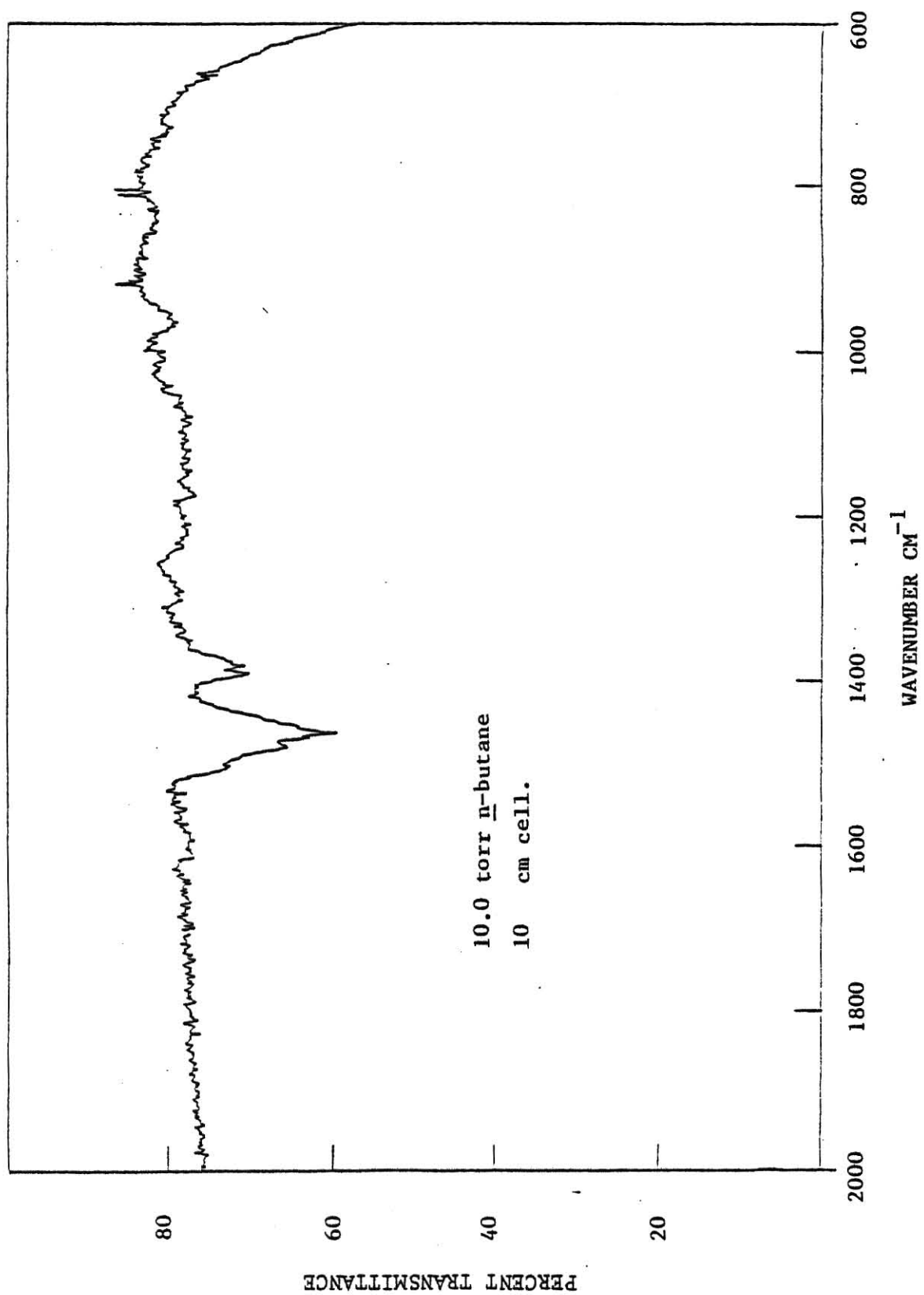
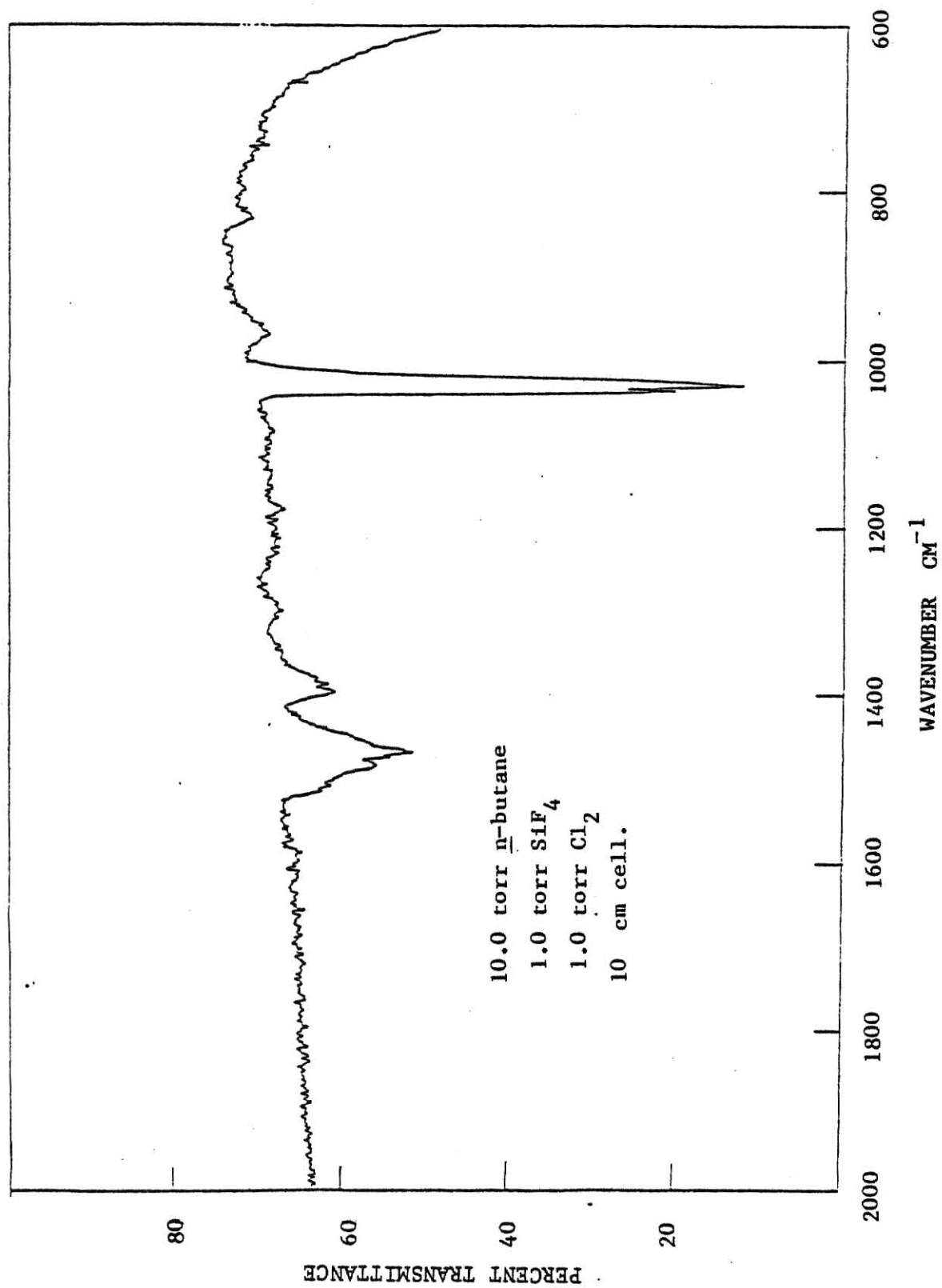


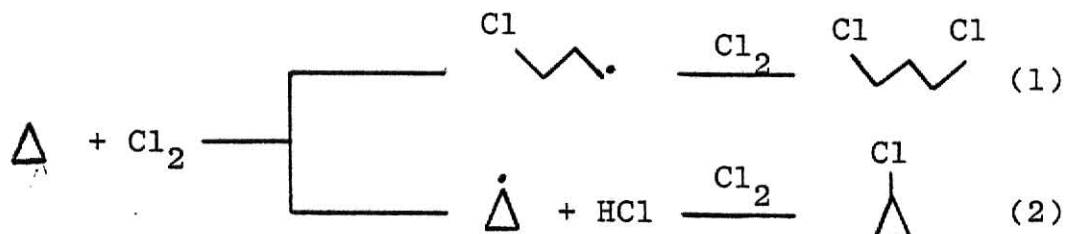
Figure 5. Infrared spectrum of 10.0 torr
n-butane, 1.0 torr SiF₄, and 1.0
torr Cl₂ in 10.0 cm pathlength
cell.



III. INFRARED LASER-INDUCED CHLORINATION OF CYCLOPROPANE

1. Literature Review

The chlorination of cyclopropane has interested a number of researchers because a number of products can be obtained.²⁸ There are two primary reaction pathways (reactions 1 and 2) possible depending on the reaction con-

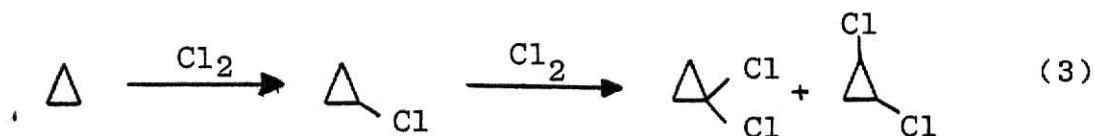


ditions. Reaction 1 is the ring-opening reaction where 3-chloropropyl radical is first formed and can further react with chlorine molecules without forming any HCl and subsequently produce 1,3-dichloropropane. Reaction 2 is a substitution reaction where the first step is a hydrogen abstraction forming cyclopropyl radical and HCl which further reacts with chlorine to form chlorocyclopropane.

Walling and Fredricks²⁶ found that chlorination of cyclopropane in carbon tetrachloride solution with Cl_2 led to a mixture of 1,3-dichloropropane and chlorocyclopropane. The temperature of the reaction affected the distribution of products. For example, at 0°C , 1,3-dichloropropane was formed in 61.4% yield compared to a chlorocyclopropane yield of 15.4%. Increasing the temperature to 68°C resulted in chlorocyclopropane being in 47.3% and only a 33.5% yield of 1,3-dichloropropane was observed. On the other hand,

chlorination of cyclopropane with t-butyl hypochloride gave mainly chlorocyclopropane. The authors²⁶ suggested that the increase in ring-opening pathway at low temperature as compared to hydrogen abstraction pathway may be attributed to lower activation energy but also low probability (A-factor) for the ring-opening reaction. This is in agreement with the heat of reaction reported by Shea and Skell²⁹ in which the heat of reaction for the ring opening chlorination was estimated to be ~ -27 kcal/mole and that for hydrogen abstraction was 0 kcal/mole. In a more recent report Baghal-Vayjovee and Benson³⁰ reported that the heat of formation of cyclopropyl radical is 3.1 ± 0.25 kcal/mole.

Most reports on the chlorination of cyclopropane have involved gas phase reactions. A number of products in addition to chlorocyclopropane and 1,3-dichloropropane were reportedly obtained, mainly derived from secondary reactions. Gustavson,²¹ Dedio, et al.,²³ Slavey,²⁴ and Stevens²⁵ obtained 1,1-dichlorocyclopropane as the major product in the photochemical chlorination of cyclopropane along with higher boiling products such as cis- and trans-1,2-dichlorocyclopropane and other polychlorinated compounds. Stevens²⁵



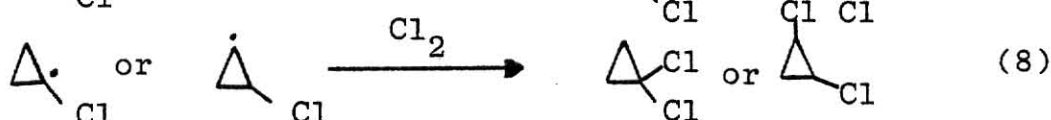
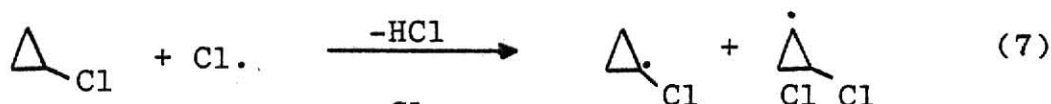
reported that the initially produced chlorocyclopropane reacted readily with more chlorine forming 1,1- and 1,2-dichlorocyclopropane in an approximate ratio of 40:1 (reaction

3). Most of these reactions were carried out in a flow system and the chlorine atoms were generated by photolysis of molecular chlorine by visible light at wavelength ~ 335 nm. Interestingly, no significant ring opening reaction was observed in these gas phase reactions. The reaction mechanism was that of a free radical chain process with chlorine atoms being the chain carrying radicals (reactions 4-8).

Initiation



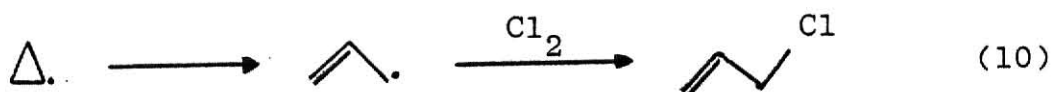
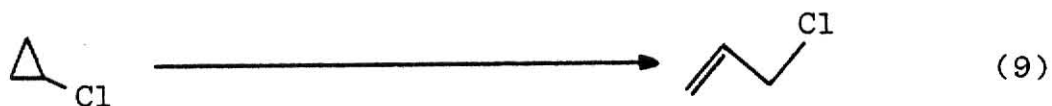
Propagation



The Arrhenius parameters for the hydrogen abstraction step (reaction 5) in the chlorination of cyclopropane are known. By competitive chlorination with either ethane or methane, Knox and Nelson³¹ found that hydrogen abstraction occurred with a rate constant of $k = 5.4 \times 10^{10} \exp(-4120/RT) \text{ M}^{-1} \text{ s}^{-1}$. Hydrogen abstraction of cyclopropane is relatively slower than the higher cycloalkane homologs, due to the higher C-H bond strength of cyclopropane compared to larger ring compounds. The bond dissociation energy of cyclopropane

was found³⁰ to be 106.3 kcal mole⁻¹ which is the highest of any saturated hydrocarbon. As a comparison, cyclobutane and cyclopentane react four and five times faster, respectively with chlorine at 300 K.

The only thermal study on the chlorination of cyclopropane was conducted by Roberts and Dirstine.²² Using a flow system, chlorine and cyclopropane were allowed to react at a temperature between 215 C to 585 C. They found that temperatures in excess of 500 C were required in order for all the chlorine to react when a five-fold excess of cyclopropane was used. Table 1 gives their results of the thermal chlorination from temperatures of 500 C to 585 C. The products obtained were similar to the results of the photolysis reaction except for the recovery of 3-chloropropene. This compound was produced largely at high temperature and/or longer contact time with the heating surface. It was apparent that this product resulted from the thermal isomerization of either chlorocyclopropane (reaction 9) or the intermediate cyclopropyl radical (reaction 10).³³ An interesting result



to note in these thermal reactions was that significantly more chlorocyclopropane was produced than 1,1-dichlorocyclopropane contrary to the photolysis reaction. They also

TABLE 1. Thermal Chlorination of Cyclopropane ^a							
Temperature °C	Residence Time sec.	Δ/Cl_2	% Reaction	% ΔCl	% $\sim\text{Cl}$	% $\text{C}\begin{smallmatrix} \text{Cl} \\ \diagdown \\ \text{Cl} \end{smallmatrix}$	% High-boiling products
500	0.1	5.85	61.0	63.0	1.0	0.2	35.8
500	0.1	5.97	42.0	55.3	1.8	0.2	42.7
510	0.3	6.42	89.5	37.0	19.6	0.5	22.9
585	0.05	1.76	64.0	29.6	11.6	0.3	58.5
100 ^b	0.9	6.37	95.6	50.5	0.1	10.9	38.5

a. From reference 22.

b. Photolysis reaction at 100° C and 0.9 s exposure time.

collected 1,3-dichloropropane, especially at higher temperatures, which constituted most of the high boiling products in Table 1.

The draw-back on the thermal method is the formation of 3-chloropropene in most cases, which cannot be separated easily as the boiling point difference is only two degrees; the boiling point of chlorocyclopropane is 43° C and that for 3-chloropropene is 45°C. Because of this practical problem the authors²² suggested the photochemical method as more convenient for the synthesis of chlorocyclopropane even though the relative yield was lower than thermally-initiated experiments.

2. Results

Preliminarily, we were looking for a bifunctional reactant to study a dual channel infrared laser-induced bimolecular reaction. Cyclopropane seems to be an appropriate choice since it has an absorption band in the CO₂ pulsed laser frequency region. Furthermore, cyclopropane was slow, at least in solution,²⁶ to react with chlorine molecules by two pathways, i.e., hydrogen abstraction and ring-opening. From these early experiments, we saw the possibility of synthesizing cyclopropane by infrared laser excitation. Cyclopropane has an infrared absorption band at 1029 cm⁻¹ and when a cyclopropane/chlorine ratio of 5.0 was irradiated at this frequency, very little chlorination reaction was observed. On the other hand, employing SiF₄ as a sensitizer enabled us to obtain a high yield of chlorocyclopropane and

only relatively small amounts of other products. We also discovered that the reaction yield could be increased dramatically by introducing a small amount of di-t-butyl peroxide. Several factors such as cyclopropane/chlorine ratio and number of pulses that affect the yield of chlorocyclopropane and the extent of secondary reactions were studied.

The first set of experiments addressed the effect of changing the cyclopropane to chlorine ratio (Table 2). The partial pressures of cyclopropane and the sensitizer, SiF₄, were maintained at 10.0 torr and 1.0 torr, respectively. The chlorine concentration was varied from 2.0 torr to 20.0 torr such that the cyclopropane/chlorine ratio was decreased from 5.0 to 0.5. The fluence was kept as constant as practical at $\sim 1.2 \text{ J cm}^{-2}$; di-t-butyl peroxide at 0.03 torr was included in the reaction mixture to initiate the reaction. At the same time, we compared the effect of increasing the number of pulses from 10 to 25.

The product was mainly chlorocyclopropane with a relatively small amount of 1,1-dichlorocyclopropane. The high-boiling products included a small amount of 1,3-dichloropropane and unidentified compounds probably cis- and/or trans-1,2-dichlorocyclopropane²⁵ and 2,3 dichloropropene (from rearrangement of 1,1-dichlorocyclopropane³⁴). These unidentified compounds are suggested in view of their relative glpc retention time as compared to the other known reaction products. The glpc response for these unknown

TABLE 2. Product distribution^a on the SiF₄ sensitized infrared laser-induced chlorination of cyclopropane at constant laser fluence ($\sim 1.2 \text{ J cm}^{-2}$), constant SiF₄ pressure (1.0 torr), and 0.03 torr di-t-butyl peroxide.

Δ (torr)	Cl ₂ (torr)	No. of Pulses	E _{abs} kcal/ mole SiF ₄	% Con- version ^b	Chlorocyclopropane ^c		Cl Δ_{Cl} % Prod- uct	High Boiling Product %	T _{eff} K	
					Absolute Yield (torr)	% Yield ^d Prod- uct				
10.0	2.0	10	62±6	75.5±9.0	1.3±0.2	65	86.1	4.0	9.9	600±20
10.0	5.0	10	80±6	57.8±7.6	2.4±0.4	48	84.5	6.2	10.4	640±20
10.0	10.0	10	86±10	34.8±2.8	2.9±0.2	29	83.3	6.9	9.8	630±30
10.0	20.0	10	93±10	41.7±3.8	3.1±0.3	31	73.4	20.1	6.5	590±20
10.0	2.0	25	80±7	87.0±2.0	1.5±0.0	75	85.1	3.4	11.5	670±30
10.0	5.0	25	74±2	58.6±0.4	2.4±0.0	48	82.9	5.8	11.3	620±10
10.0	10.0	25	68±4	38.6±1.1	3.1±0.1	31	79.5	9.3	11.1	610±10

a) The amount of products has been compensated for the dark reaction (Table 3).

b) Percent conversion based on the limiting reagent.

c) $\sim 3\%$ of 3-chloropropene was found to be present in the chlorocyclopropane observed (see Table 6 and accompanying discussion).

d) Percent yield of chlorocyclopropane based on the limiting reagent which is usually ²5% chlorine.

products were calibrated using 1,3-dichloropropane. Interestingly, the small amount of 1,3-dichloropropane formed in the laser-induced reaction was generally comparable to the dark reaction (Table 3). The amount of 3-chloropropene formed during the laser-induced reaction was determined in a similar experiment employing 10.0 torr cyclopropane, 2.0 torr chlorine and 1.0 torr SiF_4 . For 10 pulses irradiation at a fluence of $\sim 1.2 \text{ J cm}^{-2}$, $\sim 3.0 \%$ 3-chloropropene was observed.

The extent of dark reaction at various cyclopropane/chlorine ratios is reported in Table 3. Constant amounts of SiF_4 (1.0 torr) and di-*t*-butyl peroxide (0.03 torr) were included in the reaction cell. The reaction mixture was allowed to react in the dark for a similar length of time as that required to perform the laser-induced experiments, i.e., ~ 5 minutes.

At low chlorine pressure, 2.0 torr and 5.0 torr, very little dark reaction was observed. The dark reaction became significant at high chlorine pressure (20.0 torr) where as high as $\sim 13\%$ reaction was obtained. High cyclopropane/chlorine ratios yielded essentially no chlorocyclopropane but this product increased to 0.63 torr at low cyclopropane/chlorine ratio. Similar increases were observed for 1,1-dichlorocyclopropane and 1,3-dichloropropane but the other high-boiling products remained essentially constant.

As seen in Table 2, as much as 75% of chlorocyclopropane was obtained, based on chlorine as the limiting reagent.

TABLE 3. Extent of dark reaction of cyclopropane with chlorine at room temperature ($\sim 300^\circ \text{K}$) at various Δ/Cl ratio. Constant amount of SiF_4 (1.0 torr) and di-t-butyl peroxide (0.03 torr) were included in the reaction mixture

Δ (torr)	Cl_2 (torr)	%reaction	Δ_{Cl}		Δ_{Cl}		$\text{Cl} \sim \sim \text{Cl}$		"Other Products"	
			Absolute Yield (% Yield) (torr)	Absolute Yield (% Yield) (torr)	Absolute Yield (% Yield) (torr)	Absolute Yield (% Yield) (torr)	Absolute Yield (% Yield) (torr)	Absolute Yield (% Yield) (torr)	Absolute Yield (% Yield)	Absolute Yield (% Yield)
10.0	2.0	2.0	0.00 (0.0)	0.02 (1.0)	0.00 (0.0)	0.02 (1.0)	0.00 (0.0)	0.02 (1.0)		
10.0	5.0	2.0	0.03 (0.6)	0.02 (0.4)	0.02 (0.4)	0.02 (0.4)	0.02 (0.4)	0.03 (0.6)		
10.0	10.0	4.1	0.28 (2.8)	0.07 (0.7)	0.04 (0.4)	0.07 (0.7)	0.04 (0.4)	0.02 (0.2)		
10.0	20.0	13.3	0.63 (6.3)	0.58 (5.8)	0.09 (0.9)	0.58 (5.8)	0.09 (0.9)	0.03 (0.3)		

The relative per cent of chlorocyclopropane in the products was quite high, in most cases > 80%. Increasing the amount of chlorine in the reaction mixture decreased the per cent yield of chlorocyclopropane even though the absolute yield increased correspondingly with the amount of chlorine used. For instance, the absolute yield increased from 1.3 torr to 3.1 torr when chlorine was increased from 2.0 torr to 20.0 torr in experiments with 10 pulses. At low cyclopropane/chlorine ratios, i.e., high chlorine pressure, the formation of 1,1-dichlorocyclopropane became important. The amount of the high-boiling product remained essentially constant even at high chlorine pressure. Increasing the number of pulses from 10 to 25, did not effect the per cent conversion significantly except for the high cyclopropane/chlorine ratio experiments where, by increasing the number of pulses, the per cent conversion was increased by more than 10%.

The effect of increasing the number of pulses on the per cent of conversion and distribution of product can be seen in Table 4. As expected, the yield of chlorocyclopropane increased as the number of pulses was increased from 1 to 50. The effect of a single pulse in augmenting the chain reaction was much more than the subsequent pulses. With a single pulse, 0.5 torr of chlorocyclopropane was obtained, and increased to 0.9 torr and 1.3 torr when 5 and 10 pulses were applied respectively. Subsequent pulses, after the 10th pulse, resulted in very little or no additional increase in the yield of chlorocyclopropane. This result is clearly shown by the per cent conversion per

TABLE 4. Effect of number of pulses on the yield of chlorocyclopropane and percent of other products in the infrared laser-induced chlorination of cyclopropane and constant cyclopropane/chlorine ratio (10.0 torr Δ : 2.0 torr Cl_2) and laser fluence of $\sim 1.2 \text{ J cm}^{-2}$. The sensitizer SiF_4 and di-*t*-butyl peroxide is kept at constant pressure of 1.0 torr and 0.03 torr, respectively.

No. of Pulses	E_{abs} Kcal/mole SiF_4	% Conversion	Chlorocyclopropane ^a			ΔCl		High- Boiling % Prod- uct	T_{eff} K
			Absolute Yield (torr)	% CPD ^b	% Product	% Product	% Product		
1	63 $\pm$ 1	31.0 $\pm$ 1	0.5 $\pm$ 0.1	25.0	74.2 $\pm$ 6.9	4.8 $\pm$ 0.4	21.0 $\pm$ 6.6	620 $\pm$ 10	
5	60 $\pm$ 7	53.0 $\pm$ 9.0	0.9 $\pm$ 0.1	9.0	81.1 $\pm$ 3.6	3.8 $\pm$ 0.6	15.1 $\pm$ 4.2	590 $\pm$ 30	
10	62 $\pm$ 6	75.5 $\pm$ 9.0	1.3 $\pm$ 0.2	6.5	86.1 $\pm$ 3.9	4.0 $\pm$ 1.8	9.9 $\pm$ 3.0	600 $\pm$ 20	
25	80 $\pm$ 7	87.0 $\pm$ 2.0	1.5 $\pm$ 0.0	3.0	85.1 $\pm$ 2.1	3.4 $\pm$ 1.8	11.5 $\pm$ 0.6	670 $\pm$ 30	
50	74 $\pm$ 5	88.5 $\pm$ 8.0	1.3 $\pm$ 0.1	1.4	81.2 $\pm$ 4.7	4.0 $\pm$ 2.1	14.7 $\pm$ 2.7	650 $\pm$ 10	

a) The amount of 3-chloropropene was found to be $\sim 0.7\%$ for 1 pulse and increase to $\sim 3.8\%$ for 50 pulses (see Table 6).

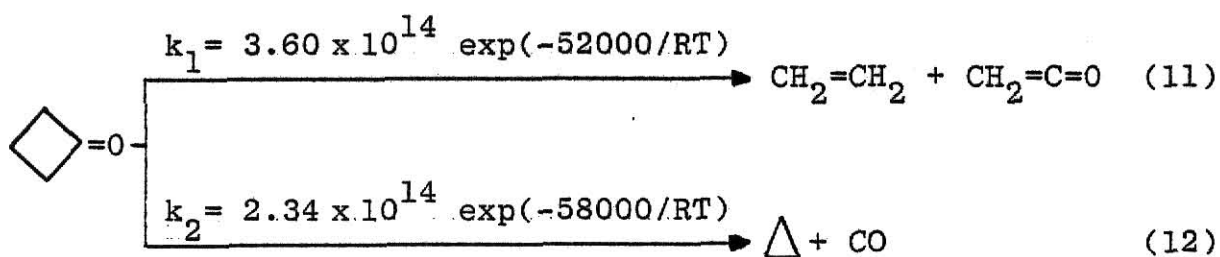
b) Percent yield of chlorocyclopropane per laser pulse.

dose (% CPD) which is the per cent yield of chlorocyclopropane per laser pulse. It can be seen that in the single pulse experiment, a 25.0% conversion was observed whereas the % CPD drop to 1.4 in the 50-pulse experiment. From these data, it can be concluded that, after the tenth pulse, the reaction was almost completed as a result of the near depletion of initiator and Cl_2 and the inhibitory effect of accumulated HCl . This set of experiments is important in optimizing the efficiency of the laser-induced reaction. The secondary reactions remained almost constant with the increase in the number of pulses as is reflected by the almost constant relative per cent of the chlorocyclopropane obtained and the per cent products of other compounds. This indicates that there was no significant decomposition of products by subsequent laser pulses which fulfills an important criterion of a useful laser synthetic process.

3. Temperature

Since temperature has an important effect on the formation of chlorocyclopropane and the extent of competing reactions, it is of significance to determine the temperature at which these reactions occurred. In a pulsed, megawatt infrared laser-induced process, there are severe temperature gradients produced during the laser pulse. The irradiated volume may attain a vibrational temperature in excess of 1000 K in $\sim 10^{-7}$ s. For total gas pressures < 0.1 torr, it has been estimated³⁵ that the irradiated volume remains at the attained temperature for 1 - 10 μs before a cooling

wave intermixes the hot and cold molecules resulting in a precipitous drop in temperature of the laser-excited molecules. Since for a unimolecular reactant, the reaction rate is an exponential function of the vibrational temperature, most reaction occurs at the maximum temperature achieved, T_{eff} . In principle, such an effective temperature, T_{eff} , can be obtained from the relative rates of two reactions with known Arrhenius parameters. A molecular reacting via two channels or two different reactants forming different products upon laser excitation can be utilized to determine T_{eff} . Most reports have employed a dual-channel unimolecular reactant.⁶ Back and Back³⁶ reported the study of direct infrared irradiation of cyclobutanone in an attempt to determine the effective temperature and the reaction time for the laser-induced decomposition reaction. The main reaction path was the decomposition of cyclobutanone to ethene and ketene and the other channel was the decomposition to cyclopropane and carbon monoxide (reactions 11 and 12).



By measuring the ratio of the two products formed via the two different channels, i.e. ethene to cyclopropane, the effective temperature can be calculated from the known Arrhenius parameters shown above. The authors found that the ratio of ethene to cyclopropane was approximately constant

at cyclobutanone pressures > 3 torr and this ratio corresponded to $T_{\text{eff}} = 830 \pm 30$ K. Since a relatively small amount of cyclopropane was produced, this estimated temperature may not be very accurate.

Steel and coworkers,³⁵ using the same reactant but employing ammonia as sensitizer, calculated the temperature of the reaction using the same procedure. Utilizing 49 torr NH_3 and 1 torr cyclobutanone, the authors determined temperatures ranging from 1027 K to 1318 K, depending on the energy absorbed. Similar to the result of Back and Back,³⁶ the small amount of cyclopropane produced in the reaction precluded an accurate estimate of the temperature.

Rosenfeld, et al.³⁷ in their study on infrared laser photodecomposition of ethyl vinyl ether observed that the ratio of products was insensitive to changes in the reactant pressure over the range of 5-440 torr. From the ratio obtained, they calculated the temperature to be ~ 1600 K.

Another method that has been employed to calculate T_{eff} in infrared laser-induced reactions employs the absorbed laser energy and heat capacities of the reaction mixture. Presses and co-workers³⁸ attempted the calculation of temperature by this method for the decomposition of perfluorocyclobutane. Temperatures of 700-1500 K were obtained depending on the energy absorbed and bath gas, argon, added to the system. Steel, et al.³⁵ employed this method to obtain T_{eff} and compared the result with the temperature obtained from the product ratio as described above. Two

different sets of temperatures were reported from the heat capacity method. One was $T_{V,R}$, where it was assumed that V-R energy relaxation was fast and only the vibrational-rotational heat capacities, $C_V(V,R)$, was in effect and utilized in the calculation. The other calculated temperature was $T_{V,R,T}$, where $C_V(V,R,T)$ was used in the calculation which assumed R-T relaxation can compete with V-R relaxation. The maximum temperature achieved under the latter conditions would correspond to complete Boltzmann equilibration. Their results indicate that $T_{V,R,T}$ from the full heat capacities was closer to the temperature obtained from the ratio of the products. This is in line with the result in which a sensitizer was used to induce the reaction indicating that translational energy played an important part in the excitation process.

Back and Back³⁶ also performed the calculation of temperature by the heat capacity method in the direct excitation of cyclobutanone. Under unfocussed condition and employing 9.5 torr of cyclobutanone, they found that the temperature depended a great deal on the laser fluence. At the highest fluence used, 1.65 J/cm^2 , the temperature was calculated to be 800 K while at low fluence of 0.40 J/cm^2 , the temperature was only 440 K.

We employed a similar method, with some modifications, to the heat capacity expression to calculate the maximum temperature for the laser induced chlorination of cyclopropane. All of the reports above employed unimolecular,

one-step processes while the chlorination reactions discussed herein are chain processes. It is almost certainly not realistic to consider T_{eff} as the reaction temperature in a chain process since the reaction probably continues even after the temperature decreases. For example, in laser-induced bimolecular chlorination of H_2S , H_2 , and CH_3SH , Nesbitt and Leone¹⁹ found that the chain lifetimes for these reactions were in the order of 500 μs as compared to $\sim 1 \mu\text{s}$ for laser-induced unimolecular decomposition. Nevertheless, T_{eff} may reflect the maximum temperature achieved by the system which in the present case may determine the amount of decomposition of unimolecular initiator, di-t-butyl peroxide.

The heat capacity of a reacting system can be obtained from the sum of the heat capacities for each component weighted by the corresponding mole of each compound as described in Appendix A. We performed temperature calculations on all of the laser-induced reactions and report T_{eff} in Tables 2, 4, 5, 6 and 7. Except where indicated, all temperatures were calculated in terms of the irradiated volume, i.e., by considering only the heat capacity of the mixture in the active volume. This seems to be justified since T_{eff} then represents the maximum temperature achieved by the system. It should be noted that the error in measuring the amount of energy absorbed was $\sim \pm 0.08$ joule which corresponds to a difference of about ± 20 K in the calculated temperature. The value to T_{eff} was rounded to 2 significant figures. In Table 2, for which a constant pressure

of SiF_4 was used, the effective temperature calculated ranges between 590 K to 670 K depending on the amount of each gas present in the reaction mixture. The error limits shown were the standard deviation from two or more experiments. The heat capacity of chlorine did not affect the total heat capacity of the system greatly and, hence, the effective temperature did not vary greatly with the amount of chlorine present.

A significant increase in T_{eff} was observed when the amount of sensitizer, SiF_4 was increased. To a lesser extent, an increase in fluence also increased T_{eff} . Table 5 shows a change in T_{eff} from ~ 500 K to ~ 1000 K by changing the SiF_4 pressure from 0.5 torr to 5.0 torr. Increasing the laser fluence from 0.62 J cm^{-2} to 2.13 J cm^{-2} while keeping the SiF_4 pressure constant at 1.0 torr increased T_{eff} from ~ 500 K to ~ 800 K. The ratio of the transmitted laser fluence to the incident fluence, I/I_0 , indicates the amount of the infrared laser radiation being absorbed. At a constant fluence of $\sim 1.2 \text{ J cm}^{-2}$, 0.5 torr SiF_4 absorbed $\sim 11\%$ and 1.0 torr SiF_4 absorbed $\sim 15\%$ of the laser energy. At higher SiF_4 pressure, much more of the energy was absorbed where, for instance, 5.0 torr SiF_4 absorbed $> 50\%$ of the laser energy. Varying the laser fluence slightly changed the I/I_0 ratio. In the high fluence (2.13 J cm^{-2}) experiment, $\sim 36\%$ of the laser energy was absorbed.

TABLE 5. Effect of SiF_4 pressure and laser fluence on product distribution and T_{eff} for 10 pulses of infrared laser irradiation. Constant amount of cyclopropane (10.0 torr), chlorine (2.0 torr) and di-*t*-butyl peroxide (0.03 torr).

SiF_4 (torr)	Fluence (J cm^{-2})	I/I_0 ^a	Total E_{abs} (joule)	E_{abs} (kcal/ mole SiF_4)	Chlorocyclopropane abs. Yield (torr)	% Yield	Chlorocyclopropane % Prod-uct	$\sim \text{Cl}$ % Prod-uct	ΔCl % Prod-uct	High- Boiling Products % Prod- uct	T_{eff} °K
0.5	1.19	0.89	0.16±0.02	78±10	0.68±0.14	34	82.9	-	3.6	13.4	510±30
1.0	1.22	0.85	0.25±0.02	62±6	1.26±0.18	63	83.5	2.6	4.0	9.9	600±20
2.5	1.24	0.66	0.60±0.01	60±1	1.00±0.15	50	64.9	7.8	7.8	19.5	850±20
5.0	1.22	0.42	0.91±0.01	46±1	0.16±0.01	8	7.7	64.5	3.8	24.0	970±10
1.0	0.62	0.78	0.17±0.00	43±1	1.19±0.01	60	87.5	-	5.1	7.4	520±10
1.0	1.22	0.85	0.25±0.02	62±6	1.26±0.18	63	83.5	2.6	4.0	9.9	600±20
1.0	2.13	0.64	0.44±0.00	110±1	1.48±0.09	74	86.1	2.3	0.6	11.0	840±10

a) The ratio of the transmittance fluence to the incident fluence.

b) Amount of 3-chloropropene was determined in separate experiments (Table 6) and calculated from the yield of chlorocyclopropane observed here.

TABLE 6. Analysis on the formation of 3-chloropropene in the laser induced reaction for 1 and 10 pulses. A constant fluence $\sim 1.2 \text{ J cm}^{-2}$ and 0.03 torr di-t-butyl peroxide were employed.

Δ (torr)	Cl_2 (torr)	SiF_4 (torr)	No. of pulses	Fluence (J cm^{-2})	% ΔCl	% $\searrow\text{Cl}$	T_{eff}
10.0	2.0	1.0	1	1.24	99.3	0.7	650
10.0	2.0	2.5	1	1.23	9.18	8.2	780
10.0	2.0	5.0	1	1.19	47.8	52.2	970
10.0	2.0	1.0	10	1.24	97.0	3.0	570
10.0	2.0	2.5	10	1.22	89.1	10.9	800
10.0	2.0	5.0	10	1.19	10.6	89.4	970
10.0	2.0	1.0	10	2.17	97.6	2.4	840
10.0	2.0	1.0	50	1.24	96.2	3.8	560

The effect of increasing T_{eff} on the reaction yield and product distribution is presented in Tables 5 and 6. Table 5 shows the complete analysis of the products in the laser-induced chlorination of cyclopropane at various SiF_4 pressures. Table 6 shows the results of separate experiments in determining the amount of 3-chloropropene formed during the laser-induced reaction. We were able to separate chloropropane and 3-chloropropene using a 20% propylene carbonate column at room temperature. Table 6 reveals that at $T_{\text{eff}} = \sim 600^\circ \text{K}$, $< 1\%$ of 3-chloropropene was formed with 1 pulse and increased to $\sim 3\%$ after 10 pulses. The amount of 3-chloropropene increased significantly when $T_{\text{eff}} > 800^\circ \text{K}$ where for instance, in the 5.0 torr SiF_4 -sensitized reaction, $\sim 52\%$ of 3-chloropropene was formed with 1 pulse and increased to $\sim 89\%$ after 10 pulses.

The amounts of 3-chloropropene observed in these experiments were then used to determine the per cent product of 3-chloropropene in Table 5. For the 0.5 torr and 1.0 torr SiF_4 -sensitized experiment, $\sim 83\%$ relative yields of chlorocyclopropane were obtained and the absolute yield was 34% and 63% respectively. No 3-chloropropene was formed with 0.5 torr SiF_4 and only 2.6% was produced at 1.0 torr of sensitizer. Increasing T_{eff} to $> 800^\circ \text{K}$ resulted in the decrease in yield of chlorocyclopropane. The primary reason, as seen in Table 6, is the formation of 3-chloropropene which is mainly due to the isomerization of chlorocyclopropane.

Many additional peaks in addition to 3-chloropropene were observed with 5.0 torr SiF_4 present. Upon condensing the reacted mixture in liquid nitrogen for injection into the GC, we observed some compounds, possibly methane or ethane that could not be condensed. Formation of methane and ethane is expected at high levels of excitation where fragmentation reactions of cyclopropane would occur.¹³ All the additional peaks were included in "high-boiling products" reported in Table 5.

Changing the laser fluence also had a significant effect on the reaction yield. Employing a constant pressure of SiF_4 (1.0 torr), and cyclopropane/chlorine ratio (5.0), the absolute yield of chlorocyclopropane increased from 60% to 74% when the fluence was increased from 0.62 J cm^{-2} to 2.13 J cm^{-2} . Interestingly, at the higher fluence, only a small amount of 3-chloropropene was formed even though $T_{\text{eff}} > 800 \text{ K}$. The other products were still about the same as compared to a typical reaction with a fluence of $\sim 1.2 \text{ J cm}^{-2}$.

4. Chainlength

Chlorination of hydrocarbons has been shown to involve long chain lengths, in some cases up to 10^7 cycles being observed.⁴³ The chainlength may be calculated from the ratio of the rate of the propagation step to the rate of the initiation step in a chain reaction. Generally, the initiation process involves the photolysis or thermal dissociation of Cl_2 molecules or other chlorination agents but other processes have also been reported including

molecular induced homolysis of Cl_2 and chemical initiation by an added initiator.²⁰ The propagation steps involve hydrogen abstraction by chlorine atoms (chain carrier) and the subsequent reaction of the alkyl radical with Cl_2 producing another chlorine atom and the chlorinated hydrocarbon. These propagation steps can proceed indefinitely, at least in theory, and thus produce a long chain process. However, in practice, the chain process is limited by termination reactions involving radical-radical combinations and the chain-length is usually determined by the extent of these reactions.⁴⁴

In the present system, we employed di-t-butyl peroxide to initiate the chain chlorination of cyclopropane. Even though the effective temperature obtained by the SiF_4 sensitized infrared laser irradiation was high enough to break the Cl-Cl bond, only a small amount of reaction was observed. On the other hand, by adding the peroxide, significantly more reaction was observed. It has been shown^{45,46} that di-t-butyl peroxide is an efficient initiator for the polymerization of styrene; the efficiency factor for di-t-butyl peroxide to initiate the reaction was close to unity. Thus, in the present experiments, we employed an initiator efficiency factor of 1.0 when calculating the chain-length for the present reaction system.

Actually, we were not able to calculate the chain-length from the ratio of the rate of propagation to that of initiation. From the mechanism and rate expression that

that will be discussed later in the discussion section, it is evident that the concentration of chlorine atoms needs to be known before the rate for the propagation step can be calculated. However, from the available data we were able to calculate the chainlength according to equation 13.

$$\text{Chainlength} = \frac{\text{amount of chlorocyclopropane formed}}{2 \times (\text{amount of di-}t\text{-butyl peroxide consumed})} \quad (13)$$

Literally, chainlength is the number of cycles the chain reaction occurs per initiator consumed. Thus, in the present system, the chainlength can be defined as the number of molecules of chlorocyclopropane produced when initiated by one t -butoxyl radical. This is a reasonable assumption considering the formation of chlorocyclopropane in high yield in these infrared laser induced reactions. In those cases where 3-chloropropene was formed, the small amount of this secondary product with one laser pulse is included in the calculation. The amount of initiating t -butoxyl radicals was taken to be twice the amount of di- t -butyl peroxide decomposed since two molecules of initiator were produced per molecule of the peroxide assuming an efficiency factor = 1.0.

Thus, for calculating the chainlength, we performed single-pulse reactions of cyclopropane and chlorine, sensitized by various amounts of SiF_4 utilizing two different amounts of di- t -butyl peroxide: 0.03 and 0.05 torr. The amount of di- t -butyl peroxide decomposed was determined from separate experiments under similar conditions as was done previously except without chlorine. The primary reason

was that we were not able to analyze the chlorinated products together with the peroxide decomposition due to these peaks having similar retention time and also the small amount of di-t-butyl peroxide to be detected compared to chlorocyclopropane produced during the reaction. The amounts of peroxide decomposed during these reactions are reported in Table 8 and will be discussed in the next section.

The single-pulse laser induced chlorination reaction is reported in Tables 7A and 7B. In Table 7A, 0.03 torr of di-t-butyl peroxide was used and various amounts of chlorine and SiF_4 were added to the reaction mixture. In the first three entries in Table 7A, 1.0 torr of SiF_4 was employed to sensitize the laser induced reaction and chlorine was increased from 2.0 torr to 10.0 torr. Under these conditions, the amount of chlorocyclopropane produced increased from 0.46 torr to 1.73 torr. This produced chainlengths ranging from 28 to 109 using a constant amount of initiator produced during the reaction (Table 8, first entry). When SiF_4 was increased to 2.5 torr, the chainlength dropped due to a greater amount of peroxide decomposed relative to the amount of chlorocyclopropane produced. For the 5.0 torr SiF_4 sensitized experiments, the amount of chlorocyclopropane dropped significantly as did the chain-lengths.

Figure 6 shows a plot of chainlength versus T_{eff} for the laser-induced chlorination of cyclopropane at various cyclopropane/chlorine ratios and utilizing 0.03 torr di-t-butyl peroxide as initiator. Overall, the chainlength

TABLE 7A. Single-pulse experiments to calculate T_{eff} and chainlength using a constant amount of di-t-butyl peroxide (0.03 torr).

Δ (torr)	Cl ₂ (torr)	SiF ₄ (torr)	Fluence (J cm ⁻²)	I/I ₀	Total E _{abs} (joule)	E _{abs} kcal/mole SiF ₄	Δ_{Cl} (torr)	T _{eff} (K)	Chain- length
10.0	2.0	1.0	1.21	0.84	0.250±0.010	63±1	0.46±0.10	620±10	28±7
10.0	5.0	1.0	1.27	0.85	0.232±0.021	59±5	1.31±0.38	560±20	82±24
10.0	10.0	1.0	1.26	0.85	0.255±0.021	64±5	1.73±0.08	550±20	109±1
10.0	2.0	2.5	1.25	0.77	0.525±0.007	53±1	0.58±0.04	800±10	18±1
10.0	5.0	2.5	1.22	0.66	0.560±0.057	56±6	1.22±0.08	790±40	40±1
10.0	10.0	2.5	1.20	0.67	0.555±0.025	56±3	2.05±0.33	750±20	67±7
10.0	2.0	5.0	1.30	0.48	0.945±0.162	47±8	0.47±0.21	980±90	13±6
10.0	5.0	5.0	1.32	0.46	0.975±0.120	49±6	0.68±0.06	970±60	18±3
10.0	10.0	5.0	1.33	0.47	0.955±0.078	48±4	0.66±0.01	920±40	17±1

TABLE 7B. Single-pulse experiments to calculate T_{eff} and chainlength using a constant amount of di-t-butyl peroxide (0.05 torr).

Δ (torr)	Cl ₂ (torr)	SiF ₄ (torr)	Fluence (J cm ⁻²)	I/I ₀	Total E _{abs} (joule)	E _{abs} kcal/mole SiF ₄	Δ_{Cl} (torr)	T_{eff} (K)	Chain- length
10.0	2.0	1.0	1.24	0.85	0.270±0.028	68±7	0.60±0.14	620±30	17±4
10.0	5.0	1.0	1.21	0.85	0.245±0.007	62±2	1.11±0.09	580±10	32±3
10.0	10.0	1.0	1.24	0.87	0.225±0.007	56±2	1.74±0.34	530±10	50±10
10.0	2.0	2.5	1.23	0.74	0.450±0.042	45±4	0.47±0.07	740±30	8±1
10.0	5.0	2.5	1.19	0.67	0.525±0.022	53±2	1.19±0.27	780±20	20±5
10.0	10.0	2.5	1.22	0.69	0.510±0.010	51±1	1.58±0.31	720±10	26±6
10.0	2.0	5.0	1.21	0.47	0.900±0.043	45±2	0.53±0.04	960±20	8±1
10.0	5.0	5.0	1.27	0.51	0.830±0.057	42±3	0.64±0.06	890±30	9±1
10.0	10.0	5.0	1.23	0.50	0.815±0.078	41±4	0.58±0.07	840±40	8±1

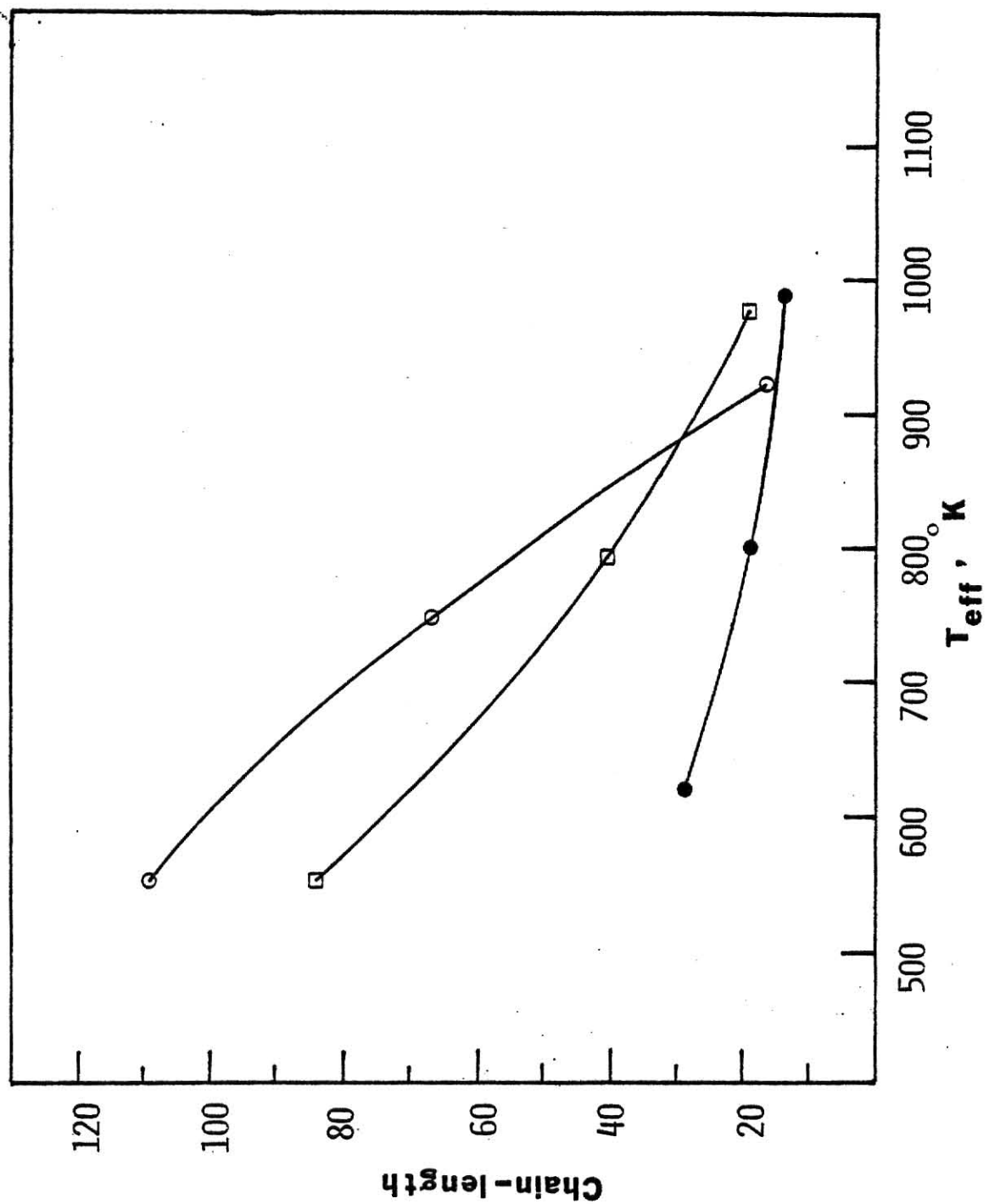
decreased with an increase in effective temperature. This was not surprising because, at high temperatures, more initiating radicals were generated which resulted in more free radicals being available and, thus, increased the extent of bimolecular termination reactions which reduce the chainlength.

A similar result was observed when 0.05 torr of di-t-butyl peroxide was utilized although, generally, the chainlength was reduced to about half of that observed with 0.03 torr of di-t-butyl peroxide (Table 7B). The chainlength dropped to only ~ 8 at 5.0 torr SiF_4 pressure. Again, these results are due to the high concentration of free radicals present at high excitation levels so that bimolecular radical-radical termination reactions become important.

5. Reaction Time

Although reaction time has not been well-defined in pulsed, infrared laser-induced processes, it has been estimated to be in the order of a few microseconds for direct excitation in unimolecular reactions at < 0.1 torr reactant pressure.^{6,35} It should be stressed that these reaction times merely represent the approximate times during which the reaction systems remain near T_{eff} . Generally, it is determined from T_{eff} and the Arrhenius parameters and accommodated for the observed yield per laser pulse. For example, Steel, et al.³⁵ reported reaction times of 2 to 20 μs for the decomposition of cyclobutanone, sensitized

Figure 6. Plot of chain-length versus T_{eff}
employing 0.03 torr di-t-butyl
peroxide at various cyclopropane/
chlorine ratios: ● $\Delta/\text{Cl}_2 = 5.0$;
□ $\Delta/\text{Cl}_2 = 2.0$; ○ $\Delta/\text{Cl}_2 = 1.0$.



by ammonia, at calculated temperatures between 1000 to 1300 K. Back and Back³⁶ estimated a reaction time of 5×10^{-4} s for direct irradiation of cyclobutanone when a calculated T_{eff} of 830 K was used. A still longer reaction time was observed by Preses, et al.³⁸ for laser-induced decomposition of perfluorocyclobutane; the reaction time was on the order of a few milliseconds with no added argon and increased to 60-80 ms with 50 torr of added argon. These reports indicate an important dependence of temperature on the reaction time where the higher the T_{eff} , the shorter is the reaction time. There is also undoubtedly a dependence of reaction time on total sample pressure since pressure will influence the nature of the cooling process.

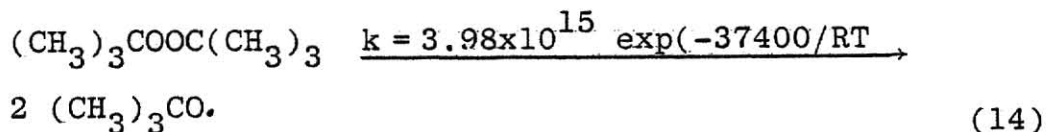
A real-time monitoring of products during a pulse laser-induced reaction should give a direct value of the reaction time. As expected, the reaction time has been shown to be dependent on the conditions and reaction system used. For example, Haas and Yahav^{47,48} using a nanosecond laser source, performed a real-time monitoring of products from the laser-induced decomposition of tetramethyldioxetane. The reaction was found to occur in two distinct stages; the first being a fast, unimolecular collision-free process which occurred during the laser pulse and the second, which the authors attributed to a collision-induced mechanism, occurred several microseconds after the laser pulse. The second process accounted for > 90% of the reaction in good agreement with previous reports of reaction time of several microseconds from the rate constant and reaction yield.

In a bimolecular reaction, it is difficult to obtain the reaction time without real-time monitoring of the appearance of products. Real time monitoring of a bimolecular reaction has been reported by Popak, et al.¹⁸ in the infrared laser-induced bromination and chlorination of chlorodifluoromethane. By recording the optical transmission of bromine and chlorine, they were able to monitor the extent of the reaction as a function of time. In the bromination reaction, they observed that the reaction did not become significant immediately after the laser pulse, but only after a lag time of $\sim 1 \mu\text{s}$ to build up the bromine atom concentration. The reaction was observed to proceed slowly, in the order of 1 ms, which agreed well with the observed yield of CBrClF_2 . For the chlorination reaction, they observed a similar behavior and the reaction time was also about 1 ms.

Another report¹⁹ deals with the study of laser-induced chemical chain reaction of chlorine with H_2 , H_2S and CH_3SH . The time development of vibrationally excited HCl product molecules was followed by detection of infrared chemiluminescence. It was observed that the photolysis of Cl_2 molecules occurred over the $2 \mu\text{s}$ duration of the laser pulse generating the initial concentration of chlorine atoms. The chain lifetimes were on the order of $\sim 500 \mu\text{s}$ for the three systems studied which is close to the value obtained by Popak, et al.¹⁸

In the present study, we were not able to calculate the chain lifetime from the available data. However, from the calculated temperature and the rate of decomposition of di-t-butyl peroxide, an estimate of the time taken to decompose the initiator can be calculated. This decomposition time, Δt , reflects the length of time the reaction system remained at T_{eff} in the irradiated volume in order to effect the decomposition of di-t-butyl peroxide. Of course, the chain process probably proceeds even after the precipitous drop in temperature resulting from the cooling process; the chain reaction is terminated by various termination processes and not by a temperature drop as in a unimolecular reaction.

The time of decomposition, Δt , of di-t-butyl peroxide was calculated from the Arrhenius parameters, T_{eff} , and the amount of di-t-butyl peroxide remaining after the laser-induced decomposition reaction (reaction 14)



Thus, by knowing the amount of di-t-butyl peroxide decomposed during the SiF_4 sensitized infrared laser irradiation, the time, Δt , can be calculated. Table 8 shows the reaction times obtained from a set of experiments using 10.0 torr cyclopropane, 0.03 torr and 0.05 torr of di-t-butyl peroxide, and various amounts of SiF_4 in order to obtain different values of T_{eff} . For example, in the first experiment, 1.0 torr of SiF_4 and 0.03 torr of the peroxide was used which gave T_{eff} of 620 K. The rate constant was then calculated

to be $2.61 \times 10^2 \text{ s}^{-1}$ and the reaction time $\Delta t = 1.2 \times 10^{-3} \text{ s}$ was obtained from equation 15.

$$\begin{aligned} \Delta t &= \frac{\ln[(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3]_0 - \ln[(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3]}{k} \\ &= \frac{\ln(2.86 \times 10^{-8}) - \ln(2.09 \times 10^{-8})}{2.61 \times 10^2} \\ &= 1.24 \times 10^{-3} \text{ sec.} \end{aligned} \quad (15)$$

When T_{eff} was increased to 810 K by using 2.5 torr SiF_4 , Δt was 2.3×10^{-6} . A still shorter time was observed at higher temperature; eg., for $T_{\text{eff}} \sim 960 \text{ K}$, Δt was found to be $\sim 8.9 \times 10^{-8} \text{ s}$. Increasing the amount of di-t-butyl peroxide to 0.05 torr still gave essentially similar values of Δt , as expected. A discussion of these results will be presented later.

6. Sunlamp-Induced Chlorination of Cyclopropane

As mentioned previously, most attempts to synthesize chlorocyclopropane have involved photolytic chlorination of cyclopropane either in a flow apparatus or static containers. It is relatively easy to induce the reaction and the chemistry is not very tedious. Even though other products are formed also and the yield of chlorocyclopropane is low, it is the easiest method available to prepare the compound. The main products of such photochlorination reactions are chlorocyclopropane and 1,1-dichlorocyclopropane; the latter is usually the major product. We were also interested in comparing the infrared laser-induced technique with the conventional photochemical method.

TABLE 8. Laser-induced decomposition of di-t-butyl peroxide in the presence of 10.0

torr cyclopropane and various amounts of SiF₄ at constant fluence of ~1.2 J cm⁻².

T_{eff} and Δt are calculated from these experiments.

$\frac{\Delta}{(\text{torr})}$	$\frac{\text{SiF}_4}{(\text{torr})}$	$\frac{+00+}{(\text{torr})}$	$\frac{\text{Fluence}}{\text{J cm}^{-2}}$	$\frac{\text{Total Eabs}}{\text{joule}}$	$\frac{\text{Eabs}}{\text{kcal/mole SiF}_4}$	$\frac{(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3}{\text{mole remained mole decomposed}}$	$\frac{\text{T}_{\text{eff}}}{(\text{K})}$	$\frac{\Delta t}{(\text{sec})}$
						(x 10 ⁻⁸)		
10.0	1.0	0.03	1.25	0.250	63	2.09+0.04	0.76+0.04	620+30 1.24x10 ⁻³
10.0	2.5	0.03	1.25	0.520	52	1.36+0.10	1.50+0.01	810+60 2.25x10 ⁻⁶
10.0	5.0	0.03	1.24	0.865	43	0.95+0.15	1.91+0.14	960+10 8.86+10 ⁻⁸
10.0	1.0	0.05	1.22	0.234	59	3.11+0.30	1.66+0.30	600+40 4.03x10 ⁻³
10.0	2.5	0.05	1.20	0.513	52	1.87+0.16	2.90+0.15	810+30 3.25x10 ⁻⁶
10.0	5.0	0.05	1.21	0.870	44	1.51+0.15	3.24+0.15	960+20 8.67x10 ⁻⁸

The sunlamp-induced reaction was performed by photolyzing the reaction mixture in a closed cell similar to that used in the laser-induced experiments for various exposure times and amount of chlorine used while keeping the cyclopropane pressure constant at 10.0 torr. The light source was a 275-watt tungsten filament General Electric sunlamp which was placed about 60-80 cm from the cell to avoid heating of the cell and reaction mixture.

Table 9 summarizes the results of the reaction performed at room temperature. The first 3 entries show the effect of increasing the amount of chlorine from 2.0 torr to 10.0 torr at constant exposure time of 30 minutes. When 2.0 torr of chlorine was used, equal amounts of chlorocyclopropane were obtained in the 55.5% reaction conversion. By increasing the amount to 5.0 torr and 10.0 torr, the percent conversion decreased slightly but the major product was 1,1-dichlorocyclopropane. For the 5.0 torr Cl_2 reaction, the 1,1-dichlorocyclopropane:chlorocyclopropane ratio was ~ 8.1 . The increase in 1,1-dichlorocyclopropane with increase in chlorine concentration is expected at high chlorine concentration since chlorocyclopropane is more reactive than cyclopropane.

Several experiments addressed the effect of time of irradiation on the reaction yield from 10.0 torr cyclopropane and 2.0 torr Cl_2 . The results showed no significant change in the reaction yield when the exposure time was varied from 15 to 60 minutes. The ratio of chlorocyclopropane to 1,1-dichlorocyclopropane remained ~ 1.0 . This indicated that the reaction was essentially completed after only 15 minutes of

TABLE 9. Product distribution from photochlorination of cyclopropane induced by a 275 watt sunlamp.

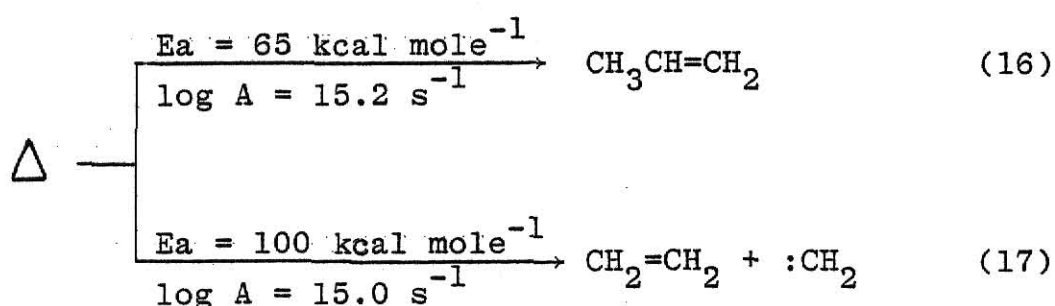
Δ (torr)	Cl_2 (torr)	Exposure Time (min)	% conversion	Δ_{Cl} % product	Δ_{Cl} % product	High-boiling products % product
10.0	2.0	30	55.5	49.5	49.5	1.0
10.0	5.0	30	49.6	26.6	71.8	1.6
10.0	10.0	30	43.8	10.7	86.5	2.8
10.0	2.0	15	53.0	54.2	45.3	0.5
10.0	2.0	30	55.5	49.5	49.5	1.0
10.0	2.0	60	58.0	51.7	44.0	4.3

irradiation with 2.0 torr of chlorine available. From the amount of chlorinated products generated, it can be calculated that $\sim 80\%$ of the Cl_2 had reacted in 15 minutes. It was not obvious why the remaining $\sim 20\%$ did not react upon longer irradiation but the question was not deemed sufficiently significant to pursue further.

No ring-opened products were observed. The small amounts of "high-boiling" products listed in the last column in Table 9 most likely were cis- and trans-1,2-dichlorocyclopropane. These products were reported by Stevens²⁵ to be present to the extent of $\sim 2.5\%$ of the 1,1-dichlorocyclopropane produced in the photochlorination of cyclopropane.

7. Discussion

Cyclopropane has been a popular molecule for infrared laser-induced studies^{50,51,52} but all investigations have involved unimolecular reactions of the molecule, e.g., reactions 16 and 17. Most studies have involved direct ir-

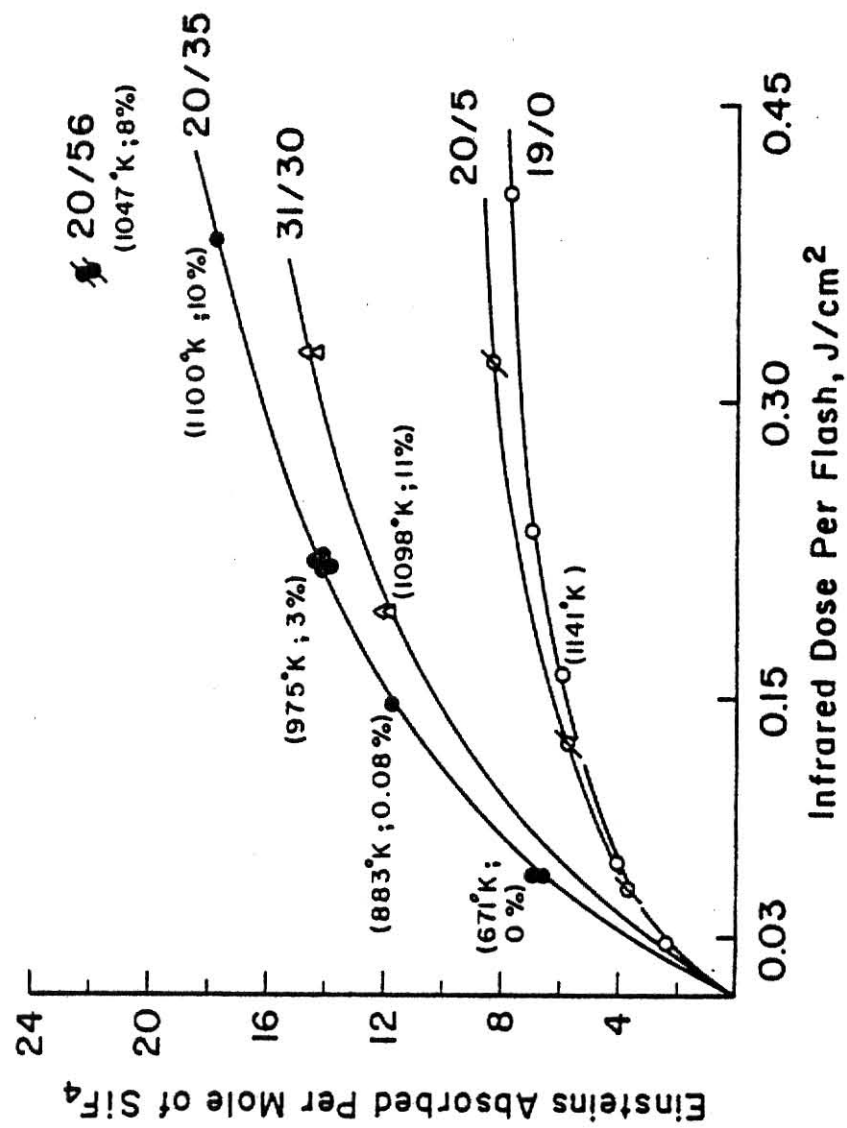


radiation of cyclopropane at high laser fluence but, by utilizing SiF_4 as sensitizer, Olszyna and co-workers¹³ were able to induce the decomposition of cyclopropane at much lower infrared power levels. At low fluence no reaction was observed but, as the fluence was increased, cyclopropane was

converted cleanly to propylene. At still higher fluence, formation of methane, ethylene and acetylene was observed. The latter products appeared to be the decomposition products of propylene. Figure 7 (from Figure 1 in reference 13) shows the percent conversion of cyclopropane in terms of the laser fluence and energy absorbed by SiF_4 . Also reported were the temperatures that would be achieved if the absorbed energy was converted adiabatically into random thermal energy. These results appear to resemble the thermal decomposition of cyclopropane⁵³ where the extent of decomposition is dependent on the temperature achieved by the system. In the SiF_4 sensitized decomposition reaction, it was observed that reaction would only occur when the "temperature" was above 900 K.

In the present study, direct excitation of cyclopropane in the presence of Cl_2 failed to produce significant chlorination products. The probably reason for no reaction would be the low excitation level achieved with an unfocused beam. We deliberately refrained from using higher laser fluences because of fragmentation reactions that might occur as observed in earlier studies of cyclopropane.^{50,51,52} Irradiation of 10.0 torr cyclopropane and 2.0 torr chlorine at 1029.4 cm^{-1} with a fluence of 1.2 J cm^{-2} resulted in an absorbed energy of $\sim 3.2 \text{ kcal/mole}$ cyclopropane which corresponded to a calculated temperature $\sim 480 \text{ K}$. Less than 2% reaction was observed after 50 laser pulses. Cyclopropane has a relatively small cross-section and the energy absorbed was not sufficient to generate free radicals to initiate the chain process.

Figure 7. Plot of energy absorbed per mole of SiF_4 as a function of infrared laser fluence (J cm^{-2}) at various SiF_4 /cyclopropane ratios. Number in brackets represent calculated temperature and percent conversion (from reference 13, Fig. 1).



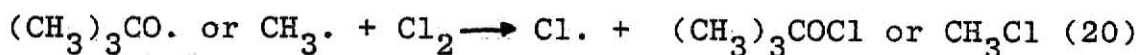
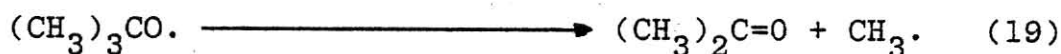
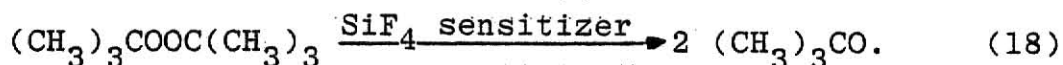
As shown by Olyszyna, et al.,¹³ using a sensitizer such as SiF_4 produces high enough temperatures to induce decomposition of cyclopropane and even propylene, $E_a \approx 65 \text{ Kcal mole}^{-1}$ and $\sim 78 \text{ kcal mole}^{-1}$, respectively. We, thus, included SiF_4 in the reaction mixture and by irradiating the mixture at 1025.3 cm^{-1} ,⁷ we observed a significant amount of reaction per laser pulse. From the energy absorbed, the calculated temperatures produced were in the range between 600 to 1000 K depending on the pressure of SiF_4 employed and the laser fluence.

Another important addition to the reaction mixture was di-*t*-butyl peroxide. As mentioned earlier, we were able to improve dramatically the yield of chlorocyclopropane by adding a catalytic amount of the peroxide which acted as a chain initiator. The advantage of utilizing di-*t*-butyl peroxide as an initiator to improve the yield is evident upon consideration of the bond energies of each reactant. The bond dissociation energies for chlorine, cyclopropane and di-*t*-butyl peroxide are 58,²⁰ 106,³⁰ and $38^{49} \text{ kcal mole}^{-1}$, respectively. In addition to bond energy, the efficiency of energy transfer from vibrationally excited SiF_4 to each reactant also plays a crucial role in initiating the chain process. Chlorine and cyclopropane, being small molecules might not undergo efficient collisional energy transfer with SiF_4 whereas the peroxide, which is definitely a large⁶ molecule would rapidly acquire vibrational excitation from the laser-activated SiF_4 . In fact, Popok et al.¹⁸ have demonstrated that chlorine and

bromine do not undergo efficient energy transfer with laser-excited SiF_4 . They observed that there was a lag time before the disappearance of bromine or chlorine after a laser pulse in SiF_4 sensitized halogenation of chlorodifluoromethane. Calculation of the percent decomposition of chlorine and di-t-butyl peroxide occurring during the estimated³⁵ 10 μs reaction time at various temperature (Table 10) reveals that decomposition of chlorine occurs significantly only at $>1000\text{ K}$ whereas di-t-butyl peroxide decomposed about 8% at 700 K and 100% at 1000 K. This demonstrated that in addition to any inefficiency in energy transfer between SiF_4 and chlorine, a much higher temperature is required for chlorine to initiate the chain reaction.

The overall mechanism for the infrared laser-induced chain chlorination of cyclopropane is summarized by reactions 18-26.

Initiation;



Propagation;



Termination;



The initiation step is the homolysis of di-t-butyl peroxide to give two t-butoxyl radicals after collisional excitation by SiF_4 . The t-butoxyl radical can undergo β -scission into methyl radical and acetone (reaction 19). From studies of the decomposition of di-t-butyl peroxide, it has been observed that, for thermal decomposition in the vapor phase, stoichiometric amounts of acetone and ethane were observed but, in the presence of a hydrogen bearing solvent,⁵⁵ the t-butoxyl radical can either abstract hydrogen directly or dissociates into acetone and methyl radical which, in turn, can abstract hydrogen from the solvent. Thus, hydrogen is abstracted in the next step by either t-butoxyl radical or methyl radical to start the chain process (reaction 21). Alternatively, either of these radicals can react with Cl_2 to produce chlorine atoms (reaction 20).

The propagation steps involve the reaction of cyclopropyl radical with chlorine (reaction 22) or chlorine atom with cyclopropane (reaction 23), to form the desired product, chlorocyclopropane, and the chain carrying radical. The Arrhenius parameters of reaction 22 have not been determined but from reports on alkyl radical abstraction of chlorine such as methyl⁵⁶ and ethyl radicals,⁵⁷ the activation energy is low, on the order of a few kcal mole⁻¹. The second propagation step has been well studied kinetically. Knox and Nelson³¹ reported that hydrogen abstraction of cyclopropane by chlorine atom has an activation energy of 4120 ± 140 cal/mole and an A-factor of 5.4×10^{10} liter/mol. sec.

TABLE 10. Percent decomposition of chlorine^a and di-t-butyl peroxide^b calculated from known Arrhenius parameters during an estimated 10 μ s reaction time at various temperature.

<u>Temperature</u> (K°)	<u>Chlorine</u> % decomposition	<u>(CH₃)₃COOC(CH₃)₃</u> % decomposition
298	0.0	0.0
500	0.0	1.8×10^{-4}
600	2.2×10^{-7}	9.5×10^{-2}
700	7.3×10^{-5}	8.0
800	5.6×10^{-3}	91.0
1000	2.4	100.0

a) rate constant for the decomposition of chlorine is

$$k = 8.7 \times 10^3 \exp (-48300/RT) \text{ from reference 53.}$$

b) rate constant for the decomposition of di-t-butyl peroxide

$$\text{is } k = 3.98 \times 10^{15} \exp (-37400/RT) \text{ from reference 49.}$$

Termination reactions are generally radical-radical combination. The primary termination process, as has been observed in many chain chlorination reactions, is chlorine atom recombination (reaction 24). The third body, M, which is necessary to render the chlorine molecule unreactive may be any unexcited molecule or the wall of the reaction cell. Some of the chlorocyclopropane might also result from the termination reaction of chlorine atom and cyclopropyl radical (reaction 25) as evident from the short chain lengths observed in the laser-induced reactions.

Cyclopropane is a strained cyclic compound and with its unsaturated character, should be expected to have a different chemistry than normal hydrocarbons or other cyclic homologs. Cyclopropane possesses a higher C-H bond dissociation energy but a lower C-C bond energy when compared to other cycloalkanes. For this reason, cyclopropane often undergoes ring-opening radical reactions whereas cyclobutane and other cycloalkane prefer hydrogen abstraction. An exception to this observation is the attack of chlorine atoms and, in certain cases, bromine atoms on cyclopropane²⁸ which results in a competition between substitution and ring-opened products.

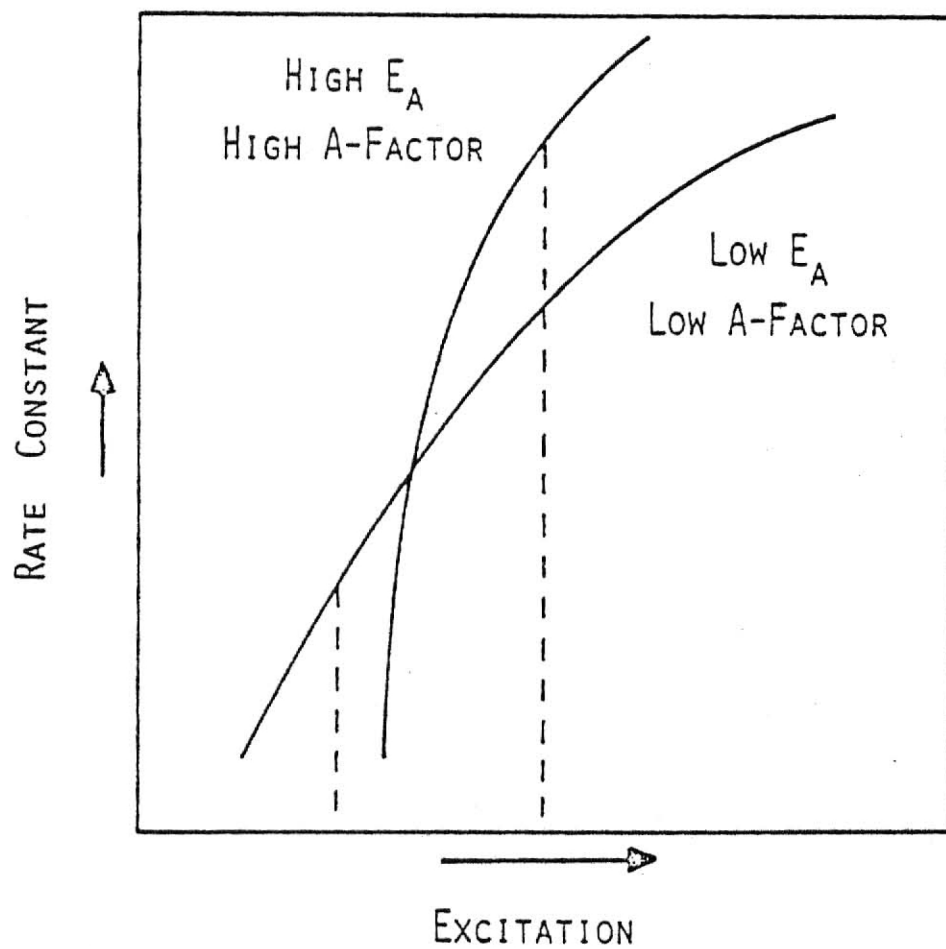
Walling and Fredricks²⁶ had demonstrated these competitive reactions for the photochlorination of cyclopropane in solution of carbon tetrachloride. They observed that these two reaction pathways depended a great deal on the temperature of the reaction. Ring-opening reaction was seen to predominate at low temperature (~273 K) but became relatively unimportant at higher temperature (341 K) where the hydrogen abstraction

reaction became the major reaction pathway. From these observations and the bond energies involved, they concluded that the ring opening reaction must have a lower activation energy than the substitution reaction but the probability (A-factor) for the former reaction to occur was smaller than the latter. Unfortunately, the Arrhenius parameters for the ring-opening reaction have not been reported but parameters for the hydrogen abstraction reaction have been reported by Knox and Nelson³¹ to be $5.4 \times 10^{10} \exp(4120/RT) \text{ M}^{-1} \text{ s}^{-1}$.

It has been shown⁶ that difference in Arrhenius parameters will affect the reaction pathway in infrared laser-induced reaction at different levels of excitation. A plot of rate constants for the two reaction pathways such as in Figure 8 illustrates how the rate of reaction changes with excitation level. At low excitation level or temperature, the low E_a , low A-factor channel predominates but at high temperature, a crossover in the rate constants occurs and the high E_a and high A-factor channel becomes competitive. In the present case, the reaction condition in the SiF_4 sensitized laser-induced chlorination of cyclopropane is such that the high energy path was followed almost exclusively.

Except for Walling and Fredricks,²⁶ previous workers did not identify 1,3-dichloropropane as a product and it was thought to be produced in negligible amount only. From our sunlamp-induced photochlorination of cyclopropane we also obtained very little of the ring-opened product.

Figure 8. Plot of rate constant versus level of excitation for two different reaction channels, one possessing a high E_a and a high A-factor while the other exhibits a low E_a and a low A-factor.



Besides competition from the high energy reaction channel, there are other possibilities that might account for the quenching of the ring-opening reaction in the gas phase. Dedio and coworkers²³ reported that, in the absence of chlorine, photobromination of cyclopropane resulted primarily in the opening of the cyclopropane ring, whereas in the chlorine-initiated photobromination, bromocyclopropane was produced. It was suggested that this may have resulted from chlorine forming a complex with cyclopropane, analogous to those with olefins and aromatic molecules;⁵⁸ cyclopropane, of course, can be considered as possessing unsaturated character. The possibility that a complex is formed in liquid phase reactions might not be true in the gas phase.

The main difference between infrared laser-induced chlorination of cyclopropane and conventional photolysis is the formation of 1,1-dichlorocyclopropane which arises from a second chlorination of the cyclopropane ring. 1,1-Dichlorocyclopropane and, to a much lesser extent, 1,2-dichlorocyclopropane, are always produced in photochlorination reaction, the former usually being the major product even with very high cyclopropane/chlorine reactant ratios. But in the infrared laser-induced reaction, only very little 1,1-dichlorocyclopropane was observed even for relatively low cyclopropane/chlorine ratios. Of course, dichlorination became more competitive at high pressure of chlorine. This is not surprising since, as more chlorine is available, a second attack of chlorine atom on the chlorocyclopropane, newly formed, is more probable. This is demonstrated in Table 2 where at

cyclopropane/chlorine ratios of 5, 2, 1, and 0.5, the chlorocyclopropane/1,1-dichlorocyclopropane product ratios are 22, 13, 12, and 4, respectively. For sunlamp-induced photochlorination utilizing cyclopropane/chlorine reactant ratios of 5, 2, and 1, chlorocyclopropane/1,1-dichlorocyclopropane ratios of 1, 0.4, and 0.1, respectively were observed. The laser-induced chlorination product ratios are comparable to the thermal reaction product ratio reported by Roberts and Dirstine²² where at cyclopropane/chlorine ratio of 6, the product ratio is 30 for the 500 C reaction. The sunlamp-induced reaction resembles the result of Dedio, et al.²³ They observed that at cyclopropane/chlorine ratios of 4.3, 1.9, 1.2, and 0.8, the chlorocyclopropane/1,1-dichlorocyclopropane product ratios were 1.9, 0.8, 0.8, and 0.7 respectively.

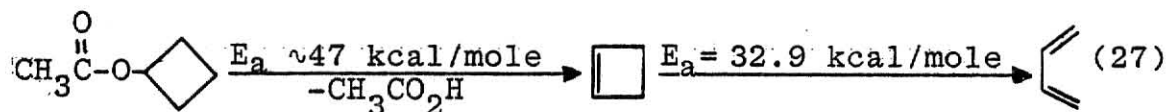
Except for chlorine concentration, no other factors appear to significantly increase the yield of 1,1-dichlorocyclopropane. Increasing the effective temperature by increasing the amount of SiF_4 used to sensitize the laser-induced reaction did not affect the amount of 1,1-dichlorocyclopropane formed.

Another major difference between the IR laser-induced chlorination and conventional thermal initiation is the reduction of ring-opened allyl chloride in the laser induced reaction, which can be attributed to the "instantaneous heating" with pulsed infrared laser and a much faster cooling rate as compared to thermal heating even in a flow system. A great advantage of the pulsed laser is the ability to control

the amount of energy deposited into the reaction system which results in a remarkable control of temperature and excitation level. This is important in our system where secondary reactions seem to depend a great deal on the reaction temperature. The isomerization of chlorocyclopropane to 3-chloropropane is the most undesired product in this synthesis. The main drawback to have the formation of allyl chloride is the destruction of the desired product, chlorocyclopropane, and practically, it is very difficult to separate the two compounds. Apparently at high temperature, specifically above 800 K, the isomerization reaction became significant and increased with the number of pulses. Thermal chlorination of cyclopropane has also been shown²² to produce significant amount of 3-chloropropane at temperature above 783 K and increase with longer contact time with the heating surface in a flow system. Grant and Swinbourne⁵⁹ reported that chlorocyclopropane isomerized at temperature above 340 K entirely to 3-chloropropane and the rate constant for this reaction was reported to be $6.3 \times 10^{14} \exp(-56200/RT)$. The high activation energy of 56.2 kcal/mole⁻¹ would cause this isomerization reaction to be unimportant at low temperatures.

An observation on the quenching of secondary reaction upon pulsed laser excitation, that may be analogous to the laser-induced chlorination of cyclopropane was reported by Nguyen and Danen.¹² They reported that under appropriate conditions, cyclobutene, uncontaminated by 1,3-butadiene, can be obtained by pulsed infrared laser irradiation of cyclobutyl acetate (reaction 27). The authors proposed that the

pulsed infrared laser can be used to synthesize an organic



compound that is thermally more reactive than its precursor. From the activation energies of the two consecutive reactions, it can be seen that the second reaction is more facile than the first but at low fluence (0.80 J cm^{-2}), they were able to eliminate the ring opening reaction and obtained the desired product, cyclobutene, almost exclusively. The extent of each reaction and the relative yields of cyclobutene and 1,3-butadiene were reported to depend on the laser fluence, reactant pressure, and CF_4 bath gas. A fluence of 2.0 J cm^{-2} and/or pressure of 2 torr resulted in 1,3-butadiene being the major product. However, the appropriate selection of laser fluence and CF_4 bath gas pressure was shown to assist in increasing the cyclobutene yield and reducing the amount of secondary reaction product. They concluded that these observations resulted from the ability of the pulsed infrared laser to induce high temperature reactions but to restrict the reaction time to a few microseconds.

The similarity in the temperature at which 3-chloropropene was formed in the thermal²² and the present laser-induced chlorination (i.e., $\gtrsim 800 \text{ K}$) support the validity of the calculated temperature presented earlier (Table 2-7). We also compared the $T_{V,R,T}^{\text{max}}$ obtained by Steel, *et al.*³⁵ with that calculated by our method and found that our T_{eff} is $\sim 2\%$ lower than their result. The difference may result from the heat capacity expression for the sensitizer, NH_3 , used

in the calculation. They used a known expression for NH_3 ⁶⁰ of $C_v = 5.12 + 6.00 \times 10^{-3}T - 0.37 \times 10^{-5}T^{-2}$ while we employed a single-power expression from the data in the JANAF table³⁹ and obtained $C_v = 0.425 T^{0.476}$ with a correlation factor of 1.00. Upon integration and evaluating the given E_{abs} , the value of T_{eff} is found to be consistently lower by ~2%. A more detailed check on this method to calculate T_{eff} in the laser-induced reaction was carried out for the chlorination of n-butane where temperatures obtained by both heat capacity and product ratio are compared; these results will be discussed in part IV of this thesis.

Tables 2-7 show the calculated temperature achieved by the reaction system by assuming that the deposited energy is randomly distributed in the constant irradiated volume. The energy absorbed by SiF_4 increased with increasing pressure of SiF_4 at a constant fluence and increased with increasing fluence at constant SiF_4 pressure (Table 5). Olszyna, et al.¹³ and results from our laboratory⁶¹ show that the absorption cross-section of SiF_4 increased with increasing pressure but decreased with increasing fluence. The amount of energy absorbed was found¹³ to increase with SiF_4 pressure and fluence in agreement with our results. The Beer's law extinction coefficient of SiF_4 at the wavelength irradiated (1025 cm^{-1}) is exceptionally high ($0.12 \text{ torr}^{-1} \text{ cm}^{-1}$). In the high SiF_4 pressure experiment, >50% of the laser energy was absorbed by 5.0 torr SiF_4 present in the 10 cm long cell. Thus we have no doubt that the laser fluence was increasingly reduced on the laser beam travelled through the

long reaction cell. As a result, more energy was absorbed at the front than the back of the cell. The severe gradients produced make the estimates of T_{eff} and Δt highly questionable for the 5.0 torr SiF_4 experiments.

The calculated temperatures obtained during the laser-induced chlorination reactions, besides being used to compare with thermal reaction, are also employed to calculate the reaction time, Δt . As mentioned earlier, the reaction time merely represents the time at which the reaction system remains at the maximum T_{eff} to effect the homolysis of di-t-butyl peroxide to initiate the chain process. As can be seen in Table 8, Δt ranges from 10^{-3} s to 10^{-7} s depending on T_{eff} . At high T_{eff} where high reactant pressure was present, Δt was found to be short and increase with decreasing T_{eff} , i.e., decreasing SiF_4 pressure. A $\Delta t \sim 10^{-7}$ s reflects a decomposition rate of $\sim 10^7 \text{ s}^{-1}$ which is near the limiting value;⁶² i.e. the rate of unimolecular decomposition of di-t-butyl peroxide approaches the rate of laser vibrational up-pumping. However, the fluence gradients mentioned previously preclude an accurate assessment of Δt for 5.0 torr SiF_4 .

The chainlength for the infrared laser-induced chlorination of cyclopropane is rather short but compatible with the results obtained by Nesbitt and Leone.¹⁹ They observed that, upon laser excitation, reaction of chlorine with CH_3SH gave a chainlength of about 150 and the $\text{Cl}_2/\text{H}_2\text{S}$ system underwent 50 cycles of chain reaction. It is not surprising to obtain short chainlengths in pulsed laser-induced reaction, especially at relatively high pressure of the reaction mixture.

Our results (Table 7) indicate a reduction in chainlength at higher initiator concentration and also at high T_{eff} . Both cases, i.e., high temperature and more di-t-butyl peroxide, resulted in more free radicals being generated which increased the rate of termination reactions and reduced the chainlength.

In the absence of a chain process, laser-induced bimolecular reactions usually undergo radical-radical coupling similar to the termination processes of the chain reaction. This reaction was found⁹ to be synthetically useful where, e.g., SF_5NF_2 was obtained in substantial amount with a single-pulse infrared irradiation of S_2F_{10} and N_2F_4 . The authors⁹ suggested that this laser-induced radical-radical combination technique can be employed synthetically to prepare compounds starting from symmetrical reactants.

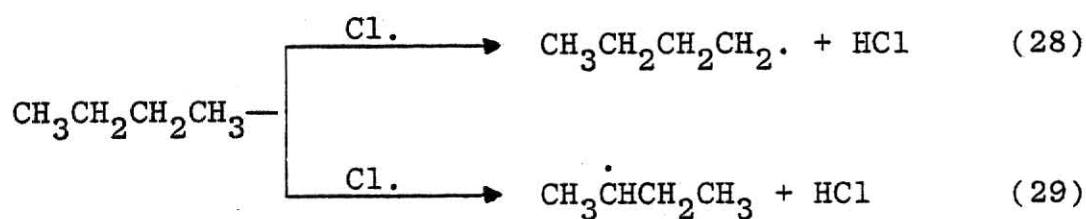
Even though a chain process, unlike a single unimolecular reaction, can extend over a considerable time period once initiated, our results indicate that the laser-induced chlorinations of cyclopropane undergo short chain cycles. Thus, the chain process appears limited by the extent of the termination process and not by the drop in temperature. The results on the chlorination of n-butane also support this speculation and will be discussed in the next section.

IV. INFRARED LASER-INDUCED

CHLORINATION OF n-BUTANE1. Laser-Induced Chlorination Reaction

Similar to cyclopropane, n-butane undergoes a free radical chain chlorination which can be induced either thermally or photolytically. n-Butane was chosen as the compound to be studied due mainly to extensive data available on its chemistry with chlorine. Considerable work on the chlorination of n-butane and related hydrocarbon had been reported, most directed to the mechanism and kinetics of the reactions.

n-Butane is a representative straight chain aliphatic hydrocarbon which reacts readily with chlorine even in the dark.⁶³ The primary products are 1-chlorobutane and 2-chlorobutane and a chain mechanism is operative similar to chlorination of cyclopropane with the hydrogen abstraction reaction being a crucial propagation step (reactions 28 and 29). By competitive chlorination, the Arrhenius parameters for the two reactions have been reported.³¹ For the primary hydrogen



abstraction, the activation energy was found to be 770 ± 140 cal/mole with an A-factor of $1.4 \times 10^{10} \pm 0.3 \text{ m}^{-1} \text{ s}^{-1}$ per hydrogen atom while for the secondary hydrogen, $E_a = 300 \pm 140$ cal/mole and the A-factor is equal to $2.4 \times 10^{10} \pm 0.5$ per hydrogen atom. Like most aliphatic hydrocarbons, the activation energies for these reactions are low so that nearly

random attack of chlorine atoms on the C-H bonds is expected. But studies have shown that there is some selectivity on the different types of hydrogens for chlorine atom abstraction.

Anson, Fredricks and Tedder²⁷ reported the relative selectivity of the hydrogen abstraction reaction on the two different types of hydrogens in n-butane by an Arrhenius form. Assuming a steady state condition in the thermal chlorination of n-butane, the ratio of the two products formed weighted by the statistical number of hydrogen atoms of each type is equal to the ratio of the rate constants for the two reactions at the same temperature. From direct experimental data, they came up with the expression shown by equation 30 for this ratio;

$$\frac{k_s}{k_p} = \frac{\left[\text{isobutane} \right]}{\left[\text{n-butane-1-chloride} \right]} \times \frac{3}{2} = \frac{(480 \pm 70)}{RT} \quad (30)$$

whereas the Arrhenius parameters above produce a calculated rate ratio as given by equation 31;

$$\frac{k_s}{k_p} = 1.71 \exp \frac{470}{RT} \quad (31)$$

These expressions are useful to our study on determining the effective temperature achieved in infrared laser-induced reactions by the product ratio method. By monitoring the two products upon laser excitation, the ratio of the two products, 1-chlorobutane and 2-chlorobutane, can be obtained and the average temperature of the reaction can be calculated. This enables us to compare the temperature from the product ratio with that calculated from heat capacities and absorbed energy and, hopefully, to assist in understanding

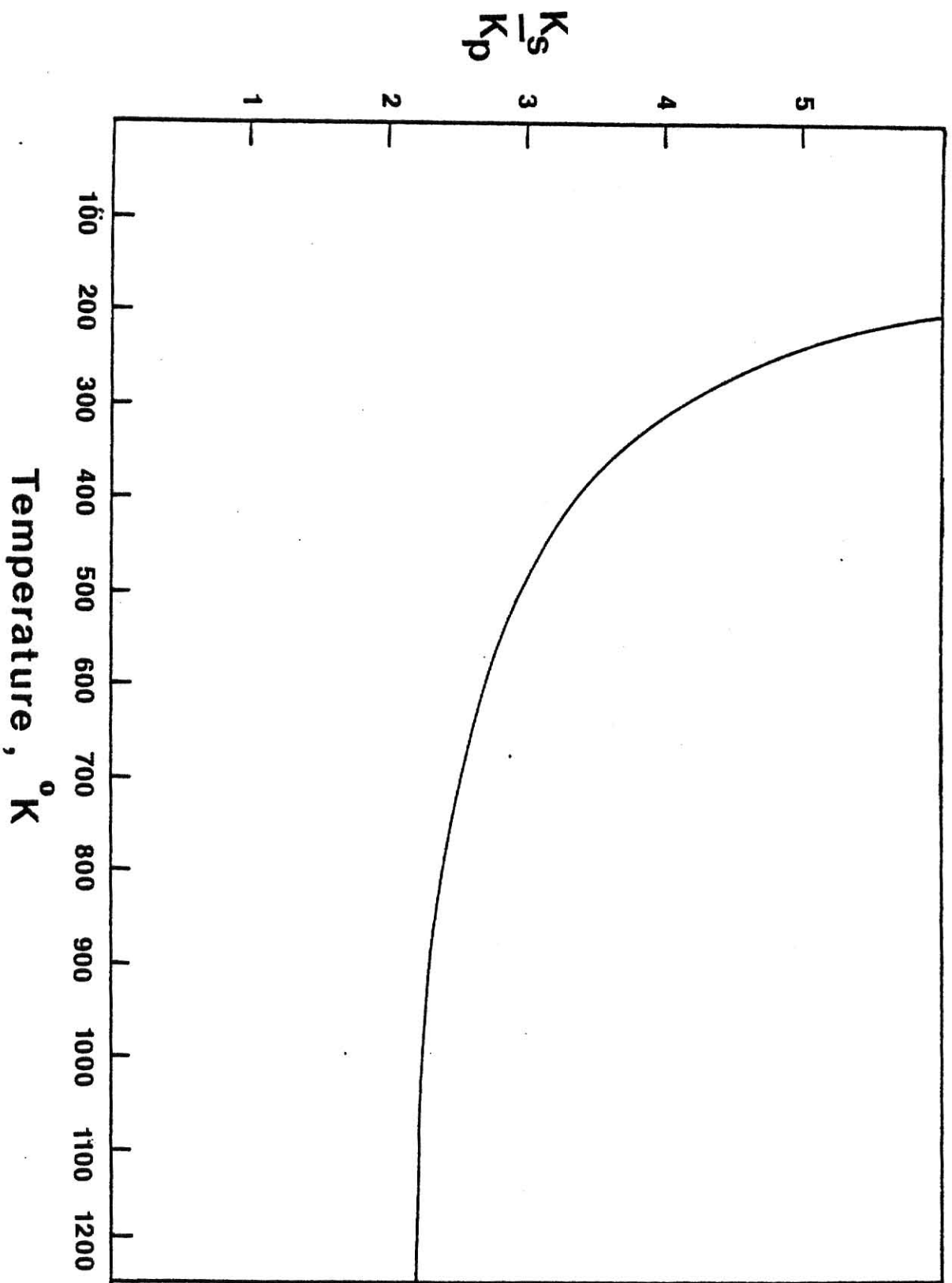
differences between laser-excited reactions and conventional thermally-induced chlorinations. Figure 9 shows a plot of the rate ratio k_s/k_p for thermal-induced chlorination of n-butane using the rate ratio reported by Anson, et al.²⁷

Except for the two products above, no other compounds, such as polychlorinated butane were observed under the present experimental conditions. Table 11 shows the set of laser-induced experiments where the SiF_4 sensitizer was varied while keeping the rest of the mixture unchanged. Each reaction mixture was exposed to a single infrared laser pulse at a fluence of 1.2 J cm^{-2} . Even though some reaction occurred without di-t-butyl peroxide, the initiator was included in the reaction mixture in order to assure similar conditions as those for the laser-induced chlorination of cyclopropane and also to calculate the chainlength and reaction time as described previously. Two sets of experiments were performed in which the amount of di-t-butyl peroxide was varied from 0.01 torr to 0.05 torr. From preliminary experiments, we found that 1.0 torr of chlorine could be used conveniently in the reactions but at higher chlorine composition the dark reaction became increasingly important. Usually, conversions of between 50 to 90 percent were obtained with a single pulse; the dark reaction was found to be ~10% depending on the time necessary to perform the experiment. The yield of the two products was corrected for the dark reaction before any calculations on temperature and chainlength were performed.

Figure 9. Plot of rate ratio k_s/k_p versus temperature for chlorination of n-butane. The rate ratio $k_s/k_p = 1.8 \exp (480/RT)^{27}$ was used.

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The main purpose for studying the laser-induced chlorination of n-butane was to obtain information on the temperature of the laser excited reaction and to verify the validity of the method to calculate temperature via the heat capacity and energy absorbed performed on the laser-induced chlorination of cyclopropane. Two different temperatures were calculated for each experiment utilizing the heat capacity method. One is T_{irr} which is the effective temperature that would be achieved by considering only the heat capacity of the system in the irradiated volume. The other is T_{tot} which is the equilibrated temperature by using the heat capacity of the total mixture present in the reaction cell. The irradiated volume was 17.7 cm^3 while the total volume of the cell used is 35.3 cm^3 . Thus, the ratio of the active volume to the total volume is 0.50.

The heat capacity of n-butane is greater than that of cyclopropane and rises faster with increasing temperature. Therefore, for the same amount of energy absorbed, the calculated effective temperature is lower than that for the cyclopropane reaction. Nevertheless, the same trend was observed, namely, that increasing the amount of SiF_4 increased the effective temperature either in the irradiated volume or the whole cell (Table 11). The equilibrated temperature T_{irr} , and the data of Table 11 illustrated the difference. T_{butane} is the temperature calculated from the butane product ratio by the expression given by Anson and coworkers (Equation 30).²⁷ The same observation that the temperature

TABLE 11. Results of the single-pulse infrared laser-induced chlorination of n-butane at constant fluence ($\sim 1.2 \text{ J cm}^{-2}$) and constant n-butane/chlorine ratio (10:1). Two different amounts of initiator were used; a) 0.01 torr di-t-butyl peroxide, b) 0.05 torr di-t-butyl peroxide.

SiF_4 (torr)	Fluence (J cm^{-2})	I/I_0	Total E_{abs} (joule)	E_{abs} (kcal/mole SiF_4)	T_{butane} (°K)	T_{irr} (°K)	T_{tol} (°K)	Chain length	Reaction time (sec)
a) 0.01 torr of di- <u>t</u> -butyl peroxide									
1.0	1.20	0.85	0.27	67.8	350+50	520	420	123	1.18×10^{-2}
2.5	1.29	0.76	0.43	43.7	500+70	610	470	124	2.50×10^{-6}
5.0	1.19	0.49	0.79	39.4	520+80	760	560	53	6.82×10^{-7}
b) 0.05 torr of di- <u>t</u> -butyl peroxide									
1.0	1.19	0.87	0.22	55.2	420+60	490	400	46	8.61×10^{-1}
2.5	1.19	0.72	0.53	53.2	520+80	690	540	24	1.79×10^{-3}
5.0	1.23	0.47	0.97	48.7	630+90	840	610	13	4.16×10^{-7}

increased with increased excitation still held by this method. The most important result, however, was how T_{butane} compared with the heat capacity temperature. Generally T_{butane} agreed reasonably well with T_{tot} especially for short chain-length reactions where the reaction time was short. T_{butane} was always lower than T_{irr} especially for the long reaction time reactions.

The chainlength for the laser-induced chlorination of n-butane was also calculated. The same method was applied as with cyclopropane but, in this case, the determination of the decomposition of t-butoxyl radicals was carried out in the presence of n-butane. The sum of the absolute yields of 1-chloro and 2-chlorobutane was used as the total yield of the products in the chain propagation steps.

From Table 11 it can be seen that the chainlengths are relatively short as compared to conventionally induced chlorination reactions of straight-chain hydrocarbon where as high as 10^7 chain cycles can be observed.⁴³ However, these results are similar to the laser-induced chlorination of cyclopropane. In Table 11 the chainlength is seen to decrease as the excitation level increases. For 0.01 torr of di-t-butyl peroxide, 1.0 and 2.5 torr SiF_4 sensitized reactions produced the maximum chain-length of ~ 120 . Increasing the pressure of sensitizer to 5.0 torr reduced the chainlength to half. When the amount of peroxide was increased to 0.05 torr, the chainlength was decreased significantly and a similar decrease in chainlength with

increasing SiF_4 pressure was observed.

The reaction time in Table 11 was calculated from the decomposition of di-t-butyl peroxide. As with that for cyclopropane, the reaction time, Δt , indicates the time at which the reaction system remained at T_{irr} to effect the decomposition of di-t-butyl peroxide. The rate constant for the decomposition of di-t-butyl peroxide (equation 14) together with T_{irr} was used to calculate Δt . As seen in Table 9, Δt ranges from 10^{-2} to 10^{-7} second, depending on T_{irr} . At low T_{irr} (~ 500 K), Δt is in the order of 10 ms, and at higher T_{irr} (~ 800 K), Δt is ~ 1 μs . In most cases, there is no significant difference in Δt when di-t-butyl peroxide was increased from 0.01 torr to 0.05 torr. In general, these reaction times are comparable to the cyclopropane experiment (Table 8) and are generally slightly longer for a similar reaction composition.

2. Sunlamp-Induced Chlorination of n-butane.

Several experiments were done on the sunlamp-induced photochlorination of n-butane at 0 C to assess the reliability of equations 30 and 31. A pyrex bulb with appropriate stoppers was utilized instead of the usual cell used in the laser-induced experiments because the reaction cell had to be kept in an ice-water bath to maintain the 0 C temperature. A constant ratio of n-butane to chlorine, i.e., 10, was irradiated with a 275 watt sunlamp for various lengths of time from a distance of 120 cm.

As seen in Table 12, the exposure time was varied from

TABLE 12. Results on sun-lamp induced chlorination of n-butane employing 10.0 torr C_4H_{10} and 1.0 torr chlorine.

Exposure Time (sec)	2-chlorobutane (torr)	1-chlorobutane (torr)	T _{butane} (°K)	T _{ratio} (°K)
15	0.59 ± 0.04	0.22 ± 0.03	300 ± 40	280
60	0.69 ± 0.04	0.27 ± 0.01	320 ± 50	290
300	0.67 ± 0.05	0.26 ± 0.03	320 ± 50	290
600	0.71 ± 0.04	0.25 ± 0.01	280 ± 40	260
Average dark R_x	0.28 ± 0.01	0.10 ± 0.01	290 ± 40	270

15 s to 10 min although almost complete reaction was observed after only 15 s irradiation. The yields of 1-chloro and 2-chlorobutane were not compensated for the dark reaction since a similar ratio as T_{butane} was obtained from the dark reaction. The extent of dark reaction is shown in the last line in Table 12 which is responsible for 40% of the observed conversion in the photolysis reaction. Two different temperatures are reported; T_{butane} is the temperature calculated from the expression of Anson, *et al.*,²⁷ (equation 30) and T_{ratio} is the temperature calculated from the rate ratio in equation 31. In all cases, T_{butane} is about 8% higher than T_{ratio} as expected from the two expressions. Although there is sizable experimental uncertainty, these temperatures are satisfyingly close to the expected temperature of 273 K. T_{butane} ranges from 283 to 318 K, while T_{ratio} is closer to 273 K, ranging from 262 to 291 K. The error limit given for T_{butane} was calculated from the error limit of equation 30; the true temperature, 273 K is within the error limits in all cases although T_{butane} always overestimated the experimental temperature.

3. Discussion.

The overall mechanism for the laser-induced and sunlamp-induced chlorination of *n*-butane is expected to be the same as that of the chlorination of cyclopropane. Since *n*-butane has two non-equivalent hydrogens, substitution by chlorine will form two primary products, namely 1-chlorobutane and 2-chlorobutane. The relative rate of the secondary hydrogen

abstraction to the primary hydrogen abstraction is 3.6 at room temperature and approaches unity at high temperature (Figure 10). The rate constants for the two reactions (Reactions 28 and 29) are known.³¹ In the present study, the n-butane/chlorine ratio employed was sufficiently high (10) that no polychlorinated butane was observed. Chlorination of n-butane occurred significantly in the dark indicating n-butane to be a more reactive substrate than cyclopropane in the chlorination reaction.

The question at hand is to determine the effective temperature during reaction by two different methods, namely chemical method (product ratio) and heat capacity method. These two methods have been described in the literature³⁵⁻³⁸ and are generally found to give comparable temperatures for a single-step unimolecular reaction. The product ratio method may be used to find the temperature of a two-channel reactant directly or a single-channel reactant with an added thermal monitor molecule;⁶ the heat capacity method may be used in any type of laser-induced reaction.

In the present study of the chlorination of n-butane, both methods were employed to obtain the effective temperature of reaction. T_{butane} is the average temperature of the reacting system determined from the ratio of 2-chloro to 1-chlorobutane formed. Two temperatures were calculated by the heat capacity method; T_{irr} reflected the maximum effective temperature achieved by the reaction mixture in the irradiated volume and T_{tot} which assumed the deposited laser energy was

randomized among all the molecules in the reaction cell.

From Table 11, it can be noted that T_{butane} is more similar to T_{tot} than T_{irr} which may indicate that the free radical chain chlorination reaction continues even after the drop from T_{irr} . Cooling processes intermix the excited molecules in the irradiated volume with the surrounding cold molecules but the low E_a for the chain-propagation steps (equations 28 and 29) in the chlorination of n-butane permit the reactions to ensue even at reduced temperature. Thus, T_{butane} , derived from the 2-chlorobutane/1-chlorobutane ratio is a composite or average temperature for the reaction within the irradiated volume as well as after intermixing with molecules in the unirradiated volume. As mentioned earlier, a bimolecular free radical halogenation reaction is quenched primarily by termination reactions and not by a temperature drop. The present results strongly support this argument. For instance, in 1.0 torr SiF_4 and 0.01 torr di-t-butyl peroxide reaction, T_{butane} is seen to be lower than even T_{tot} and the chainlength is the maximum obtained in these laser-induced reactions. This may result from slow termination reactions due to relatively low concentrations of free radicals so that reaction continues significantly even after the system reaches T_{tot} . In all the other reactions using higher SiF_4 pressure and/or higher di-t-butyl peroxide concentration, T_{butane} is generally higher than T_{tot} which results from faster termination processes because of higher steady-state concentration of free radicals during the reaction.

In the sunlamp-induced chlorination of n-butane, T_{butane} is somewhat higher than the experimental 273 K temperature. On the other hand, T_{ratio} which is obtained directly from the ratio of the rate constants, seems to be more compatible to the expected temperature. This raises the question of the accuracy of the expression (equation 30) reported by Anson, et al.²⁷ which was obtained directly from experimental data. However, if the error limits on the exponential part of the expression (equation 30) is taken into consideration, T_{butane} would be very similar to the experimental temperature. This observation should be extended to T_{butane} derived from the laser-induced chlorination of n-butane to obtain a better value of the average reaction temperature for the infrared laser-induced chlorination of n-butane.

V. CONCLUSION

From the present study on the infrared laser-induced and sunlamp-induced chlorination of cyclopropane and n-butane, several conclusions can be made. The two primary aims of this thesis were, first, to explore the potential application of pulsed infrared laser irradiation in organic synthesis particularly for free radical chain reactions and, secondly, to determine the effective reaction temperature and chain lengths in such laser-induced chlorination reactions.

The pulsed infrared laser-induced reaction of cyclopropane and chlorine has been shown to produce chlorocyclopropane in high yield and reasonable purity. This is the first non-unimolecular, organic transformation of synthetic utility which, to our knowledge, cannot be better accomplished by conventional means. The results of the laser-induced reaction in some aspects resemble the thermal reaction but the unique ability of the pulsed infrared laser to provide instantaneous heat directly to the molecules without heating the reaction cell eliminates any significant secondary reactions. The chain nature of this reaction makes this method relatively efficient in terms of quantum yield as compared to a non-chain process and scaling up of the laser synthesis of chlorocyclopropane would appear feasible.

In the present study, we found that a sensitizer was needed to effectively initiate the chain reaction. Direct excitation of cyclopropane did not produce a good yield of

chlorocyclopropane. In addition to the SiF_4 sensitizer, a catalytic amount of di-butyl peroxide was also found to further increase the yield of chlorocyclopropane. The ratio of cyclopropane/chlorine was also important primarily in quenching the di-chlorination of the cyclopropane ring. A typical reaction mixture that gave a good yield included 10.0 torr cyclopropane, 2.0 torr chlorine, 1.0 torr SiF_4 , and 0.03 torr di-t-butyl peroxide. The yield of chlorocyclopropane is limited by the 2.0 torr of chlorine used and depended on the number of pulses applied. With proper caution, the yield of chlorocyclopropane can be increased by increasing the amount of chlorine to a maximum of 10.0 torr; i.e., a cyclopropane/chlorine ratio of 1. An efficient use of laser photons should also be taken into consideration. In the present case, a compromise between good conversion per pulse and a good total yield is obtained when ~ 10 pulses are applied.

We have also demonstrated that the approximate temperature of the laser-induced reaction can be calculated by two different methods. A simple method to calculate the reaction temperature is by the absorbed energy and heat capacity method. Even though this method has been reported in the literature, some modification was made to make it more practical to our system where a number of reactants are present in significant amount. The primary modification is with the heat capacity expression. Writing the heat capacity versus temperature data into a single-power expression provided a simpler integration and yielded a better correlation

coefficient. This method of calculating the temperature can be applied to any laser-induced reaction provided that the heat capacity of the irradiated mixture is known. An accurate measurement of the energy deposited into the reaction system is an important prerequisite to a good value of the reaction temperature.

Another method of calculating the temperature involves the analysis of the products for two competitive reactions with known Arrhenius parameters. The product ratio defines the temperature of reactions. Both methods of calculating the temperature were used in the n-butane/chlorine system. The free radical chain nature of the chlorination reaction precluded obtaining a comparable temperature between the two methods, i.e., T_{butane} and T_{irr} , as the reaction is not quenched by a drop in temperature. T_{butane} obtained from the ratio of the two products, 2-chlorobutane/1-chlorobutane, was concluded to be the average temperature during which the reaction occurred while T_{irr} represented the maximum temperature achieved briefly within the irradiated volume.

The chainlengths of the laser-induced chlorination of cyclopropane and n-butane were found to be relatively short. A maximum chain cycle of ~ 120 was observed in the laser-induced chlorination of cyclopropane employing 0.03 torr of di-t-butyl peroxide. The chainlength decreased when more of the initiator was present, and/or high T_{eff} (high SiF_4 pressure) where termination processes became important. The reaction time, Δt , defined as the time of decomposition of the initiator, ranged from $\sim 10^{-2}$ s to 10^{-7} s as T_{eff}

increased from ~ 600 K to 1000 K.

APPENDIX A

T_{eff} was calculated from the absorbed energy and heat capacities of compounds in the reacting mixture. Heat capacities for chlorine and SiF_4 were obtained from JANAF Tables,³⁹ n-butane from the API Tables,⁴⁰ and cyclopropane calculated from group-additivity tables by O'Neal and Benson.⁴¹ All of these heat capacities were reported in tabular form as a function of temperature. Usually, the temperature dependence of the heat capacities are reported as power series expressions such as equation 32.

$$C_v = a - R + bT + cT^2 + \dots \quad (32)$$

For most compounds, these relationships have not been expressed in any form. Our attempt to express heat capacities versus temperature data into a power series expression was tedious. A simpler formulation of a single power expression such as equation 33

$$C_v = aT^b \quad (33)$$

was found to give a better correlation upon a power curve fitting especially in the temperature range of 298 to 1200°K. The constants a and b can be easily obtained graphically or from a programmed calculation.

The expressions for each of the compounds present in the reacting system are as given by equations 34-37. The energy deposited into the reacting system is related to C_v

$$C_v(\text{c-C}_3\text{H}_6) = 0.1194 T^{0.8166} \quad (34)$$

$$C_v(\text{SiF}_4) = 3.2969 T^{0.2792} \quad (35)$$

$$C_v(\text{Cl}_2) = 3.5518 T^{0.0982} \quad (36)$$

$$C_v(\text{n-C}_4\text{H}_{10}) = 0.3866 T^{0.7099} \quad (37)$$

and temperature by;

$$E_{\text{abs}} = \int_{298}^{T_{\text{eff}}} C_v \, dT \quad (38)$$

For a mixture of gases with certain moles of each component, the equation becomes;

$$E_{\text{abs}} = \int_{298}^{T_{\text{eff}}} [xC_v(X) + yC_v(Y) + zC_v(Z) + \dots] dT \quad (39)$$

where x, y, and z represent the number of moles of each component. Substituting C_v of each component into its corresponding temperature expression, aT^b etc., yield equation 40;

$$E_{\text{abs}} = \int_{298}^{T_{\text{eff}}} [xaT^b + ycT^d + zgT^h + \dots] dT \quad (40)$$

where a, b, c, d, g, and h are constants obtained from the curve-fitting calculation previously. Evaluating the integral, one obtains equation 41;

$$E_{\text{abs}} = \left[x \frac{a}{b+1} T^{b+1} + y \frac{c}{d+1} T^{d+1} + z \frac{g}{h+1} T^{h+1} \right]_{298}^{T_{\text{eff}}} \quad (41)$$

Knowing the energy absorbed, the temperature T_{eff} , can then be easily obtained by evaluating the above equation. We employed a root-finding program⁴² which calculated the temperature by an iterative method.

For example, in a standard mixture of 10.0 torr cyclopropane, 1.0 torr SiF_4 , and 2.0 torr chlorine, the typical amount of energy absorbed was 0.25 joules which is equal to 0.060 calories. The number of moles of each gas present in the irradiated volume of 17.7 cm^3 was calculated from the ideal gas equation. For 10.0 torr of cyclopropane, the number of moles is 9.52×10^{-6} ; 1.0 torr SiF_4 corresponds to 9.52×10^{-7} mole, and 2.0 torr Cl_2 corresponds to 1.90×10^{-6} mole.

Therefore, from equation 40;

$$E_{\text{abs}} = \int_{298}^{T_{\text{eff}}} [(9.52 \times 10^{-6})(0.1194 T^{0.8166}) + (9.52 \times 10^{-7})(3.2969 T^{0.2792}) + (1.90 \times 10^{-6})(3.5518 T^{0.0982})] dT \quad (42)$$

evaluating equation 42;

$$E_{\text{abs}} = [(9.52 \times 10^{-6})\left(\frac{0.1194}{1.8166} T^{1.8166}\right) + (9.52 \times 10^{-7})\left(\frac{3.2969}{1.2792} T^{1.2792}\right) + (1.90 \times 10^{-6})\left(\frac{3.5518}{1.0982} T^{1.0982}\right)]_{298}^{T_{\text{eff}}} \quad (43)$$

Applying the value of $E_{\text{abs}} = 0.060$ cal., by iterative method, the root, T_{eff} , was found to be 605 K.

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PULSED INFRARED LASER-INDUCED CHLORINATION REACTIONS.

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT.

The pulsed infrared laser-induced chlorinations of cyclopropane and n-butane were studied to characterize the main features of such laser-induced chain reactions including the effective temperature, chain-length and reaction products. A laser-induced synthesis of chlorocyclopropane is reported in which the product was obtained in high yield and relatively free of impurities as compared to conventional procedures. Silicon tetrafluoride excited by the pulsed CO₂ laser at 1025.3 cm⁻¹ was used to sensitize the chlorination reactions. In the laser-induced chlorinations, a catalytic amount of di-*t*-butyl peroxide was found to increase the formation of products significantly. Yields of chlorocyclopropane as high as 74% with 25 laser pulses were observed under appropriate conditions. Sunlamp-induced photochlorination was conducted to compare to products formed via laser inducement. 1,1-Dichlorocyclopropane was the major product from sunlamp-induced chlorination of cyclopropane, especially at low cyclopropane/chlorine ratios.

The effective reaction temperature was calculated from the heat capacity of the reacting system and the laser energy absorbed. In the chlorination of n-butane the temperature was also determined from the 2-chlorobutane/1-chlorobutane product ratio and known Arrhenius parameters. The effective temperature obtained from the energy absorbed and the heat capacity of the reactants in the irradiated volume ranged from ~600 K to ~1000 K depending on the absorbed energy and reactant pressure. Comparison of the temperatures obtained

by the two methods in the chlorination of n-butane demonstrated that the product ratio temperature, T_{butane} , was closer to T_{tot} , calculated from the heat capacity of the total cell volume, and always lower than T_{irr} , calculated from the heat capacity in the irradiated volume only.

The chainlengths for chlorination of both cyclopropane and n-butane were comparable and relatively short, ranging from 8 to ~120 depending primarily on the effective temperature. Such short chainlengths indicate effective termination reactions resulting from the high concentration of radicals produced by the pulsed laser initiation. The reaction time, Δt , determined from the decomposition of di-t-butyl peroxide, ranged from a few milliseconds to several microseconds which may reflect the time during which the reaction mixture remained at the maximum effective temperature.