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FINAL REPORT

"DURIP FTIR STUDIES OF SOLID STATE REACTION DYNAMICS"

submitted to

Air Force Office of Scientific Research
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EQUIPMENT ACQUIRED BY DURIP GRANT

1)	FTIR Spectrometer (Mattson Model Polaris/Icon)	25221.40
2)	Analytical Computer (Zenith Model Z-386)	4380.00
3)	Computer Workstation (Sun SparcStation-1)	5818.25
	w/ ethernet peripherals (Cabletron, Inc.)	1202.88
4)	SpectraCalc Software (Galactic Industries)	1042.00
5)	LaserJet II printer (Hewlett-Packard)	2665.00
	TOTAL	40329.53
	DURIP-AFOSR FUNDS	34800.00
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RESEARCH SUPPORTED BY DURIP EQUIPMENT GRANT

Completed Projects

During the performance period, a study of photochlorination reactions in low-temperature films was completed using the instrumentation acquired by the DURIP grant. The purpose of the study was to survey reactions induced by 308 nm photolysis of binary solid solutions of simple hydrocarbons with molecular chlorine. We investigated the effects of varying the sample temperature and photolysis wavelength on reaction product branching ratios and quantum yields for several different hydrocarbons. Detailed results and conclusions are presented in a paper to be published in the Journal of Physical Chemistry. This manuscript is attached as Appendix A of this report.

The results of this study are of significance to the Air Force High Energy Density Materials program to identify potential candidates for advanced propellants. Our studies of solid-state reactions are aimed at understanding the fundamental characteristics of low-temperature chain reactions which could potentially degrade the performance of solid propellants at cryogenic temperatures. This particular study confirmed our earlier hypothesis that initiation of chain reactions in solids requires a specific mechanism for separating radical pairs in the solid state.

Under normal conditions, chain reactions and their associated undesirable effects on propellant performance are not expected to play a significant role in the chemistry of amorphous (disordered) solids.

Ongoing Projects

Three on-going projects are being supported by equipment acquired with DURIP grant funds. Each of these projects is supported by a research contract from the Air Force Astronautics Laboratory (F04611-87-K-0023).

1. Cluster Formation in Vapor-deposited Solids. The FTIR spectrometer is currently being used to support a study of water cluster formation during vapor deposition of H_2O/N_2 mixtures onto cryogenic substrates. At the same time, the physical process of vapor deposition is being modelled by computer simulations on the Sun computer workstation purchased with DURIP funds.

2. Theory of Chain Reactions in Disordered Solids. A percolation theory of solid state chain reactions is now under development in our group. Although the theory itself is analytical, it is being compared with numerical simulations of chain reaction processes computed on the Sun workstation. The workstation is indispensable for this project because it has sufficient memory (8 Mbytes RAM) and computing speed (12 million instructions per second) to perform the simulations. It is hoped that the theory will provide a basis for understanding general characteristics of solid state chain reactions (kinetic chain lengths and chain length distributions) for interpretation of future experimental data.



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3. Mechanism of Photopolymerization Reactions in Amorphous Solids. The FTIR spectrometer, Analytical computer, and SpectraCalc software have also been used to investigate the mechanisms of photopolymerization reactions in amorphous formaldehyde at cryogenic temperatures (10-150 K). Photochemical quantum yields, effects of sample annealing, variations in photolysis wavelength and initiator concentration have all been supported by this equipment. The results are now being written up for publication.

Support of Proposed Research

Three additional projects have recently been funded in our research group which will utilize the FTIR spectrometer system purchased with DURIP equipment funds. The first of these, entitled "Stability of High Energy Amorphous Materials", will be sponsored by the Air Force Astronautics Laboratory starting February 1990 (pending negotiation). This project will investigate the sensitivity of amorphous films of ozone and fluorine azide towards laser-induced detonation. The FTIR system will be used to evaluate the extent of reaction and reaction product branching ratios where pertinent.

The second project, entitled "Thin Film Laser Pyrolysis of Nitramine Propellants", will be supported by the Army Research Office (pending negotiation of the contract). The focus of this project is to determine (by FTIR) the initial reaction pathways important in the decomposition of RDX and HMX propellants during the initial stages of heating in the solid state.

The third project, entitled "Structure and Reactivity of Amorphous Solids", is supported by the National Science Foundation. This project is designed to investigate new types of photochemically induced chain reactions in order to better understand the fundamental relationships between structure and reactivity in the solid state, particularly at low temperatures. Determination of photochemical quantum yields by FTIR will be a major focus of the work.

Appendix A

PHOTOCHLORINATION OF SIMPLE ALKANES IN CRYOGENIC SOLIDS

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Abstract

Photochemical reactions have been induced by laser photolysis of amorphous binary solids composed of chlorine mixed with propane, n-butane, iso-butane, n-pentane, cyclopentane, n-hexane, or cyclohexane at 10-150 K. In each case, the laser dissociates the chlorine into atoms which react with the alkane to form HCl and the corresponding chloroalkane.

Quantum yields for these reactions are in most cases less than or approximately unity. The results are consistent with a radical recombination reaction mechanism. There is some evidence for the existence of short chain reactions in samples of n-hexane and chlorine which produce up to 5 product molecules per absorbed laser photon. At 10 K, chlorine atoms react with primary, secondary, or tertiary H atoms. However, at temperatures near the melting points of the solids, reaction to form the lowest energy radical is strongly preferred. The dependence of photochlorination yields on photolysis wavelength shows that chlorine atoms, not electronically excited chlorine molecules, are responsible for initiating the reaction.

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Introduction

Photochemistry of disordered molecular solids represents a convenient method of inducing transient or irreversible changes in the chemical composition of a wide variety of materials utilizing the high spatial, temporal, and wavelength selectivity of lasers. Potential applications include photolithography, optical data storage and processing, photosensitization and solar energy conversion, and laser-induced detonation of explosives or propellants. Fundamental studies of solid state photochemical mechanisms provide an important knowledge base from which problems of commercial and technological interest like these can be addressed.

We recently reported that photochemical chain reactions can be induced in amorphous solid films formed by vapor deposition of chlorine with simple hydrocarbons onto the surface of a cryogenic optical window.^{1,2} Quantum yields for photochlorination of cyclopropane can be as high as 30 product molecules (1,3-dichloropropane) for each 308 nm photon absorbed by the sample. In mixtures of cyclobutane with chlorine, quantum yields for formation of cyclobutyl chloride as high as 7.4 were observed in samples which were rich in the hydrocarbon fraction. In each instance, the yields were determined by obtaining transmission FTIR spectra of samples before and after UV laser photolysis.

Chain reactions involving chlorination of chlorobutane in polycrystalline solids irradiated by gamma rays have been reported by Barkalov and co-workers.^{3,4,5} They have postulated that reaction occurs as a result of mechanical disruption and fracture of the solid. The same group has reported chain polymerization reactions in polycrystalline solids^{6,7,8,9} at temperatures as low as 4 K. They have shown that kinetic chain lengths of hundreds or thousands of steps can be achieved in polycrystalline solids. Comparison of our results¹⁰ in amorphous solids with related experiments like these suggests that

molecular disorder severely restricts the reactivity of solids by localizing chain reactions near the site of initiation (UV photon absorption). We note that the concept of localization is endemic to disordered solids. It is reflected in many physical properties of amorphous materials including electrical conductivity, exciton transport, and magnetic properties.^{11,12,13,14,15,16,17,18}

Although we reported the first example of photochemical chain reactions in amorphous solids, it is apparent that chain mechanisms are not generally applicable to photochlorination of hydrocarbons in disordered media. When we reported the cyclopropane results we noted that similar n-propane experiments resulted in very low quantum yields for formation of HCl and chloropropanes.¹ The yields were consistent with a radical recombination mechanism shown schematically in Figure 1. Many Cl atom pairs formed by UV laser photolysis undergo geminate recombination to Cl₂. In a small fraction of events (about 12% in 1:1 mixtures of propane:chlorine at 77 K) chlorine atoms abstract an H atom from a neighboring propane molecule forming HCl. The propyl radical thus formed may recombine with the partner Cl atom in the caged environment of the solid, producing either 1-chloropropane or 2-chloropropane as the final product.² We investigated the branching ratio of these two products and concluded that Cl atoms produced at 77 K exhibit a very high selectivity for abstraction of secondary H atoms from propane in the initial step of the reaction mechanism.¹⁹

A few other research groups have also been investigating chemical reactions in glasses.^{20,21,22} Ingold and co-workers have studied the kinetics of H atom abstraction by methyl radicals in alcohols, and have been able to relate some of the features of structural disorder to kinetically inequivalent species in the solid state.^{23,24,25} Willard and co-workers have also investigated several different photochemically induced reactions in

glasses,^{26,27,28,29} including photochlorination of hydrocarbons.³⁰ These workers noted that the chain reaction operative in liquid solutions of Cl_2 in 3-methylpentane was reduced to a "concerted" photochlorination reaction with greatly diminished quantum yields when the temperature of the solution was lowered to its glass transition temperature (T_g).

The exact interpretation of the term "concerted" is not clear from their paper. However, the term suggests an alternative interpretation of our own results for photochlorination of propane. That is, it is possible that instead of forming Cl atom pairs by laser photolysis of molecular chlorine, reaction could proceed by a 4-center metathesis reaction of electronically excited Cl_2 with propane forming HCl and chloropropane. Detailed studies of electronically excited states of Cl_2 have been reported by several research groups and it is clear that some of these states live long enough in rare gas matrixes^{31,32,33} or are sufficiently reactive³⁴ to make such a mechanism in hydrocarbon matrixes quite plausible.

The present study was undertaken for two principal reasons. First, we wanted to conduct a survey of photochlorination reactions with several different hydrocarbons in disordered solids to see if other chain chlorination reactions (besides cyclopropane and cyclobutane) could be detected. The principal evidence for this would be measured photochlorination quantum yields in excess of unity. No conclusive evidence for chain reactions was found for any of the hydrocarbons investigated in this study with the possible exception of n-hexane.

The second motivation for this study was to determine whether reactions not involving chain mechanisms proceed via radical recombination (as we previously postulated)² or perhaps involve reaction of electronically excited Cl_2 molecules. We found that the wavelength dependence of the photochlorination reaction strongly supports the participation of Cl atoms and radical recombination processes in the reaction mechanism.

Experimental Section

The experimental apparatus and techniques have been described previously.^{1,19} Briefly, a binary mixture of the purified gases is prepared in a glass vacuum manifold at room temperature in a darkened room. The mixture is then slowly deposited (2-4 monolayers/s) onto the surface of a CsI optical window mounted in a copper retainer at the base of a closed-cycle helium refrigerator. In many experiments, a similar dewar vessel cooled by liquid nitrogen is utilized. The vacuum shroud is equipped with one quartz window through which the samples are photolyzed. Two CsI windows mounted on opposite sides of the shroud are used to obtain transmission infrared spectra (Bio-Rad Model FTS-40 or Mattson Model Polaris/Icon spectrometers). The sample may be rotated under vacuum to face any of the windows or the vapor deposition tube. The relative concentrations quoted are mol:mol ratios based on the measured partial pressures of each reagent in the sample preparation manifold prior to deposition. Measurements of film densities and thicknesses by laser interferometry strongly suggest that the sticking coefficients for a variety of compounds under our experimental conditions is near unity,³⁵ and we believe that the relative concentrations of chlorine and alkanes in the film are accurately represented by the respective partial pressures in the sample preparation manifold.

Ultraviolet absorption spectra of representative samples are obtained in a similar manner by depositing the film onto a Suprasil quartz window and placing the vessel in a standard UV absorption spectrometer (Varian Model Cary 17 or Model DMS-90).

Each sample is photolyzed with a laser at low average power to avoid bulk heating of the solid films. At 308 nm (XeCl excimer laser, Questek Model 2200) the fluence was typically 1-3 mJ/cm²/pulse and the laser was operated at 2-5 Hz. At 355 nm (Nd:YAG laser,

3rd harmonic, Molelectron Model MY-21/10) the fluence was typically $3.8 \text{ mJ/cm}^2/\text{pulse}$ at 10 Hz. At 337 nm (Nitrogen laser, Laser Science Model VSL-100) the fluence was typically $20 \text{ } \mu\text{J/cm}^2/\text{pulse}$ at 20 Hz. In some experiments, continuous irradiation was provided by an argon ion laser (Spectra-Physics Model 165-09) at 458, 488, or 514 nm. Intensities at these wavelengths were in the range $6\text{-}110 \text{ mW/cm}^2$. In all cases, it was necessary to expand the laser beam to irradiate the sample, which had an area of 2.8 cm^2 . The average laser intensity was measured in each case by replacing the sample by a 1.27 cm^2 iris and measuring the transmitted laser power using a Scientech Model 38-01 absorbing disc calorimeter.

Results

Three different types of experiments were carried out in this study. Photochemical quantum yields were determined for 1:1 mixtures of chlorine with several different hydrocarbons. Secondly, quantum yields were determined for samples of propane and chlorine at a variety of relative concentrations. Several experiments were also performed with pentanes and hexanes in different mixtures with chlorine. Finally, the product branching ratio between 1-chloropropane and 2-chloropropane was determined for photolysis of propane/chlorine samples at several different wavelengths.

Quantum Yield Measurements. We define photochemical quantum yield as the average number of hydrocarbon molecules reacting per photon absorbed by the sample. The procedure for determining quantum yields from transmission FTIR spectra obtained before and after laser photolysis is straightforward and has been described previously.^{1,2} The results of these experiments are summarized in Table I for photochlorination of several hydrocarbons containing 3-7 carbon atoms. All of the experiments described in this section

were performed using 1:1 mixtures of the hydrocarbon with Cl_2 , and all were photolyzed at 308 nm.

In many cases, it was possible to measure the quantum yield for formation of chloroalkane or HCl products. This is often a more reliable measurement, particularly under conditions where only a small fraction of the sample is reacted. In cases where both measurements were carried out, the quantum yields for reactant disappearance were in agreement with those for product appearance. This verifies that no significant laser vaporization of the samples took place and that all major product channels are taken into account. In the case of samples prepared with pentane, hexane and heptane, the large number of possible products (and the variety of their conformations) made it impractical to determine product yields for each individual product channel.

The results in Table I may be summarized as follows. In most cases, the photochlorination quantum yield is less than or approximately equal to one. Quantum yields for experiments conducted at low temperatures (15 K for small alkanes, 77 K for the higher melting alkanes) were generally about 0.6, except for that of n-hexane which was somewhat higher. At 15 K, the selectivity for forming secondary vs. tertiary chloroalkanes (versus primary chloroalkanes) was modest. The values listed in Table I are raw yields and are not corrected for the greater number of primary H atoms in the alkanes. At high temperatures (77, 125, and 108 K for propane, butane and isobutane, respectively) the selectivity for formation of secondary and tertiary products was markedly higher. For butane and isobutane, the quantum yields at 77 K were lower than quantum yields at higher and lower temperatures. The quantum yield for propane was also lower at 77 K than at 15 K, but experiments could not be carried out at higher temperatures for propane due to vaporization of the sample.

Concentration Dependence. Mixtures of chlorine and propane were prepared at different relative concentrations ranging from 7:1 to 1:7 (mole:mole). Most of the experiments described in this section were carried out at 77 K. Quantum yields for 308 nm photolysis were determined by FTIR spectroscopy. Diminution of propane was followed by measuring the integrated IR band intensity at 747 cm^{-1} . Formation of 1-chloropropane and 2-chloropropane products was monitored by measuring the integrated intensity of their absorption bands at 785 and 610 cm^{-1} , respectively. The IR spectra exhibited no evidence for formation of other products.

In 1:1 mixtures, the diminution of propane and the appearance of products (1-chloropropane and 2-chloropropane) are both approximately linear with increasing total laser fluence (number of laser pulses). These experiments were carried out by obtaining FTIR spectra of each sample following successive photolysis periods until approximately 20% of the sample had reacted. The measured quantum yield is 0.12 ± 0.04 .

In propane-rich samples, similar behavior is observed when only a small fraction of the samples are converted to products. A representative plot of reactant and product relative concentrations vs. cumulative laser fluence is shown in Figure 2. In 3:1 mixtures of propane:chlorine, the quantum yield for product formation is 0.13 ± 0.04 , while the quantum yield for propane consumption is 0.10 ± 0.04 . These values were determined under conditions where less than 20% of the propane had reacted. Exhaustive photolysis confirms that the formation of products is ultimately limited by the amount of chlorine in the samples. In 7:1 mixtures of propane:chlorine, only about 5% of the propane reacts to form products, even when samples are subjected to extensive photolysis. In the early stages of photolysis the quantum yield was determined to be 0.5 ± 0.2 .

In chlorine-rich samples, the initial quantum yield for reaction of propane appeared to be somewhat higher than in equimolar samples. In a 1:3 sample of propane:chlorine, the quantum yield at 5% conversion was measured to be 0.3 ± 0.2 . The extent of reactant loss was consistent with product formation, but both were distinctly non-linear functions of total laser fluence. As the samples were photolyzed, the apparent quantum yield decreased until about half of the propane had reacted. The remaining 50% appeared to be unreactive, or had a photochemical quantum yield which was too small to measure using our technique. In 1:7 mixtures of propane:chlorine, similar behavior was observed. Only about 50% of the propane appeared to be reactive in spite of the large excess of chlorine in the solids.

A series of experiments was performed to probe concentration effects with n-pentane, cyclopentane, n-hexane, and cyclohexane. In these experiments, samples prepared at 77 K were photolyzed with the XeCl excimer laser for typically 10,000 pulses at an incident fluence of 10 mJ/cm². The quantum yields reported in Table II are calculated on the basis of alkane molecules reacted per absorbed laser photon. Because the detailed fluence dependence of the quantum yield was not investigated, the values in Table II must be regarded as semi-quantitative. Nevertheless, the fact that most of the quantum yields in Table II are not significantly greater than 1.0 suggests that chain mechanisms do not play a significant role in the photochlorination reactions. The apparent exception is for chlorination of n-hexane, for which quantum yields in hydrocarbon-rich samples appear to be significantly greater than 1.0, as shown in Figure 3.

No evidence was found for formation of dichloroalkane products in any of the experiments. In most cases photolysis was stopped after only 5-20% conversion to products in order to avoid secondary reactions. It is possible that some of these products

could have been formed from the heavier alkanes (pentanes, hexanes, and heptane), but the large number of possible isomers and conformers would make it difficult to detect and identify those which are produced in small yields.

Two experiments were performed with n-hexane-d₁₄ to determine the effects of isotopic substitution on the measured quantum yields. In a 5:1 mixture of C₆H₁₄:Cl₂, the photochemical quantum yield was measured to be 2.5 ± 1 (on the basis of hydrocarbon diminution) and 1.3 ± 1 (on the basis of formation of DCI product). These values are less than half of the corresponding hexane-h₁₄ values, indicating that there is a significant isotope effect. The DCI quantum yields were corrected for the fact that the IR absorption coefficient of DCI is about 3 times weaker than that of HCl.³⁶ In a second experiment, a mixed isotopic sample was prepared (C₆H₁₄:C₆D₁₄:Cl₂ = 2.5:2.6:1). The overall quantum yield for product formation was 3.7 ± 2 (comparable to the hexane-h₁₄ experiments), but the branching ratio for HCl:DCI products was about 2.7:1, strongly favoring H atom abstraction.

Wavelength Dependence. Several experiments were conducted in order to study the effect of changing photolysis wavelength. Four different lasers were utilized at 6 wavelengths. Two experiments were performed at 337 nm (nitrogen laser) and two at 355 nm (Nd:YAG laser, 3rd harmonic). Formation of products was qualitatively consistent with the 308 nm results, but no attempt was made to measure the quantum yields due to variations in spatial and temporal profiles of the laser beams and different absorption coefficients of Cl₂. The branching ratio between 2-chloropropane and 1-chloropropane is 5 ± 1 and 6 ± 1 at 337 and 355 nm, respectively. This is the same as for 308 nm photolysis (5 ± 1), and we expect that the quantum yield is the same as well.

Five experiments were conducted by photolyzing samples with an argon ion laser at 458, 488, and 514 nm. The results are summarized in Table III. Products were easily observed after 458 nm photolysis. The absorption coefficient at this wavelength was too small to be measured directly in the solid state, but the photochlorination quantum yield was estimated to be 0.2 ± 0.03 on the basis of the gas phase absorption coefficient. We measured this by obtaining the UV spectrum of a 1 atm sample of chlorine at 295 K. The results in the near-UV are in close agreement with literature values.³⁷ The 458 nm quantum yield is only about twice the value at 308 nm, suggesting that the solid state absorption coefficient is actually about half the gas phase value at 458 nm. The branching ratio at 458 nm was determined to be 4 ± 2 , in good agreement with the UV results. One experiment was performed in which a sample was photolyzed at 15 K at 458 nm (21 J/cm^2), but no product was observed. At 10 K, photolysis at 308 nm resulted in a quantum yield of about 0.8 and branching ratio of about 2.3, as reported previously.¹⁹

At 488 nm, product was observed only after extensive photolysis at 77 K. The fluence in this experiment was 750 J/cm^2 , or about 100 times the fluence typically used in the UV experiments. The quantum yield was estimated (again on the basis of the gas phase absorption coefficient) to be 0.04 ± 0.02 . The branching ratio was determined to be 3 ± 2 .

At 514 nm, no product was observed after 750 J/cm^2 photolysis at 77 K. On the basis of the gas phase absorption coefficients, we estimate that the quantum yield for photochlorination at this wavelength could not be greater than 0.002.

Discussion

The general objective of this study is to discern details of the photochemical mechanisms for photochlorination of simple alkanes in solid state mixtures with chlorine. Specifically, we want to learn whether chlorine atoms or electronically excited molecules are responsible for initiating the reaction. Also, we want to determine whether any of the simple alkanes besides cyclopropane and cyclobutane might participate in free radical chain reactions in the solid state. Our principal observable is the photochemical quantum yield, as measured by infrared absorption spectroscopy. We have observed the effects of changing photolysis wavelength, photolysis temperature, and chlorine concentration for several cyclic and acyclic hydrocarbons. Each of these effects will be discussed in turn, as they provide information concerning the mechanism of photochlorination in the solid state.

Wavelength Dependence. Molecular chlorine has a broad absorption band peaked near 330 nm which extends into the visible region of the spectrum. In rare gas matrixes, it has been shown that fluorescence from the $A'(^3\Pi_{2u})$ state is observed when the molecule is excited above or below the threshold for photodissociation.^{32,33,38} Above threshold, the caged Cl atoms undergo recombination to the excited state. Photobleaching experiments show that recombination in solid argon is extremely efficient,³² and that the fraction of molecules undergoing irreversible photodissociation is less than 10^{-6} . We note that photolysis of Cl_2 in xenon induces the formation of various excimer species with nearly unit quantum efficiency.^{39,40,41,42,43,44}

The gas phase bond dissociation energy of Cl_2 is 58 kcal/mol, which corresponds to the energy of a 493 nm photon. In our experiments, photochlorination products are observed for 458 and 488 nm photolysis, but not at 514 nm. If electronically excited Cl_2 ($A'(^3\Pi_{2u})$) molecules were responsible for the photochlorination reaction, we would expect that reaction could be initiated at all of these wavelengths. The fact that reaction is only

observed at wavelengths which are above the photodissociation threshold provides clear evidence that Cl atoms are responsible for initiating the reaction.

Additional support for this conclusion comes from the temperature dependence of the branching ratios listed in Table I. It is unlikely that changes in temperature could strongly affect the reactivity of electronically excited Cl_2 molecules towards primary, secondary or tertiary H atoms in the hydrocarbons. However, the temperature of the solid and its ability to thermalize hot Cl atoms is a likely source of temperature dependence, and support our conclusion.

Quantum Yields. Almost all of the photochlorination yields measured in this study were of the order unity or less. The qualitative conclusion to be drawn from this is that chain reactions do not play a major role in the photochlorination reaction mechanism. Because the products formed in each case (HCl + chloroalkanes) are the same as for the chain reaction mechanism, the magnitude of the quantum yields provides the principal basis for this conclusion. It is possible, of course, that chain propagation steps play a minor role in product formation. We cannot definitively rule this out. However, we have no conclusive evidence for the participation of chain propagation in the reaction and the results are qualitatively consistent with the type of radical recombination mechanism outlined in the introduction of this paper and proposed for propane in a previous paper.²

The one possible exception to this is chlorination of n-hexane. In this case, the quantum yields appear to be significantly higher, about 4-5 product molecules formed per UV laser photon absorbed by the sample. Formation of HCl seems to be favored over formation of DCI from hexane- d_{14} , possibly due to a lower C-H bond dissociation energy compared with C-D (a zero point energy effect). It is clear from an examination of Figure 3 that there is considerable uncertainty in the measured yields. It is possible that very short

chain reactions participate in the reaction mechanism, but the effect is certainly small compared with kinetic chain lengths of 10^4 - 10^7 typically observed in the gas phase and liquid solutions.

Temperature Dependence. In a previous paper, we noted that the branching ratio between 2-chloropropane and 1-chloropropane exhibits a pronounced temperature dependence.¹⁹ The branching ratio simply reflects the selectivity of Cl atoms for abstracting primary or secondary H atoms from the hydrocarbon in the initial step. The primary or secondary alkyl radical thus formed undergoes recombination with the "partner" Cl atom formed in Cl_2 photolysis to form the corresponding alkyl chloride.

At low temperatures (15-50 K) the branching ratio between 2-chloropropane and 1-chloropropane products is 0.8 ± 0.2 . At 77 K, the branching ratio is 5 ± 2 . The higher selectivity was attributed to thermalization of the Cl atoms in the slushy solid which is probably near its glass transition point.¹⁹ The low selectivity at low temperatures was attributed to reaction of "hot" Cl atoms which retained at least some of the excess energy from the photodissociation event. The rigidity of the amorphous solid at very low temperatures is thought to enhance the "hot" Cl atom effect on photochlorination branching ratios.

An alternative explanation is that the higher selectivity at low temperatures is due to diffusion in the slushy solid which allows a Cl atom to "find" a secondary H atom with which to react. However, this explanation fails to account for the fact that the quantum yields at low temperature are about 6-fold higher than at high temperature.¹⁹ The diffusion argument would predict the opposite temperature dependence. While we do not yet fully understand the reaction mechanism, the thermalization mechanism is most consistent with the experimental results obtained to date.

The results presented in Table I show that this type of temperature dependence is not peculiar to propane. Both n-butane and isobutane exhibit markedly enhanced selectivity for formation of secondary or tertiary chlorides at temperatures approaching the melting point of the solid. The effect is quite dramatic in the case of isobutane. The hydrocarbon has only one tertiary H atom, and increasing the photolysis temperature from 15 to 108 K results in a nearly 60-fold increase in the probability of chlorination at that site. The large number of possible products (isomers and conformers) makes determination of branching ratios for pentanes and hexanes difficult using this technique. However, we expect that the greater selectivity for H atom abstraction from secondary and tertiary sites at high temperatures (near T_g of the binary solid) is quite general.

Concentration Dependence. The detailed results for concentration-dependent quantum yields must be interpreted with caution. This is because changes in concentration are unavoidably accompanied by changes in other physical properties of the vapor-deposited samples, such as the melting point and glass transition temperature. Consider, for example, the freezing point of an ideal solution of two components A and B. An elementary freezing point depression analysis predicts that as small amounts of A are added to an otherwise pure solution of B, the freezing point of B is reduced as shown in Figure 4. The freezing point depression is a consequence of the entropy of mixing, which lowers the chemical potential of the liquid relative to the pure crystalline solid. The enthalpy of mixing is zero for an ideal solution.

While the melting point of an ideal mixture is a non-linear function of temperature, the glass transition point (T_g) should be linearly dependent on composition, as indicated in Figure 4. This is because the entropy of a liquid is similar to that of a glass (cooling is not accompanied by large changes in the structure of the system). In addition, changes in

enthalpy are linearly dependent on composition and are approximately independent of temperature.

The main point we wish to make here is that changes in composition may result in some solids which are well below the glass temperature while others may be near or above it. The chlorine/propane system is particularly susceptible to this effect. In propane-rich samples the melting point is about 85 K. Samples prepared at 77 K are almost certainly above the glass temperature. On the other hand, the melting point of chlorine-rich samples is near 170 K, and samples formed at 77 K are likely to be below T_g .

Keeping this sort of limitation in mind, it is worthwhile to consider some qualitative aspects of the experimental results. For higher-melting compounds (i.e., pentanes and hexanes in Table II and Figure 3), we note that the general trend is toward higher quantum yields in hydrocarbon-rich samples. This is easily rationalized by the following argument. In chlorine-rich samples, Cl_2 molecules which are dissociated by the laser are more likely to be caged by other (non-reactive) chlorine molecules rather than by (reactive) hydrocarbon molecules. Chlorine atoms have a greater opportunity for reaction in hydrocarbon-rich samples and this is reflected in the increased quantum yields. We note that chain reactions would normally be expected to exhibit the opposite concentration dependence. Chain chlorination of cyclopropane, for example, exhibits its maximum yield for an equimolar mixture of reagents.¹ This observation provides additional support for our conclusion that chain reactions do not play a major role in product formation.

In 1:1 propane/chlorine mixtures, the fraction of propane reacted was approximately proportional to the cumulative laser fluence at low to moderate levels of conversion (less than 30% reacted). For optically thin homogeneous samples we expect an exponential decay in the propane fraction, but we don't regard the observed behavior to be a dramatic

departure from the "expected" results. Photochlorination in propane-rich samples was limited by the amount of chlorine, as expected, though it is not clear whether reaction occurs in the solid or liquid phase (*vide supra*). In chlorine-rich samples about 50% of the propane molecules seem to be unreactive. We do not understand the origin of this effect, since phase separation (trapping of propane molecules in the interior of hydrocarbon clusters) would appear to be less likely under these conditions compared with possible chlorine aggregation in low-melting solids rich in the hydrocarbon fraction.

Conclusion

Photochlorination reactions of solid propane, n-butane, isobutane, n-pentane, cyclopentane, cyclohexane, and n-heptane exhibit no conclusive evidence for the participation of chain propagation reactions in the mechanism. With few exceptions the measured photochlorination quantum yields are less than or approximately equal to 1.0. The results are consistent with a reaction mechanism involving recombination of radical species at the local site of photolytic dissociation of Cl_2 . In samples of n-hexane and chlorine somewhat higher yields are observed, and it is possible that short chain reactions contribute to the mechanism producing as many as 5 molecules per photon. The fact that photochlorination of propane is observed only when the photolysis laser photon energy exceeds the dissociation energy of chlorine strongly implicates chlorine atoms as the active species, not electronically excited chlorine molecules.

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Table I. Quantum Yields for Photochlorination of Alkanes in 1:1 Mixtures with Molecular Chlorine.

Alkane	m.p.	T _{exp}	$\Phi(\text{alkane})$	R(2°/1°)	R(3°/1°)
propane	85	15	0.7 ± 0.1	0.8 ± 0.2	
		60		1.5 ± 0.5	
		77	0.12 ± 0.04	5. ± 2.	
n-butane	135	15	0.6 ± 0.2	1.3 ± 0.4	
		77	0.2 ± 0.1	1.3 ± 0.4	
		125	1.1 ± 0.2	15. ± 3.	
isobutane	113	15	0.6 ± 0.2		0.07 ± 0.02
		77	0.0 ± 0.2		0.9 ± 0.2
		108	1.9 ± 0.5		4. ± 1.
n-pentane	143	77	0.5 ± 0.2		
cyclopentane	179	77	0.8 ± 0.2		
n-hexane	178	77	1.7 ± 0.3		
cyclohexane	280	77	0.6 ± 0.2		
n-heptane	182	77	1.6 ± 0.4		

melting pt of chlorine is 172 K.

Table II. Quantum Yields for Photochlorination of Pentanes and Hexanes versus Relative Chlorine Concentration at 77 K.

$X(\text{Cl}_2)^{\text{a}}$	n-pentane	cyclopentane	n-hexane	cyclohexane
0.17	0.6 ± 0.1	1.2 ± 0.2	4.6 ± 0.9	1.6 ± 0.3
0.25	0.5 ± 0.1	1.1 ± 0.2	4.7 ± 1.0	1.0 ± 0.2
0.33	—	1.0 ± 0.2	1.8 ± 0.4	—
0.50	0.5 ± 0.1	0.8 ± 0.2	1.7 ± 0.3	0.6 ± 0.2
0.75	0.4 ± 0.1	0.5 ± 0.1	0.9 ± 0.2	0.5 ± 0.1

a) mole fraction of chlorine in sample

Table III. Wavelength Dependence for Photochlorination of Propane at 77 K.

λ nm	σ^a cm ² , base e	Fluence J/cm ²	Quantum Yield	R(2°/1°)	No. expts.
308	1.5×10^{-19}	4	0.12 ± 0.04	5 ± 2	5
458	$3. \times 10^{-21}$	53	0.20 ± 0.03^b	4 ± 2	3
488	$7. \times 10^{-22}$	750	0.04 ± 0.02^b	3 ± 2	1
514	2.3×10^{-22}	750	< 0.002	—	1

^a) Absorption cross section measured for Cl₂ (1 atm, 295 K, 10 cm path). The value at 308 nm is in good agreement for the measured solid state cross section (77 K, 50% propane), and with gas phase data in ref. 37.

^b) The stated uncertainty reflects the precision of the measurement. The accuracy of the value is uncertain because the gas phase absorption cross section was used in the calculation of the quantum yield.

Figure Captions

Figure 1. Schematic representation of the proposed radical recombination mechanism for photochlorination of amorphous solid chlorine/propane films (see text for details).

Figure 2. Relative concentrations of propane (circles), 2-chloropropane (squares), and 1-chloropropane (triangles) as a function of cumulative laser fluence. The sample was formed from a 3:1 mixture of propane:chlorine deposited onto a CsI substrate at 77 K. The unphotolyzed sample contained 1.9×10^{16} propane molecules/cm² at the center of the sample window. The 308 nm laser fluence was 4.15×10^{15} photons/cm²/pulse.

Figure 3. Plot of photochlorination quantum yield vs. mole fraction of molecular chlorine in samples mixed with n-hexane. The circles represent yields based on depletion of n-hexane whereas the squares represent yields calculated on the basis of HCl formation.

Figure 4. Schematic diagram of the freezing point depression and glass transition temperature as a function of composition in an ideal two-component mixture of two substances A and B.

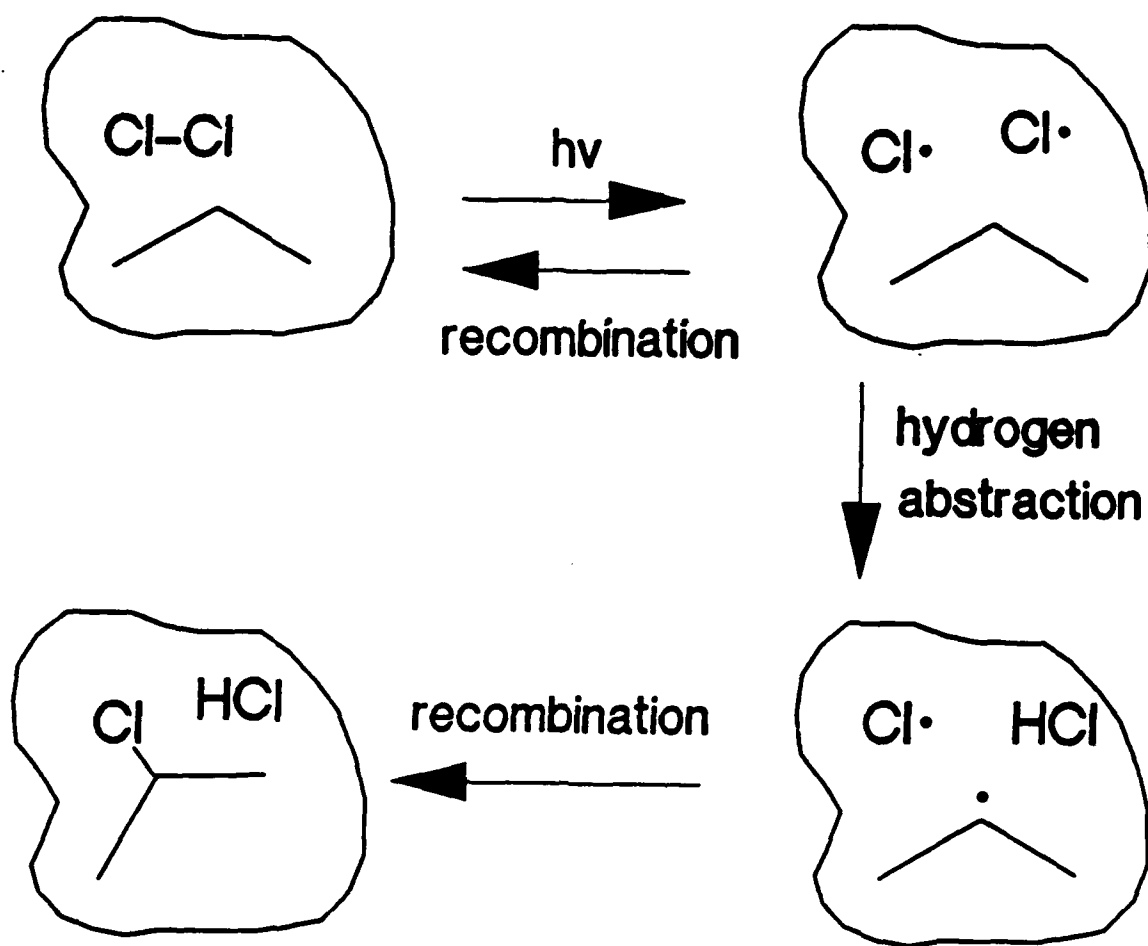


Figure 1

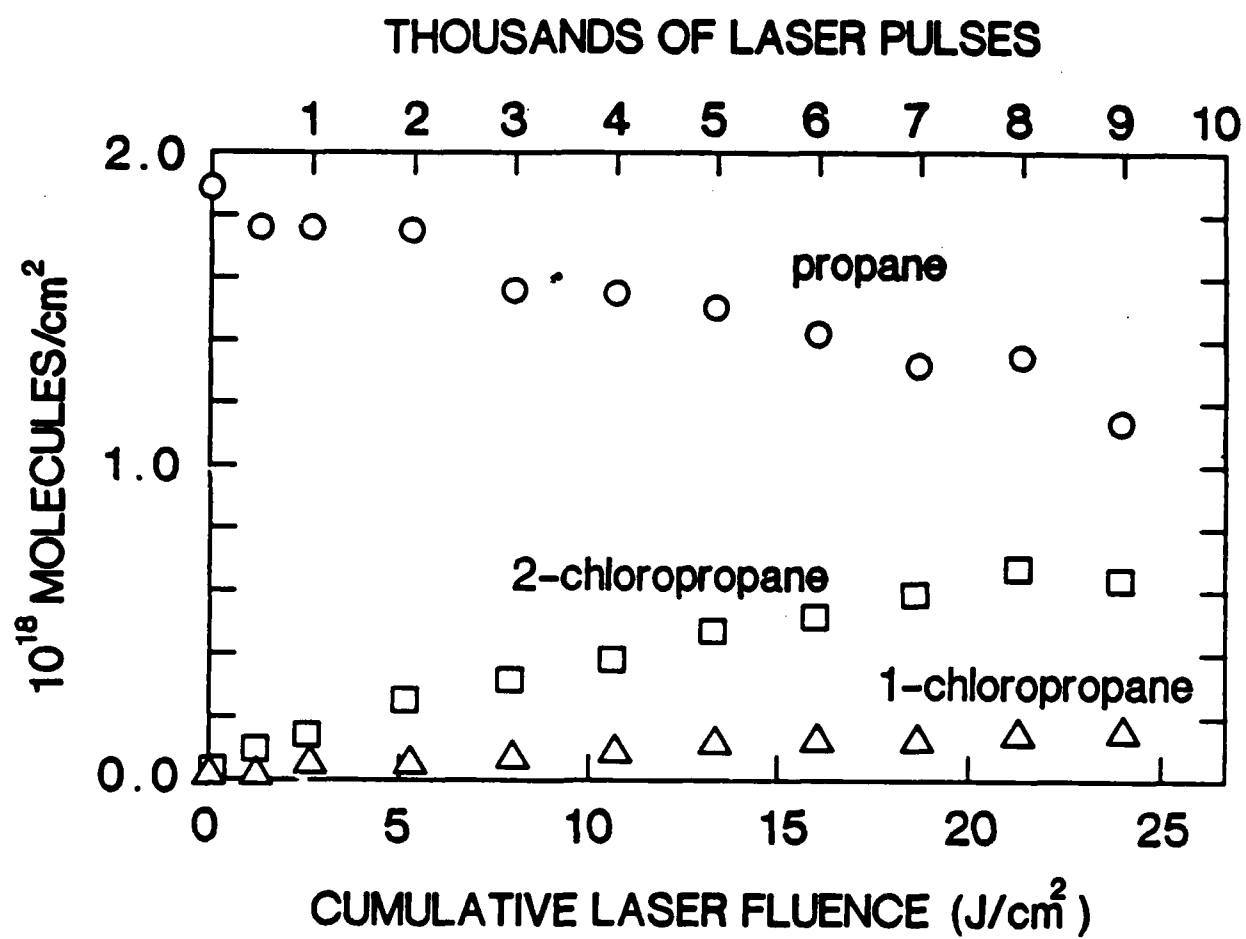


Figure 2

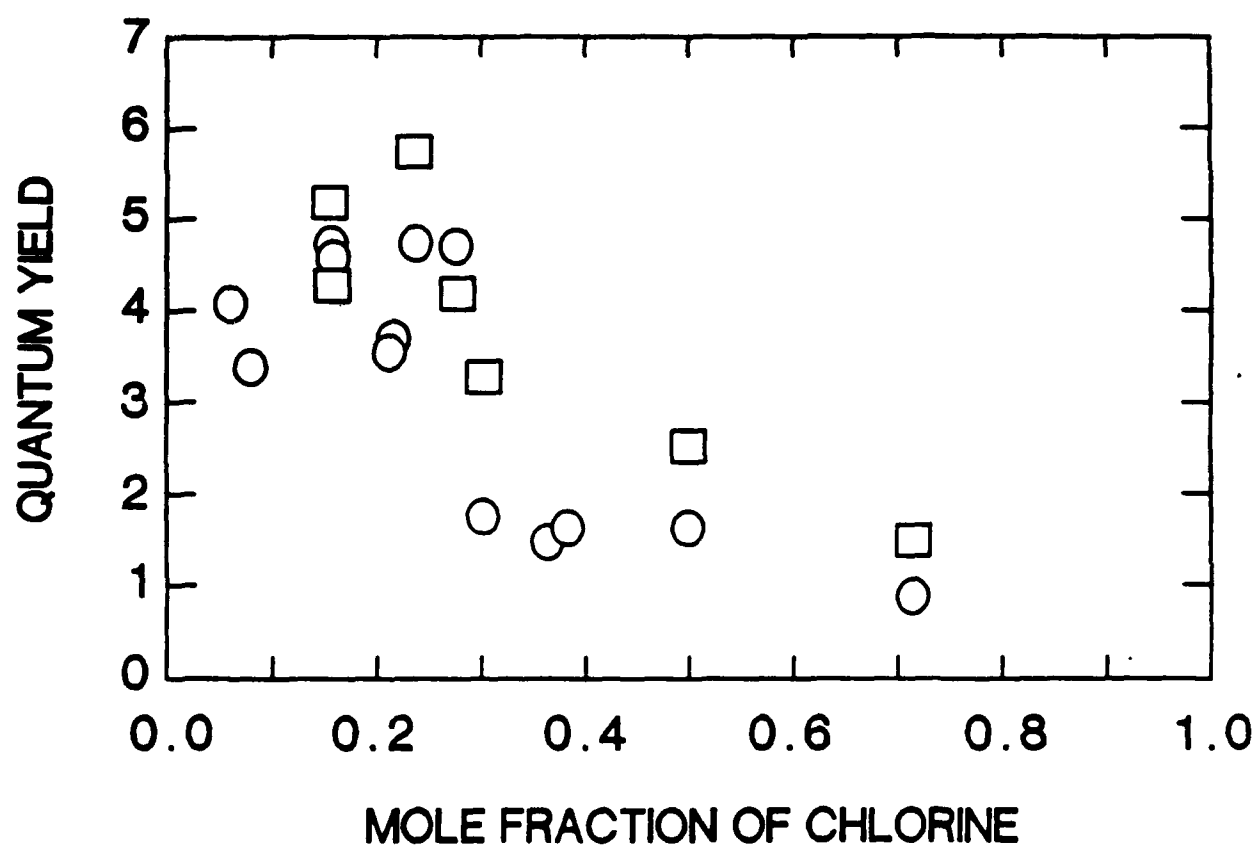


Figure 3

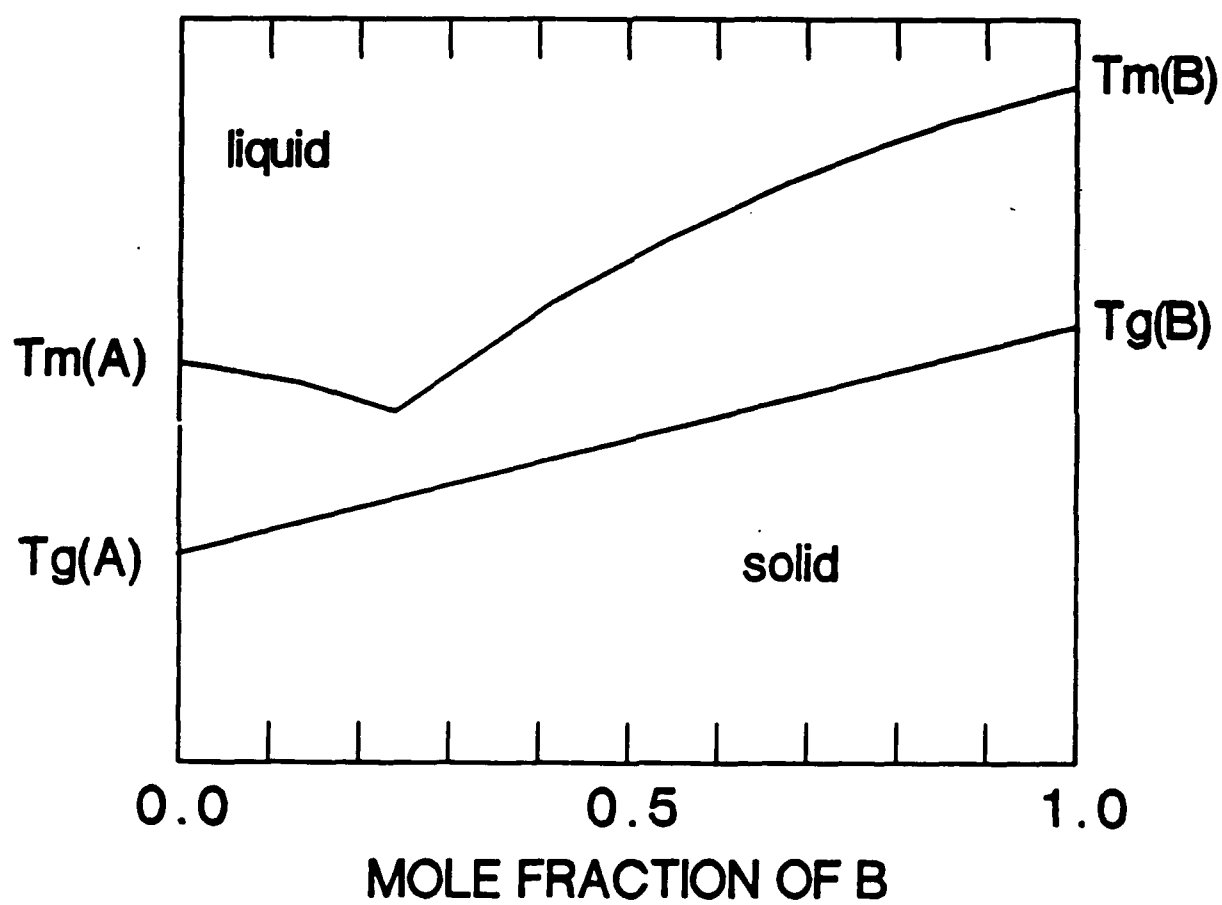


Figure 4