Conformational Selectivity in the Solid-State Photochlorination of Cyclopropane

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The solid-state free-radical chain reaction of chlorine with cyclopropane has been investigated with the use of pulsed UV laser photolysis and transmission FTIR spectroscopy. The photochemical quantum yield for an equimolar mixture of the two reagents prepared as a thin film by vapor deposition at 77 K is 52 ± 8 . Samples prepared at this temperature form the anti, anti conformer of 1,3-dichloropropane as the initial reaction product, even when the photolysis is carried out at temperatures as low as 10 K. However, selective formation of the gauche, gauche conformer is observed in the early stages of photolysis for samples that are prepared and photolyzed at 10 K. Continued photolysis of the 10 K sample leads to a sudden burst of reactivity (microexplosion) in which HCl and chlorocyclopropane are formed in addition to distributions of 1,3-dichloropropane conformers. The results indicate that the control of conformational selectivity in this reaction is governed by the influence of temperature and sample density on elementary steps in the reaction mechanism.

Introduction

In two previous reports from our laboratory, we described UV laser-initiated free-radical chain reactions in mixtures of cyclopropane and chlorine formed as a low-temperature solid film via vapor deposition.^{1,2} This photochlorination reaction proceeds via a ring-opening addition mechanism:

$$Cl_2 + h\nu \rightarrow 2Cl^*$$
 (1)

$$Cl' + cyclo-C_3H_6 \rightarrow ClCH_2CH_2CH_2$$
 (2)

$$ClCH_2CH_2CH_2^{\bullet} + Cl_2 \rightarrow ClCH_2CH_2CH_2Cl + Cl^{\bullet}$$
(3)

in which 1,3-dichloropropane is the only observed product at 77 K. One of the intriguing aspects of this reaction is that in the initial stages of laser photolysis, only the anti, anti (AA) conformer of the product is formed. Two other lower energy conformational isomers, gauche, gauche (GG) and anti, gauche (AG), emerge only after continued photolysis. These conformers do not interconvert in the low-temperature solid environment, and they are distinguishable on the basis of their infrared spectra in the region of the C-Cl stretching vibrations.^{3,4}

High selectivity for formation of particular conformational isomers of reaction products in solid-state chain reactions has also been observed for photochlorination of acetylene,⁵ ethylene,⁶⁻⁸ propylene,⁶ methylcyclopentane,⁹ and methylcyclohexane.⁹ At temperatures below about 30 K, these reaction systems exhibit sudden bursts of reactivity (microexplosions) during the photolysis period.¹⁰⁻¹³ The high product conformational selectivity is lost during these events, and distributions of product conformers have been observed in all cases. From these results we have inferred that microexplosions create a relatively high-temperature, highmobility environment for chain reactions to take place.

With these results in mind, we have revisited the chlorine/ cyclopropane system to examine the reaction product distributions as a function of sample temperature during photolysis. We anticipated that in addition to the various possible conformers of 1,3-dichloropropane, the microexplosions might open an entirely new product channel forming HCl and chlorocyclopropane via the chain propagation sequence

 $Cl^* + cyclo - C_3H_6 \rightarrow HCl + cyclo - C_3H_5^*$ (4)

$$cyclo-C_3H_5 + Cl_2 \rightarrow cyclo-C_3H_5Cl$$
 (5)

This substitution channel is reported to be a major reaction pathway in room-temperature solutions.¹⁴

In this paper we report conformational distributions for the ring-opening channel as a function of sample temperature and thermal history. We describe how the conformational product distributions can be controlled by varying the sample preparation conditions. We have also found evidence for the substitution channel, reactions 4 and 5 under microexplosion conditions.

Experimental Section

Thin amorphous films of chlorine and methylcyclopropane are prepared by deposition of the premixed gases directly onto the surface of an optical window. The deposition rate of the reagent mixture is typically 0.3–0.7 mmol/h, and the total amount of sample deposited is typically 0.06 mmol. The room is kept dark during premixing and sample deposition to prevent chain reactions from occurring in the gas phase. The sample window is mounted in a copper retainer at a cold tip in high vacuum, which is cooled either by liquid nitrogen or by a closed-cycle helium refrigerator. The outer shroud can be rotated under vacuum so that the sample faces the deposition port or a quartz window through which samples are photolyzed, or a pair or KBr windows for obtaining transmission FTIR spectra (Mattson Model Polaris FTIR spectrometer).

For experiments requiring FTIR spectra, the samples are deposited onto the surface of a CsI optical window. A CaF_2 substrate is used for experiments in which an optically flat substrate is required (e.g., for ellipsometry measurements or for monitoring interference fringes in the specular reflection of a He–Ne laser beam from the sample during deposition).

Samples are photolyzed using a pulsed nitrogen laser (Laser Science Inc. Model VSL-337) operating at 337 nm. Pulse repetition rate and fluence are typically 10 Hz and 0.022 mJ/ cm^2 , respectively.

Results

Laser photolysis of glassy cyclopropane/ Cl_2 mixtures at 337 nm and 77 K causes the characteristic infrared bands of cyclopropane to diminish in intensity. At the same time, bands characteristic of AA-1,3-dichloropropane appear. After continued photolysis, we see an emergence of bands characteristic of the AG and GG conformers. The product bands are identified by comparison with the literature values.^{3,4} Samples are typically photolyzed to the extent that about 60% of reactants are converted to products. It was not possible to achieve more than 85% conversion, even after extended photolysis periods. The observed products were formed in amounts consistent with reactant loss

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TABLE I: Quantum Yields and Conformational Distributions for Photochlorination of Cyclopropane

deposition temp (K)	photolysis temp (K)	ratio of conformers (AA:AG:GG) ^a	quantum yield
10	10	0:1:10	0.6 ± 0.1
20	20	2:1:0	0.7 ± 0.1
30	30	1:1:0	1.5 ± 0.2
45	45	0:10:1	3.2 ± 0.5
60	60	4:1:0	20 ± 3
77	10	10:1:0	1.3 ± 0.2
77	45	10:1:0	2.7 ± 0.4
77	77	10:1:1	52 ± 8

^a Zero for a conformer population indicates that the respective conformer was produced in such small quantities as to be undetectable. These distributions are determined by dividing integrated band intensities for each conformer (given in Table II) by their relative absorption coefficients. These distributions are determined during the initial period of laser photolysis. In some cases the distributions change with continued photolysis.

 TABLE II:
 Band Positions and Relative Absorption

 Coefficients for the Reaction Products

product	freq (cm ⁻¹)	rel abs coeff
AA-1,3-dichloropropane	697, 780	1.0
AG-1,3-dichloropropane	656, 727	3.0
GG-1,3-dichloropropane	642,679	3.8
нсі	2697	18.7
chlorocyclopropane	939	0.4

based on measurements of the relative infrared absorption band intensities obtained from authentic samples of 1,3-dichloropropane deposited directly onto the sample window. There was no evidence of sample vaporization during laser photolysis.

During photolysis, the IR band intensities of the reaction products exhibit an exponential increase, approaching a final asymptotic value. The infrared band at 1278 cm⁻¹ is used to monitor 1,3-dichloropropane production because this band is common to all conformers. The cyclopropane concentration is monitored by its characteristic band at 1022 cm⁻¹, which exhibits an exponential decrease during the photolysis period. Because the samples are optically thin at the laser wavelength, a phenomenological photoreactive cross section can be obtained for the reactants or products from a nonlinear least-squares fit of the data (integrated IR band intensity vs cumulative incident laser fluence) to an exponential decay or rise, respectively. The ratio of the photoreactive cross sections to the absorption cross section of chlorine at the photolysis wavelength^{15,16} is equal to the photochemical quantum yield, or number of molecules formed per photon absorbed by the sample. Results for reactant and product bands were averaged to obtain the final quantum yields listed in Table I. The yields are typically larger than unity because repetition of the chain propagation steps, reactions 2 and 3, can convert many reactants to products for each laser photon absorbed by the sample.

The data in Table I show that the overall photochemical quantum yields are small and approximately independent of photolysis temperature below about 30 K, regardless of the sample preparation conditions. Above 30 K the yields increase rapidly with increasing temperature.

Also listed in Table I are the branching ratios for the three conformers formed during the photochemical reaction. Determination of branching ratios for conformer production is possible because each conformer exhibits characteristic C-Cl stretching vibrational bands in the infrared region as listed in Table II. In cases where more than one product conformer is observed, the integrated intensities of these bands were divided by their characteristic absorption coefficients in order to obtain the reported conformational distributions.

Perhaps the most striking feature of the data is that samples prepared and photolyzed at 10 K selectively form the lowest energy GG product conformer, whereas the higher energy AA conformer is the principal product formed from samples prepared by vapor



Figure 1. Infrared spectra of a 1:1 mixture of cyclopropane and chlorine at 10 K prior to photolysis (bottom), after 9000 pulses of 337-nm laser light at 0.022 mJ/(cm² pulse) (middle) and after a microexplosion (top). Each division in the vertical scale represents 0.3 (left) and 0.1 (right) absorbance units. Bands characteristic of AA (697 and 780 cm⁻¹), AG (656 and 727 cm⁻¹), and GG (642 and 679 cm⁻¹) 1,3-dichloropropane are evident in the top spectrum. The broad band at 2697 cm⁻¹ in the top spectrum is the HCl absorption band.

deposition at 77 K but photolyzed at 10 or 45 K. When samples are formed and photolyzed at 45 K, the AG conformer is the principal product.

In some experiments, the conformational distribution changes with the extent of photolysis. For example, in experiments where photolysis was carried out at 77 K, we observe initially AA-1,3dichloropropane formation, but absorption bands characteristic of the more stable AG and GG conformers begin to emerge after continued laser photolysis. Samples formed and photolyzed at 60 K yield initially both AA and AG conformers of 1,3dichloropropane. Those formed and photolyzed at 45 K initially AG with the emergence of GG only after about 26 000 laser pulses. Experiments conducted at 20 and 30 K yield AA and AG throughout laser photolysis. The distributions listed in Table I were determined from integrated band intensities obtained early in the photolysis period in order to reflect the initial conformational distributions as much as possible.

In the case of deposition and photolysis at 10 K, the high conformational selectivity for the GG product occurs only in the initial stages of the reaction. After exposure to a cumulative fluence of about 0.44 J/cm², the sample undergoes a microexplosion. The irradiated area changes in appearance from nearly transparent to milky white (translucent). Infrared spectra obtained immediately following a microexplosion indicate the presence of all three conformational isomers. In addition, infrared absorption bands due to HCl and chlorocyclopropane are observed after the microexplosion but are not produced by the ordinary photochemical chain mechanism in the range 10-77 K; this is illustrated in Figure 1. The assignments of the chlorocyclopropane and HCl bands were verified by comparison with the literature values.¹⁷ Approximately 16% of the reactants are consumed during the microexplosion, and branching between the addition and substitution channels is approximately 1:1. The branching ratio of conformers of 1,3-dichloropropane after the microexplosion is 1:3:3 for AA:AG:GG. There was no evidence for loss of reactants due to vaporization during the microexplosion.

Ellipsometry measurements were performed to determine the refractive index of samples prepared at 10–77 K. For vapor depositions at 10–45 K, an apparent refractive index of 1.06 was obtained. Depositions at 77 K yielded an index of refraction of 1.15. By comparison, the index of refraction for CaF₂ at 77 K is 1.4353.¹⁸ The values obtained for these vapor-deposited samples are much lower than one can reasonably expect for condensed phase materials. The anomalous results are most likely due to inhomogeneities in sample density along the surface normal. We have previously observed this phenomenon in mixtures of methylcyclopropane and chlorine.¹⁹



Figure 2. Plot of specular reflectivity of a 1:1 sample of cyclopropane and chlorine during vapor deposition. Deposition onto a CaF₂ window at 45 K begins at t = 5 s (top panel). The sinusoidal waveform is the result of interference between reflections of the He-Ne probe laser beam from the front and back surfaces of the growing sample. Note that the reflected intensity decreases initially. For deposition at 77 K (bottom panel), the fringe pattern increases upon initiation of sample deposition at t = 35 s. The noise in the bottom panel is due to vibration of the apparatus by the piston in the closed-cycle refrigerator.

Examination of the interference fringes obtained from reflection of a He-Ne laser beam from the sample surface during deposition provides an important clue to the true refractive indices of the samples. We found that samples prepared at 77 K yielded an interference fringe pattern that begins with an increase in sample reflectivity at the start of deposition, as shown in Figure 2. Conversely, an initial decrease in reflectivity occurs at deposition temperatures of 45 and 10 K. This result shows that samples deposited at 77 K have a refractive index that is higher than the substrate, whereas those deposited at 10 and 45 K have indexes lower than CaF₂, at least in the immediate region of the sample/ substrate interface.

Discussion

Conformational Selectivity. One of the interesting aspects of the cyclopropane/ Cl_2 system is the fact that the distribution of product conformational isomers is dependent on the temperature of the substrate during sample deposition. Conversely, the results show that after 77 K deposition, the photolysis can be carried out at lower temperatures without affecting the conformational distributions. We therefore conclude that the conformational distributions are governed not only by changes in temperature but also on the physical structure on the solid formed during the deposition process.

The interferometry (reflectivity) measurements show that samples formed at 77 K have higher refractive indexes and therefore higher densities than those formed at lower temperatures. We believe that the relatively dense packing in these samples strongly hinders rotational motion about the C-C bonds of the 1,3-dichloropropane product, thereby trapping the initially formed AA conformer. On the other hand, the extra void volume incorporated into samples formed at low temperatures relaxes the steric constraints on rotational isomerization, allowing the formation of the lower energy GG conformer. It is possible that the excess energy of the photolysis photon aids the isomerization process, since the quantum yields at 10 K are low and the reaction is highly localized near the original site of photon absorption. However, at 77 K the quantum yields are relatively large; therefore, most products are formed in regions that are both spatially and temporally well separated from their respective initiation events.

There is ample evidence that the initial conformer formed by the reaction is AA. For example, solution phase stereochemical studies have shown that $S_H 2$ reaction of a Cl atom on cyclopropane occurs with inversion of configuration at the carbon atom that is attacked.²⁰ This forms a 3-chloropropyl radical in which the newly formed C-Cl bond has an anti spatial relationship to the radical center. We have argued in a previous paper that expansion of the carbon backbone as a result of the ring opening leaves a vacancy on the endo side of the radical, and the formation of a second C-Cl bond occurs preferentially on the exo side, thereby forming the AA conformer of 1,3-dichloropropane.¹ In samples prepared at intermediate temperatures (45 and 60 K) the corresponding densities may be low enough to relax this exo/ endo selectivity, resulting in enhanced formation of the AG conformer. In fact, the surprisingly high selectivity for AG formation at 45 K could be due to low-energy pathways that lead to formation of an anti center in reaction (2) and a gauche center in reaction (3).

Experiments conducted at 20 and 30 K give rise to conformational distributions that do not seem to make sense in terms of relaxation of the AA conformer to lower energy forms. We note that in this temperature range the distributions are probably subject to opposing factors of decreasing temperature and decreasing density, making the actual distributions difficult to predict.

In principle, the differences in conformational selectivity could be due to formation of different crystal structures of the solid, which influence the reaction mechanism and thereby control the conformational distribution. We believe that this is not the case for the following reasons. First, the infrared bandshapes for the various types of samples are all consistent with formation of disordered (glassy) mixtures of the chlorine and hydrocarbon. No obvious site splittings and/or band narrowing were observed. Second, a set of samples photolyzed at 10 K but formed at a range of temperatures from 10 to 77 K all exhibit comparable (though not identical) quantum yields. It seems to use that if each conformer were formed by a different reaction mechanism (due to differences in crystal structure) then substantial differences in the quantum yields might be expected. Third, the anomalous results obtained in the ellipsometry experiments imply that the density of the samples is not homogeneous but is instead lower near the substrate compared with regions near the vacuum interface. This type of inhomogeneity could be caused by variations in the extent of local relaxation that takes place when each molecule lands on the cold surface, especially if the thermal conductivity of the sample is much less than that of the substrate. In any case, inhomogeneities in sample density are not compatible with the formation of a crystalline structure and therefore indirectly support the idea that an inhomogeneous disordered solid solution is formed by vapor deposition.

Microexplosions. The microexplosions that occur in samples formed at 10 K allow us to refine our qualitative model for what causes this interesting phenomenon. We have previously presented evidence for transient liquefaction occurring during microexplosions.^{9,10} We speculated that the heat of reaction coupled with a catastrophic release of lattice energy allows liquefaction to occur. During this liquefaction, a scrambling of conformers has been observed. Our study of isomeric product distributions in the chain reaction of acetylene with chlorine showed that the liquefaction directly influences the mechanism of product formation and does not simply scramble the isomers after they are formed.⁵ This was because the product, 1,2-dichloroethylene, does not undergo thermally activated cis-trans isomerization at cryogenic temperatures.

In this investigation not only do we find a scrambling of conformers (AA, AG, and GG are observed after the microexplosion) but for the first time we have seen a new reaction channel open that takes place during microexplosions but not during the ordinary photochemical chain reactions, even at temperatures as high as 77 K. The activation energy for the substitution



Figure 3. Plot of the natural logarithm of the quantum yield versus inverse absolute sample temperature. The solid curve is a weighted nonlinear least-squares fit of the experimental results to eq 6.

mechanism, reaction 4 is 17 kJ/mol.^{21,22} This is significantly higher than for the ring-opening addition mechanism, reaction 2, which has $E_a = 7.1$ kJ/mol.²³ We therefore conclude that the transient heating that occurs during the microexplosions must raise the temperature of the sample well in excess of 77 K in order for the two channels to be competitive, as observed in this study.

Temperature Dependence of the Quantum Yields. Because we have not measured the rates of solid-state reactions in real time, we cannot directly determine the activation energy for the solid-state chain reactions. However, if the quantum yield were proportional to the initial reaction rate, then a semilogarithmic plot of quantum yield as a function of inverse absolute temperature should afford a similar quantity. Such a plot is illustrated in Figure 3.

The quantum yields are insensitive to changes in temperature below 30 K. A similar result obtained previously for the reaction of ethylene and chlorine was interpreted in terms of a heavyparticle quantum tunneling mechanism for the chain extension reaction.^{24,25} However, in this case the quantum yield at low temperature is less than 1.0, and the result can be understood in terms of a localized reaction activated by the energy of the UV photon deposited by the laser rather than by ambient thermal energy of the solid. We find no compelling evidence for participation of quantum tunneling in this reaction.

In the temperature range 45-77 K, the quantum yields are strongly temperature dependent. This suggests that the overall temperature dependence of the quantum yield can be expressed in the form

$$\Phi(T) = \Phi(0) + \Phi(\infty) \exp(-E_a/kT)$$
(6)

where the first term reflects the photon activated portion of the quantum yield, and the second term represents the thermally activated extension of the chain. The data in Table I were subjected to a weighted nonlinear least-squares fit to eq 6, and the result is presented as the solid curve in Figure 3. The free parameters determined from this fit are $\Phi(0) = 0.73 \pm 0.07$, $\Phi(\infty) = 3100 \pm 300$, and $E_a = 2.61 \pm 0.05$ kJ/mol. We stress that E_a cannot be a true activation energy, because the measurements are for quantum yields, not rates. Also, the reactions take place under conditions that are far from thermodynamic equilibrium. Interestingly, the apparent activation energy is substantially less than the true activation energy determined previously for the solution phase reaction, 7.1 kJ/mol.²³ It is also less than the standard enthalpies of fusion for chlorine and cyclopropane (6.4 and 5.4 kJ/mol, respectively).²⁶

In a previous study of temperature-dependent quantum yields for solid-state photochlorination of methylcyclopropane, we suggested that the apparent activation energy for chain extension was due to barriers to rotational motion in the solid.¹³ The rationale is that orientational disorder can inhibit chain extension by preventing neighboring molecules from adopting favorable geometries for reaction, but thermally activated librations and rotations can overcome this restriction, even at temperatures that essentially prevent translational diffusion (i.e., below the melting point). The spatial and orientational disorder that is characteristic of vapor-deposited samples ensures that there is a distribution of barriers to rotation, so that on a laboratory time scale each chain reaction appears to stop when the intermediate radical is formed in a particularly unfavorable geometry. The observed temperature dependence simply reflects the fact that some rotational barriers are more difficult to overcome than others. Therefore, the apparent activation energy reflects the ability of the system to overcome the effects of structural disorder rather than the barrier to reaction itself. The results presented in this paper for photochlorination of cyclopropane are consistent with this interpretation.

Acknowledgment. We thank the reviewers for suggestions that led to a significant improvement in the paper. This research is supported by the National Science Foundation under Grant CHE-8918733.

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