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Laser-Initiated Chain Reactions of Chlorine with Propane and Cyclopropane in Amorphous Films at 77 K

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Abstract: Free radical reactions of chlorine with propane and cyclopropane deposited as amorphous thin films at 77 K have been investigated. Reactions are initiated by pulsed laser photolysis of the chlorine molecules at 308 nm. Product yields and branching ratios have been determined by Fourier transform infrared absorption spectroscopy of the films following irradiation. The Cl_2/propane system is characterized by low product yields consistent with a local radical recombination mechanism. However, the Cl_2/cyclopropane reaction proceeds via a true chain reaction mechanism involving ring opening of the hydrocarbon. The dominant product of the reaction is the anti,anti conformer of 1,3-dichloropropane. Product yields have been determined as a function of the mole fraction of chlorine in binary mixtures of the reagents. The results are consistent with a simple statistical model for free radical trapping in nonreactive sites within the amorphous films.

Investigations of chemical reactivity in the solid state are beginning to unravel some of the effects of rigid structured environments on reaction mechanisms. A detailed knowledge of such effects will undoubtedly have a profound impact on solid-state physics and materials science, particularly in devising strategies for synthesizing new materials. In addition, the insight gained from such studies will be valuable for investigating biochemical reactions, which typically occur in environments that are highly restricted by noncovalent binding to enzymes.

One of the important contributions that chemists can make in this area is to develop models of solid-state reactions that relate macroscopic observables to the molecular properties of the solid. It is especially important to cultivate an appreciation for the spatial (stereochemical) properties of molecules in order to establish relationships between the topology of the solid state and the steric requirements of reaction mechanisms. Recent progress in the study of reactions in crystalline solids has been reviewed by McBride et al.[1]

We recently initiated a research project to investigate free radical chain reactions between chlorine and small hydrocarbons deposited as thin films on a cryogenic substrate. Part of the motivation for choosing these systems is that the kinetics and reaction mechanisms in the gas phase and in solution have been well characterized.[2,3] Following radical initiation, the chain propagation reactions (eq 1 and 2) are mainly responsible for product formation. Chain termination typically occurs via radical–radical recombination to form Cl_2, R_2, and RCl, or by reaction at the walls of the vessel. The first step, hydrogen atom abstraction from the hydrocarbon, is usually rate limiting, and Arrhenius parameters for many such reactions have been reported.[4] A recent development by Leone and co-workers was to monitor the formation of vibrationally excited product molecules in real time by infrared fluorescence.[5-7] A pulsed laser was used to initiate the reaction by dissociation of Cl_2, eliminating the requirement for an additional radical precursor, as was typically used in the classical studies.

$$Cl^{\bullet} + RH \rightarrow HCl + R^{\bullet} \quad (1)$$

$$R^{\bullet} + Cl_2 \rightarrow RCl + Cl^{\bullet} \quad (2)$$

In our work, we have carried out similar studies by initiating free radical reactions in mixtures of chlorine with propane or cyclopropane frozen on an optical window at 77 K. The product yields and branching ratios are determined by infrared absorption spectroscopy of the thin films before and after irradiation with the 308-nm output of a XeCl excimer laser. The principal goal of the project is to elucidate the effects of restricted mobility in the solid state on the ability of these reagents to participate in free radical chain reactions. Our results demonstrate that in propane/chlorine mixtures, the reaction mechanism is dominated by radical recombination. Reaction with cyclopropane, however, provides a mechanism for separation of the radical pairs by ring opening, resulting in efficient chain reactions and high product yields. The results are interpreted in terms of a simple statistical model of free radical chain propagation in amorphous solids.

Experimental Section

Thin amorphous films of chlorine and hydrocarbon were prepared by mixing appropriate quantities of the gases in a glass vacuum manifold and spraying them onto a CsI window at 77 K. The deposition rate of the reagent mixture is typically 0.3–0.7 mmol/h, and the total amount

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(1) McBride, J. M.; Segmuller, B. E.; Hollingsworth, M. D., Mills, D. E.; Weber, B. A. *Science* **1986**, *234*, 830.

(2) Pryor, W. A. *Free Radicals*; McGraw-Hill: New York, 1966; series in Advanced Chemistry.

(3) Walling, C. *Free Radicals* in *Solution*; Wiley and Sons: New York, 1957.

(4) Knox, J. H.; Nelson, R. L. *Trans. Faraday Soc.* **1959**, *55*, 937.

(5) Nesbitt, D. J.; Leone, S. R. *J. Chem. Phys.* **1980**, *72*, 1722.

(6) Nesbitt, D. J.; Leone, S. R. *J. Chem. Phys.* **1981**, *75*, 4949.

(7) Nesbitt, D. J.; Leone, S. R. *J. Phys. Chem.* **1982**, *86*, 4962.

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of sample deposited is typically 0.06 mmol. The room is kept dark during premixing and deposition of the samples to prevent chain reactions from occurring in the gas phase. The window is held by a copper mount at the end of a stainless steel dewar. Good thermal contact is provided by thin strips of indium foil around the edges of the cold window and between the copper mount and dewar. The entire assembly is mounted within a stainless steel vacuum shroud. The shroud is equipped with one fused silica window through which the samples are irradiated and two CsI window for obtaining transmission infrared absorption spectra of the films. The dewar can be rotated while under vacuum so that the window faces the reagent deposition line, the photolysis window, or the CsI infrared windows. In some experiments, the sample was deposited on a quartz window for obtaining ultraviolet absorption spectra.

Irradiation of the films is accomplished by using an excimer laser operating at 308 nm (Questek Model 2200). After sample deposition, the reaction vessel is closed off and removed from the vacuum manifold. The vessel is placed directly in front of the laser. Samples of propane with chlorine were typically irradiated for 100–1000 pulses while samples of cyclopropane and chlorine were irradiated for 1–10 pulses. Each pulse is approximately 15 ns in duration and has a total energy of about 100 mJ. The pulse energy is measured by using the internal energy meter on the laser and was verified with an absorbing disc calorimeter (Scientech Model 38-01). The optical density of the samples is typically 0.24 at 308 nm such that 40% of the laser photons are absorbed.

Reaction product yields and branching ratios were determined by Fourier transform infrared absorption spectroscopy (Biorad/Digilab Model FTS-40). Spectra were recorded before and after sample irradiation, and the integrated areas of individual reactant and product bands (in absorbance mode) were used to monitor the extent of reaction. Control experiments in which samples of pure propane or cyclopropane were irradiated exhibited slight (1–4%) decreases in the areas of the hydrocarbon absorptions. No product bands were observed in these experiments, and the decrease could be attributed either to a slight annealing of the samples or to vaporization of a small fraction of the sample by the laser pulse. This effect was taken into account for samples rich in hydrocarbon when reaction yields were calculated on the basis of diminution of reactant band intensities.

All reagent gases were obtained from Matheson and have a minimum stated purity of 99.5%. Chlorine was subjected to repeated freeze/pump/thaw cycles to remove noncondensable impurities. Samples of 1-chloropropane, 2-chloropropane, and 1,3-dichloropropane were obtained from Aldrich (Gold Label, 99%) and were used without further purification.

In order to calculate the reaction yields in the experiment, it is necessary to estimate the number of reagent molecules deposited per unit area at the center of the cold window. Assuming that the sample emerges from the deposition tube with a cosine angular distribution and has unit sticking coefficient, the fraction of the total sample which is deposited in 1 cm^2 at the center of the cold window is calculated to be 11%. This is an approximate value since it is based purely on geometric considerations. As a check, the absorbance of a sample containing a known total amount of Cl_2 was measured with a Varian Model Cary 17 UV absorption spectrometer. By using the gas-phase photoabsorption cross section[8] it was found that 14% of the molecules are deposited per cm^2 at the center of the window. While there is no guarantee that the photoabsorption cross section of gaseous Cl_2 at room temperature is the same as that mixed with solid hydrocarbon at 77 K, the good agreement between the two independent methods indicates that our estimate of the two-dimensional sample density is not grossly in error. The 11% figure was used in all of the calculations of product yields.

Results

Propane + Chlorine. Infrared spectra are presented in Figure 1 for a mixture of chlorine and propane frozen onto a CsI optical window at 77 K. The spectrum recorded prior to laser photolysis is consistent with the vibrational frequencies and spectral assignments for propane, according to Flurry[9] and Comeford and Gould.[10] All of the absorption bands are found to be red shifted by 5–15 cm^{-1} from their gas-phase values. Molecular chlorine, being a homonuclear diatomic, is transparent in the infrared.

After photolyzing the sample with 1000 laser pulses at 308 nm, the absorption bands of propane are diminished in intensity. Also, the spectrum exhibits characteristic absorptions due to the major products, 1-chloropropane, 2-chloropropane, and HCl, as shown in Figure 1. The product peaks were identified by comparison to assignments in the literature[11-16] and were verified by obtaining infrared spectra of the authentic compounds deposited directly onto the CsI optical window at 77 K. No evidence of polychlorinated propanes was found in the spectra.

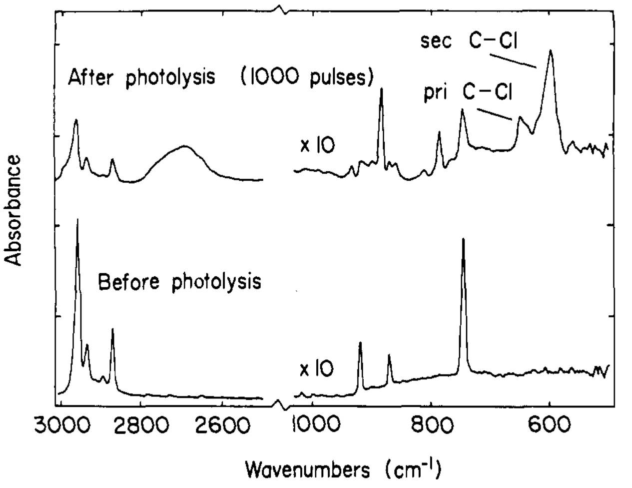
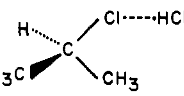


Figure 1. Infrared spectra of an equimolar mixture of propane and chlorine prior to photolysis and after 1000 pulses of 308 nm laser light. The average pulse fluence is 35 mJ/cm^2. Each division on the vertical scale represents 0.2 absorbance unit on the left-hand side of the figure and 0.02 absorbance units on the right-hand side.

The two C–Cl stretching frequencies of 1-chloropropane at 737 and 650 cm^{-1} are associated with the anti and gauche conformers, respectively. The absorption band at 605 cm^{-1} is due to 2-chloropropane, which has only one conformer. Examination of Figure 1 reveals that the 605-cm^{-1} band is considerably larger than the other two, suggesting that 2-chloropropane is the major product of the reaction. By comparing the intensities of the product absorption bands with the spectrum of a 1:1 mixture of the authentic compounds, it was found that the reaction produces 5.7 ± 0.3 times as much 2-chloropropane as 1-chloropropane. The marked preference for chlorinating propane at a secondary site is in spite of the fact that there are three times as many primary hydrogen atoms that can be abstracted by chlorine atoms produced by laser photolysis of molecular chlorine. The inherent reactivity of chlorine atoms toward secondary vs. primary hydrogen atoms, when corrected for the greater number of primary sites, is 17:1.

The other major product of the reaction is HCl, which exhibits a diffuse absorption band in the region 2580–2810 cm^{-1}. In authentic samples of HCl in propane, the HCl absorption shows up as a pair of well-resolved bands at 2758 and 2712 cm^{-1}, as shown in Figure 2. Samples of HCl in 2-chloropropane, however, exhibit a broad, unstructured band similar to the reaction product. This result indicates that HCl formed in the reaction of chlorine with propane is strongly associated with the chloropropane reaction product, perhaps forming a hydrogen bond as shown schematically below.



Such a hydrogen-bonding scheme could also account for the red shift of the HCl frequency of the reaction product relative to that

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[8] Okabe, H. *Photochemistry of Small Molecules*; Wiley (Interscience): New York, 1978.

[9] Flurry, R. J. *J. Mol. Spectrosc.* **1975**, *56*, 88.

[10] Comeford, J. J.; Gould, J. H. *J. Mol. Spectrosc.* **1960**, *5*, 474.

[11] Rasanen, M.; Bondybey, V. E. *J. Phys. Chem.* **1986**, *90*, 5088 and references therein.

[12] Bentley, F. F.; Smithson, L. D.; Rozek, A. L. *Infrared Spectra and Characteristic Frequencies 730–300* cm^{-1}; Wiley (Interscience): New York, 1968.

[13] Shipman, J. J.; Folt, V. L.; Krim, S. *Spectrochim. Acta* **1962**, *18*, 1603.

[14] Mizushima, S.; Shimanouchi, J.; Nakamura, K.; Nayashi, N.; Tsuchiya, S. *J. Chem. Phys.* **1957**, *26*, 970.

[15] Brown, J. K.; Sheppard, N. *Trans. Faraday Soc.* **1954**, *50*, 1164.

[16] Sheppard, N. *Trans. Faraday Soc.* **1950**, *46*, 533.

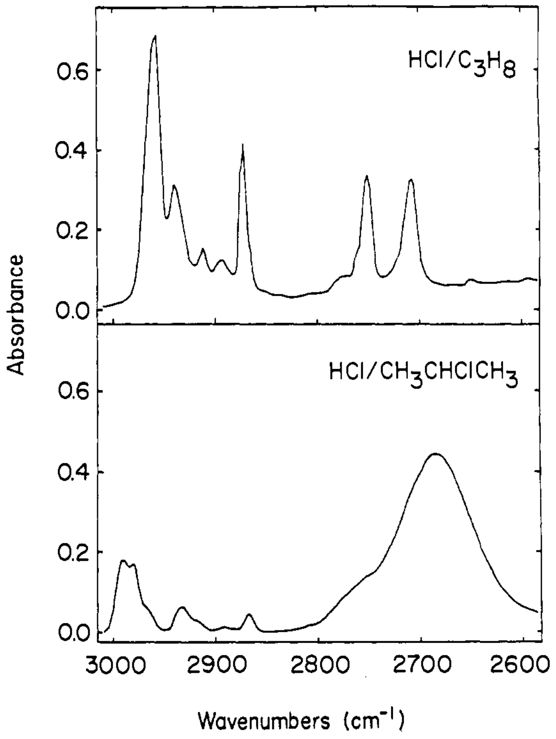

Figure 2. Infrared spectra of HCl co-deposited with propane and 2-chloropropane directly onto a CsI window at 77 K. Absorption by HCl in propane occurs as a pair of well-resolved bands at 2758 and 2712 cm^{-1}. In 2-chloropropane, the HCl absorption is diffuse and red-shifted, possibly due to a hydrogen-bonded complex.

found in propane or in the gas phase.

True free radical chain reactions, as illustrated in reactions 1 and 2, are characterized by formation of large amounts of product from small amounts of free radicals. The average turnover number for these reactions is termed the reaction chain length. Yuster and Reyerson[17,18] investigated the thermal chlorination of propane and calculated a chain length of approximately 10^7. In our experiments, we are able to directly determine the product yields by measuring the intensity of absorption bands due to the products, or reduction of absorption bands due to reactants. The number of chlorine atoms formed by photolysis is calculated by measuring the absorbance of the sample at 308 nm and the incident laser pulse energy, assuming a 100% quantum yield for photodissociation of each chlorine molecule into two chlorine atoms.[8] The two-dimensional density of chlorine molecules at the center of the optical window is estimated from the total amount of sample deposited and the deposition geometry, as outlined in the Experimental Section. Averaging over 100 laser pulses, the quantum yield for the product formation in the chlorine/propane system was found to be 0.12 ± 0.01. That is, an average of only 0.12 chloropropane molecule is formed for each photon absorbed by the sample. In a few experiments, the laser fluence was lowered from 35 to 1 mJ/cm^2 and the number of laser pulses increased to 10^4. The reaction product yields and branching ratios were the same as in experiments performed at higher fluence.

Since we find no evidence for any reaction products other than HCl and monochloropropanes, the low product yield suggests that most of the chlorine atoms immediately recombine to form Cl_2. A small fraction of the chlorine atoms abstract an H atom from nearby propane molecules, forming HCl and a primary or secondary propyl radical. Either 1-chloropropane or 2-chloropropane can then be formed by recombination of the propyl radical with the second Cl atom generated from photolysis of the Cl_2 molecule. In a sense, the reaction is self-terminated by radical recombination, so that product formation is confined to the site of chlorine photolysis. The experiments provide no direct way to confirm this proposed self-termination mechanism. However, the small product yields that are measured make it unlikely that free radical chain propagation occurs in our low-temperature films in the same way that reaction takes place in liquids and gases.

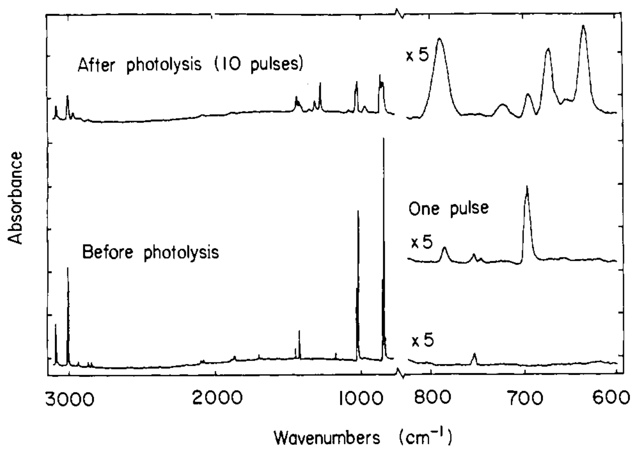

Figure 3. Infrared spectra of an equimolar mixture of cyclopropane and chlorine before and after 308 nm laser photolysis. The middle trace shows a spectrum obtained after a single laser pulse, while the top spectrum was obtained of the same sample after nine additional pulses. The average pulse fluence is 35 mJ/cm^2. Each division on the vertical scale represents 0.2 absorbance units, except on the right-hand side of the figure, where each division is 0.04 absorbance units.

Cyclopropane + Chlorine. Photochlorination of cyclopropane can occur by a mechanism similar to that for propane, yielding HCl and chlorocyclopropane as products. However, an alternative mechanism is also possible, involving addition of a chlorine atom to cyclopropane accompanied by ring opening:

$$Cl^\bullet + c\text{-}C_3H_6 \rightarrow ClCH_2CH_2CH_2^\bullet \quad (3)$$

$$ClCH_2CH_2CH_2^\bullet + Cl_2 \rightarrow ClCH_2CH_2CH_2Cl + Cl^\bullet \quad (4)$$

In the gas phase, chlorocyclopropane is formed in high yield.[19] Both mechanisms have been found to contribute to product formation in the liquid phase.[20] The ring-opening mechanism accounts for 50–85% of the products, depending on the solvent and reaction temperature. Lowering the temperature has the effect of increasing the yield due to the ring-opening mechanism.[20]

Our laser photolysis experiments of low-temperature films of cyclopropane and chlorine show that the major product is 1,3-dichloropropane formed by the ring-opening mechanism. The most dramatic difference between experiments performed with propane and cyclopropane is the much higher product yields of the latter. Conversion of reactants to products can be as high as 25% when a single laser pulse with cyclopropane is used, whereas more than 100 pulses are required to observe appreciable formation of products in the case of propane.

Infrared spectra obtained in the cyclopropane/chlorine experiments are shown in Figure 3. The infrared bands of cyclopropane were identified by using the assignments of Breher et al.,[21] who obtained spectra of cyclopropane in the gas, liquid, and crystalline phases. Assignment of the reaction product spectra was made by comparing the experimental spectra to those of 1,3-dichloropropane,[22,23] chlorocyclopropane,[24,25] allyl chloride,[26] and other polychlorinated propanes[22,23] and cyclopropanes.[24,25] Analysis of the spectra showed that no significant amount of any

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(17) Yuster, S.; Reyerson, L. H. *J. Phys. Chem.* **1935**, *39*, 859.
(18) Yuster, S.; Reyerson, L. H. *J. Phys. Chem* .**1935**, *39*, 1111.

(19) Roberts, J. D.; Dirstine, P. H. *J. Am. Chem. Soc.* **1945**, *67*, 1281.
(20) Walling, C.; Fredricks, P. S. *J. Am. Chem. Soc.* **1962**, *84*, 3326.
(21) Breher, C.; Krikorian, E.; Blane, J.; Halford, R. S. *J. Chem. Phys.* **1961**, *35*, 1097.
(22) Thorbjørnsrud, J.; Ellostad, O. H.; Klaboe, P.; Torgrimsen, T. *J. Mol. Struct.* **1973**, *15*, 61.
(23) Brown, J. K.; Sheppard, N. *Proc. R. Soc. (London)* **1955**, *A231*, 555.
(24) Green, W. G.; Wurry, C. J.; Kalasinsky, V. F. *J. Raman Spectrosc.* **1985**, *16*, 177.
(25) Rothschild, W. G. *J. Phys. Chem.* **1966**, *70*, 1712.
(26) Melachlan, R. D.; Nyquist, R. A. *Spectroschim. Acta* **1967**, *24A*, 103.

Table I. Experimental Determinations of Reaction Yields[a] in Mixtures of Cyclopropane and Chlorine at 77 K Following a Single 308 nm Laser Pulse

		yield	
C_3H_6:Cl_2[b]	X[c]	reactants[d]	products[e]
0.20:1	0.83	1.3 ± 0.3	2.8 ± 0.6
0.50:1	0.67	3.8 ± 0.8	5.1 ± 1.0
1.0:1	0.509	15 ± 3	13 ± 3
2.0:1	0.33	8.4 ± 1.7	9 ± 2
5.0:1	0.17	3.5 ± 0.6	7 ± 3
9.0:1	0.10	3.1 ± 1.5	5.6 ± 3

[a] Determined on the basis of number of chlorine atoms formed by photolysis. [b] Relative pressures of reagents in sample prior to deposition. [c] Mole fraction of chlorine in sample. [d] Determined from diminution of cyclopropane absorbance at 3090 and 1425 cm^{-1}. [e] Determined from intensity of 1,3-dichloropropane absorbance at 780 and 697 cm^{-1}.

Table II. Characteristic C–Cl Stretching Frequencies for Conformers of 1,3-Dichloropropane

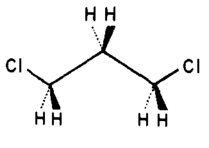
conformer	freq (cm^{-1})[a]
AA	697, 780
AG	656, 727
GG	642, 679

[a] Reference 22.

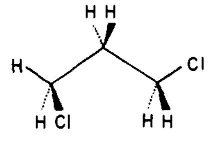
product other than 1,3-dichloropropane is formed in the reaction. In one experiment, the sample was exhaustively photolyzed with 100 laser pulses, and a small, diffuse band at 2580–2850 cm^{-1} due to HCl was observed. However, it is not known whether this is due to H atom abstraction from cyclopropane or whether all of the HCl product can be attributed to H atom abstraction from the relatively large amount of 1,3-dichloropropane in the photolyzed samples.

The reaction yields for single pulse irradiation of the samples were determined by measuring the decrease in the integrated intensity of cyclopropane bands at 3090 and 1425 cm^{-1} and by the integrated intensities of 1,3-dichloropropane bands at 780 and 697 cm^{-1}. As before, the intensities of the bands are calibrated by obtaining spectra of samples containing known quantities of the authentic compounds. For a 1:1 mixture of cyclopropane and chlorine, the product yield is 13 ± 3 as determined by product formation or 15 ± 2 for reagent consumption. That is, for every Cl atom formed by laser photolysis of Cl_2, about 15 molecules of cyclopropane are destroyed and 13 molecules of 1,3-dichloropropane are formed. The quantum yield based on the number of product molecules formed per photon absorbed by the sample is 26 ± 6. Since the reaction yield is greater than unity, true chain propagation of the reaction by free radical intermediates must be occurring in the solid. The reaction yield is sensitive to the relative amounts of chlorine and cyclopropane in the film, as summarized in Table I. Note that while reaction yields in the propane experiments are calculated on the basis of Cl_2 molecules dissociated, the yields in cyclopropane are calculated per Cl atom formed since independent chain reactions are initiated by each atom in the latter.

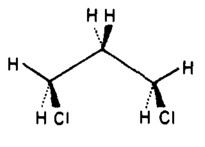
Although 1,3-dichloropropane is the only major product formed in the reaction of cyclopropane with chlorine, several different conformers of this molecule can be distinguished by infrared absorption spectroscopy. The four distinct conformers are denoted by the spatial relationship (anti or gauche) of each terminal chlorine atom with the chloromethyl group at the opposite end of the molecule. The GG′ conformer is energetically unfavorable due to strong 1,3 parallel repulsions of the chlorine atoms.[15] This conformer is not expected to be formed in significant amounts. Of the remaining three conformers, the AA conformer is highest in energy, while the GG conformer is the most stable.[22,23] Each conformer exhibits characteristic symmetric and asymmetric C–Cl stretching frequencies in the infrared spectrum, as summarized in Table II. Comparison of these stretching frequencies with our results shows that the chain reaction produces exclusively the AA conformer of 1,3-dichloropropane after a single laser pulse. If the sample is then photolyzed with 9 additional pulses, the bands at 697 and 780 cm^{-1} are replaced by two pairs of peaks at 635, 679 cm^{-1} and 653, 725 cm^{-1}, corresponding to the more stable GG and AG conformers. The apparent change in the intensity ratio of peaks at 700 and 790 cm^{-1} after subsequent laser pulses is attributed to the overlap of the CH_2 wag of the GG conformer (784 cm^{-1}) with the C–Cl stretch of the AA conformer (780 cm^{-1}). Energy deposition from laser pulses occurring after product formation is sufficient to anneal the solid, permitting rotation about the C–C bonds and formation of the more stable conformers of 1,3-dichloropropane. The fact that only the AA conformer is observed following a single laser pulse demonstrates that the energy released by the chain reaction itself is insufficient to allow transitions to the lower energy conformers at 77 K. One experiment was conducted in which the sample was photolyzed for 35 pulses at 1 mJ/cm^2 (versus 1 pulse at 35 mJ/cm^2 in the typical experiment). The infrared spectrum showed formation of mainly the AA conformer with only minor yields of the AG and GG conformers.



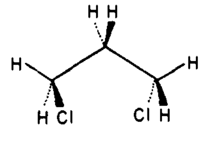
AA



GA



GG′



GG

In most of the experiments performed with chlorine and cyclopropane, the samples were irradiated with only a single laser pulse. This procedure simplifies calculation of the product yields since only one conformer (AA) of 1,3-dichloropropane is formed under these conditions. In some experiments it was noted that the reaction yields for the second and third laser pulses were somewhat larger than those for the first pulse. This effect could be due to a slight annealing of the solid. Chain reactions could be initiated not only by chlorine photolysis but also by releasing free radicals trapped in the solid as a result of previous pulses.

One experiment was performed by depositing chlorine with propane and cyclopropane in a 2:1:1 ratio. Single-pulse irradiation resulted in a 15% decrease in the cyclopropane absorption intensity and corresponding appearance of the AA conformer of 1,3-dichloropropane. There was no decrease in the propane absorption bands and no detectable formation of 1-chloropropane or 2-chloropropane.

Discussion

Propane + Chlorine. The two most important features of the photoinduced reaction of chlorine with propane are the low reaction yield and the high selectivity for abstracting a hydrogen atom at the secondary position. The fact that the reaction yield is only about 12% suggests the following plausible mechanism for product formation on the basis of radical recombination.

When a chlorine molecule absorbs one of the laser photons at 308 nm, it immediately dissociates into two chlorine atoms. In 88% of these events, the two chlorine atoms recombine to form Cl_2. In 12%, one of the chlorine atoms abstracts an H atom from a nearby molecule of propane, forming HCl and a propyl radical. Presumably, the two chlorine atoms have equal probabilities of undergoing reaction with propane, so the probability that both Cl atoms will react with different propane molecules is $(0.06)^2$, or 0.4%. This is too small to be detected in our experiments. Since the propyl radical and the unreacted chlorine atom occupy adjacent sites in the amorphous film and are separated at most by a molecule of HCl, it is reasonable to postulate that the final product, 1-chloropropane or 2-chloropropane, is formed by recombination of the propyl radical with the chlorine atom. Consequently, each individual reactive event is restricted to one site, and propagation of a chain reaction through the film probably does not occur.

The HCl product absorption spectra lend support for this type of mechanism. There is a strong similarity between the HCl reaction product spectrum and that obtained when HCl is deposited with 2-chloropropane directly onto the cold window. This suggests that the C–Cl bond of the chloropropane reaction product is formed in the immediate vicinity of the HCl product, allowing the two to form a hydrogen-bonded complex. This is consistent with our postulated radical recombination mechanism in which each chloropropane molecule is formed by radical recombination in the presence of one HCl molecule.

The other major feature of the reaction is the high selectivity for abstraction of secondary vs. primary hydrogen atoms. Knox and Nelson[4] examined the chlorination of propane in the gas phase as a function of temperature and obtained Arrhenius parameters for abstraction of primary and secondary H atoms to form HCl. The parameters reflect the inherent reactivity of chlorine atoms toward primary and secondary H atoms, accounting for the fact that there are three times as many of the former as the latter in each propane molecule. The activation energy for abstraction of a secondary H atom is somewhat lower than that for a primary H atom, presumably due to the greater stability of secondary alkyl radicals compared with primary radicals. Therefore, the selectivity for secondary H atoms increases as the temperature is lowered. The relative rates of abstraction from secondary and primary positions can be calculated from the parameters given by Knox and Nelson. When the result is extrapolated to 77 K, the selectivity is predicted to be 17.2:1 in favor of the secondary site. This value is in remarkable agreement with our experimental value of 17:1. Such agreement suggests that chlorine atoms formed by dissociation of Cl_2 are thermalized to the characteristic temperature of the environment (77 K) on a time scale that is short compared with that of H atom abstraction.

It is important to recognize that the Arrhenius parameters reported by Knox and Nelson were obtained at much higher temperatures than 77 K. However, to the extent that their results are valid at our experimental temperatures, the remarkable (perhaps fortuitous) agreement of the prediction with our experiments suggests a somewhat indirect method of estimating the lifetime with respect to recombination of two chlorine atoms produced by UV photolysis in an amorphous film of propane and Cl_2.

Molecular chlorine has a bond energy of 238 kJ/mol, and the energy of a 308-nm photon is 388 kJ/mol. Therefore, a considerable amount of excess translational energy must be dissipated by low-frequency modes of the film. Thermalization of the atoms typically occurs in about 10^{-12} s.[27] Since the selectivity of attack is characteristic of a 77 K temperature, the lifetime of each chlorine atom must be at least several picoseconds. According to our postulated reaction mechanism, the lifetime is limited by the total rate constant for reaction, either by recombination to Cl_2 or by H atom abstraction from propane. We can estimate the rate constants for reaction with propane at primary and secondary sites using the Arrhenius parameters of Knox and Nelson with an isolated binary collision model of reactions in condensed media.[28-31] The pseudo-first-order rate constant for each reaction pathway is given by

$$k(\mathrm{s}^{-1}) = Z\langle P\rangle \qquad (5)$$

where Z is the effective collision frequency and $\langle P\rangle$ is the probability that reaction occurs in any given collision. A crude estimate of Z is obtained by dividing the average relative velocity of a chlorine atom and propane molecule by one-half the average collision diameter.[32,33] This yields $Z \sim 1.4 \times 10^{12}$ s^{-1}. The reaction probability is calculated from the ratio of the reaction cross section (obtained from Arrhenius parameters)[4] to the hard sphere collision cross section. Using this approach we estimate that the first-order rate constant for reaction of a chlorine atom with propane in the film (including both channels leading to primary and secondary propyl radicals) is 6×10^9 s^{-1}. Our experimental measurement of the reaction yield shows that recombination of the two Cl atoms is 7.3 times faster than reaction so the first-order rate constant for recombination of two Cl atoms is approximately 4.4×10^{10} s^{-1}. The corresponding recombination lifetime of 23 ps is in qualitative accord with recent measurements of I_2 recombination rates in solution.[34-38]

Since the experiments are performed at a nominal temperature of 77 K and the melting point of propane is about 85 K, there is a legitimate question of whether the samples are truly in the solid state, especially in the moments immediately following laser photolysis.

Using the standard theory of freezing point depression we estimate the melting point of a 1:1 mixture of propane and chlorine to be only 2 deg below that of pure propane. The eutectic point occurs at a 9:1 ratio of the two components, respectively.

The heat capacity of the solid is estimated to be 25 J/(mol·K), ignoring contributions from internal vibrational modes of the molecules. Taking into account the number of molecules per unit area in our samples we estimate that the temperature rises by 6 deg for each mJ of energy per cm^2 deposited by the laser. In experiments conducted at 1 mJ/cm^2 laser fluence, only 40% of the energy is absorbed by the sample. The temperature rise is only 2.4 deg and no melting occurs. Most of the experiments were conducted at 35 mJ/cm^2 laser fluence. Using 3.5 kJ/mol as the heat of fusion of propane,[32] we estimated that as much as 20% of the sample may be melted under these conditions. The experimental results are the same for experiments conducted at high and low fluence. This suggests either that a small degree of melting does not significantly alter the character of the solid (at least insofar as the reaction mechanism is concerned) or at temperatures near 77 K the binary mixture does not adopt distinct solid or liquid phases and the actual environment exhibits some characteristics of each.

The time required to cool the sample is calculated to be about 2 ms on the basis of the sample thickness and estimating the thermal conductivity of the film from that of small alkanes in the liquid state (typically 0.15 W/(cm·K).[32]

Cyclopropane + Chlorine. The fundamental differences between the propane and cyclopropane systems are that, in the latter case, reaction proceeds by a ring-opening mechanism and it is characterized by true chain propagation within the solid. In fact, the ring-opening step is probably crucial to the initiation of free radical chain processes because it provides an efficient mechanism for separation of the two radical sites. Radical recombination, which dominates the reactive mechanism in the case of propane, is effectively inhibited in cyclopropane.

One of the advantages of monitoring the reactions by infrared absorption spectroscopy is that it is often possible to distinguish particular conformers of the product molecules frozen in the solid. This, in turn, provides a rather detailed probe of the topology of the reaction as it proceeds in this restricted environment.

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(27) Bamford, C. H.; Tipper, C. F. H. *Comprehensive Chemical Kinetics*; Elsevier, Scientific Publishing Co.; New York, 1980; Vol. 22.

(28) Litovitz, T. A. *J. Chem. Phys.* **1956**, *26*, 469. Madigosky, W. H.; Litovitz, T. A. *J. Chem. Phys.* **1961**, *34*, 489.

(29) Krueger, H.; Knudtson, T.; Vlahoyannis, V. P.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 204.

(30) Lupo, D. W.; Lucas, D. *J. Phys. Chem.* **1986**, *90*, 5105.

(31) Abdel-Halim, H.; Ewing, G. E. *J. Chem. Phys.* **1985**, *82*, 5442.

(32) *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1980.

(33) Hirschfelder, J. O.; Curtis, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.

(34) Abul-Haj, N. A.; Kelley, D. F. *J. Chem. Phys.* **1986**, *84*, 1335.

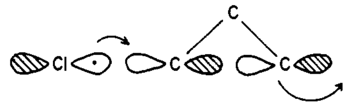
(35) Kelley, D. F.; Abul-Haj, N. A.; Jang, D. J. *J. Chem. Phys.* **1984**, *80*, 4105.

(36) Nesbitt, D. J.; Hynes, J. T. *J. Chem. Phys.* **1982**, *77*, 2130.

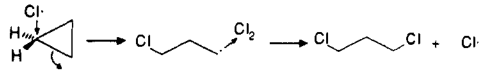
(37) Chuang, T. J.; Hoffman, G. W.; Eisenthal, K. B. *Chem. Phys. Lett.* **1974**, *25*, 201.

(38) Langhoff, C. A.; Moore, B.; Nugent, W. In *Picosecond Phenomena II*; Hochstrasser, R., Kaiser, W., Shank, C., Eds.; Springer: Berlin, 1980; p 249.

The reaction of chlorine with cyclopropane forms the AA conformer of 1,3-dichloropropane as the sole product. Attack of a chlorine atom at one of the carbon atoms can be described as a partial donation of the unpaired electron into an unoccupied



molecular orbital of cyclopropane.[39] This molecular orbital exhibits antibonding character between two of the carbon atoms, providing a low-energy pathway to ring opening. The C–C bond that breaks must be the one directly opposite the attacking chlorine atom in an S_N2-type displacement. This forms a chloropropyl



(6)

radical in which the newly formed C–Cl bond bears an anti spatial relationship to the radical center. The radical center is also removed from the original site of Cl_2 photolysis which, unlike the reaction with propane, inhibits recombination of the alkyl radical with the partner chlorine atom formed by photolysis of Cl_2. The chloropropyl radical attacks another molecule of chlorine forming the final 1,3-dichloropropane product, regenerating a chlorine atom to propagate the chain reaction. For reasons that are not entirely clear to us, this second step must involve formation of the second C–Cl bond exclusively from the exo side of the radical in order to form the observed AA conformer of 1,3-dichloropropane.

Recently, Ault[40] published an infrared absorption study of bimolecular complexes of chlorine and cyclopropane isolated in inert gas matrices. The spectra were consistent with a structure in which the chlorine molecule is situated at the midpoint of one of the C–C bonds in a C_{2v} geometry. One might naively expect that photolysis of a chlorine molecule in this geometry would result in electrophilic attack of one Cl atom on the adjacent C–C bond followed by ring opening. Recombination of the chloropropyl radical with the partner chlorine atom would then form the 1,3-dichloropropane product. However, our results contradict this simple picture on two counts. First, one would expect that such a mechanism would directly form the lowest energy GG conformer of 1,3-dichloropropane, in disagreement with our observations. Second, such a mechanism could form at most one product molecule per photon absorbed by the sample whereas the measured yield is 26 ± 6. Therefore, if the reaction is initiated by photolysis of a chlorine molecule in the geometry inferred in the matrix study,[40] then the two resulting chlorine atoms must initiate separate chain reactions that propagate independently through the solid.

The issue of whether the reaction occurs in the liquid or solid state is much simpler to address for cyclopropane than for propane. The melting point of pure cyclopropane is 146 K and our freezing point depression analysis indicates that the eutectic point of the binary mixture occurs at a 3:2 ratio of cyclopropane:chlorine. The solid begins to melt at 137 K, about 60 K above the nominal temperature of the experiment. For experiments using a laser fluence of 1 mJ/cm^2 the bulk heating is negligible. Samples irradiated at 35 mJ/cm^2 are significantly elevated in temperature but the substantial heat of fusion for cyclopropane, 10.8 kJ/mol,[32] limits the extent of melting to less than 6% of the sample. Our experimental observations corroborate the calculations insofar as relaxation of the AA conformer of 1,3-dichloropropane to lower energy forms does occur in the high fluence experiments but not in experiments conducted at 1 mJ/cm^2.

Radical Chain Trapping. Finally, we consider a model that describes the mechanism by which the chain reaction of cyclopropane with chlorine is halted. In the gas and liquid phases, the reaction chain lengths are typically of the order of 10^4–10^7, and the principal termination mechanisms are radical–radical recombination and reactions at the walls of the vessel. The reaction chain lengths measured in our experiments range between 1.5 and 15, depending on the relative concentrations of cyclopropane and chlorine in the film, as shown in Table I. These chain lengths are too short to be explained by radical–radical recombination, especially at low laser fluences, so other processes must be operative in the solid state which restricts the length of the chain reactions.

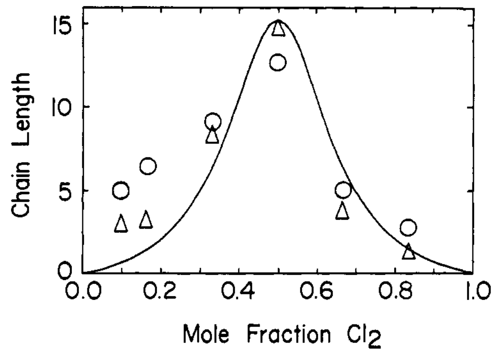


Figure 4. Plot of reaction chain length for mixtures of chlorine and cyclopropane as a function of mole fraction of chlorine in the unphotolyzed samples. Samples are irradiated with a single 308 nm laser pulse. The circles represent experimental determinations based on the intensity of 1,3-dichloropropane product absorptions. The triangles are based on diminution of cyclopropane reactant absorptions. The solid curve is calculated on the basis of a simple statistical model of radical trapping with no adjustable parameters (see text).

A simple model consistent with our results is easily derived by assuming that propagation of the radical center continues until it is trapped in a site in which all of its nearest neighbors are unreactive. We first make the assumption that every free radical in the solid film has six nearest neighbors with which it interacts closely. One of these sites is always occupied by an unreactive molecule which is the product of the previous step in the chain reaction (1,3-dichloropropane). Therefore, each radical is surrounded by five sites that may contain potential reaction partners. In the case of a chlorine atom, the probability that any one of its five neighboring sites is occupied by an unreactive Cl_2 molecule is simply equal to the mole fraction of molecular chlorine in the film. The probability that all five of the neighboring sites are occupied by Cl_2 molecules is the fifth power of the mole fraction of chlorine. In this instance, we consider the chlorine atom to be trapped in a nonreactive site, and that particular radical chain reaction is stopped. Similarly, there is a finite probability that a chloropropyl radical will be generated in a site that is completely surrounded by cyclopropane molecules. Likewise, the radical will be trapped and the chain reaction stopped. It is worth noting that any activation energy in excess of about 10 kJ/mol is sufficient to render the radicals unreactive at 77 K.

Mathematically, the probability that a chlorine atom will successfully complete reaction 3 is simply

$$P(3) = 1 - (X)^5 \tag{7}$$

where X is the mole fraction of Cl_2 in the film. Similarly, the probability that a chloropropyl radical will successfully complete reaction 4 is

$$P(4) = 1 - (1 - X)^5 \tag{8}$$

Both steps of the chain cycle are required to produce a single molecule of 1,3-dichloropropane, and the probability of completing k complete cycles of the chain reaction is simply $[P(3)P(4)]^k$. The total number of 1,3-dichloropropane molecules formed for each chlorine atom generated by UV photolysis is termed the chain length of the reaction

$$\text{chain length} = \sum_{k=1}^{\infty} [P(3)P(4)]^k = P(3)P(4)/[1 - P(3)P(4)] \tag{9}$$

The reaction chain length, or reaction yield, is thus predicted to be a simple function of the composition of the binary film. To compare the predictions of the model with our experimental results,

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[39] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.

[40] Ault, B. S. *J. Phys. Chem.* **1986**, *90*, 2825.

the data from Table I are plotted in Figure 4, along with a solid curve calculated from eq 9. The agreement, while not quantitative, is nevertheless quite good considering the model has no adjustable parameters other than the choice for the number of nearest neighbors, which we feel is quite reasonable.

The model quite accurately predicts the experimental results for samples containing a high percentage of chlorine. In samples where the concentration of cyclopropane is high, the yields are somewhat less reproducible and are nearly always higher than the yields predicted from eq 9. Part of the discrepancy might be due to the different sizes of cyclopropane, chlorine, and the two free radicals and how these species are able to interact with their nearest neighbors. A chloropropyl radical may, in some cases, be able to attack cyclopropane to escape a radical trapping site in which there are no chlorine molecules in its shell of nearest neighbors. Also, the model assumes that the identity of the nearest neighbors in each step is completely independent from all other steps. This is obviously not the case since each step propagates the radical site only a finite distance in the film. Some of the nearest neighbors in one step will also be present in a subsequent step, and this causes the identity of nearest neighbors to be somewhat correlated. These are all minor considerations, however. The model in its simplest form provides a qualitatively accurate description of the chain propagation and termination in the solid film.

According to the model, there should be approximately equal concentrations of chlorine atoms and chloropropyl radicals trapped in unreactive sites following completion of the chain reactions. We have not been able to detect these radicals directly by infrared absorption spectroscopy, perhaps because the concentrations are low, and many of the chloropropyl radical absorptions may be obscured by absorptions due to 1,3-dichloropropane. Also, preliminary attempts to detect the radicals by ESR spectroscopy have been unsuccessful.[41] Indirect evidence for the existence of these radicals stems from measurements of the reaction yields on subsequent laser photolysis pulses. We have observed that the apparent reaction yield for the second laser pulse is larger than that of the first pulse. It is postulated that the second pulse, in addition to creating new chlorine atoms by photolysis of Cl_2, also anneals some of the sites in which radicals from the first pulse are trapped. Since these liberated radicals can then continue the chain reaction process, the overall yield from subsequent pulses should be greater than that from the first pulse, until the concentrations of reagents become depleted. This annealing process is consistent with our observation that the AA conformer of 1,3-dichloropropane originally produced in the chain reaction is able to relax to the more stable GG and AG conformers.

One of the implicit assumptions of our model for chain termination is that the chlorine atoms produced by photolysis all react with cyclopropane. None recombine to regenerate Cl_2 as in the case of propane. Actually, the model is not sufficiently quantitative to rule out Cl_2 recombination entirely, but the good agreement of predicted and observed reaction yields suggests that reaction with cyclopropane competes effectively with recombination. Were this not the case, the chain lengths for the reactions would have to be much greater than those predicted by the model in order to produce the high overall yields observed in the experiments.

In previous studies, Arrhenius parameters for reaction of chlorine atoms with cyclopropane have been determined only for the H atom abstraction channel in the gas phase,[4] not for the associative ring-opening mechanism. However, Walling and Fredricks[20] determined the branching ratio between the two mechanisms at two different temperatures in liquid CCl_4. Using these data to estimate Arrhenius parameters for ring opening, we find that reaction of a Cl atom with cyclopropane is predicted to be more than an order of magnitude slower than reaction with propane. This calculation suggests that in cyclopropane, chlorine atom recombination should be much faster than ring opening, and the chain lengths would have to be of the order of 2000 to produce the high observed reaction yields.

In order to test this hypothesis, an experiment was performed with a mixture of Cl_2, propane, and cyclopropane in a 2:1:1 ratio. The objective of the experiment was to set up a direct competition of reaction of Cl with propane and cyclopropane. The cyclopropane provides a mechanism for generating chain reactions, but once initiated, the branching ratio would depend only on the relative reaction rates of Cl with the two different hydrocarbons. After a single laser pulse, 15% of the cyclopropane was found to react via the usual ring-opening mechanism, but no detectable reaction of propane occurred. This experiment shows that reaction of Cl with cyclopropane is indeed much faster than reaction with propane. Therefore, in the chlorine/cyclopropane experiments initiation of the chain reactions probably competes effectively with chlorine recombination, in qualitative agreement with our model.

Conclusions

The photoinitiated reaction of propane with chlorine produces HCl, 1-chloropropane, and 2-chloropropane in low yields consistent with a localized radical recombination mechanism. The relative reactivity of secondary and primary H atoms on propane is found to agree remarkably well with that predicted from gas-phase Arrhenius parameters. This agreement suggests that chlorine atoms produced in the film are thermalized to 77 K on a time scale that is fast compared with H atom abstraction from propane. With use of an isolated binary collision model to estimate the rates of reaction in the film, the lifetime of a chlorine atom with respect to recombination of Cl_2 is calculated to be 23 ps.

The reaction of chlorine with cyclopropane proceeds via a true chain reaction mechanism involving ring opening of the hydrocarbon upon addition of a chlorine atom. The final reaction product is the anti–anti conformer of 1,3-dichloropropane, which subsequently relaxes to the more stable gauche–gauche and anti–gauche conformers. Formation of the higher energy conformer in the reaction is consistent with an S_N2-type description of the ring-opening reaction. This provides an efficient mechanism for separating the free radical sites, inhibiting radical recombination, and promoting free radical chain reactions in the amorphous solid. The reaction yields are sensitive to the relative concentrations of chlorine and cyclopropane in the film and are qualitatively consistent with a simple statistical model of free radical trapping in unreactive sites within the solid.

With use of infrared absorption spectroscopy to characterize product branching ratios and overall reaction yields, it is possible to construct a rather detailed description of free radical reaction dynamics in thin films of chlorine and simple hydrocarbons. One of the most powerful aspects of the method is the ability to distinguish particular conformers of molecules in the solid. This enables us to relate the reaction dynamics to the spatial properties of molecules and the way in which they are able to undergo chemical reactions. We anticipate that the method can be generalized to investigate other types of reaction systems. It may eventually develop into a valuable probe of chemical reaction dynamics in environments where molecular motion is restricted, such as in enzyme catalysis or synthesis of solid-state materials.

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(41) Knight, L., private communication.