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## Free radical chain reactions of chlorine with cyclobutane in the solid state: Evidence for radical migration via H atom transfer

Arthur J. Sedlacek and Charles A. Wight Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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In the study of solid state reaction mechanisms, a fundamental question sometimes arises as to how reaction partners come into contact with one another in the absence of diffusion. Dole and co-workers<sup>1</sup> have proposed a mechanism in which free radicals may abstract hydrogen atoms from nearby sites, allowing the radical center to migrate within the solid. Reactions can thus occur without requiring movement of heavy atoms or rearrangement of the solid. Clough<sup>2</sup> has also obtained evidence for hydrogen hopping mechanisms by observing H/D exchange in gamma irradiated solids. Validation of this type of reaction mechanism continues to be an active and controversial area of research.

In this Communication we report that solid state chlorination of cyclobutane produces chlorocyclobutane and HCl via a radical chain mechanism, reactions (1) and (2):

$$\mathbf{C} \cdot + \square \longrightarrow \mathbf{H}\mathbf{C} + \square$$
(1)

$$\Box + Cl_2 \longrightarrow \Box + Cl \qquad (2)$$

Measurements of the reaction quantum yield as a function of the relative concentrations of chlorine and cyclobutane strongly implicate the participation of H atom transfer reactions between cyclobutane and cyclobutyl radical.

The experimental apparatus and techniques have been described previously.<sup>3</sup> Briefly, thin amorphous films are formed on a 77 K CsI window by spray deposition of a binary mixture of the gas phase reagents. The films are then photolyzed at 308 nm (Questek Model 2200 excimer laser) to initiate reactions by dissociating some of the chlorine molecules. Reaction product quantum yields are determined by comparing integrated intensities of reactant and product infrared absorption bands (Digilab/Biorad Model FTS-40 spectrometer), combined with measurements of the laser fluence and absorption coefficient of the samples at 308 nm.

Infrared spectra for a 1:1 mixture of cyclobutane: chlorine before and after photolysis are presented in Fig. 1. The absorptions in the lower trace are characteristic of cyclobutane.<sup>4-6</sup> Chlorine is transparent in the infrared. Product bands appearing after photolysis (upper trace) are identified as chlorocyclobutane using previous spectral assignments.<sup>7-9</sup> This was confirmed by depositing an authentic sample of chlorocyclobutane onto the CsI window and comparing with the product spectrum. In addition, a broad diffuse product band at 2750 cm<sup>-1</sup> is attributed to HCl. No evidence for any other products is observed. Quantum yields (numbers of chlorocyclobutane molecules formed per laser photon absorbed) are listed in Table I for various relative concentrations of the two reagents. The quantum yield is greatest in samples which are rich in cyclobutane. The first step in the reaction mechanism is undoubtedly abstraction of a hydrogen atom from the hydrocarbon, reaction (1). The cyclobutyl radical can then react with molecular chlorine to form chlorocyclobutane and another chlorine atom, reaction (2). This is the classic chain reaction sequence observed in gases<sup>10</sup> and solutions.<sup>11</sup> Alternatively, chlorocyclobutane can be produced in the solid state via radical recombination since the cyclobutyl radical in reaction (1) is formed adjacent to the partner chlorine atom produced by photodissociaton of  $Cl_2$ . However, the maximum quantum yield for this mechanism is unity. Since our measured quantum yields are as high as 7.5, true chain reactions must be occurring to at least some extent in the solid state.

A curious aspect of our results stems from the fact that reaction yields are greatest in the limit of low chlorine concentration. Under these conditions it is relatively unlikely that a cyclobutyl radical will be near enough to a chlorine



FIG. 1. Infrared absorption spectra of 1:1 sample of  $Cl_2/cyclobutane$  before (A) and after (B) pulsed laser photolysis at 308 nm. The sample was subjected to 20 000 laser pulses at a fluence of 0.51 mJ/cm<sup>2</sup>. Absorption features marked with an asterisk are assigned to chlorocyclobutane product molecules. Each division on the vertical axis represents 0.1 absorbance units.

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TABLE I. Photochemical quantum yield as a function of composition of the amorphous films.

Cyclobutane:chlorine*	Quantum yield <sup>b</sup>
0.5:1	0.8 ± 0.3
1:1	$1.1 \pm 0.3$
2:1	$2.6 \pm 0.5$
3:1	$3.9 \pm 0.7$
5.25:1	$6.2 \pm 1.1$
11.5:1	$7.4 \pm 0.8$

\* Mole ratio based on relative pressures of gas phase reagents.

<sup>b</sup> Average number of chlorocyclobutane molecules formed per 308 nm photon absorbed by the sample.

molecule to react. For example, in experiments where the  $Cl_2$  mole fraction is 0.08, the probability that a cyclobutyl radical will find a chlorine molecule among its 12 nearest neighbors is only 63%. The expected quantum yield under these conditions is calculated to be less than 2 and should increase with increasing chlorine concentration. The measured yields are larger than this and exhibit the opposite concentration dependence.

The apparent ability of cyclobutyl radicals to react with chlorine molecules in relatively low concentration suggests that cyclobutyl radicals are mobile in the solid. Physical diffusion is highly unlikely since the temperature is well below the melting point of cyclobutane (223 K). The photolysis is carried out at low fluence (0.5 mJ/cm<sup>2</sup>) to eliminate the effects of transient heating by the laser pulse.

A likely explanation for the apparent mobility of cyclobutyl radicals arises from H atom transfer, reaction (3):

$$\Box + \Box \longrightarrow \Box + \Box \qquad (3)$$

Successive transfer steps allow the radical site to migrate until a chlorine molecule is encountered with which it may react. The free radical chain reaction of chlorine with cyclobutane is the first such system for which we have observed evidence of intermolecular H atom transfer. In a previous study of  $Cl_2$ /cyclopropane reactions,<sup>3</sup> the product yield was found to be a maximum for equimolar mixtures of reagents. No evidence for H atom migration was found, probably because of a higher activation energy. This is reasonable since the C-H bond dissociation energy of cyclopropane exceeds that of cyclobutane by 41 kJ/mol.<sup>12</sup> Reactions having activation energies greater than about 12 kJ/mol are not expected to occur on normal laboratory time scales at 77 K.

Our future plans include studies of H/D exchange reactions of cyclobutane and other hydrocarbons to further quantify the role of intermolecular H atom transfer reactions in solid state chemistry. These results will be presented in a full paper in the near future.

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## Investigation of finite size effects in a first order phase transition: High pressure Raman study of CdS microcrystallites

B. F. Variano, N. E. Schlotter, D. M. Hwang, and C. J. Sandroff Bell Communications Research, Inc., Red Bank, New Jersey 07701

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A large body of theoretical work has appeared on how the character of phase transitions is affected by the finite size of physical systems.<sup>1-6</sup> Generally, the effect of finite size is to broaden the transition region for both first and second order phase changes though the scaling relationship between physical size and the extent of broadening is expected to be different for the two cases. This Communication presents preliminary results from experiments designed to probe finite size effects in a first order phase transition in the solid state.

Instead of the usual temperature variations we induced the solid/solid phase transformations through variations in the external pressure. The CdS samples used in our study had been prepared at room temperature in the form of colloidal microcrystallites ranging in diameter from 30 to 300 Å. For colloids on the larger end of this range we added 48 cc of 0.01 M Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O to a solution containing 100 cc of water, 48 cc of 0.01 M Na<sub>2</sub>S·9H<sub>2</sub>O, and 48 cc of 0.01 M (NaPO<sub>3</sub>)<sub>6</sub> as a colloid stabilizer. The colloidal suspensions were loaded into a diamond anvil cell of the Merrill–Bassett type, and the pressures were measured by the ruby fluorescence method.<sup>7</sup>

Bulk CdS undergoes a structural first order phase tran-