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Mendeleev Commun., 1993, 3(1), 5–7

Mendeleev Communications

Solid-state Chain Photochlorination in Recrystallized Mixtures of Ethene and Chlorine at 30 K

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Binary solid films of chlorine with ethene have been deposited in excess argon and subsequently recrystallized by warming and evaporation of the argon solvent. This novel recrystallization procedure results in a dramatic increase in the quantum yield and degree of conversion for long stereospecific chain photochlorination with the exclusive formation of the *trans*-1,2-dichloroethane.

The existence of the quantum low temperature limit of the rate constant in principle enables the observation of chemical conversions near absolute zero.[1] Current cryochemical methods make it possible to obtain unique solid mixtures of reactants. Low-temperature tunneling reactions in such mixtures bring about the creation of new substances, which is impossible at high temperatures in liquid or gas phases. Of special interest are solid state chain reactions. In spite of some attempts to observe chain growth at liquid helium temperatures, there have as yet been no direct observations of this process with high degrees of conversion. The principal obstacle to this is the difficulty of preparing a regular alternating arrangement of reactants which permits the conversion without reactant diffusion. Perfect equimolar mixed crystals of reactants are required for this experiment, and this prompted us to attempt a recrystallization experiment in a low-temparature solid sample. In this communication we present the first successful example of a solid state recrystallization process for the preparation of such mixed crystals, along with preliminary observations of long chain conversion of C_2H_4:Cl_2 (1:1) crystals to *trans*-1,2-dichloroethane.[2]

In condensed mixtures[3,4] donor–acceptor complexes C_2H_4:Cl_2 are formed, which can organize themselves in regular alternating structures, such as in Hassel crystals.[5] It was shown[2] that in equimolar mixtures at $T \leq 45$ K the reaction takes place only under chlorine photolysis. The chain reaction product *trans*-conformer is formed through addition of chlorine atoms belonging to different Cl_2 molecules adjacent to C_2H_4 as a result of successive chemical stages, reactions (1) and (2).

$$Cl + C_2H_4 \rightarrow C_2H_4Cl \qquad (1)$$

$$C_2H_4Cl + Cl_2 \rightarrow C_2H_4Cl_2 + Cl \qquad (2)$$

A simulation of the model mixed crystal and the geometry of chain growth was presented in ref. 6. The high commensurability of the lattices of reactant and product crystals as well as the linear (one-dimensional) propagation of isolated chains along the shortest diagonal of the *ac*-plane (101 axis) established in these calculations, enables one to hope that for perfect crystal preparation it will be possible to obtain long chains and high degrees of conversion, analogous to those in the high temperature topochemical polymerization of diacetylenes.[7]

A standard method of transforming molecular glasses into crystalline solids is by thermal annealing at temperatures above the glass transition. However, in the case of many small organic compounds, sublimation of a thin film occurs at temperatures far below the glass transition, making crystal formation under high vacuum difficult. An alternative procedure is to deposit the sample onto a low-temperature substrate in the presence of excess inert material such as argon. Heating the sample will cause the argon to sublime, thus providing conditions for crystal formation in a manner which is analogous to standard

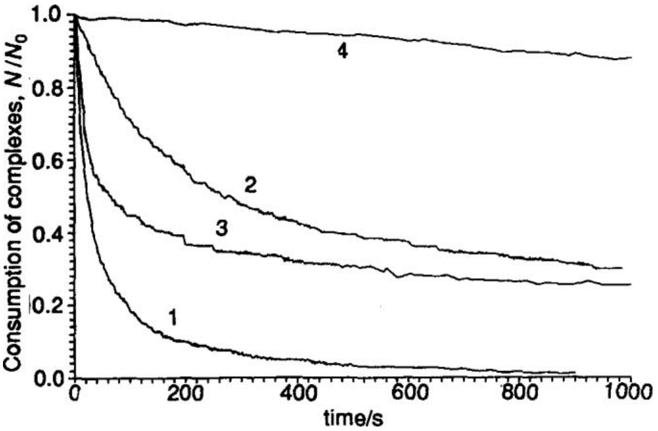

Fig. 1 Kinetics of complex consumption at 30 K in the recrystallized sample (1); in sample deposited in the absence of argon (2); in the same sample previously annealed at 60 K (3); in the ternary mixture $Ar:C_2H_4:Cl_2 = 60:1:1$ (4). $I = 3 \times 10^{15}\ cm^{-2}\ s^{-1}$, sample thickness *ca.* 0.5 μm

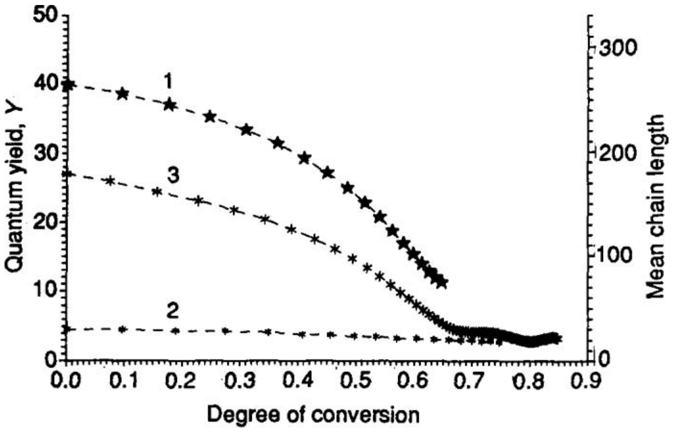

Fig. 2 The dependence of quantum yield and mean chain length on degree of conversion in samples shown in Fig. 1

recrystallization techniques by liquid solvent evaporation, but in the absence of a true liquid.

In this study, we prepared solid films of chlorine and ethene in argon by twin-beam vapour deposition onto an infrared transparent substrate (BaF_2 or KBr) in a vacuum 10^{-6} Torr. The mole fractions of Cl_2 and C_2H_4 were approximately equal in each case, but argon was included at concentrations as high as 50-fold excess. The temperature of the substrate in the liquid helium cryostat was kept at 22–24 K during sample deposition to minimize the mobility of molecules during this period. A typical sample thickness was 0.5 microns after evaporation of the argon, and the rate of film growth was *ca.* $4\ nm\ s^{-1}$. Following deposition, the samples were slowly ($1\ K\ min^{-1}$) warmed. At 35 K the argon began to sublime at a noticeable rate, as registered by the pressure increase in the cryostat. As the sample became more concentrated in the chlorine-ethene complexes, the sublimation temperature of the argon steadily increased. When the sample reached 60 K all of the argon had evaporated and the sample was re-cooled to 30 K.

Photolysis was carried out using an N_2-pulsed laser ($\lambda_2 = 337$ nm, repetition frequency 1 kHz) in the chlorine dissociative absorption band (cross section $\sigma = 2 \times 10^{-19}\ cm^2$). The reactant consumption and product accumulation kinetics were registered by real time changes in the optical density of the appropriate IR-bands. The accuracy of optical density measurements was $\Delta D = 2 \times 10^{-3}$ at time resolution 1 s. The absolute values of the cross-section σ_i of the main characteristic IR-bands of the C_2H_4, C_2H_4–Cl_2 complexes and *trans*-1,2-dichloroethane have been the subjects of preliminary measurments with an accuracy of *ca.* 20%.[8] The high transparency of the sample remained up to high conversion degrees $\xi = 1 - N/N_0$ (N_0 is the initiation concentration of complex). The optical density changes in the 600–1000 cm^{-1} region due to light scattering were less than 0.03 at $\xi = 0.8$–1.0. This background variation was taken into account in IR-band intensity measurements. The quantum yields were calculated from the relation $Y(\xi) = (\sigma_i I)^{-1} \Delta D_i / \Delta t$, where I is the photolizing light intensity absorbed in the sample, $\Delta D_i / \Delta t$ is the rate of optical density variation of the corresponding IR-band at time t, with degree of conversion ξ. The balance of consumption of C_2H_4:Cl_2-complexes and *trans*-1,2-dichloroethane storage is retained during photolysis and no *gauche*-conformer formation can be detected with the above-mentioned accuracy.

The diminution of the reactant during the photolysis at 30 K was monitored by time-resolved IR-absorption in the region of the ν_7 vibrational mode of ethene at 955 cm^{-1}, as shown in Fig. 1. In recrystallized samples the consumption of complexes is the fastest: $Y(\xi = 0) = 40 \pm 3$ and conversion degree reaches $\xi_{max} = 1.0$. The sample, which was deposited in the absence of argon, exhibits quantum yield $Y(0) = 5 \pm 0.5$, *i.e.* 8–10 times lower than in the recrystallized sample. The value of ξ_{max} is equal to 0.75. The rest of the complex is not consumed even under prolonged photolysis, which corresponds to $Y \leqslant 10^{-2}$. Photolysis of the ternary mixture $Ar:Cl_2:C_2H_4 = 60:1:1$ results in an extremely slow reaction ($Y = 0.3 \pm 0.1$) with the same product formation. These data demonstrate unequivocally that sublimation of argon from a ternary solid solution can allow crystal growth to occur which directly results in a 10-fold increase in the photochemical quantum yield of a low-temperature chain reaction.

The main chain length will, in general, be greater than Y due to the possibility of geminate recombination of the two Cl atoms formed upon photodissociation. The fact that some samples exhibit Y as low as 0.3 means that this value represents an upper bound to the efficiency of chain initiation. Furthermore, the fact that only the *trans* conformer of the chain reaction product is observed suggests that the minimum chain length is two and that the initiation efficiency is less than $Y_0 = 0.15$. This value allows one to determine the lower limit of the mean chain length $\nu = Y/Y_0$. In recrystallized samples $\nu(\xi = 0)$ is 250 steps.

Changes in Y and ν in the course of conversion are shown in Fig. 2. At $\xi = 0.5$ the mean chain length decrease is not greater than 50%. Nevertheless, the diminution of function $\nu(\xi)$ for the recrystallized sample is the sharpest, so at $\xi \geqslant 0.7$–0.8 mean chain length in all samples can not be distinguished. By comparing these data with computer simulation results,[6] the above-mentioned long-chain growth is suggested to occur due to alternating reactant packing being commensurate with product lattice. The chain termination is suggested to result from defects randomly distributed in the bulk and from breakage of one-dimensional propagation.

The above date show that the proposed method is appropriate for preparation of crystals possessing high reactivity. Because the crystal growth occurs at helium temperatures, it is possible to obtain new energy-enriched crystalline or fractal structures, the preparation of which is enormously difficult under other conditions because of the high reactivity of the original chemical compounds.

Partial support for this work was provided by the US National Science Foundation and the Alfred P. Sloan Foundation.

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Received: Moscow, 23rd July 1992
Cambridge, 25th August 1992; Com. 2/04569I