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A SINGLE CRYSTAL STUDY OF A SOLID-STATE POLYMERIZATION REACTION

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Abstract

Halogenoacetates are known to undergo a solid-state elimination reaction to metal halide and poly(hydroxyacetic acid), polyglycolide. Earlier studies have shown that the reaction takes place exclusively in the solid-state without the occurrence of liquid intermediates. Single crystals of sodium chloroacetate and silver chloroacetate were reacted and studied with X-ray diffractometry, scanning electron microscopy and thermomicroscopy. The results show that the reaction leads from single crystals to a composite of polyglycolide and metal halide. Neither the salt nor the polymer exhibit a preferred crystallographic orientation, therefore it must be concluded that the crystal lattice is not preserved during the reaction.

Keywords: diffractrometry, polymerization, single crystals, solid-state reactions, topochemistry

Introduction

We have recently reported in a series of papers about the thermally induced solid-state elimination reaction in salts of halogenoacetic acids [1–8]. This reaction, known for potassium chloroacetate since 1857 [9], leads quantitatively to poly(hydroxyacetic acid), polyglycolide. Equation 1 shows the principal reaction scheme as exemplified for sodium chloroacetate:

$$\mathrm{Cl{-}CH_2COO^{-}+\,Na_{(s)}} \rightarrow \mathrm{NaCl_{(s)}} + 1/n[\mathrm{-CH_2-COO-}]_{\mathrm{n(s)}} \qquad (1)$$

Our previous results that were obtained with a multitude of modern analytical techniques have demonstrated convincingly that this reaction occurs indeed in the solid state, without liquid intermediate. Crystal structure determinations on silver chloroacetate [5] and sodium chloroacetate [10] suggest a topochemical mechanism for this unusual polymerization reaction. The metal halide (NaCl in Eq. (1)) is precipitated as small crystals (diameter about 1 μm) in a matrix of polyglycolide. Washing out the salt with water leaves a matrix of highly porous polyglycolide with cubic holes of the same size as the salt crystals. Polyglycolide is of high practical interest as biomaterial (e.g., in surgery [11–13]), as it is well degraded in the body to non-toxic products.

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As all previous investigations were carried out on microcrystalline samples, not on single crystals, it is of considerable interest, from a solid-state chemical point of view, to study the question whether the reaction occurs in a topotactical way, i.e. whether the crystal structure of the parent compounds determines the structure of the products. Clearly, as the elimination reaction leads to a heterogeneous mixture of two components (salt and polyglycolide), a single-crystal-to-single-crystal reaction, as found in some photochemically induced solid-state polymerization reactions [14–16], is impossible. One may, however, suspect that the precipitated salt crystals or the polymer could be formed in a preferential crystallographic orientation with respect to the halogenoacetate crystal. Consequently, we have prepared and reacted single crystals of silver chloroacetate and of sodium chloroacetate.

Experimental

Sodium chloroacetate and silver chloroacetate were prepared as described in [3]. A single crystal of silver chloroacetate was grown in a gel consisting of water, ethanol, tetraethylorthosilicate and triethylamine [5] (see [17] for a general overview). A single crystal of sodium chloroacetate was obtained by very slow cooling of a solution of sodium chloroacetate in acetic acid.

Bragg rotating crystal pictures were obtained with a Stoe camera using CuK_α radiation (λ=154.178 pm; 5–65° 2Θ; 12 h measuring time).

Scanning electron microscopy was carried out with a Philips SEM 515 on gold-sputtered samples. Thermomicroscopy was carried out on a Mettler FP 80/84 hot stage instrument in sapphire crucibles.

Results and discussion

Halogenoacetates tend to crystallize as thin platelets. This makes it generally difficult to grow crystals that are suitable for X-ray structure analysis. Actually, the structure of sodium chloroacetate could only be solved from synchrotron powder data [10]. The crystals that were used in this study were obtained by gel crystallization (silver salt) and by slow cooling crystallization (sodium salt). Figure 1a shows a representative view of smaller silver chloroacetate single crystals as they are obtained from aqueous solution if it is slowly cooled. Note the almost ‘two-dimensional’ crystal morphology. The surface of the crystals is not as smooth as it appears in Fig. 1a. Figure 1b shows a magnified view of the surface where rectangular kinks, possibly from the crystallization process, can be seen. Silver chloroacetate crystallizes in the orthorhombic space group $Pbc2_1$, a fact that supports the assumption of a crystallographically defined surface texture resulting from crystal growth.

Silver chloroacetate reacts to polyglycolide and silver chloride. Figure 1c shows the surface of such a reacted single crystal of silver chloroacetate (reacted at 120°C). Although the distinction between polyglycolide and AgCl is not possible from this picture, it is obvious that no preferred orientation exists in the formed heterogeneous mixture.

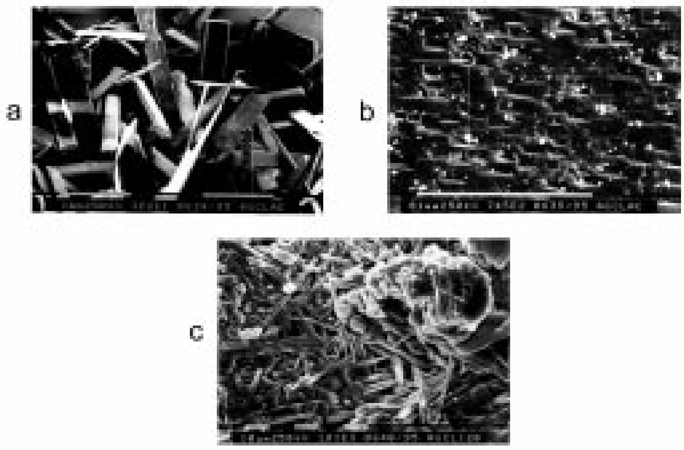

Fig. 1 Scanning electron micrographs of single crystals of silver chloroacetate AgOOC–CH_2–Cl. a – Unreacted silver chloroacetate crystals (magnification 30.2×); b – Surface of an unreacted silver chloroacetate crystal (magnification 745×); c – Surface of a reacted silver chloroacetate crystal (=polyglycolide+AgCl) (magnification 1010×)

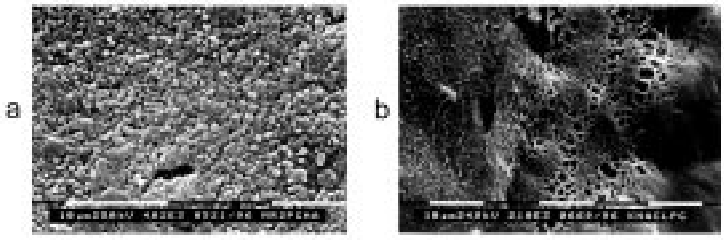

Fig 2 Scanning electron micrographs of single crystals of sodium chloroacetate NaOOC–CH_2–Cl. a – Surface of a reacted sodium chloroacetate crystal (=polyglycolide+NaCl) (magnification 4020×); b – Surface of a reacted sodium chloroacetate crystal that was extracted with water (=porous polyglycolide) (magnification 2100×)

Silver chloride is poorly soluble in water, and therefore difficult to extract (however, it can be done with water that contains complexing agents, like CN^-). An easier case is sodium chloroacetate where the formed sodium chloride can be more easily washed out. Figure 2a shows the surface of a reacted sodium chloroacetate crystal (reaction conditions: heated with 5 K min^{-1} from 30 to 210°C, then 10 min at 210°C). The cubic salt crystals are dominating the picture, and again, no preferred orientation can be observed. Figure 2b shows the surface of a reacted single crystal of sodium chloroacetate that was thoroughly washed with water. All NaCl has been removed, and the cubic pores remain where the salt had been before. If at all, an orientation exists only in limited regions of the sample.

Scanning electron microscopy is a highly useful tool for examination of surface morphologies. However, the pictures that we took of crystal surfaces may not be representative for the whole crystal, as surface effects are well known in solid state chemistry. A look ‘inside’ a crystal is possible by diffraction methods, provided that the crystal is small enough not to absorb too much of the radiation. This was the case in the following studies.

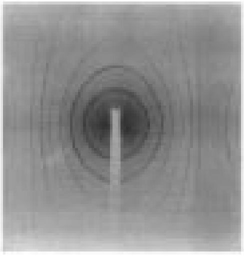

Fig. 3 Bragg rotating crystal pictures taken on a reacted single crystal of sodium chloroacetate (=polyglycolide+NaCl). The precipitated NaCl (predominant in the scattering pattern) does not show a preferred crystallographic orientation, i.e., the crystals and domains are randomly oriented

Single crystals of silver chloroacetate and sodium chloroacetate were subjected to Bragg rotating crystal examinations. Single crystals give discrete spots on the film, whereas polycrystalline material without special orientation gives diffraction fringes. Such a picture was obtained for a single crystal of sodium chloroacetate (not shown). Figure 3 shows a picture of a reacted single crystal of sodium chloroacetate (=polyglycolide+NaCI). The diffraction pattern is dominated by sodium chloride (scatters more strongly than the polymer), that, obviously, does not show a preferred but a random orientation (no diffraction spots but diffraction fringes). If NaCl is washed out, the more weakly scattering polyglycolide can be seen. Again, no preferred crystallographic orientation of the polyglycolide domains is detectable, as only diffuse diffraction fringes are observed (picture not shown). The same observations were made for silver chloroacetate.

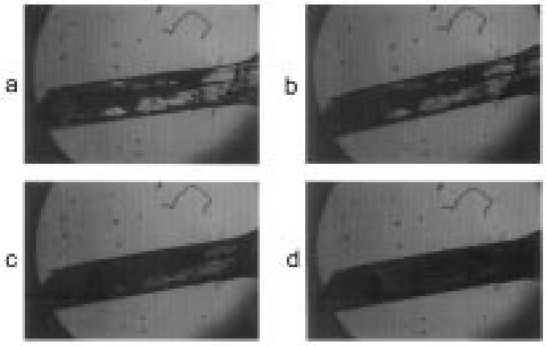

Fig. 4 Thermomicroscopy on a single crystal of sodium chloroacetate (length about 2.5 mm). Temperature program: 170 to 180°C with 0.5 K min^{-1}, then kept at that temperature. The crystal is initially transparent and then turns opaque and finally dark due to the transformation into an intimate mixture of NaCl microcrystals and polyglycolide. a – Unreacted crystal (171.5°C; *t*=3 min); b – Partially reacted crystal (174.5°C; *t*=9 min); c – Partially reacted crystal (180°C; *t*=20 min); d – Fully reacted crystal (180°C; *t*=25 min)

Thermomicroscopy was carried out on a single crystal of sodium chloroacetate. The sample was heated from 170 to 180°C with 0.5 K min^{-1} and kept at that temperature. Figure 4 shows four representative pictures. The crystal does not change its shape, i.e., it does not melt during the reaction. It can be seen that the crystal is fragmented into small statistically oriented domains (4b and 4c). The formerly transparent crystal turns first opaque and finally dark. This is due to light scattering at the formed salt crystals. The true color of the crystal changes from white to yellowish. After washing with water, the crystal of now pure polyglycolide turns white again. This experiment shows that we most likely have a true solid state reaction without temporary liquefaction.

Conclusions

Our results show that the reaction does not lead from a single crystal of halogenoacetate to a single crystal of polyglycolide, and that neither the formed salt crystals nor the domains of polyglycolide are not formed in an oriented way. A probable explanation could be as follows: The reaction starts at some sites of the crystals where the local energy is raised, e.g., at defects. At these sites, nuclei of eliminated salt are formed that continue to grow as eliminated ions (e.g., Na^+, Cl^-) diffuse through the lattice. It is probably easier for the ‘salt’ to migrate through the reacting crystal and to attach to an already present crystal than to form a new nucleus. This phase separation must lead to stress in the crystal, as a new phase is formed and the remaining polyglycolide phase is shrinking (the net volume change of the whole crystal is small). This stress is likely to induce new defects in the crystal where other nuclei are formed. This could explain some local order in the precipitated salt microcrystals (see the linear arrangement in Fig. 2b). Such ‘feed-back’ mechanisms have been proposed earlier for solid-state reactions [18, 19].

The concept of nucleation at defects is corroborated by the observation that the average salt crystal size decreases considerably if crystals of sodium chloroacetate are ground before the reaction [7]. By grinding, many defects and potential nucleation sites are created.

We believe that this nucleation at many different sites in the crystal, combined with strong local stress, causes the loss of the structural integrity of the crystal, and consequentially a random orientation of the products. The reaction occurs topochemically, but not topotactically [20, 21].

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