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Morphology of Solid Photochemical Decomposition Products of Silver Carboxylates

B. B. BOKHONOV, O. I. LOMOVSKY, V. M. ANDREEV, AND V. V. BOLDYREV

Institute of Solid State Chemistry of Siberian Branch of the Academy of Sciences of the USSR, 630091, Novosibirsk 91, Derzhavina 18, USSR

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The formation of solid photochemical decomposition products of silver carboxylates with long linear hydrocarbon chains and its variation in the course of reaction was investigated. At the initial stage of photolysis, particles of silver are formed with the overall situation analogous to that in the case of other silver salts. After the degree of decomposition has reached 20%, the formation of a space-ordered structure of solid products in the form of alternating volume lamellae of paraffin and silver is observed. The average distance from one lamella edge to the next lamella edge is dependent upon the length of the methylene chains of silver carboxylates and the intensity of irradiation. The results obtained are discussed from the point of view of possible spinodal character of decomposition of intermediate solid solution paraffin–silver carboxylate.

Introduction

Silver carboxylates (SC) with carboxylic acids having 12–22 carbon atoms in the linear carbon chain are one of the basic components of thermodeveloped photomaterials (*1*). The reduction of these salts in the process of the development of photolayers results in the formation of metallic silver which creates a visible image. Photochemical decomposition of SC leads to a decrease in the photostability of layers. The study of SC photochemical decomposition is of scientific interest because in this very case, in contrast to the traditional photochemical processes in which the compounds are decomposed according to the solid + gas scheme, a solid hydrocarbon is formed along side with the formation of metallic silver and gaseous product.

The aim of this work was the clearing up of the formation character of SC decomposition solid products in the course of the reaction.

Experimental

SC samples—laurate, stearate, and behenate—were synthesized in a water medium by means of exchange reactions between natrium salts of the corresponding acids and silver nitrate at 60°C. The initial reagents of "chemically pure" quality were recrystallized from water. SC single crystals were grown by slow cooling in a saturated 10 : 1 ethanol : pyridine mixture. The crystals are not sensitive to visible light, but are decomposed by ultraviolet light. The irradiation of crystals was carried out by the wide spectrum of the mercury lamp with an

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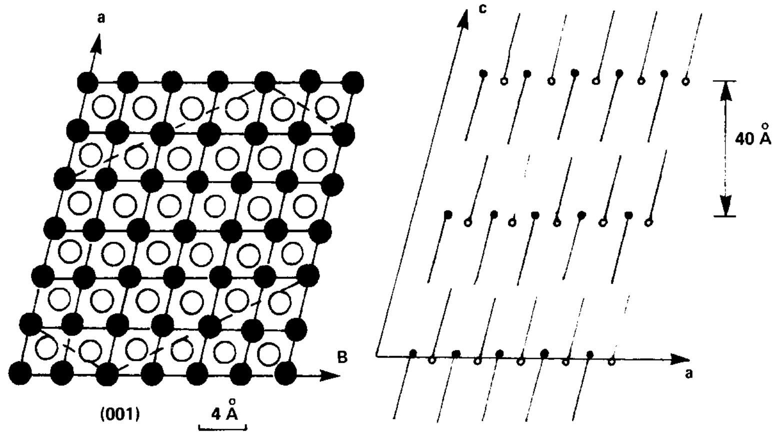

FIG. 1. Scheme of crystalline lattice of silver carboxylates. The open circles and the dark circles represent silver atoms in double silver layers: (*ab*) plane—left, (*ac*) plane—right. The stright lines on the right side of the figure represent methylenic chains.

illumination energy of 1.02×10^{-3} W/cm^2. To avoid heating of the crystals, a heat filter and intensive air cooling of the samples have been used. The intensity of the incident light was varied by changing the distance between the source and the sample. Irradiation time was varied in the range 0–360 min. Irradiation intensity was defined by means of chemical ferrioxalate dosimeter. Electron microscopic investigations were carried out with the help of scanning electron microscope JSM-T-20 and electron optical installation EF-4. Electron diffraction patterns were measured after the irradiation of samples.

Results and Discussion

The following background information is known. Unit cells of SC containing more than six atoms of carbon in the methylene chain belong to the triclinic class and contain two formula units. Silver carboxylates have a lamellar structure consisting of alternating double silver layers being separated by methylenic ends (*2*). Silver layers are placed within the (*ab*) plane. Methylene chains are arranged at an oblique angle to the plane (Fig. 1).

The absorption spectra of all SC have a maximum at 250–260 nm (*3*). The photochemical decomposition is carried out according to the scheme

$$\text{R–COOAg} \xrightarrow{h\nu} \text{Ag} + \text{R}\cdot + \text{CO}_2$$

The obtained silver atoms aggregate into metallic particles, and hydrocarbon radicals mainly recombine with the formation of paraffin.

In this investigation it was discovered that the observed electron microscopic picture of the solid products formed changes with the degree of the photochemical decomposition of crystals. At the initial stages of transformation the morphology change of the basic (001) face does not take place. By means of transmission electron microscopy under these conditions, the formation of small silver particles reaching the size ~100 Å being distributed in the layer near the outside edge of a parent SC crystal has been discovered (Fig. 2). Further irradiation leads to an increase in the number of particles, but with essentially no enlarge-

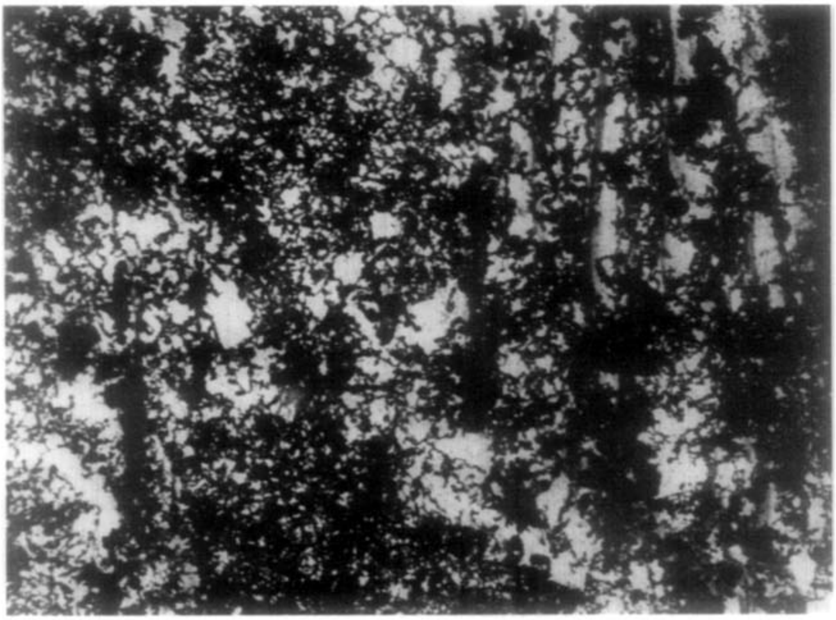

FIG. 2. Carbon replica of crystal of silver stearate decomposed by ultraviolet light: intensity 1.02 × 10^{-3} W/cm^2, irradiation time 270 min, temperature 20°C. Photochemical decomposition degree (α) is 15%, magnification 25,000×. Dark areas are silver particles.

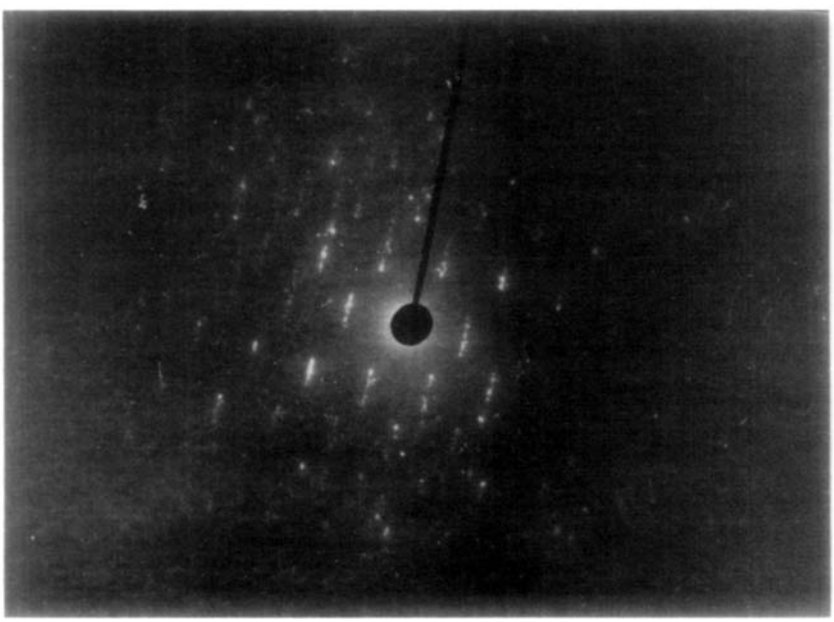

FIG. 3. Electron diffraction pattern of crystal of silver stearate, $\alpha = 15\%$. Decomposition parameters are the same as in the case of Fig. 2. Wandering of the spots is a consequence of formation of solid solution.

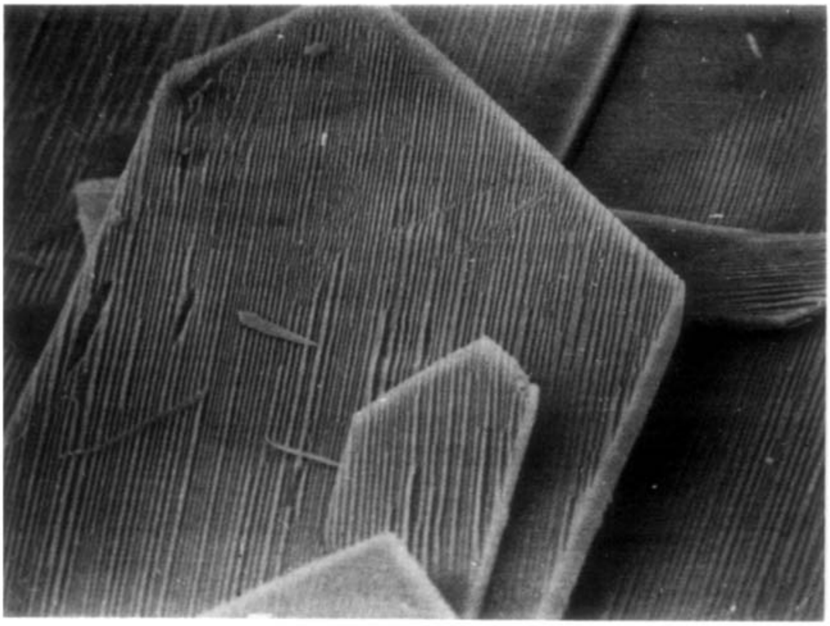

FIG. 4. Structure of surface of (001) face of crystal of silver, stearate, α = 20%. Irradiation time is 360 min, decomposition parameters are as in the case of Fig. 2. Magnification 1500×.

ment in their size. These observations correlate with a change of optical reflection spectra of the crystals as observed under photolysis (*3*). In these spectra there also appears a new wide absorption band in the region 420–480 nm characteristic of the formation of colloidal silver particles (*4*). In the course of photolysis a uniform intensification of this band occurs which also points to the accumulation of numbers of particles, but not to their growth in size. When the degree of transformation reaches the 15–20% range, a shift of reflections of the initial lattice takes place on the electron diffraction patterns (Fig. 3) which can be the consequence of the formation of the solid solution of paraffin in the initial SC lattice.

As the degree of photochemical transformation of samples reaches 20% or more, the character of the space distribution of the decomposition solid products changes essentially. On the (001) face the formation of an ordered structure is observed. The structure consists of alternating volume paraffin lamellae, separated by cracks which are decorated by small dispersed silver particles (Fig. 4). The lamellae formed on the (001) face are placed at an angle of ~150° to the **a** axis of the initial SC.

The parameter of the space ordering, i.e., the average distance from one lamella edge to the next lamella edge, depends upon the length of the SC methylene chain. For irradiation of the samples under the conditions mentioned above, the distance between the lamellae is 0.4, 0.9, and 1.5 μm for laurate, stearate, and behenate of silver, respectively. The lengths of the methylene chains of laurate is 35 Å, stearate is 50 Å, and behenate is 60 Å. It is seen that the increase in the length of the SC methylene chain causes the parameter of space ordering to increase. The electron diffraction patterns obtained for the case of SC decomposition by ~20% and more (Fig. 5) point to the presence of the initial SC, paraffin, and metallic silver.

It was discovered in this investigation

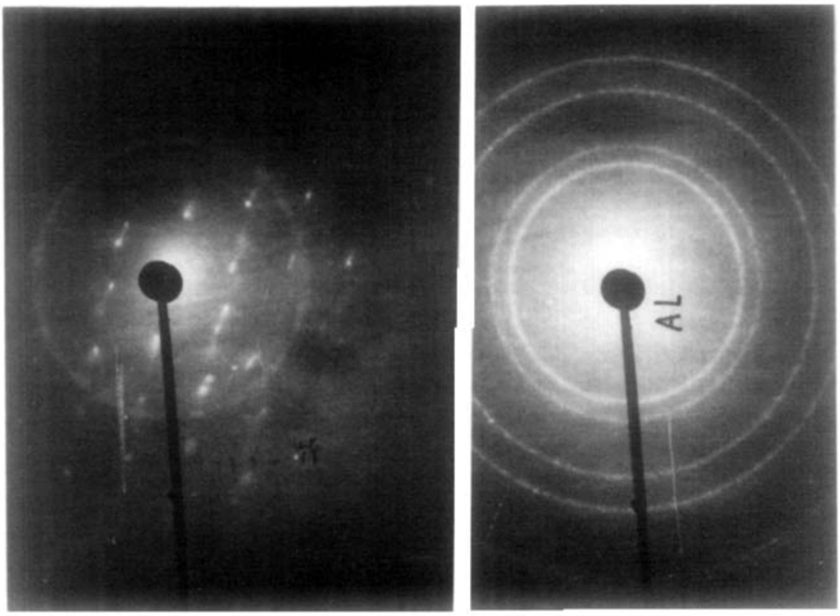

FIG. 5. Electron diffraction pattern of crystal of silver stearate, $\alpha = 20\%$ (decomposition parameters are the same as in the case of Fig. 4) and calibration electron diffraction pattern of aluminum film.

that heating for 1 hr at 90°C of SC crystals already photochemically decomposed by 15% (for which the ordered structure of the reaction product has not yet formed), results in the formation of such a structure. This points to an important role of the mobility of the reaction products for the formation of the ordered structure.

The parameter of the space ordering of the photochemical reaction products depends on the intensity of irradiation. For example, an increase in the energy of illumination from 1.02×10^{-3} to 5.2×10^{-3} W/cm^2 leads to a decrease of the ordering parameter from 0.9 to 0.5 μm in the case of silver stearate.

To sum it up we should note that in all these new findings in the initial stages of transformation the morphology of the products of the SC photochemical decomposition is analogous to that which is observed under the photolysis of other silver salts, silver halides or silver oxalate, for example. As to the morphology in the case of higher degrees of SC photochemical decomposition, three main peculiarities of the formation of the solid products of the reaction have been discovered which require an explanation. They are: (i) a formation of a lamellar structure of the photolysis products; (ii) the steric orientation of the growing lamellae relative to crystallographic axes of the initial crystal of SC; and (iii) the variation of the ordering parameter with the intensity of irradiation.

In the discussion we note the following. In the initial stages of irradiation in the surface layer of the crystal, silver atoms, hydrocarbon radicals, and CO_2 are formed. Silver atoms being mobile, associate into metallic particles. Perhaps hydrocarbon radicals move and recombine forming the solid solution of paraffin in the initial SC. At ~20% photolytic decomposition of SC, the decomposition of the solid solution with the formation of lamellae of the phases take place. Silver particles in this case are displaced and decorate the structure formed.

One can suppose that the orientation of the growing lamellae is determined by the relation of the initial SC crystallographic lattices and those of paraffin. New paraffin structure formation occurs by the way of the smallest change of the mutual arrangement of hydrocarbon chains in the SC and paraffin structures.

One usually considers two most probable mechanisms for formation of new phases. First, the decomposition of the paraffin solid solution in SC may proceed by means of fluctuating formation of the nuclei of a new phase, being characterized by the interface presence and its further development. The phenomenon described is commonly called "nucleation-and-growth" mechanism. The disordered arrangement of the new phase particles having different sizes is usually observed by microscopy in this case.

The second possible mechanism is analogous to that of spinodal decomposition of a solid solution. The distinct peculiarity of such a decomposition is the formation and development of fluctuations in the solid solution composition with a small deviation from the average composition, but being characterized by extended size and spatial ordering. Fluctuation waves can be transformed into particles of the new phases simultaneously in large parts of a crystal. The formation of the spatially ordered products of reactions which was previously observed through microscopy under the decomposition of metallic solutions (*5, 6*), glasses (*7*), and silicates (*8*) is similar to that discovered in our work and was explained just this way. Nevertheless, it is impossible to make a synonymous conclusion about the character of the decomposition only on the basis of electron microscopic investigations of the spatial distribution of the reaction products. In our case, the observed dependence of the ordering parameter on the intensity of irradiation speaks in favor of the second mechanism (*9–11*) for paraffin–silver carboxylate solid solution decomposition.

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