

THERMAL DECOMPOSITIONS OF SILVER CARBOXYLATES

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The thermal decompositions of the even silver dicarboxylates from silver oxalate to silver sebacate were studied. In vacuum, the dicarboxylates decomposed to give metallic silver, CO₂ and organic diradicals as primary products, and polymers as secondary products. The higher silver dicarboxylates were much more stable to thermal treatment than silver oxalate, probably due to the initiation of decomposition of all carboxylates except silver oxalate by the rupture of a Ag–O and not a C–C bond.

A study of the thermal decomposition (TD) reactions of the silver salts of monocarboxylic acids in the homologous series from silver acetate to silver behenate has shown that the thermal stability of the salts increases as the length of the methylene chain is increased [1]. It has been found that, prior to the beginning of the TD reaction, a disordering occurs first in the packing of the methylene chains, and then within the silver layers, i.e. the TD of Ag monocarboxylates proceeds in a mesomorphic state [2].

It appeared of interest to study the TD reactions in a homologous series of silver salts of dicarboxylic acids, to determine the relationship between their thermal stabilities and the lengths of the methylene chain, and to find some physico-chemical properties of the salts. The present paper describes a study of the TD reactions of silver dicarboxylates (SDC) with the general formula C_nH_{2n-4}O₄Ag₂ for *n* = 2 (silver oxalate), *n* = 4 (silver succinate), *n* = 6 (silver adipate), *n* = 8 (silver suberate) and *n* = 10 (silver sebacate).

Experimental

The salts used were synthesized by a procedure described elsewhere [1]. The TD reactions were studied by means of IR spectroscopy, X-ray diffraction phase analysis, mass spectrometry, DTA and DSC.

The kinetics of the reaction was studied in vacuum by thermogravimetry under isothermal conditions. The synthesized salts were identified on the basis of chemical analysis and IR spectroscopic data.

Results and discussion

There is no information in the literature on the structure of the SDC, with the exception of silver oxalate [3], the molecule of which is packed in a crystal as a polymer chain to form layers with a certain displacement. As the length of the methylene chain increases, the SDC can exhibit a layer structure of packing, similar to that of silver monocarboxylates [4], which may be determined by X-ray diffraction. Figure 1 gives the interplanar distance d_{001} as a function of the number of carbon atoms. It is seen that, beginning with $n=4$, the interplanar distance increases by 2.5 Å as n rises by 2, which corresponds to the unit length of one zigzag of the methylene chain.

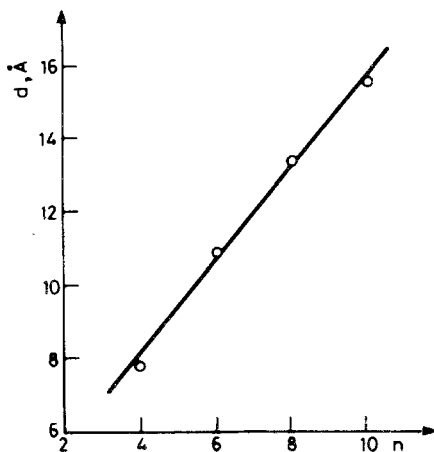


Fig. 1 Interplanar distance d_{001} as a function of the number of carbon atoms in SDC

Thus, on passing from silver oxalate to the other SDC, the packing of the molecules in the crystal changes from a chain to a layer. Further, the linear dependence of d_{001} on n , at $n \geq 4$, can be regarded as evidence that all the SDC studied, with the exception of silver oxalate, have the same crystalline modification. A determination of its type was not intended in this work.

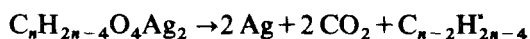
Taking into account the layer structure (a property common to the SDC and silver monocarboxylates) and the presence of a methylene chain, one might expect similar behaviour on heating. In this connection, it was of interest to establish the

existence of mesomorphic transitions and disordering in the crystal lattice of the SDC on heating. The DTA and DSC data prior to the beginning of the TD reactions showed none of the thermal effects which usually accompany structural changes in a crystal. When the SDC were heated to the temperatures of decomposition, the X-ray patterns did not change, in contrast with those of the monocarboxylates with the same chain length. All these results attest to the fact that the SDC do not undergo mesomorphic transition before their TD, and the reaction begins in the crystalline state.

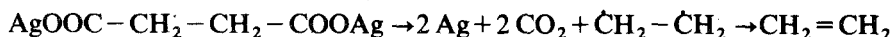
X-ray diffraction analysis of the solid products of SDC decomposition showed that only metallic silver was formed in vacuum. Upon decomposition of the SDC with $n \geq 4$ the metallic silver was accompanied by white, unidentified organic products that condensed on the cold walls of the reactor. These melted between 118° and 140°.

Mass spectrometry of the gaseous products of decomposition gave the following results. Earlier [5], and in our experiments on the decomposition of silver oxalate, the evolution of CO₂ alone was found, which is only one of the gaseous products for all the other SDC. Further, for each individual salt, the evolution of typical fragments was found. Thus, in the case of silver succinate, ion-radicals were evolved with $m/e = 28, 27, 26$ and 25 , corresponding in percentage ratio to a mass spectrum of ethylene, together with ions with $m/e = 55, 56$ and 57 , corresponding to C₄H₇⁺, C₄H₈⁺ and C₄H₉⁺. In the case of silver adipate, ions with $m/e = 26, 27, 28, 39, 41, 53, 56$ and 57 were evolved. The decompositions of the SDC with $n = 8$ and $n = 10$ gave CO₂ and ions with $m/e = 27, 28, 29, 41, 42, 43, 55, 56, 57, 69, 70$ and 71 , relating to fragments of the methylene chain.

On the basis of the data obtained, the TD reaction can be presented as the following scheme:



where C_{*n*-2}H_{2*n*-4}[·] is a diradical of the methylene chain with two unpaired electrons, which can recombine intramolecularly. This is confirmed by the evolution of ethylene in the thermal decomposition of silver succinate:



Differences in the thermal stabilities of the SDC, evaluated via the temperatures of the beginning of weight loss in the thermoanalytical curves (heating rate 5 deg min⁻¹) and via their half-life at 250° in a mass spectrometer (through the kinetics of CO₂ evolution) (Fig. 2), are most pronounced for the first terms of the series. Thus, the introduction of a methylene chain into the SDC, on passing from silver oxalate to succinate, leads to a rise in the temperature of the beginning of decomposition by more than 100 deg. As the length of the methylene chain

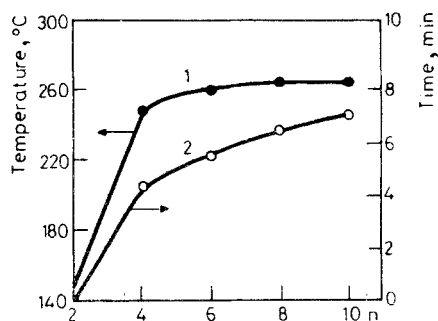


Fig. 2 Thermal stability of the homologous series of SDC based on TG data – 1, on half-life period at $T = 250\text{ }^{\circ}\text{C} - 2$

increases further, the thermal stabilities of the salts rise only slightly. Let us try to explain this behaviour of the dependence of the thermal stabilities of the SDC on the basis of some literature data and our own experimental results.

When considering the mechanisms of the TD reactions of different metal oxalates, Boldyrev et al. [6] hypothesized that the initial stage in the chemical reaction is the rupture of the C—C bond in an oxalate ion. On the other hand, in a study of the TD reactions of silver malonate [7] and copper malonate [8], Galwey et al. introduced homolytic rupture of the O—Ag and O—Cu bonds in order to explain the reaction products. There are no indications in these papers, however, as to which bond, O—M or C—C, is broken first. Direct evidence of the primary rupture of the O—Ag bond in Ag carboxylates was obtained by Fields and Meyerson [9], who studied the TD of 15 carboxylates, mainly aromatic, mono- and polycarboxylates. They showed that the initial stage in the chemical reaction was the homolytic rupture of the O—Ag bond, with the formation of the acyloxy radical R—COO·.

A correlation of the given data suggests that the sharp increase in thermal stability on passing from the oxalate to the other salts is associated with the change in the initial stage of bond rupture. In silver oxalate, the two carboxyl groups exhibiting a strong electron-acceptor induction effect are located near each other, which leads to an elongation and weakening of the C—C bond, the rupture of this initiating the TD reaction. The introduction of a methylene chain into silver oxalate sharply decreases the mutual influence of the carboxyl groups on each other and raises the temperature of the beginning of the reaction by more than 100 deg. We presume that the initial stage in the TD reaction of the SDC with $n = 4$ is rupture of the O—Ag bond, followed by decarboxylation of the acyl radical. The radical formed is unstable and is quickly decomposed to Ag, CO₂ and the fragment of the methylene chain. The induction effect is transmitted to more than 4 carbon atoms,

and therefore elongation of the methylene chain has no effect on the thermal stabilities of the SDC with $n \geq 4$, which are determined by the strength of the O—Ag bond.

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Zusammenfassung — Die thermische Zersetzung der geradzahigen Silberdicarboxylate Silberoxalat bis -sebacinat wurde untersucht. Unter Vakuum zersetzen sich die Dicarboxylate zu metallischem Silber, CO_2 und organischen Diradikalen als Primärprodukt und Polymeren als Sekundärprodukt. Die höheren Silberdicarboxylate sind wesentlich stabiler als das Oxalat, wahrscheinlich weil bei ihnen die Zersetzung von der Spaltung einer Ag—O-Bindung und nicht einer C—C-Bindung wie beim Oxalat ihren Anfang nimmt.

Резюме — Изучено термическое разложение дикарбоксилатов серебра, начиная от оксалата серебра до себацината. В вакууме соли разлагаются с образованием металлического серебра, углекислого газа и органических бирадикалов как первичных продуктов и полимеров — как вторичных продуктов. Соли серебра с дикарбоновыми кислотами с более длинной углеродной цепью были намного более устойчивыми к термической обработке, по сравнению с оксалатом серебра. Возможно, что это обусловлено начальным разложением всех карбоксилатов, исключая оксалат, путем разрыва связи Ag—O, а не связи C—C.