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Thermal decomposition of silver oxalate

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Abstract

This is a review of the studies of the thermal decomposition of silver oxalate from 1950s through the 1990s. The role of various factors, which have influence on the thermal decomposition rate, is discussed. A detailed mechanism of the reaction is proposed, unsolved problems are summarised. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; Silver oxalate; Polarisation; Effect of dopant; Preliminary irradiation; Electric field on the thermal decomposition

1. Introduction

Thermal decomposition of silver oxalate is a typical model reaction accompanied by the migration of ions over the lattice. The mechanism of silver oxalate thermal decomposition can be best considered in terms of general notions of how any oxalates decompose.

In [1] we proposed a classification for oxalate thermal decompositions according to which all oxalates can be divided into three groups. The first group comprises the thermal decomposition of oxalates of alkaline metals and alkaline earth. They usually decompose to form a carbonate and carbon oxide:

$$MeC_2O_4 \rightarrow MeCO_3 + CO$$

The second group incorporates the thermal decomposition of the oxalates that decompose forming metal oxide as a solid product and a mixture of carbon monoxide and dioxide as gaseous products:

$$MeC_2O_4 \rightarrow MeO + CO + CO_2$$

This is how the oxalates of transition metals usually decompose.

Finally, the third group includes the thermal decomposition of the oxalates giving rise to metal as the solid product and carbon dioxide as the gaseous product:

$$MeC_2O_4 \rightarrow Me + 2CO_2$$

This is the way for the decomposition of the oxalates of heavy metals, including silver oxalate.

In [2] it was assumed that the primary stage for the thermal decomposition of all oxalates is the breakage of the C–C bond in the oxalate ion, because this bond is the weakest. The data of [3] also indicate that this stage is the most probable one. These authors demonstrated that for the thermal decomposition of an oxalate ion present in a potassium bromide matrix the primary process is rotation of the carboxylic group around the symmetry axis of the oxalate ion. During this process, at first the oxalate ion becomes not flat; then the C–C bond breaks. The kinetics of this process are described by the first-order equation with an activation energy of 60–63 kcal/mol. Bond breakage results in the formation of two CO_2^- radicals. The

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presence of these radicals was detected in thermal decomposition of strontium oxalate [4]. The interaction of the radicals can lead either to the formation of carbonyl carbonate:

$2CO_2^- \rightarrow CO_3CO^-$

or to the return to the initial state of the system:

$2CO_2^- \rightarrow C_2O_4^{2-}$

One more possibility occurs, if there is an acceptor of electrons in the vicinity of oxalate ion, for example a cation having a high ionisation potential; then the breakage of the C–C bond occurs simultaneously with electron transfer from oxalate ion to acceptor, resulting in the formation of two carbon dioxide molecules. The latter possibility is likely to be realised also in the case of silver oxalate.

2. Physicochemical properties of silver oxalate

Silver oxalate is a transparent crystal that can be prepared by pouring together aqueous solutions of silver salts and soluble oxalates or oxalic acid itself [5]. The appearance of crystals (habitus) is shown in Fig. 1. Depending on the synthesis method (the rate and order in which the solutions are poured together, the composition of solution with respect to the anion component of the silver salt and the cation component of the oxalate), the physicochemical properties of different silver oxalate preparations can differ substantially [6–12]. In some cases, a slow decomposition of the ammonia complex can be used to prepare silver oxalate crystals.

The synthesised crystals are aged during their storage [7]. It was stated that the ageing of crystals is not accompanied by changes in the habitus and crystal size; the outer surface area does not change. Observed changes of the physicochemical properties of silver oxalate, in particular the change of thermal decomposition rate, are likely to be connected, similar to the case of lead oxalate, with the redistribution of defects in the crystal, in particular polygonization [14].

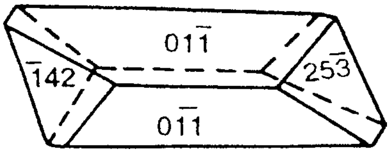


Fig. 1. Habitus of silver oxalate crystal.

Crystal density is 5.005 g/cm^3, molecular volume is $V = 60.7$ cm^3/mol. After recrystallization from ammonia solution, the density increases to 5.029 g/cm^3, and the molecular volume decreases correspondingly to 60.3 cm^3/mol. The refractive index is 1.843. The infrared spectrum contains bands corresponding to the twisting (79 and 145 cm^{-1}), stretching (268 cm^{-1}) and bending (525 cm^{-1}) O–C–O vibrations in oxalate ion [15].

The edge of absorption band is at 298 nm; besides, there are minima at 350 and 312 nm in the spectrum. The photochemical sensitivity limit of oxalate is 492 nm [16,17]. It was believed for a long time that photoconductivity was absent from silver oxalate [9,17]. However, it was demonstrated that the photoelectric effect is observed in silver oxalate [18,19]. Its spectral distribution is located in the short-wavelength region at $\lambda < 280$ nm ($h\nu \sim 4.4$ eV). The measured current was of the order of 10^{-12} A. Voltammetric characteristics are ohmic below a field strength of about 10^2 V/cm. The investigation of the effect of gases, including acceptors (I_2, Br_2) and donors (H_2, NH_3) on the photoconductivity of silver oxalate demonstrated that it is a n-type photoconductor.

Luminescence is observed under excitation in the region of inherent absorption [20]. A more detailed study of the luminescence [21,22] confirmed earlier an assumption [9,17] concerning the exciton character of excitation. At 77 K, excitation with the 365 nm light, silver oxalate produces luminescence in the orange region. Near room temperature, the luminescence weakens and shifts into the red region [22].

Dark conductivity strongly depends on the prehistory of the preparation and is provided by the transfer of silver ions. The investigation of the concentration dependence of conductivity exhibited by solid solutions of silver oxalate with the addition of hetero-valent ions Ca^{2+}, Cu^{2+}, Pb^{2+} demonstrated that the conductivity of oxalate at first decreases with increasing the concentration of the additive, passes through a minimum and then increases. Since this behaviour of the isotherm corresponds to the Koch–Wagner model [23], it implies that the initial decrease of the conductivity of crystals is explained by the decrease of the concentration of the most mobile interstitial ions and the following increase is due to

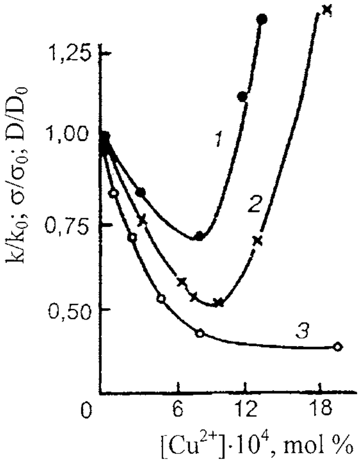


Fig. 2. Koch–Wagner isotherm for silver oxalate with Cu^{2+} additive. Relative change of the: diffusion coefficient D/D_0 (1); conductivity σ/σ_0 (2); rate constant of thermal decomposition k/k_0 (3), where $k = 1/\tau$.

the increase of the concentration of cationic vacancies. The Koch–Wagner method was used to determine the concentrations of interstitial ions and their mobility [17,24].

Fig. 2 shows an example of one such isotherm obtained by adding the ions of divalent copper into silver oxalate. Since Cu^{2+} is a paramagnetic ion, the concentration of divalent copper ions that entered the silver oxalate lattice could be determined accurately by measuring the amplitude of ESR spectrum [25]. As one can see in Fig. 2, the minimum is observed as the plot of conductivity changes, versus the concentration of copper that entered the lattice, at 9×10^{-4} mol% Cu^{2+}. Using these figures, the concentration of interstitial ions was calculated to be 2.5×10^{-4} mol%, or 1.5×10^{18} ions/mol; the conductivity coefficients for interstitial ions and cation vacancies were 7×10^{10} and 5.7×10^{11} cm^2/s, respectively. This figure also shows the curve for the self-diffusion coefficient of the ^{110}Ag isotope in silver oxalate with increasing concentration of the additive. One can see that both curves exhibit similar behaviour, and the measured diffusion coefficient $(2 \pm 0.5) \times 10^{11}$ is close to that calculated from electroconductivity data using the Einstein equation $D \sim (\sigma kT/Ne^2) = (1.16 \pm 0.3) \times 10^{11}$. The activation energies of conductivity (89.9 ± 10.5 kJ/mol) and self-diffusion (100.3 ± 1.3 kJ/mol) are also similar.

The presence of Frenkel defects in silver oxalate was confirmed also by other methods. It is known that the thermoelectrete state (the appearance of internal polarisation in strong electric field) can be created in ionic crystals containing Frenkel defects. The reason for this state is the shift of interstitial ions and vacancies under the action of an electrical field [26].

In order to check the existence of the thermoelectrete state in silver oxalate, a tablet 0.2 mm thick prepared by pressing oxalate powder was placed into a measuring capacitor with Dacron gaskets which was then held in a cryostat. The locking contacts prevented injection of charge carriers from electrodes to the sample and allowed obtaining a hetero-charge in the sample. A thermoelectrete state was created by superimposing an electrical field onto the sample, followed by cooling the sample from room temperature to 77 K. Then the field was switched off. As the sample was defrosted, the discharge currents were measured with the electrometric amplifier. The curve of depolarisation current (Fig. 3) discovered by us in silver oxalate [27] agrees well with the shape of the curve usually observed in such cases.

The introduction of cadmium ions into the lattice causes a sharp drop of the depolarisation current curve at about 240 K, and the appearance of a new peak at

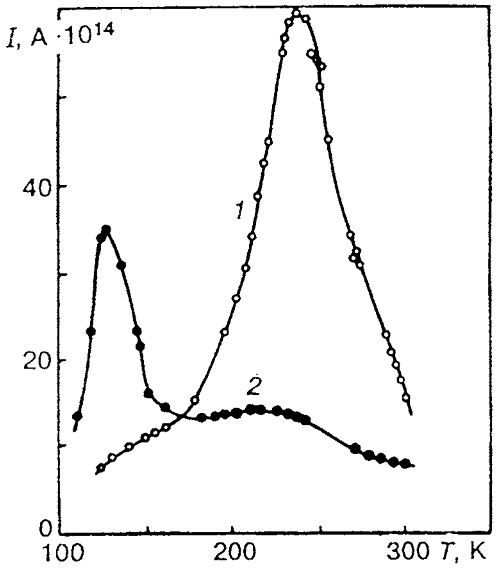


Fig. 3. Thermodepolarization current in silver oxalate: (1) initial sample and (2) the sample with 1 mol% Cd^{2+} added.

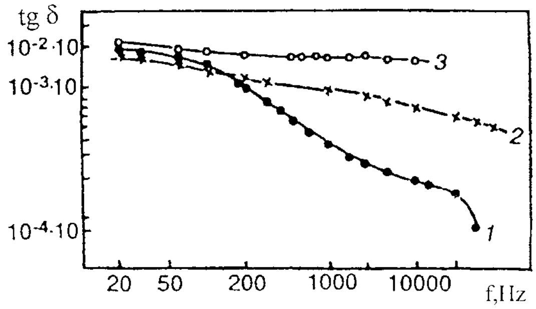


Fig. 4. Frequency dependence of the tangent of losses angle for oxalates: (1) PbC_2O_4; (2) $Ag_2C_2O_4$; (3) $Ag_2C_2O_4$ + 1.2% PbC_2O_4.

120 K which is likely to be connected with the formation of the complex $Cd^{2+}/\square_K$ during doping [27]. A similar effect is observed in the treatment of silver oxalate crystals with solutions containing mercaptotetrazol and ⟨sta-salt⟩, compounds that bind the surface active silver ions. Along with this process, the decrease in the conductivity of silver oxalate occurs. Treatment in silver nitrate solution, from which an additional amount of silver ions can be adsorbed on the silver oxalate surface, leads to the increase of discharge flow that characterises a thermoelectrete. The conductivity of the sample also increases.

The data of [28] are also evidence of the presence of Frenkel defects in the lattice. According to these data, silver oxalate is a crystal exhibiting the frequency–temperature dependence of the dielectric constant, *e*, within the range 70–370 K and a frequency range from the sonic to 300 MHz that is characteristic of the crystals with ionic polarisation. The tangent of the loss angle for $Ag_2C_2O_4$ is $(1.88\text{–}1.9) \times 10^{-2}$ within the frequency range 0.02–0.2 kHz and decreases as the frequency increases (Fig. 4). At lower frequencies, *e* is a function of the electronic, ionic and interlayer polarisation and is determined by the presence of weakly bound charge carriers which are interstitial silver ions. All these data are evidence that silver oxalate is Frenkel-disordered where the major charge carriers are interstitial silver ions.

3. Crystal structure of silver oxalate

The first investigation of the crystal structure of silver oxalate were carried out by Griffith in 1943 [29]. According to those data, crystalline silver oxalate has a monoclinic lattice with the parameters: $a = 0.346 \pm 0.0002$ nm, $b = 0.646 \pm 0.002$ nm, $c = 0.947 \pm 0.004$ nm, $\beta = (76 \pm 1)^\circ$. Each elementary cell contains two molecules. The spatial position of the atoms in the silver oxalate lattice form molecular chains connected through Ag–O bonds into a three-dimensional structure.

Since the data of Griffith did not agree with the results of the studies into the structure of other oxalates, Kolesnikov and Baumer [30] investigated silver oxalate structure and stated that the data of Griffith are incorrect and require substantial corrections. They are first of all connected with the angle in the monoclinic syngony, as well as the positions and orientation of the anions $C_2O_4^{2-}$ in the lattice.

Naumov et al. came to similar conclusions [31,32]. The silver oxalate structure proposed by Naumov differs from that proposed by Kolesnikov since it involves a shift by 1/2 of the short period and the change of axes when passing from the spatial group $P2_1/c$ to $P2_1/b$. Fig. 5 shows projections of the $Ag_2C_2O_4$ structure on the monoclinicity plane according to the structural models proposed by the three authors cited.

The first conclusion that is essential for the estimates of the reactivity of silver oxalate, and follows from the works of Kolesnikov and Naumov, is that the oxalate ion of the $Ag_2C_2O_4$ structure is flat and the C–C bond is longer than the usual value characteristic of an isolated ion, therefore, it can be broken more easily.

Efficient dimensions, distances between ions, valence angles and ion packing in the new model of structure differ from those that follow from the Griffith model. A feature of the new model is the presence of channels that stretch along [100]. The ribbons composed of silver cations are located in the channels. The width of ribbons is determined by the shortest distance between silver cations which is 0.2945 nm. This value exceeds the distance in the metal by only 0.0056 nm. So, the lattice already contains dimers, intermediate products that can provide topotaxial growth of the product in the case if the third silver atom is added to these two. Another conclusion is the discovery of channels along which silver ions can move freely (Fig. 6).

Finally, a very important conclusion is the position of interstitial silver ion in the lattice stated by Naumov.

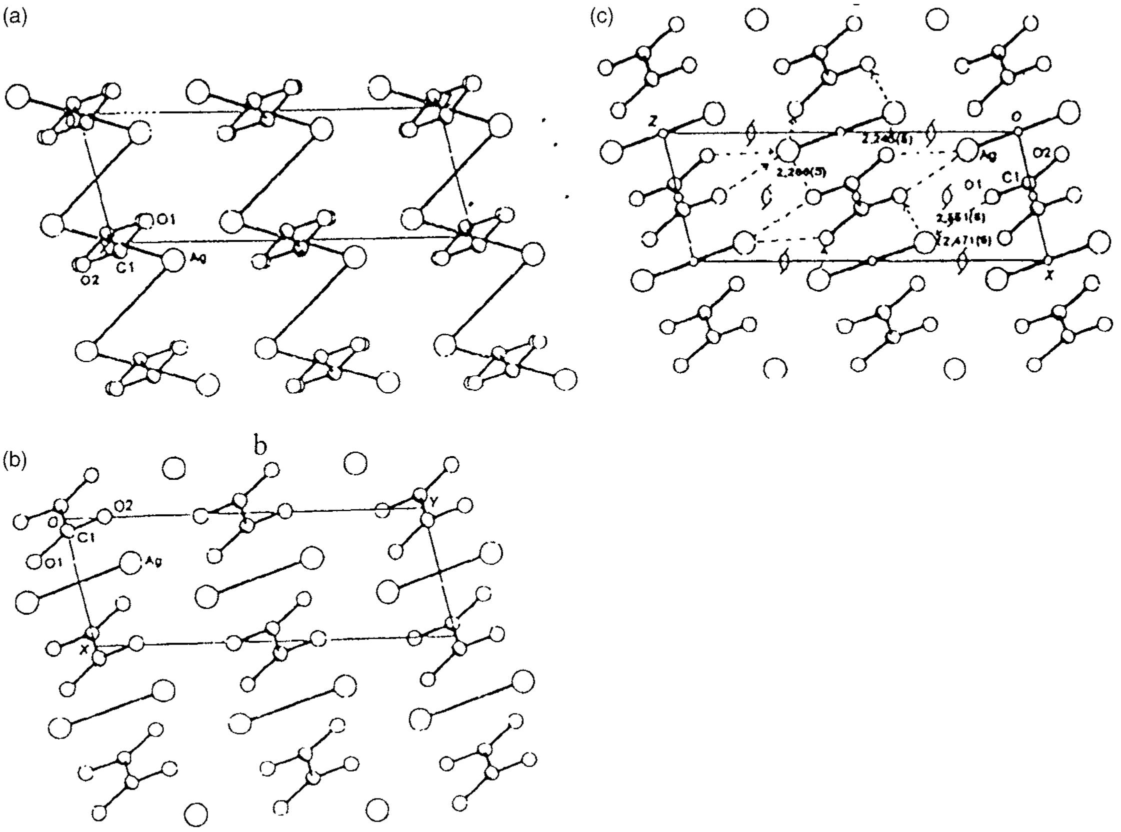


Fig. 5. The projections of $Ag_2C_2O_4$ structure on the monoclinicity plane according tot he models proposed by Griffit (a); Kolesnikov (b); Naumov (c).

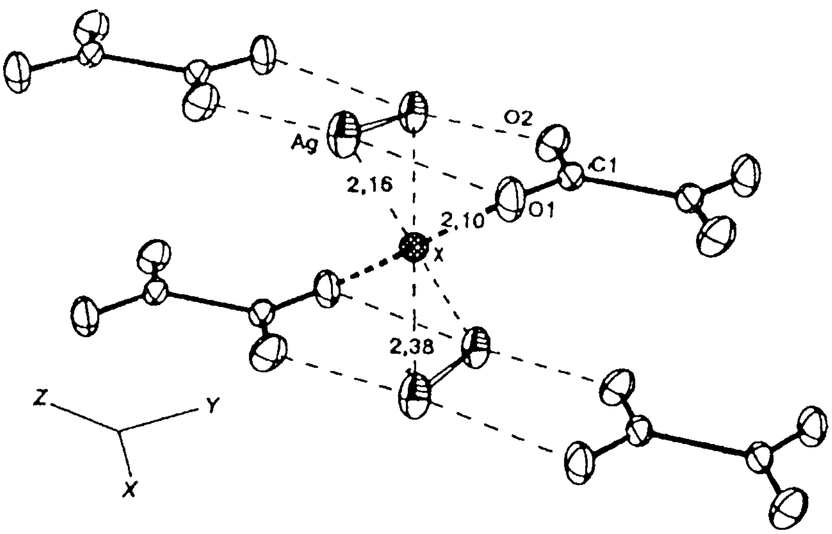


Fig. 6. The surroundings of the most probable position X of interstitial Ag^X ion in $Ag_2C_2O_4$ structure.

This position implies a close contact between silver and the oxygen of oxalate ion providing the possibility of preferential electron transfer from an oxalate ion to a silver ion located in interstices.

4. The features of thermal decomposition: the morphology of the initial stage

Even the first studies of the kinetics of silver oxalate thermal decomposition [33] pointed to a specific character of the kinetic curve. After some induction period, the rate of the process increases to a maximum value, then decreases. As an example, the plots of pressure and rate versus time taken from [7] are shown in Figs. 7 and 8. This shape of thermal decomposition curves, which resembles those characteristic of autocatalytic reactions, as in the case of potassium permanganate, predicts a chain and autocatalytic mechanism of the reaction [6,13,33].

The methods to investigate the thermal decomposition of silver oxalate can be different: in some cases, the amount of gas evolved during decomposition is determined with the help of gas burette (volumetric method); in other cases, the changes of pressure caused by gas evolution in a closed system are measured; the changes of mass during the reaction are determined in the third group of methods (gravimetry).

The application of these classical methods does not ensure the information necessary for the investigation of the mechanism of silver oxalate thermal decomposition that is known to proceed via a complicated sequence of electronic and ionic stages. Because of this, along with these methods intended for the estimates of the overall kinetics of the process, other physical methods are used to study the thermal decomposition (the studies of electrical conductivity, absorption spectra, dielectric losses, electron paramagnetic resonance spectra, etc.). These methods, directed at the investigation of separate stages in the thermolysis, were an inherent part of the overall program aimed at the investigation of silver oxalate thermal decomposition.

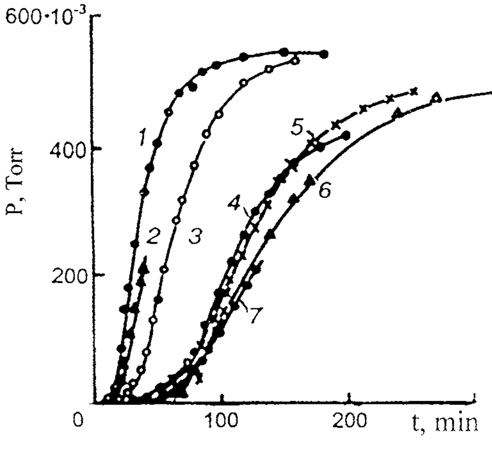


Fig. 7. Plots of pressure vs. time for $Ag_2C_2O_4$ decomposition: (1 and 2) 125 °C; (3) 120 °C; (4 and 5) 115 °C; (6 and 7) 110 °C.

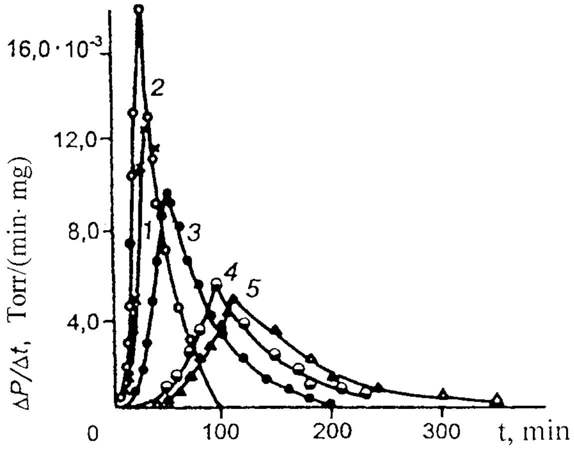


Fig. 8. Plots of rate vs. time for silver oxalate decomposition at different temperatures: (1) 125 °C; (2 and 3) 120 °C; (4) 115 °C; (5) 110 °C.

Thermal decomposition of silver oxalate was found to be very sensitive to the "life story" of the preparation: the method of its preparation [31], storage [7], preliminary treatment with chemical reagents [34,35], irradiation [36,37], mechanical action [38–43], and the properties of the medium in which the decomposition was carried out [12,44,45]. These factors are especially essential at the beginning of the process when they determine the duration of induction period preceding the decomposition, and the kinetics of the initial period of thermal decomposition, which can be described by either exponent or power function [37]. The questions under discussion were: (i) whether the nuclei of metallic silver are formed during the thermal decomposition, and if yes, (ii) where they are formed, within the volume or at the crystal surface, and (iii) whether crystal chemical correspondence (topotaxy) exists between the lattice of the metallic silver formed and the lattice of the initial oxalate [9,32,34].

As regards to the differences between the exponent and power function of the decomposition, it was found that the decisive factors are the real structure of the initial lattice and defect content. The thermal decomposition of freshly prepared silver oxalate crystals obtained at high supersaturation (for example, by pouring the solutions together rapidly) is better described at the initial stage of the reaction by an exponent, because the development of the reaction along linear defects randomly distributed in the crystal (dislocations) correspond better to this case [37]. The crystals grown under the conditions where there are only few defects, or those that have been aged (when the defects get ordered and some of them disappear due to polygonization) decompose according to the power law.

MacDonald [13] who studied the behaviour of silver oxalate crystals heated under the microscope reported that the crystal gets darker throughout its volume during the decomposition, changing its colour from reddish-brown to opal. MacDonald did not succeed in discovering the formation of separate nuclei during the decomposition. Tompkins [6] who studied silver oxalate decomposition under the action of light came to a similar conclusion. However, Griffith [46] who studied the structure of silver oxalate and structural changes during thermal decomposition, indicates that silver nuclei are formed as face-centred metallic silver. When they reached a size of 10^{-5} m they stopped growing. Other evidence of the formation of nuclei during the decomposition appeared [37] with a reference to unpublished Barthlet's work, in which he described the observation of nuclei of the reaction product on carefully grown defect-free crystals kept for some time after being grown. These nuclei were miniature blocks that stopped growing when they reached a definite size.

A final conclusion that the thermal decomposition of silver oxalate proceeds via the formation and growth of nuclei was made after Branitsky et al. [47] reported their optical and electron microscopic studies of the structural and morphological features of silver oxalate decomposition under heat, light and reduction by hydroxylamine. Silver oxalate preparations obtained by different methods were used in the investigation. In one case, the preparation was obtained by simultaneous slow addition of 1.2 M solutions of silver nitrate and oxalic acid (preparation No. 1), in another, material from preparation No. 1 was recrystallized from ammonia as this was done in [13]. This preparation was called No. 2. Preparation No. 3 was obtained by rapid destruction of the ammonical complex by an excess of oxalic acid. Preparation No. 4 was prepared by means of the counter diffusion of Ag^+ and $C_2O_4{}^{2-}$ ions through a layer of pure water for 2 months, then the crystals were isolated, washed with water and dried.

Since silver oxalate is sensitive to the action of electrons and decomposes rapidly, the surface was investigated by self-shaded carbon replicas. The observations of the silver oxalate surface revealed that the surface of the crystals of preparation No. 1 is more perfect than that of preparation Nos. 2 and 3. The most perfect surface is that of preparation No. 4 that was used for further investigations. The crystals were heated for several hours in air at a temperature of 120–140 °C.

The results demonstrated that it is really impossible, as MacDonald indicated [13], to detect silver nuclei with a usual microscope. However, electron microscopic observations showed that the nuclei are formed during thermal decomposition as small silver particles. The nuclei usually appear at the surface sites where defects are present, or in the vicinity of sites where dislocations come onto the surface; the latter can be detected at etch spots. The number of nuclei gradually increases during the decomposition. An important result obtained by the authors of this work is the observation that new nuclei are formed in the vicinity of the old ones, thus forming the so-called swarm-like congregations [48]. After each nucleus reaches the size of 0.2–0.5 μm, their growth decelerates substantially and soon stops completely. The picture observed during the photolysis of silver oxalate under the UV light is similar in general, but the mean particle size at which the growth stops is much less and varies within the range of 5–200 nm. Besides, no swarm-like congregations are observed during photolysis. The observations of Branitsky were generally confirmed by later investigations of the nucleation during the thermal decomposition of silver oxalate carried out by Leiga [49,50]. An important item of Leiga's investigations was the fact that the nuclei were oriented along the *c* axis of crystal. Besides, it was demonstrated that silver was released in two forms during thermolysis. The first type of nuclei was a well-crystallised face-centred silver crystal. The crystals of the second type looked like spots of irregular, often random shape; they were also cubic-structured silver having interatomic distances differing from those existing in the usual silver lattice and are intermediate with respect to the distance between silver atoms in metal and in oxalate.

The author of [47] assumes that after the removal of CO_2 from the lattice the silver ion passes into the space between silver layers already existing in the lattice. The distance between silver atoms becomes 0.310 nm, which is less than the distance between silver atoms in oxalate lattice but more than the lattice of metallic silver (0.288 nm). An orientational correspondence is observed between the lattices of silver and silver oxalate.

Thus formed silver is in metastable state and differs by its physicochemical characteristics from compact silver. The most striking difference is high catalytic activity [51]. After the decomposition has started, changes occur in the electrical, optical and spectral properties of silver oxalate.

The change of conductivity occurs during the first moments of thermal decomposition, which is likely to be due to the absorption of transfer-carrying interstitial silver atoms by the growing nuclei. Then after the minimum value is achieved, the conductivity increases due to the formation of metallic silver particles (Fig. 9) [52].

The investigation of the kinetics of thermal decomposition in parallel with the conductivity of crystals with the help of contact-free pondermotive method showed that after thermal decomposition has started, the correlation between reaction rate and the concentration of interstitial silver ions, typical of the initial period of the reaction, now disappears (Fig. 10) [53]. The assumed reason of this phenomenon was the change of the limiting stage of this reaction that occurred when the interface between the initial silver oxalate and the reaction product (metallic silver) appeared. Under new conditions, due to the possibility of topotaxial transition from the initial silver oxalate structure to the structure of reaction product [32], the concentration of interstitial ions stops being a decisive parameter. However, this assumption was not verified.

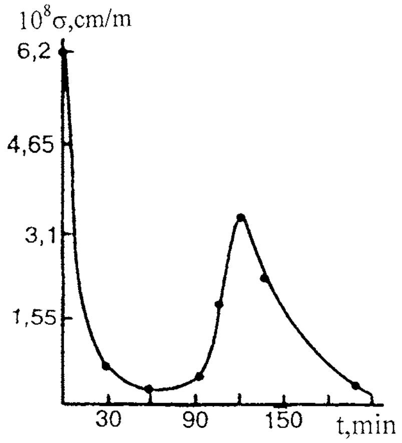


Fig. 9. The change of specific conductivity of silver oxalate single crystal during its thermal decomposition.

The data on dielectric losses during thermal decomposition is in agreement with these data (Fig. 11). At first the dielectric constant decreases, then increases. It is important to note that these changes in the dielectric constant not always remain constant during the process. If the thermal decomposition of silver oxalate is interrupted, the character of changes in dielectric constant during the storage of a partially decomposed sample for 24 h will be different [54].

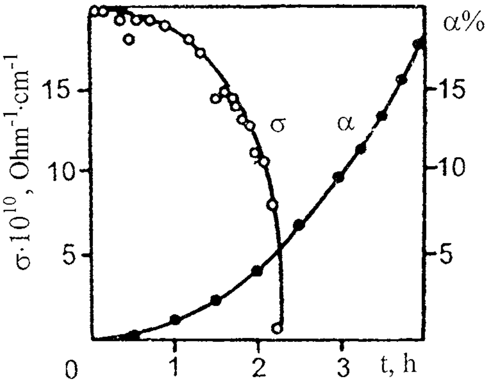


Fig. 10. The change of ion conductivity of silver oxalate during its thermal decomposition in vacuum at 135 °C: (α) curve corresponding to thermal decomposition; (σ) conductivity at alternating current with a frequency of 400 Hz.

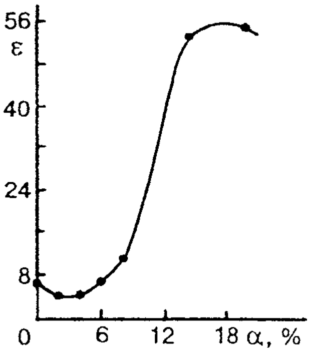


Fig. 11. The dependence of dielectric constant (ε) of $Ag_2C_2O_4$ on the decomposition extent (α).

The changes in the curve of thermodepolarization currents occur during thermal decomposition (Fig. 12). At early stages of thermolysis, thermodepolarization current decreases [53]. While photo-current is not detected in the initial silver oxalate until the wavelength of the falling light decreases to 600 nm, the photo-current appears in partially decomposed silver oxalate. When heated to 210 K, photo-current decreases sharply but thermoionic current appears instead (Fig. 13). The reasons causing photo-current and thermoionic current are likely to be connected with the ionisation of silver particles under the action of light and heat [53].

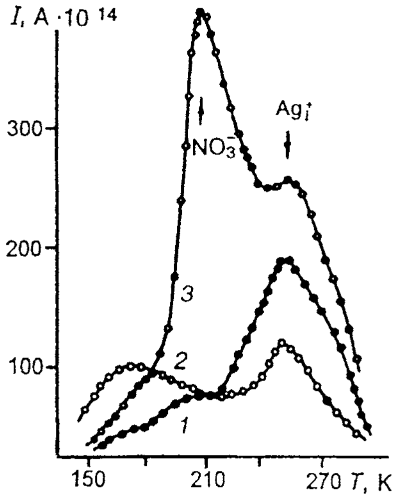


Fig. 12. Thermodepolarization current $Ag_2C_2O_4$: (1) initial silver oxalate; (2) silver oxalate partially decomposed (thermally) till $\alpha = 5\%$; (3) silver oxalate treated with $Ag(NO_3)$ solution (0.1N).

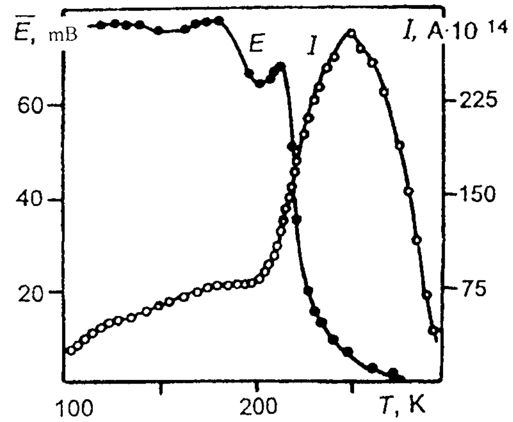


Fig. 13. Temperature dependence of photo-EMF (*E*) and thermoion current (*I*) in $Ag_2C_2O_4$ partially decomposed thermally.

5. The effect of preparation method: the effect of environment

It was demonstrated in the first studies of the kinetics of thermal decomposition that the reactivity of silver oxalate was extremely sensitive to the method of its preparation. For example, it was found [8,13,33] that silver oxalate obtained by pouring together $AgNO_3$ and $Na_2C_2O_4$ under the excess of oxalate ion decomposes, other conditions being kept constant, more rapidly than that prepared from the solution containing silver nitrate in excess. The fact that the observed effect is due not to the presence of nitrate ions but to silver ions in excess is proved by similar results obtained in the case when silver oxalate is prepared from silver sulphate solutions. It was also discovered that if the decomposition was carried out under fused paraffin, the decomposition rate was slower than in vacuum. However, this was not observed under a layer of gelatin.

MacDonald and Sandison [34] studied the effect of the liquid medium on the rate of silver oxalate thermal decomposition in more detail. They found that paraffin, dichlorobenzene and dibenzyl decelerate the reaction while phenol, saccharose or glucose syrup, aniline and benzaldehyde accelerate it. Commenting on these data Erofeev et al. [7] noted that the reducers accelerate thermal decomposition while the substances exhibiting oxidative action act as inhibitors.

The effect of preparative conditions on the rate of silver oxalate thermal decomposition was studied

Table 1
The formation of $Ag_2C_2O_4$ crystals depending on the nature of the depositing agent, concentration of initial solutions and the order of pouring them together

Pouring order	Concentration (N)	Crystal shape	Mean size (μm)
Simultaneous pouring of the solutions: $AgNO_3$ and $Na_2C_2O_4$	0.1	The major part of crystals are rhombs; prisms and hexagons are also present	1–2
	0.01	Rhombs, prisms, hexagons	4–6
Addition of $AgNO_3$ solution to $Na_2C_2O_4$ solution	0.1	Rhombs, prisms	2–4
	0.01	Rhombs, prisms	6–10
Addition of $Na_2C_2O_4$ solution to $AgNO_3$ solution	0.1	Indefinite shapes	1
	0.01	Rhombs, prisms	1–2
Simultaneous pouring of $AgNO_3$ and $H_2C_2O_4$ solutions	0.1	Rhombs, hexagons	10–12
	0.01	Prisms	8–10
	0.1	Rhombs, hexagons	6–8
Addition of $AgNO_3$ solution to $H_2C_2O_4$ solution	0.01	Rhombs, prisms	4–8
	0.1	Rhombs	16–20
Addition of $H_2C_2O_4$ solution to $AgNO_3$ solution	0.01	Rhombs, prisms	12–14

rather thoroughly by Eroshkin [11]. He demonstrated that the preparation conditions affect first of all the shape (habitus) and size of the resulting crystals; this fact alone can cause the change of the process rate. The results obtained by Eroshkin are shown in Table 1. One can see that the composition, concentration and the order of pouring the components together have a strong effect on both the size and habitus of silver oxalate crystals. This influences the rate of thermal decomposition (Fig. 14). It follows from the data shown here that the highest decomposition rate is exhibited by silver oxalate crystals obtained by adding a 0.1N $Na_2C_2O_4$ solution to 0.1N $AgNO_3$ solution (curve 1). The crystals obtained by simultaneous pouring these solutions together are decomposed slower (curve 2). The addition of 0.01N $AgNO_3$ solution to 0.01N sodium oxalate solution gives a sample corresponding to curve 3. Silver oxalate obtained from 0.01 N solution of oxalic acid (curve 4) decomposes slower than that obtained from the sodium salt. The preparations obtained from more concentrated solutions decompose slower (curve 5). The lowest decomposition rate is exhibited by the sample obtained by adding a 0.1N solution of oxalic acid to 0.1N $AgNO_3$ solution.

A substantial effect on crystal size is caused by pH of the solution. When the pH changes from 7 to 1, the size of crystals increases. According to this, the ratio of crystal surface to volume changes, which finally leads to the decrease of silver oxalate thermal decomposition rate (Fig. 15, Table 2). For other later works dealing with the influence of preparative method and the medium on thermal decomposition of silver oxalate, see also [12].

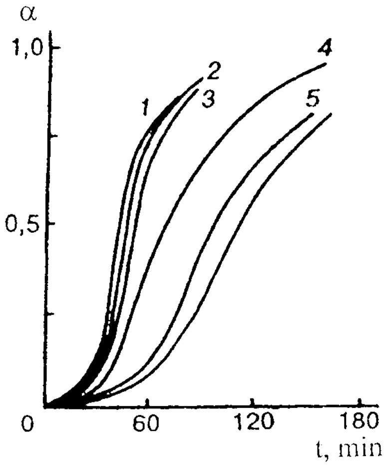


Fig. 14. The effect of preparation method on the rate of thermal decomposition of silver oxalate at 134 °C. For explanations, see text.

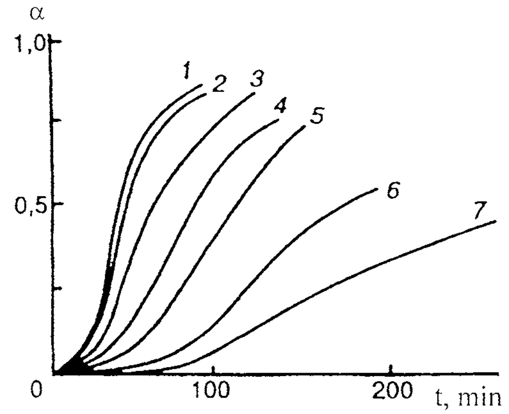


Fig. 15. The effect of pH of initial solutions on the decomposition of $Ag_2C_2O_4$ at 134 °C: (1) pH = 7.1; (2) pH = 3.6; (3) pH = 2.9; (4) pH = 2.1; (5) pH = 1.83; (6) pH = 1.2; (7) pH = 1.0.

The thermal decomposition of silver oxalate is sensitive to the composition of the atmosphere that surrounds the substance. The process is accelerated in the presence of helium, argon and neon but slightly decelerates in the presence of krypton and xenon in comparison with the process carried out in vacuum [44,45]. In hydrogen, thermal decomposition proceeds at a much higher rate than in vacuum. Vice versa, oxygen is a strong inhibitor of the process. Oxygen has a strong effect not only on the initial period of reaction but also on its further development. It was believed [13,36,45,55] that the inhibiting action of oxygen was due to the poisoning of active centres or to the formation of electron scavengers on the silver surface competing with silver centres, thus causing the disappearance of the autocatalytic character of decomposition.

Table 2
Specific surface of the preparations obtained by pouring together the solutions $Na_2C_2O_4$ and $AgNO_3$, depending on the solution pH

Preparation No.	pH	m^2/g
1	7.1	2.67
2	5.52	2.17
3	4.56	2.05
4	3.6	1.5
5	2.9	0.9
6	2.1	0.5
7	1.83	0.32
8	1.1	0.15
9	1	0.1

Nitrogen is inert and does not have any substantial effect on thermal decomposition rate [55]. The same is true for the effect of CO_2 on thermolysis rate [33,44,50]. Nitrogen oxides have a decelerating effect on the decomposition rate of both the pure silver oxalate and its mixtures with $Hg_2C_2O_4$ [56]. The explanation of the decelerating action of nitrogen oxides is the same as that for oxygen [57]. Water vapour decelerates the decomposition of silver oxalate [58]. A strong accelerating action is caused by mercury vapour [13].

6. The mechanism of silver oxalate thermal decomposition

The authors of the earliest works dealing with thermal decomposition of silver oxalate tried to describe the mechanism of thermal decomposition within the Herny–Mott model that was previously used successfully to interpret the photolysis mechanism of silver halides and the photochemical and thermal decomposition of the azides of heavy metals [59–61]. The essence of this model is a sequence of alternating processes taking part at defects and involving the formation and capture of an electron that passed into the conductivity zone as a result of the anion excitation. Since the capture center becomes more negative than the rest of the lattice, mobile cations approach it and get stuck to it. After the addition of a cation, the charge of the center becomes more positive, compared to the surrounding sites, and it becomes a scavenger for the next electron, etc. This special internal electrolysis causes the formation and growth of the reaction product nucleus. This special internal electrolysis causes the formation and growth of the reaction product nucleus. However, when the Herny–Mott model was transferred to thermal decomposition of silver oxalate, the growth of nucleus was stipulated to occur in this case not due to the transfer of cations but due to the deformation of the lattice resulting from the removal of two CO_2 molecules during decomposition [9]. Later, when silver oxalate was found to possess no photoconductivity, the model of silver oxalate thermal decomposition was modified by introducing the notion of electron excitation during photolysis and thermolysis not into the conductivity zone but into an exciton state [9]. For oxalate photolysis, the following description is valid:

$OX^{2-} + h\nu \xrightarrow{k_1} [OX^-]^-$,

the formation of a stabilized exciton

$[OX^-]^- \xrightarrow{k_2} OX^{2-}$, recombination of an exciton

$[OX^-]^- + h\nu \xrightarrow{k_3} [OX]^{2-}$, double exciton

$[OX]^{2-} \xrightarrow{k_4} [OX^-]^-$, and its recombination

$[OX]^{2-} \xrightarrow{k_5} 2CO_2 + 2e^-$,

chemical reaction with the formation of anion vacancy and two electrons

For the steady state, the decomposition rate will be expressed as:

$$R = \frac{k_1 k_3 k_5 N I^2}{(k_2 + k_3 I)(k_4 + k_5)}$$

Here N is the number of vacancies per cm^2, k_1 and k_3 the probabilities of the excitation of oxalate ion in the neighbourhood of the anion vacancy, and I is the intensity of photolyzing light.

Since the reaction rate is proportional to I^2, we can conclude that $k_2 \gg k_2 I$ and $k_4 \gg k_5$. Then the rate equation will be:

$$R = \frac{k_1 k_3 k_5 N I^2}{k_2 k_4}$$

A similar scheme was proposed [17,62] for the thermal decomposition of silver oxalate. This scheme took into account specific features of silver oxalate thermal decomposition that were discovered in our works, and first of all the fact that efficient centres of exciton trapping are interstitial silver ions, and the sensitivity of the process to the addition of electron donors and acceptors.

$OX^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [OX]^{2-}$	The formation of exciton
$2Ag^+ + [OX]^{2-} + T \xrightarrow{k_3} 2Ag + C_2O_4{}^0$	The decomposition of exciton at traps, i.e. interstitial ions
$\square_K + T \xrightarrow{k_4} \square_K/T$	Recombination of interstitial silver ion and the cation vacancy
$C_2O_4{}^0 \xrightarrow{k_5} 2CO_2 + \square_A$	The decomposition of oxalate radical with the formation of anion vacancy gaseous CO_2 molecules
$C_2O_4{}^0 + \square_K \xrightarrow{k_6} M$	The formation of a hypothetical product due to the capture of positive hole by a cation vacancy

For the steady state of exciton formation and the decomposition of radicals formed as a result of electron loss by excitons, introducing some simplifying assumptions (for details, see [55]), the rate can be expressed as:

$$V = \frac{k_1 k_3 k_5 [OX^{2-}]}{k_2 k_4 + k_3 \delta (k_5 + \square_K k_6)}$$

where

$$\delta = \frac{\square_K}{Ag^+/\square_K}$$

Though in comparison with the previous scheme this one is undoubtedly a substantial step ahead, it is not free from shortcomings. One of them is the assumption that the $C_2O_4{}^0$ radical decomposes only after the oxalate ion looses two electrons, though it can be assumed rather reasonably that the decomposition can take place when only one electron is lost. It is clear that the probability of this process is larger. Besides, the physical sense of the constant k_6 remains obscure.

Vagueness concerning the possibilities and limits of the existence of the center that captures a positive hole on a cation vacancy corresponds to the uncertainty in the estimates of the role of this center in changing thermal stability. It is indicated in [17] that the fixing of a positive hole should lead to the increase of oxalate thermal stability while the reverse is proved in [63].

As in the models considered earlier, the exciton scavenger (interstitial ion) is immobile while the exciton is mobile. Because of this, it is not clear how the metallic silver lattice is formed from the silver oxalate lattice. The limiting stage is assumed to be the decomposition of $C_2O_4^0$ radical at a rate constant k_5.

The notion of the exciton mechanism for the thermal decomposition outlined was used by Leiga [49,50] to build a scheme for the thermal decomposition mechanism. According to his scheme:

1. At first, oxalate ion is excited due to the fluctuation of phonons:

   $C_2O_4^{2-} \rightarrow (C_2O_4^{2-})^*$

2. This excitation can be localised on the scavenger (an impurity of crystal defect):

   $(C_2O_4^{2-})^* + T \rightarrow (C_2O_4^{2-})^*T$

3. An interstitial ion moves to the site of exciton capture:

   $(C_2O_4^{2-})^*T + 2Ag^+ \rightarrow Ag_2T + C_2O_4^0$

4. This results in the formation of silver clusters and $C_2O_4^0$ radicals. $C_2O_4^0$ radical decomposes:

   $C_2O_4^0 \rightarrow 2CO_2$

5. The localisation of oxalate ion excitation occurs at a site neighbouring to the metal particle; this is followed by the addition of silver ions:

   $Ag_2T + (C_2O_4^{2-})^* \rightarrow (Ag_2TC_2O_4^{2-})^*$

   $(Ag_2TC_2O_4^{2-})^* + 2Ag^+ \rightarrow Ag_4T + 2CO_2$

The works that appeared by this time [64–66] proved that electron excitation was only a background at which the consequent chemical reactions developed; these studies stimulated the elaboration of an alternative mechanism of thermal decomposition. In the aforementioned model, the main attention was paid to the fate of the exciton state of oxalate ion while no special attention was paid to the formation of a new phase (metallic silver) [24]. Two important features of the thermal decomposition of silver oxalate were taken into account in this case: first, the substantial role of interstitial silver ions, more mobile in comparison with other silver ions, in the formation of a nucleus; second, a stop of the nucleus growth when it reaches some critical size (about 200–500 nm).

According to this model, the growth of the silver nucleus occurs mainly due to the migration of interstitial ions to the site of exciton capture. Depletion of the interstitial ion concentration in the region adjacent to the nucleus while the nucleus grows, and especially while the nuclei begin to compete with each other, is the reason why the growth of the nucleus stops, according to [24]. Evidence in favour of this hypothesis is the calculation of nuclei size performed taking account of the known diffusion coefficients and concentrations of interstitial silver ions; the results of these calculations demonstrated the correspondence with the data on nucleus growth rate measured experimentally. An indirect confirmation of the model can also be the fact that the critical size of nuclei depends on the concentration of interstitial ions in the lattice governed by the addition of dopants.

As regards the chemical stage of exciton decomposition, i.e. the breakage of bonds inside an oxalate ion (either excited or the one that has lost one or two electrons) this item was omitted in [24]. This question remains not clear even now, to say nothing of the data indicating that the primary process in the decomposition of oxalate ion is the breakage of C–C bond which is longer in the crystal structure than its normal length in an isolated ion.

Some progress in the understanding of the mechanism for the decomposition of silver oxalate was outlined in connection with the results of the investigations of the silver oxalate crystal structure performed recently [31,32]. The results of these investigations showed that the hypothesis concerning the possibility of the topotaxial transition of silver oxalate structure into metallic silver structure has been confirmed experimentally. Moreover, the routes (channels) along which interstitial ions can move have been shown, and the position of an interstitial silver ion in the lattice has been determined at which the distance between it and the site of electron density localisation in the $C_2O_4^{2-}$ ion (oxygen atom) decreases to 0.21 nm [32].

Due to the investigations carried out in [18,19], a substantial progress was achieved in the understanding of the mechanism of the photochemical decomposition of silver oxalate. However, the scheme of the mechanism of the thermal decomposition of silver oxalate still is not completed yet.

This allows expecting that the creation of a model describing the mechanism of the thermal decomposition of silver oxalate (involving the necessary quantum-chemical calculations of electron transfer from oxalate ion to silver ion, and a more detailed consideration of a crystal chemical mechanism describing the growth of metal nucleus, along with the determination of reasons for the limit of nucleus growth and a swarm-like character of their occurrence) will be continued in the nearest future to its completion.

7. The effect of heterogeneous inorganic additives

The effect of heterogeneous inorganic additives on the rate of the thermal decomposition is well known. The reasons for this phenomenon can be different. This may be the consequence of the contact potential difference which, in turn, causes the change of local concentrations of electrons and holes in the near-contact region [67,68], binding of electrons on free d-orbitals of the additive atoms [69], ion diffusion through the contact surface [70] and chemical interaction between the additive and the decomposing substance [71].

The effect of oxide heterophase additives on the rate of silver oxalate thermal decomposition was considered in detail in [68]. These authors performed a special series of experimental studies to reveal how heterophase additives can affect thermal decomposition of silver oxalate. Oxide and sulphide powders were used as mechanical impurities. They were semiconductors of either n-type (ZnO, Ag_2S) or p-type (NiO, Cu_2O). They were added to oxalate particles by mixing during the crystallisation of silver oxalate preparation by pouring together $AgNO_3$ and $H_2C_2O_4$ solutions, which provided larger contact in comparison with usual mechanical mixing. The rate of thermal decomposition was measured in vacuum at 136 °C with the help of Mac–Ben type quartz balance. Besides, experiments were carried out aimed at the determination of the delay to ignition of silver oxalate with additives.

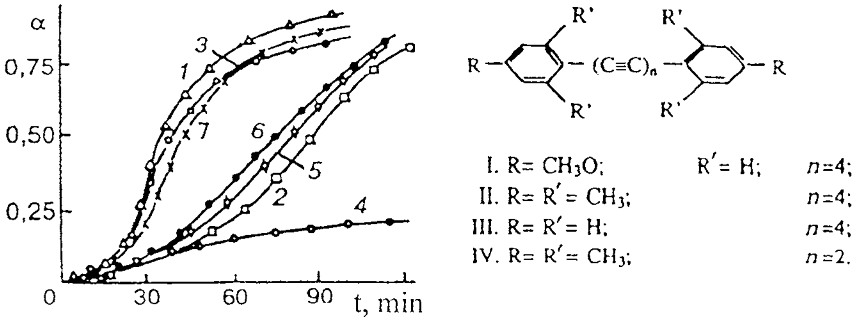
The results of experiments carried out by the authors of [68] showed that the contact of silver oxalate with additives having a higher work function of electrons than silver oxalate (NiO, Cu_2O) accelerates the reaction while with the additives having lower work function of electrons (ZnO, Ag_2S) the rate of thermal decomposition decreases. The results are interpreted as a consequence of semiconductor catalysis of the thermal decomposition. The authors of [68] think that the limiting stage of this process is either the formation or the following decomposition of the $C_2O_4^0$ radical.

These data are in contradiction with the results of Sheppard and Vanselow [35] who demonstrated that the addition of Ag_2S accelerates thermal decomposition of silver oxalate. Still less clear is the effect of metal powders as additives. According to the data of [72], metal powders either have no effect (Mg, Al) on thermal decomposition or slow it (Pb, Fe, Cu).

8. The effect of organic additives on the rate of silver oxalate thermal decomposition

The aforementioned data concerning the influence of inorganic oxide additives, electron donors or acceptors, call to the data on the effect of organic additives with the same properties. Organic dyes are usually used as these additives. Their advantage is the possibility to deposit them onto oxalate surface from solutions thus providing the contact between the salt and the additive at the atomic level which is very difficult to achieve in the case of oxide additives.

The first data on the effect of organic additives were reported by MacDonald and Sandison [34] who demonstrated that phenol, glucose, aniline and benzaldehyde accelerate thermal decomposition of silver oxalate while nitrobenzene, dibenzyl, paraffin decelerate it. The circumstance that reducers accelerate the decomposition and the oxidisers decelerate it was used later to work out a hypothesis concerning the reaction mechanism based on the assumption that the limiting stage of the reaction is the addition of an electron to a silver ion forming metal atom [45]. The effect of organic additives was studied in more detail in the works of Leiga and our laboratory. It was demonstrated in the works of Leiga [49,50] that organic dyes that are electron donors, such as triphenylamine, acridine orange and rhodamine B accelerate the thermal decomposition of silver oxalate while electron acceptors (tetracyanoethylene, Bengal rose and erythrosine B) decelerate the process. It was demonstrated in [73,74] that the addition of polyines slows the thermal decomposition of silver oxalate, the efficiency of deceleration increasing with the increasing length of the polyine chain in the molecule and



I. R= CH₃O; R'= H; n=4;
II. R= R'= CH₃; n=4;
III. R= R'= H; n=4;
IV. R= R'= CH₃; n=2.

Fig. 16. The kinetics of silver oxalate thermal decomposition at 133 °C without additives (1) and with the additives: 5 at.% HgI_2 (2); PbI_2 (3); as well as the substances I (4); II (5); III (6); IV (7).

with introducing electron donor substituents into *para-* and *ortho-*positions of the end aromatic rings (Fig. 16).

A more detailed investigation of the action of organic additives demonstrated that their action is much more diverse than it was assumed earlier, and can manifest itself in both the ionic and electronic stage of silver oxalate thermal decomposition.

8.1. The influence of additives on the ionic stage of the process

The influence of organic acid additives on the ionic stage of silver oxalate thermal decomposition was studied for the examples of dyes: xanthene (uranin, eosin, erythrosine, Bengal rose), oxyanthraquinone (alizarin) and azo dyes (methyl red, methyl orange, alizarin yellow, Congo red, tropeolin, acid chromium black, magnezon, zircanon) [75–77]. It was demonstrated that mechanical addition of dye powder up to 5% does not cause substantial changes in the rate of thermal decomposition but the introduction of dye by the deposition from solution at a concentration of 5×10^{-3} mol/l causes a substantial increase of the induction period, i.e. slows thermal decomposition. Fig. 17 shows the results of the studies of kinetics of the thermal decomposition of silver oxalate at 134 °C, after treatment with a solution of methyl red. The positions of kinetic curves demonstrate that the addition of dye slows the decomposition, the braking effect being higher for higher concentration of the solution.

The studies of the spectra of dyes in solution and in the adsorbed state on inert substrate (glass) and on oxalate crystals were carried out with the SF-10 and SFD-2 spectrophotometers and demonstrated that the adsorption of a dye on silver oxalate causes a shift of the absorption band to longer wavelength. This effect, which was observed earlier in the investigation of dye adsorption on silver halides [78], is evidence that chemical interaction takes place between the oxalate and the dye adsorbed on its surface. This interaction can be represented best of all as the addition of surface silver ion to the charged carboxylic group of the dye. This interaction is accompanied by the rearrangement of the molecular structure from benzoid into quinoid which is the reason for the shift of adsorption to longer wavelengths.

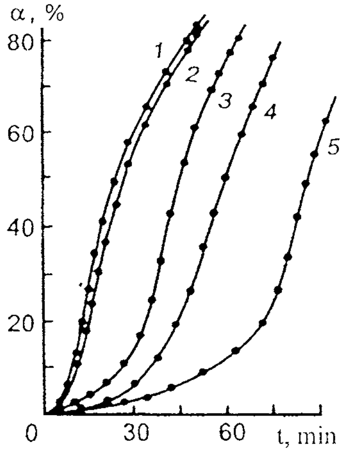


Fig. 17. Kinetic curves of thermal decomposition of silver oxalate at 134 °C with methyl red added: (1) the sample without additives; (2) 5% of dye added as a mechanical mixture; (3–5) after the treatment with aqueous solutions of methyl red with concentrations 7.4×10^{-4}, 5.0×10^{-3} and 1.0×10^{-2} mol/l, respectively.

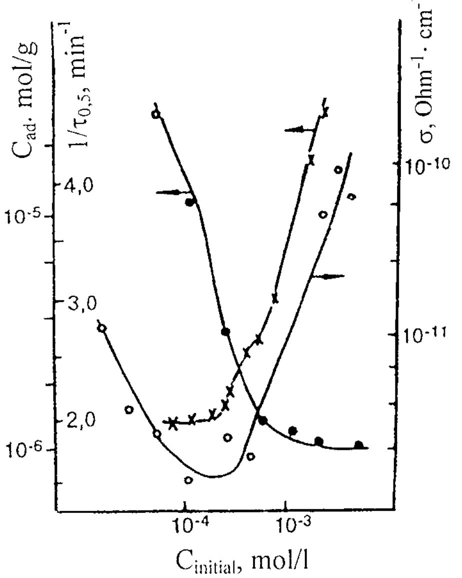


Fig. 18. The effect of erythrozine additive adsorbed from solution on the conductivity (empty circles) and thermal stability of silver oxalate (expressed as $1/\tau_{0.5}$; black circles); C is the concentration of the adsorbed dye (crosses).

Together with this, a decrease of the ionic conductivity of silver oxalate occurs. This is attributed to interstitial silver ions and weakly bound silver ions present at the defect sites (the contribution from the latter is clearly exhibited in the changes of conductivity with alternating current [79]).

The acid dyes of the uranin series have a similar effect on the rate of thermal decomposition. These dyes include erythrosine, its inhibiting action on the thermal decomposition of silver oxalate was noticed by Leiga [50]. Fig. 18 shows how the rate of thermal decomposition expressed as $1/\tau_{0.5}$ ($\tau_{0.5}$ being half-life of silver oxalate) decreases with increasing concentration of erythrosine in solution. In parallel, electrical conductivity of silver oxalate decreases which is the evidence that the dye binds mobile silver ions. The latter circumstance forces one to revise the explanation of the inhibiting action of erythrosine considering only its electron acceptor properties. A similar effect was observed when the additive was 5-methyl-7-oxy-1,3,4-triazaindolycin (sta-salt used in silver bromide photoprocesses as stabilizer) and its homologs were used as additives [74].

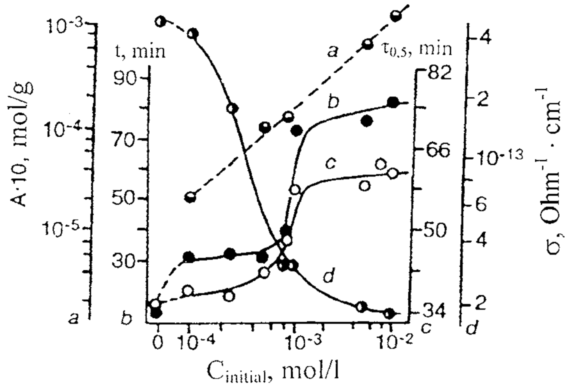


Fig. 19. The effect of the adsorption of sta-salt from aqueous solutions on physicochemical properties of oxalate: (a) the amount of sta-salt adsorbed per 1 g of oxalate; (b) the tendency to chemical reduction in hydroquinone solution; (c) oxalate half-life with respect to thermal decomposition at 135 °C; (d) dc conductivity of $Ag_2C_2O_4$.

It was found that, similarly to the interaction of sta-salt with the crystals in the photographic process, the adsorption of sta-salt and its homologs on the surface of silver oxalate leads to strong inhibition of silver oxalate thermal decomposition and to the decrease of the rate of its reduction in hydroquinone solution. The inhibition during the adsorption of sta-salt is accompanied by a strong decrease of the conductivity (Fig. 19). The binding of mobile interstitial ions is likely to be the reason of the observed inhibition in this case, too.

8.2. The influence of additives on the electronic stage of the process

We have already mentioned the known works of MacDonald and other authors in which the reducers (electron donors) accelerate silver oxalate thermal decomposition and the acceptors (electron acceptors) slow this process. These data, as well as our opinion on the mechanism of silver oxalate thermal decomposition [45] were in contradiction with the data on the influence of inorganic additives on the rate of silver oxalate thermal decomposition suggesting that electron donors should decelerate thermal decomposition while acceptors, to the contrary, should accelerate it.

In order to perform a test of how the additives of various organic reducers and oxidizers affect the rate

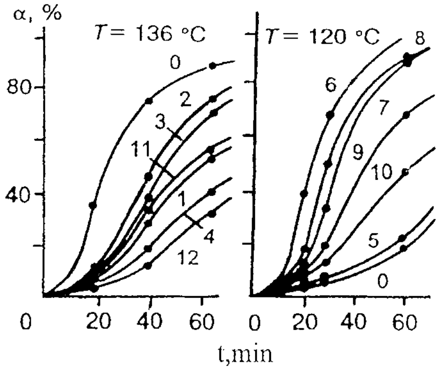


Fig. 20. The kinetics of $Ag_2C_2O_4$ thermal decomposition in the presence of electron donors and acceptors: (0) initial $Ag_2C_2O_4$; with additives: (1) *p*-benzoquinone; (2) fluoranile; (3) chloranile; (4) tetracyanethylene; (5) diphenylamine; (6) benzidine; (7) tetramethyl-*p*-phenylenediamine; (8) *n*-phenylenediamine; (9) *n*-aminophenol; (10) glycine; (11) hydroquinone; (12) pyrogallol.

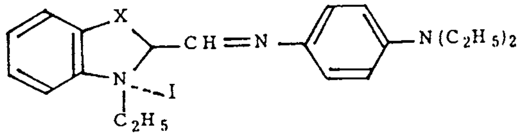
of thermal decomposition, experiments were performed to reveal the effect of the addition of electron donors and acceptors on the thermal decomposition of silver oxalate. The experiments involved electron donors (diphenylamine, benzidine, tetramethyl-*p*-phenylenediamine) and acceptors (*p*-benzoquinone, fluoranile, chloranile, tetracyanethylene). The data on thermal decomposition of silver oxalate into which 5 mass% of an additive was introduced are shown in Fig. 20. One can see from these data that electron donors accelerate thermal decomposition while acceptors decelerate it.

The authors of [80] tried to decide what happened as a result of the interaction between an additive and silver oxalate surface. They used a typical electron donor diphenylamine and a typical acceptor tetraethylacetylene. The additives were adsorbed on silver oxalate surface from the gas phase. The colour of oxalate changed after the adsorption of donors. Its surface became blue. The change of adsorption spectrum corresponded to the formation of the oxidised form of diphenylamine [76]. It is evident that partial reduction of silver oxalate and the formation of metal nuclei catalysing further thermal decomposition should have taken place. Unlike the behaviour of donors, the adsorption of acceptors does not lead to any changes in the spectrum of the adsorbed substance. This may be due to the fact that the action of electron acceptor is exhibited not before thermal decomposition as it is the case with electron donors, but in its course since this is the stage that competes with the formation of thermal decomposition centres.

8.3. *The influence of additives sensitising thermal decomposition*

As we have already mentioned when describing the properties of silver oxalate, the width of the prohibited region for the electron transition from the valence zone to the conductivity zone is rather large in comparison with the phonon excitation. Besides, electron excitation in the oxalate ion and its transfer to a silver ion proceed via an intermediate exciton stage. Excitation of the oxalate ion, localisation of this excitation on a scavenger followed by the decomposition of oxalate ion with electron transfer to silver ion, determine the initiation of thermal decomposition process. Because of this, it should be expected that the additives simplifying electron transition but remaining unchanged themselves would provide multiple use of the additive during the process [81].

These additives were proposed by Mikhailov [82,83]. Relying on the similarity of the electron stages in photolysis and the thermal decomposition of silver oxalate, Mikhailov proposed to use spectral sensibilizers that are applied in the conventional silver bromide photographic process. A series of arylmethane, quinone–imine, polymethyne, azomethine, and azo dyes were used as additives:



azomethine dye

where X = -S-

As in the case of acid additives, the dyes were deposited on the silver oxalate surface from solution. The dependence of the acceleration of silver oxalate thermal decomposition on the extent of surface filling showed that a plateau was achieved when the concentration of additive increased till it formed a monolayer. It was shown in special experiments that up to 10% of the additive remained unchanged during the thermal decomposition of silver oxalate.

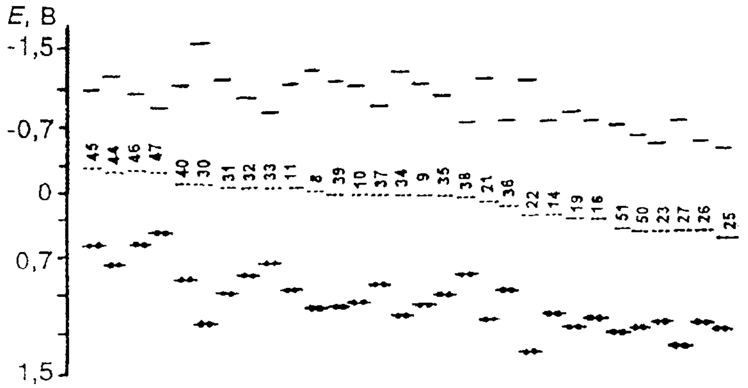


Fig. 21. The diagram of electron levels of dyes in the scale of redox potentials: (upper) the lowest vacant levels ($\varepsilon_{\mathrm{IV}}$); (lower) the highest populated levels ($\varepsilon_{\mathrm{ho}}$); (middle) redox potentials (E_{hyper}); (8) uranin; (9) eosin; (10) erythrosine; (11) Bengal rose; (14) malachite green; (16) crystal violet; (19) pyronin G; (21) acridine orange; (22) acriflavin; (23) thionine; (25) methylene blue; (26) capry blue; (27) phenosafranine; (30) 3,3′-diethylthiacyanine iodide; (31) 3,3′-diethylthiacarbocyanine iodide; (32) 3,3′-diethylthiadicarbocyanine iodide; (33) 3,3′-diethylthiatricarbocyanine iodide; (34) 3,3′-diethyloxacarbocyanine iodide; (35) 3,3′-diethyloxadicarbocyanine iodide; (36) 3,3′-diethyloxatricarbocyanine iodide; (37) 3,3′-diethylselendicarbocyanine iodide; (38) 3,3′-diethylselentricarbocyanine iodide; (39) 1,1′-diethyl-2,2′-quinocyanine iodide; (40) 1,1′-diethyl-2,2′-quinocarbocyanine iodide; (44) 1,1′-diethyl-4,4′-quinocyanine iodide; (45) 1,1′-diethyl-4,4′-quinocarbocyanine iodide; (46) 1,1′-diethyl-4,4′-quinodicarbocyanine iodide; (47) 1,1′-diethyl-4,4′-quinotricarbocyanine iodide; (50) azomethine dye (for the structural formula, see Section 8.3); (51) same as azomethine dye with X = –CH=CH–.

The mechanism of the accelerating action of the additives was considered from two points of view: on the basis of redox potentials of the dyes and from the viewpoint of the zone theory. The consideration based on redox potentials starts from the comparison of polarographic half-wave potentials of dye reduction ($E_{1/2}$) and the excitation energy (E_{max}) corresponding to energy difference between the upper filled electron levels and the lowest vacant ones. As in the case of silver halide photolysis [84], it was demonstrated that there was a correlation between the acceleration of silver oxalate thermal decomposition by an additive and which was called the hyper-redox potential. The highest activity was demonstrated by the additives with low-lying hyper-redox potential levels and E_{max} (Fig. 21).

A similar result was obtained on the basis of the zone scheme. The calculation procedure was described in [83]. The final result of the calculations was the comparison between the zone diagram in silver oxalate (composed according to the spectral dependence of photolysis and work function of electrons) and electron levels of dyes adsorbed on silver oxalate (Fig. 22). One can see that an additive accelerates thermal decomposition if its Fermi quasi-levels lie below the Fermi level of silver oxalate. The same compounds have the deepest vacant electron levels.

The action mechanism of these additives is assumed by Mikhailov to occur in two versions [82]. The first one involves the transition of an electron from silver oxalate to the dye under thermal excitation. As a result of electron capture, the system of electronic levels of the dye changes since ionisation potential decreases. The positive hole (which is $C_2O_4^-$ ion) formed as a result of the electron loss by silver oxalate lattice undergoes chemical transformation (decomposes with the evolution of two CO_2 molecules and transfer of the electron to silver ion) and thus disappears. The electron from the dye passes into the silver oxalate lattice where it is captured by a silver ion. The transfer of electron from dye to the silver oxalate results in the recovery of the basic state of the dye molecule. As a result of multiple repetition of these acts, the nuclei of metallic silver are formed in the silver oxalate lattice; they catalyse the further progress of the process.

In the second version for the sensitisation of silver oxalate thermal decomposition by dye additives, it is assumed that at first the electron subsystem of the additive gets excited. The electron passes from the excited additive molecule to the silver oxalate lattice where it is captured by a silver ion. The hole formed in

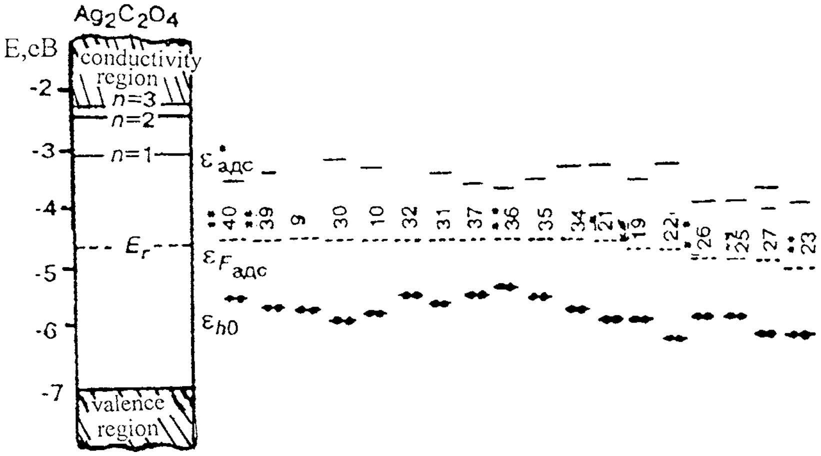


Fig. 22. The diagram of energy zones of silver oxalate and electron levels of dyes in the adsorbed state (on silver oxalate); $n = 1, 2, 3$—exciton levels (for detail, see caption of Fig. 21).

the dye acts as electron acceptor for a $C_2O_4^{2-}$ ion; it passes its electron to the dye and decomposes.

So, the basis of the model describing the action of sensitisers is a simultaneous manifestation of their donor–acceptor properties with respect to silver oxalate which provides a multiple use of the dye molecule to simplify electron transition from an oxalate ion to silver.

9. The influence of homophasic additives

The effect of the additives introduced into silver oxalate lattice during its preparation had been known since the earliest investigations dealing with the thermal decomposition of silver oxalate. We have already cited the works of MacDonald and Hinshelwood, as well as later investigators who pointed to a substantial dependence of the rate of thermal decomposition on the method of silver oxalate preparation, including the presence of foreign ions in solution. For example, the presence of nitrate ions in excess during the deposition of silver oxalate makes the thermal decomposition rate decrease [10,11,13]. To the contrary, the excess of oxalate ions during the preparation causes an increase in the rate of consequent thermal decomposition of silver oxalate [7]. The introduction of sodium ions from sodium oxalate and silver nitrate solutions into the synthesised silver oxalate lattice causes a decrease of thermal stability of the resulting oxalate [85].

The introduction of the ions with different valence (most often cations) into silver oxalate lattice causes the formation of additional ionic defects in the lattice. To understand how this happens, let us consider the addition of cadmium ions from solution into the silver oxalate lattice during its deposition. Since the radii of Ag^+ and Cd^{2+} ions are similar (0.113 and 0.103 nm), one should expect the substitution of a part of silver ions by cadmium ions in the lattice. Since the electrical neutrality condition must be met, the introduction of a doubly charged cation instead of single-charged cation should cause the formation of cation vacancy in addition to those already present in the lattice. The binding energy of this cation vacancy to the ion with different valence present into lattice is usually low, so the complex ⟨hetero-valent ion–vacancy⟩ dissociates. Whether the complex dissociates completely or only partially, will depend on the bond energy and on the conditions in which the solid substance is present.

As we mentioned at the beginning of this chapter, if the crystal contains Frenkel defects, i.e. the major point defects are interstitial ions and cation vacancies, the addition of supplementary cation vacancies during doping should cause the decrease of the concentration of interstitial ions.

The addition of cadmium into the silver oxalate lattice causes a strong decrease in the rate of silver oxalate thermal decomposition, especially at the initial stage. The concentration of interstitial ions determined according to [23] decreases in phase with this decrease.

Similar results are observed when Pb^{2+} and Cu^{2+} ions are introduced into silver oxalate. With increasing concentration of these dopants, the rate of thermal decomposition decreases. A feature of the system $Ag_2C_2O_4 + Cu^{2+}$ is the fact that Cu^{2+} ions are paramagnetic, so the amount of ions that got into the lattice can be measured as the intensity of ESR signal; thus these ions can be separated from the total number of ions deposited together with silver oxalate during its preparation. The data obtained by us demonstrated that there was a clear correlation between the change of interstitial silver ion concentration and the change of the decomposition rate of undoped silver oxalate.

10. The effect of preliminary irradiation with light, ionising radiation, or electron beam on the rate of silver oxalate thermal decomposition

The sensitivity of silver oxalate to irradiation with visible light was mentioned in the earliest works dealing with the investigation of silver oxalate properties [86]. Attempts were made, on the basis of those studies, to prepare photographic emulsions involving silver oxalate [87,88], but due to its low sensitivity to light this idea did not receive further development (quantum yield of silver oxalate photolysis at 25 °C and wavelength of 370 nm is 0.1 mol CO_2 per quantum [36]).

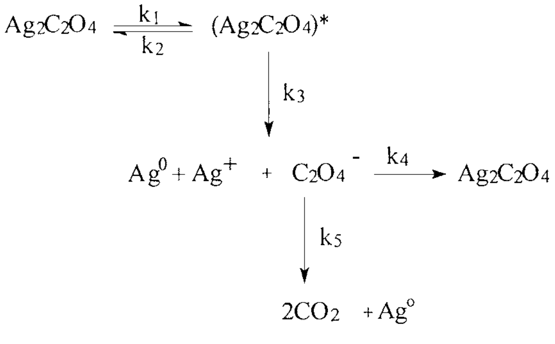
Electron microscopic studies of the initial stage of silver oxalate photolysis showed that metallic silver nuclei formed during photolysis are located mainly on the surface defects (vicinals, dislocation outlet sites) [49,89–91].

Silver oxalate is much more sensitive to UV light than to visible light. When irradiated with UV light, similarly to the case of visible light, metallic silver is evolved at dislocation lines as nuclei with a size from 5 to 200 nm. The nuclei stop their growth after having reached 200 nm. This stop is explained by the transition of metal silver from metastable state to a stable one, like the case of thermal decomposition [89]. However, unlike in thermal decomposition, no swarm-like positions of silver nuclei are observed during photolysis [91].

According to [9,92], the photolysis of both the pure and doped silver oxalate occurs linearly with time; according to [9], the reaction rate is proportional to the intensity of the light to the second power, which was considered as confirmation of the fact that the decomposition of silver oxalate occurred as a result of a bimolecular reaction. It was demonstrated in later and more detailed investigations that the kinetics of photolysis in fact are not linear at the earliest stages, photolysis rate increases within 1.5–2 min then reaches its steady level [18].

Clearly exhibited absorption peaks are observed in the plots of the quantum yield of photolysis versus wavelength. These peaks fit well within the series of exciton excitations in Vanie–Mott model. The authors believe that an exciton in silver oxalate is an excited state of oxalate ion with partial transfer of electron to Ag–O bond; this state migrates over the lattice. Exciton migrates till it meets a scavenger where it decomposes. The electron is transferred from the exciton to silver ion with the formation of a silver atom and a $C_2O_4^-$ radical. The formation of this radical was detected in silver oxalate photolysis as described in [93].

The general scheme of silver oxalate photochemical decomposition can be represented as:



Unlike the model of Finch et al. [9], the model proposed by Galitsyn and Poshevnev does not involve a bimolecular stage of oxalate ion excitation which is of low probability. The rate of exciton excitation is proportional not to the square light intensity but to its first power. Galitsyn and Poshevnev demonstrated that this dependence is really observed if the irradiation is carried out not by a continuous UV spectrum but by monochromatic light which was a more correct version of experiment.

The radiolysis of silver oxalate was also the subject of investigation. It was demonstrated that silver oxalate was characterised by moderate sensitivity to radiation. During the radiolysis it decomposes to form the same products as those formed during photolysis, namely, metallic silver and carbon dioxide [92,94]. The radiolysis rate was studied in [92]. According to these data, the radiolysis rate remained constant during the process, except for the first 5 min period. Unlike photolysis and thermal decomposition, the radiolysis of silver oxalate is not limited by the surface but occurs over the volume. Electron microscopic studies show that in this case, too, nuclei of metallic silver are formed, but their size is much less than under photolysis (∼100 nm as a maximum). These nuclei, similar to photolysis, are located mainly along dislocation lines [95].

Two signals are recorded in ESR spectrum during the radiolysis of silver oxalate [92]. One of these signals is attributed to $C_2O_4^-$ radicals localised at cation vacancies.

Measurement of the conductivity of a silver oxalate single crystal during the radiolysis using X-ray apparatus RUT-200 showed that after 30 min, before any changes of mass or the volume of the gas released can be detected by means of gravimetry of volumetry, electrical conductivity of silver oxalate is changed substantially (Fig. 23). The plot of conductivity versus time is wave-like. A similar wave-like character is observed during thermal decomposition, which is an evidence of the similarity of the mechanisms of these two processes [52].

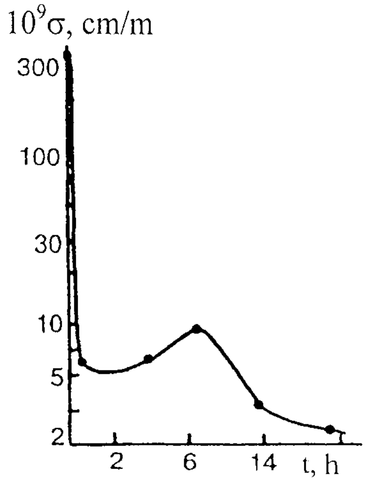


Fig. 23. The change of specific conductivity (300 Hz) of $Ag_2C_2O_4$ single crystal after irradiation with X-ray apparatus RUT-200, dose rate 1500R/min.

When discussing these results, it was proposed that the initial drop of silver oxalate conductivity during radiolysis, similarly to thermal decomposition, is connected with the absorption of mobile silver ions from the lattice by the growing nuclei of metallic silver. These mobile ions are likely to be responsible for interlayer polarisation and throughout conductivity. Further changes in conductivity were found to be due to the accumulation of metallic silver and the transformation of the metal from a metastable form into a stable one.

Similarly to the case of thermal decomposition of silver oxalate, both photolysis and radiolysis are affected by doping when homophase additives are introduced into the lattice. However, the action of these additives is different by its character. The introduction of cadmium ions into silver oxalate lattice causes strong deceleration of thermal decomposition; its effect on the photolysis rate is not so significant (Fig. 24); the effect on radiolysis rate is even smaller (Fig. 25) [92]. The addition of bivalent lead ions decelerates thermal decomposition but accelerates photolysis and radiolysis. For the latter, the effect of lead addition is most striking: the introduction of only 1 at.% Pb^{2+} causes an increase of radiolysis rate by a factor of 35 (Fig. 26) [92]. The same is observed with the addition of bivalent copper ions to silver oxalate. Thermal decomposition of silver oxalate is

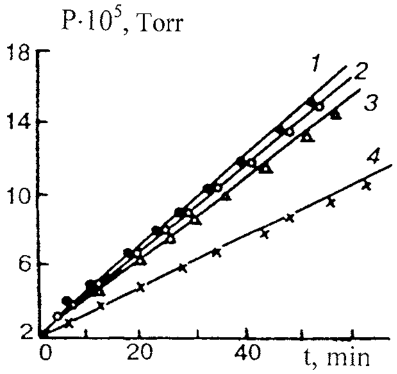


Fig. 24. The effect of the addition of Cd^{2+} ions co-precipitated with silver oxalate on the rate of silver oxalate photolysis at 95 °C: (1) pure $Ag_2C_2O_4$; (2–4) containing 1, 5 and 10 mol% Cd^{2+}, respectively.

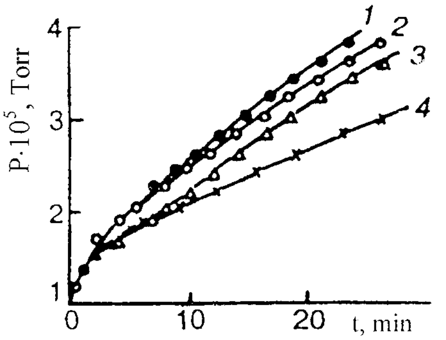


Fig. 25. The effect of Cd^{2+} additive on the radiolysis of $Ag_2C_2O_4$: (1) oxalate without additives; (2–4) co-precipitated with 1, 5 and 10 mol% Cd^{2+}, respectively.

decelerated by this additive while photolysis and radiolysis are accelerated by it [91].

The general trend to change the sign of the effect of an additive in oxalate solid solutions in the sequence—thermal decomposition, photolysis, radiolysis—was explained in [92] in the following way. The effect of the addition of bivalent ions that substitute for silver ions in the silver oxalate lattice is due to many factors. According to the known principle of lattice electrical neutrality, the doping of silver oxalate lattice should cause an increase in the number of cation vacancies. The accumulation of cation vacancies in the lattice should decrease the concentration of interstitial silver ions thus slowing the process. However, cation vacancies are at the same time efficient scavengers for $C_2O_4^-$ radicals; the presence of such scavenging centres was confirmed, as we have mentioned, by the investigations of electron paramagnetic resonance spectra of the irradiated silver oxalate samples with the addition of Cd^{2+} and Pb^{2+} and the curves of their defrosting that characterise the accumulation of radicals during irradiation and their stability. Because of this, the probability of exciton decomposition on the scavenger and the probability of electron transfer to the metal ion should increase, so that the rate of oxalate decomposition should increase [96]. Besides, the ions introduced into the lattice can participate in the processes changing electron–hole equilibrium. For example, Cu^{2+} ions are themselves electron acceptors and can affect the process rate. So, the action of additives on thermal, photochemical and radiation decomposition should be considered as several overlapping factors that act in opposite directions. The resulting effect is what we observe (Fig. 27). It is very important to take this circumstance into account when considering the effect of preliminary radiation on the rate of silver oxalate thermal decomposition.

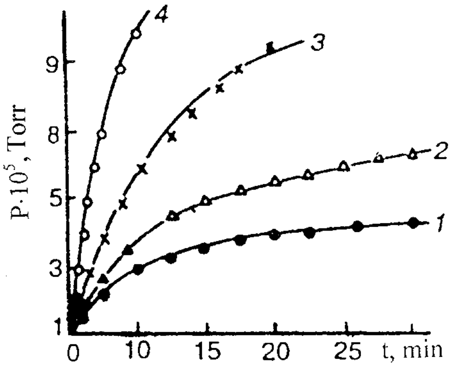


Fig. 26. The effect of Pb^{2+} on $Ag_2C_2O_4$ radiolysis: (1) radiolysis of the oxalate without additives; (2–4) with co-precipitated PbC_2O_4, 0.2, 0.8 and 5 mol%, respectively.

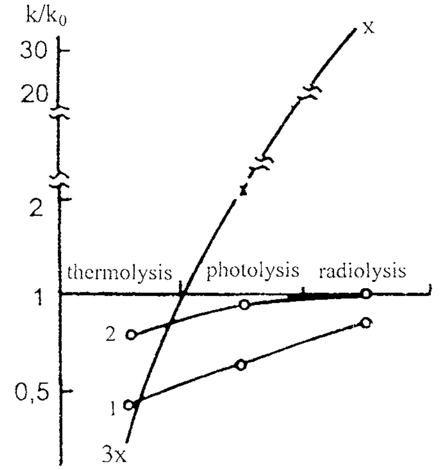


Fig. 27. The change of relative (k/k_0) character of the effect of bivalent ions introduced into silver oxalate lattice during co-precipitation, in the process row: thermal decomposition, photolysis, radiolysis; (1) system 90% $Ag_2C_2O_4$ + 10% CdC_2O_4; (2) 99% $Ag_2C_2O_4$ + 1% CdC_2O_4; (3) 99% $Ag_2C_2O_4$ + 1% PbC_2O_4.

11. The influence of preliminary radiation on the rate of thermal decomposition of silver oxalate

The effect of preliminary irradiation with both the visible and ultraviolet light was known long ago [33].

Benton and Cuningham [36] found that preliminary irradiation with UV light provides a substantial increase of the rate of the following thermal decomposition of silver oxalate by decreasing the induction period at the initial stage of the process.

Similar results were obtained in other works [6,56,97–103] dealing with the thermal decomposition of silver oxalate. The irradiation by γ-^{60}Co and X-rays also causes acceleration of the thermal decomposition not only at the initial stage but also at the next stages of the process. The irradiation with accelerated electrons and the irradiation in nuclear reactor channel (with thermal neutron beam and γ-radiation) cause the same effect (Fig. 28). In the latter case it was noticed that after the irradiation, the period of acceleration for the silver oxalate thermal decomposition is described, not by an exponential function of time, but by a cubic time function [37].

Comparison of the effect of irradiation during thermal decomposition with preliminary irradiation with X-rays (γ-quanta energy being 0.2 MeV) did not indicate any substantial differences between these two kinds of treatment [96]. Similar results were obtained for the action of light [97]. This was the grounds to doubt that the stage of electron excitation was limiting in thermal decomposition of silver oxalate [104].

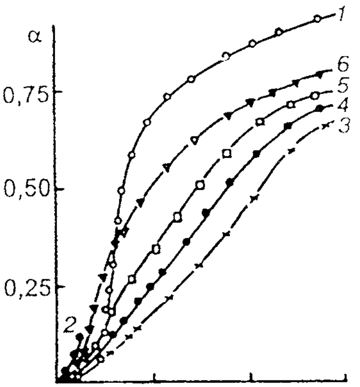


Fig. 28. The influence of irradiation with γ-^{60}Co rays on silver oxalate thermal decomposition at 158 °C (1 and 2) pure silver oxalate: (1) unirradiated and (2) irradiated with a dose of 43×10^{3}R; (3–6) silver oxalate with cadmium admixture: (3) unirradiated, (4) irradiated with a dose of 43×10^{3}R, (5) irradiated with a dose of 240×10^{3}R and (6) irradiated with a dose of 300×10^{-3}R.

The irradiation of silver oxalate, in which a part of the silver was replaced in the lattice by cadmium ions, with γ-^{60}Co rays and light demonstrated that the observed decrease of the rate of thermal decomposition caused by the additive was due mostly to its effect on the thermal decomposition rate than on photolysis and radiolysis processes [97].

Two opinions existed concerning the reasons for the effect of preliminary irradiation on the rate of silver oxalate thermal decomposition, similar to the case of thermal decomposition of potassium permanganate considered in the previous section. According to one of them [105], the observed effect of the acceleration of silver oxalate thermal decomposition is the consequence of the release of energy accumulated during irradiation shifting silver ions from their normal positions in the nodes of the lattice into interstices. According to the second point of view, the effect of preliminary irradiation is reduced to the accumulation of metallic silver in silver oxalate lattice during irradiation, which catalyses further thermal decomposition [106]. At present, as a result of the accumulation of new experimental data, the second point of view is generally acknowledged.

12. The effect of electric field on thermal decomposition of silver oxalate

The opinion that silver oxalate thermal decomposition is the sum of electronic and ionic processes stimulated experimental investigations of the action of an electric field on the thermal decomposition.

One of the first indications of the effect of electric field appeared in [107]. These authors studied the conductivity during thermal decomposition and noticed that, while in the absence of electrical field silver oxalate tablets went on decomposing slowly after they reached a maximum decomposition rate within temperature range 105–120 °C. They exploded when the field was superimposed. However, it remained unclear whether the transition from thermal decomposition to an explosion was the consequence of the effect of electric field on silver oxalate thermal decomposition, or was the consequence of electrical breakdown between metallic silver particles growing during thermal decomposition.

Thermal decomposition of silver oxalate was studied in [108] under the action of a constant electric

Table 3
The effect of electric field on thermal decomposition of $Ag_2C_2O_4$

The action of electric field (80 V/cm)	Ignition temperature (°C)	Time from the start of heating to the ignition temperature (min)	CO_2 pressure at the ignition moment (mmHg)
Without field	143 ± 4	173 ± 8	~0.8
Field applied for a short time	130 ± 2	155 ± 3	~0.8
Field applied constantly	122 ± 2	143 ± 3	~0.8

field, in a periodic field and in the absence of any field. The results are shown in Table 3. It follows from these data that, when silver oxalate is placed in an electric field, the rate of thermal decomposition increases. Since the amount of carbon dioxide released before the explosion occurs is quite the same, it was concluded that the field affected ion and electron processes during thermal decomposition but not the shape of silver nuclei formed during decomposition, as was assumed earlier.

A more detailed investigation of the effect of electric field on thermal decomposition of silver oxalate was carried out in [109] using a specially constructed set-up allowing one to change the field direction. Volume charge arises in silver oxalate when the field is superimposed. The field of this volume charge is opposite to the external field. The authors demonstrated that by changing the field direction one can govern thermal decomposition of silver oxalate. In the case of cathode polarisation, the process accelerates; in the case of anode polarisation, it is slowed [108].

An accelerating effect of electric field on silver oxalate thermal decomposition was stated in the works of Deren and Mania [110] and Saveliev et al. [111]. It was stated in the latter work that electric field of 10 kV/cm accelerates thermal decomposition of silver oxalate at 145 °C. The activation energy of thermal decomposition decreases from 118.3 to 114.5 kJ/mol. The field affects kinetic curves by changing the induction period.

The authors of the aforementioned works think that this effect is connected with the changes in lifetimes of electrons and holes in the silver oxalate lattice. However, recent works that demonstrated the presence of a thermoelectrete state in silver oxalate [27], and the negative result of the attempt to affect the formation of latent photographic image by posing pulse electric field [112] are evidence that the observed effects of the field are connected not with the electron stage of the process but with the ionic stage, namely, with local changes in the concentration of interstitial silver ions in crystals.

The effect on the electronic stage of the process can be expected in crystals only in the case of a very strong electric field when the conditions for Frantz–Keldysh effect [113] can be realised (this effect implies the shift of the absorption band edge to longer wavelengths under the action of a field due to the increased probability of tunnelling when an electron passes from the valence zone to the conductivity region).

13. The effect of preliminary mechanical treatment on thermal decomposition of silver oxalate

The effect of preliminary mechanical treatment on the thermal decomposition of silver oxalate was the subject of several experimental investigations carried out in the 1970s [38–43] within the frame of joint investigations in the Institute of Solid State Chemistry (SB of the Academy of Sciences of the USSR) and the Institute of Physical Chemistry (the Academy of Sciences of the DDR). A substantial result obtained in course of these investigations was the effect of preliminary mechanical treatment on the silver oxalate thermal decomposition was found to be more substantial that if it was simply due tot he increase of specific surface of silver oxalate powder because of dispersing that accompanied mechanical treatment. It was found that mechanical treatment resulted in substantial disordering of silver oxalate crystals. It is essential whether silver oxalate is mechanically treated in air or in vacuum. Mechanical activation in vacuum with a EI-type planetary mill caused a substantial acceleration of silver oxalate thermal decomposition at 139 °C [38], often passing to explosion (Fig. 29). The activation in air caused not so substantial acceleration of

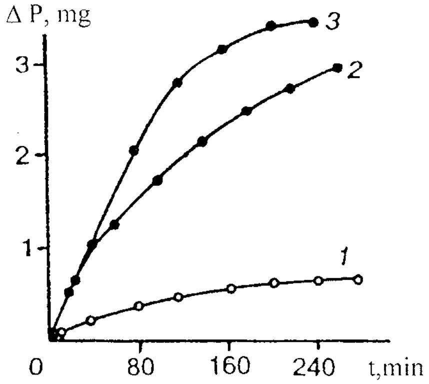


Fig. 29. Kinetic curves of thermal decomposition of different $Ag_2C_2O_4$ samples at $T = 139\,^{\circ}C$, $P = 3 \times 10^{-2}$ mmHg: (1) initial powder; (2) activated for 1 min; (3) activated for 20 min.

decomposition but it caused the changes in the mechanism of thermal decomposition: a part of silver oxalate was decomposed to give not metal silver and carbon dioxide but silver oxide and a mixture of carbon oxides (Fig. 30).

Another feature of the thermal decomposition of silver oxalate activated mechanically is the dependence of the kinetic effect on the type of treatment. For example, the treatment in a planetary mill (shock-attrition regime) and pressing (shift deformation) lead, other conditions being kept constant, to different changes in the kinetic curve of thermal decomposition. At short time of mechanical treatment, the curve of thermal decomposition can be divided into regions corresponding to faster decomposition of oxalate on defect-containing regions of crystals and slower decomposition on more perfect regions that had not enough time to mechanically deform.

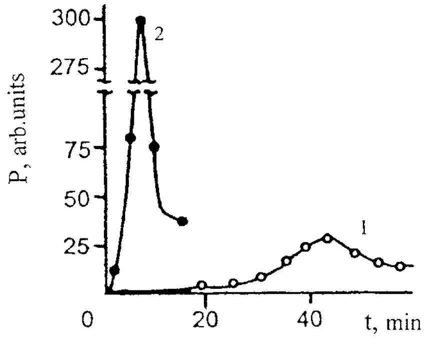


Fig. 30. The rate of CO and CO_2 evolution at thermal decomposition of $Ag_2C_2O_4$ in high vacuum at 136 °C: (1) CO_2 evolution from unactivated powder; (2) the evolution of CO_2/CO mixture from the sample activated for 20 min.

14. Unsolved problems

The following problems outlined in the previous sections remain unsolved in the studies of thermal decomposition of silver oxalate:

1. Further investigations are necessary into the mechanism of the growth of silver nucleus, starting from the formation stage when the concentration of interstitial ions is important, and the growth stage when this concentration has no effect. The question concerning the mechanism by which the change of limiting stage occurs remains open at a level of the hypotheses and assumptions waiting for being verified.
2. The same is true when speaking of the mechanism of exciton decomposition. This implies the mechanism of bond breakage in the oxalate ion, either excited or ionised partially or completely. The same is true for the mechanism of the influence of heterophase additives, both organic and inorganic, on the thermal decomposition of silver oxalate.
3. The reasons for the stop in the growth of silver cluster when it reaches some critical size, and the reasons for the transition from usual process character typical for topochemical reactions to swarm-like character, remain unclear yet.
4. The reasons for the catalytic action of the products of photolysis and radiolysis of silver oxalate on the rate of the following thermal decomposition remains still at the level of assumptions.

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