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Study of the Mechanism of the Effect of Preliminary Irradiation on the Thermal Decomposition of Silver Oxalate Containing a Cadmium Impurity

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In paper (^{2}) it was shown that the introduction of a cadmium impurity into silver oxalate leads to a decrease in the effect of preliminary irradiation on the rate of subsequent thermal decomposition of this salt. Along with this, it was established (^{1,9}) that an impurity of cadmium ions decreases both the rate of thermal decomposition and the rate of the processes of photolysis and radiolysis of silver oxalate crystals, which lead to the appearance of initial centers that catalyze the subsequent thermal decomposition of this salt. Since the decrease in the rate of thermal decomposition of preliminarily irradiated silver oxalate containing a cadmium additive may therefore be a consequence both of a decrease in the rate of the processes occurring upon irradiation in the presence of the additive and of a decrease in the rate of the thermal decomposition process itself, it was of interest to determine which of these two causes is the principal one.

Samples of pure silver oxalate and samples containing an additive in amounts of 0.1; 0.5; 1; 5; 7.5; and 10 mole percent were obtained by coprecipitation, as described in paper (^{3}). X-ray analysis of the samples obtained showed the formation of solid solutions in the region of small amounts of the introduced additive. At additive concentrations exceeding 1 mole %, lines appear on the Debyegrams of the samples corresponding to the separation of cadmium oxalate as a separate phase. The rates of photolysis and radiolysis were studied on high-vacuum apparatuses by measuring the pressure of the evolved gas in the range $5 \cdot 10^{-6}$–$5 \cdot 10^{-5}$ mm Hg. As the source of ultraviolet light, an SVDSh-1000 lamp was used; as the source of X-radiation, an RUP-2 unit operating at 200 kV and 20 mA. The results of the experiments on photolysis and radiolysis at 67° of silver oxalate containing a cadmium additive are shown in Fig. 1 and Fig. 2. From the position of the curves in Fig. 1 it is seen that the cadmium additive markedly decreases the rate of photolysis of silver oxalate. The introduction of a cadmium additive has a smaller effect on the rate of radiolysis, as can be seen from the relative position of the radiolysis curves in Fig. 2.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The rate of thermal decomposition was studied in the same way as in papers ([1,2]), by the gravimetric method at temperatures of 132, 136, and 140 ± 0.2°. Preliminary irradiation of the samples with γ-radiation from Co^{60} was carried out on a K-2000 installation for radiation-chemical investigations ([4]), with doses of $9.9 \cdot 10^5$, $1.0 \cdot 10^7$, and $9.4 \cdot 10^7$ r/g at dose rates from 27 r/sec to 270 r/sec. Study of the thermal decomposition of irradiated and unirradiated samples showed that the effect of the additive and the effect of preliminary irradiation are manifested primarily at the initial stage of the reaction and have almost no effect on its subsequent course. The result of introducing the cadmium additive is an increase in the duration of the induction period. Preliminary irradiation shortens this period, but the character of its change is different for samples with different impurity contents (Fig. 3).

The dependence of the magnitude of the induction period on the logarithm of the absorbed dose for samples containing up to 1 mole % impurity is described

by the equation $y = ax + b$ (where y is the duration of the induction period in minutes, x is the logarithm of the absorbed dose) with an almost unchanged slope coefficient (1.85 for pure silver oxalate, 1.68 for oxalate with 1 mol.% impurity). For specimens with an impurity content

Fig. 1. Effect of the addition of CdC_2O_4 on the course of photolysis of silver oxalate.
1 – $Ag_2C_2O_4$, 2 – 99% $Ag_2C_2O_4$ + 1% CdC_2O_4, 3 – 95% $Ag_2C_2O_4$ + 5% CdC_2O_4, 4 – 90% $Ag_2C_2O_4$ + 10% CdC_2O_4

Fig. 2. Effect of the addition of CdC_2O_4 on the course of radiolysis of silver oxalate.
1 – $Ag_2C_2O_4$, 2, 3, 4 – silver oxalate containing CdC_2O_4 at 1, 5, and 10 mol.% respectively

Fig. 3. Dependence of the duration of the induction period on the logarithm of the dose of preliminary irradiation.
1 – $Ag_2C_2O_4$, 2 – 99.9% $Ag_2C_2O_4$ + 0.1% CdC_2O_4, 3 – 99.5% $Ag_2C_2O_4$ + 0.5% CdC_2O_4, 4 – 99% $Ag_2C_2O_4$ + 1% CdC_2O_4, 5 – 95% $Ag_2C_2O_4$ + 5% CdC_2O_4, 6 – 90% $Ag_2C_2O_4$ + 10% Cd^+

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 4. Change in the rate constant of thermal decomposition of oxalates after irradiation.
1 $-Ag_2C_2O_4$, $2, 3, 4, 5, 6$ $-$silver oxalate containing CdC_2O_4 at 0.1, 0.5, 1, 5, and 10 mol.% respectively

greater than 1 mol.%, the indicated dependence is disrupted as a result of a more pronounced shortening of the induction period upon irradiation.

Figure 4 presents the results of a kinetic analysis of the experimental data, carried out according to the equation $\alpha = 1 - \exp(-kt^n)$ (5), which satisfactorily describes decomposition from 15 to 85%, with calculation of the rate constant from the relation $K = n \cdot k^{1/n}$ (6). As can be seen from this figure, preliminary irradiation increases the rate of thermal decomposition of mixed oxalates with an impurity of not more than 1% only slightly more than the decomposition rate of pure silver oxalate;

In specimens with an impurity content of more than 1 mole %, the changes in rate upon irradiation are greater.

A comparison of the results obtained on the effect of the additive on the rate of photolysis and radiolysis of silver oxalates with the results of experiments on the thermal decomposition of solid solutions makes it possible to answer the question posed at the beginning of this work: what is primarily affected by the additive—the processes occurring during preliminary irradiation, or the subsequent thermal decomposition. In the case of preliminary irradiation with ultraviolet light, the additive exerts an inhibiting effect both on the rate of photolysis of silver oxalate (Fig. 1), thereby decreasing the number of centers from which thermal decomposition can subsequently begin, and on the rate of the process of thermal decomposition itself of silver oxalate. The decrease, observed in our experiments ([2]), in the rate of thermal decomposition of silver oxalate pre-irradiated with ultraviolet light and containing cadmium impurity, as compared with the pure preparation, may therefore be regarded as the combined action of the additive, inhibiting both the photolysis and the thermal decomposition of silver oxalate.

On the basis of the results presented above from experiments on the radiolysis of silver oxalate with a cadmium additive, one may expect that, after irradiation with ionizing radiation, the relative retardation of the rate of thermal decomposition caused by small amounts of impurity will not change substantially. This is confirmed by the experimental results shown in Figs. 3 and 4, from which it is evident that both the length of the induction period and the rate constant for the pure preparation and for preparations containing additive up to 1 mole % change in the same way with increasing dose.

On the basis of the foregoing, it may apparently be assumed that the change in the rate of thermal decomposition of crystals of AgC_2O_4 containing cadmium impurity and pre-irradiated with γ-radiation is connected mainly with the influence of the impurity on the thermal decomposition of the salt. As for the reason for the decrease in the inhibiting influence of the additive when its amounts exceed 1%, it is probably connected with the separation of CdC_2O_4 as an independent phase. The phase boundaries in mixed-oxalate crystals may be centers for the accumulation of silver liberated during radiolysis by a mechanism probably similar to the mechanism of decoration of dislocations by means of partial photolysis ([7,8]). This should lead to improved conditions for the formation of initial centers during the subsequent thermal decomposition, which as a result will be accelerated mainly through an increase of the rate in the initial stage; this is confirmed by our data on the preferential influence of irradiation and impurity on the induction period and on its change upon irradiation of oxalates with a high impurity content. Changing the dose rate of irradiation from 27 r/sec $\cdot$ g to 270 r/sec $\cdot$ g does not lead to any noticeable change in the accelerating effect of irradiation, which indicates the irreversible character of the radiolysis of silver oxalate.

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