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Abstract

Full Text

PHYSICAL CHEMISTRY

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APPLICATION OF IONIZING RADIATION TO THE STUDY OF THE DECOMPOSITION PROCESSES OF COPPER AND NICKEL OXALATES

It is of interest to investigate whether there is a difference in the character of the topochemical decomposition processes of solid inorganic compounds occurring under electron irradiation and in their usual thermal conduct. The action of fast electrons on a solid leads to the appearance of excess charge carriers—secondary electrons and holes—and, in addition, is associated with the formation of radiation defects, i.e., with disturbance of the periodic structure of crystals.

These factors may influence the rate of topochemical processes under the action of ionizing radiation, as well as the structural and chemical characteristics of the products formed. Although radiation defects and the primary active forms arising in a solid under the influence of ionizing radiation are unstable ([1]), they may nevertheless lead to the formation of secondary, more stable forms of the type of latent-image centers in the photographic process and others, which affect the rate of topochemical processes. It should be pointed out that additional charge carriers may participate in certain stages of topochemical processes. This is of interest in connection with the views, repeatedly expressed recently, concerning the substantial role of electronic stages in the topochemical decomposition processes of compounds of the type of azides and oxalates ([2–5]).

In the present investigation the objects of study were copper and nickel oxalates, prepared by precipitation of $0.2\,N$ solutions of copper and nickel nitrate salts with a $0.4\,N$ solution of oxalic acid at 50°. According to X-ray structural analysis data, the phase composition of copper oxalate corresponded to the formula $CuC_2O_4 \cdot \frac{1}{2}H_2O$, and that of nickel oxalate to $NiC_2O_4 \cdot 2H_2O$.

Irradiation of the oxalates was carried out in air with fast electrons having energies from 0.6 to 2 MeV. The uniformity of the beam density was determined photometrically from the darkening of a photographic plate or film. At higher dose rates ($\sim 10^6$ rad/sec), the irradiated preparations were placed in an open metal apparatus provided with a massive extension and immersed in liquid nitrogen or solid carbon dioxide. At lower dose rates (10^4 rad/sec), irradiation was carried out in open test tubes or cuvettes made of molybdenum glass, cooled with solid carbon dioxide or a stream of cold air.

The temperature inside the powdered samples during irradiation was measured with a thermocouple. With intensive heat removal by liquid nitrogen it was 40—50°, and it was established that there was correspondence between the amount of energy received by the solid and that expended on evaporation of the nitrogen. With less intensive heat removal the temperature inside the sample was 100—150°. The thickness of the layer of powdered samples corresponded approximately to the free path length of electrons of the given energy. The dose was determined by calculation from the current strength and by a chemical dosimeter (recommended by the L. Ya. Karpov Physicochemical Institute) having the following composition: 0.02 mol/l $CuSO_4$; 0.002 mol/l $FeSO_4$; 0.02 N H_2SO_4. The yield of Fe^{3+} was determined on an SF-4 spectrophotometer, $G = 0.65$.

Irradiated samples were subjected to kinetic and X-ray diffraction study in order to determine the depth of transformation and the phase composition of the products formed. The decomposition kinetics of both unirradiated and preliminarily irradiated samples was studied in a vacuum apparatus with quartz spiral balances.

Topochemical processes of decomposition of copper and nickel oxalates may proceed with formation of a mixture of metals and oxides

$$MeC_2O_4 \longrightarrow Me + 2CO_2; \tag{1}$$

$$MeC_2O_4 \longrightarrow MeO + CO + CO_2. \tag{2}$$

In the present work it was established that, in the decomposition of copper oxalate, a third reaction also proceeds—cuprous oxide is also formed.

$$2MeC_2O_4 \longrightarrow Me_2O + CO + 3CO_2. \tag{3}$$

The rate of the processes and their direction depended to a great extent on the experimental conditions: temperature, gaseous medium, and the action of ionizing radiation. Thus, thermal decomposition of unirradiated copper oxalate in vacuum proceeded mainly according to reactions (1) and (3) and began at 225°. Nickel oxalate in vacuum decomposed predominantly with formation of metallic nickel (1); decomposition began at 240°. Decomposition of both oxalates in air began at a measurable rate at higher temperatures (250°—copper oxalate; 300° —nickel oxalate). In the first case the products formed consisted of CuO and Cu_2O; in the second, of NiO.

Radiation decomposition of the oxalates in air occurred at temperatures 200-250° lower than thermal decomposition, with formation of products of a different phase composition. The depth of decomposition increased with increasing dose. The radiation-chemical yield of decomposition of the oxalates was several tenths of a molecule per 100 eV.

A summary of data characterizing the phase composition of the products of radiation and thermal decomposition of copper and nickel oxalates is given in Table 1. The data were obtained on the basis of X-ray structural analysis.

Table 1

Phase composition of the products of radiation and thermal decomposition of copper and nickel oxalates in air and in vacuum

Substance	Radiation decomposition: temp., °C	Radiation decomposition: dose, rad	Radiation decomposition: composition, %	Thermal decomposition: temp., °C	Thermal decomposition: composition, %
Copper oxalate	100 (in air)	$3.6 \cdot 10^9$	Cu, 30Cu$_2$O, 30Undecomp., 40	300 (in air)	Cu$_2$O, 50CuO, 50
Copper oxalate	100 (in air)	$1 \cdot 10^{10}$	Cu, 90Undecomp., 10	280 (vacuum)	Cu, 85Cu$_2$O, 15
Nickel oxalate	100–150 (in air)	$8 \cdot 10^9$	Ni, 5Undecomp., 95	310 (in air)	NiO, 10
Nickel oxalate	100–150 (in air)	$3 \cdot 10^{10}$	Ni, 80Undecomp., 20	280 (vacuum)	Ni, 95NiO, 5Undecomp.
Nickel oxalate	40–50 (in air)	$3.3 \cdot 10^{10}$	Ni, 80Undecomp., 20		

It is evident from Table 1 that radiation decomposition of the oxalates in air proceeds toward formation of metals—according to reaction (1) for nickel oxalate, or of the metal and cuprous oxide (reactions 1 and 3) for copper oxalate. Formation of NiO and CuO was not observed. Since the radiation topochemical process proceeded at low temperature, oxidation of the decomposition products —the metals—apparently occurred only to a small extent, and the formed

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

oxides were not detected by X-ray diffraction. As was established in special experiments, oxidation of dispersed copper and nickel obtained upon decomposition of oxalates (in vacuum) begins at 175° and proceeds vigorously at 200°.

It should be noted that thermal decomposition of oxalates in vacuum, carried out at higher temperatures than radiolytic decomposition, also led mainly to the formation of metal in the case of nickel oxalate and of a mixture of metal and cuprous oxide in the case of copper oxalate.

Fig. 1. Kinetic curves of the decomposition of copper oxalate in vacuum: 1 —at 280°, 2 —263°, 3 —240°, 4 —225°

To clarify the influence of preliminary irradiation on the kinetics of the topochemical processes under study, kinetic curves were obtained for the decomposition of nonirradiated and preliminarily irradiated copper oxalate in vacuum over the temperature interval 225–280°. Before the measurements, the samples were subjected to prolonged conditioning to constant weight at 150° in order to remove crystallization water.

As follows from Fig. 1, the kinetic curves of decomposition of nonirradiated copper oxalate at low temperatures have a typical autocatalytic form and are characterized by the presence of a long induction period (about 100 min at 220°). With increasing temperature the duration of the induction period decreases. The activation energy of decomposition of copper oxalate, calculated from the reciprocal times required to reach the maximum rate, is 29 kcal/mole. Figure 2 gives the kinetic curves of decomposition of nonirradiated and preliminarily irradiated (in air) samples of copper oxalate. The decomposition was carried out in vacuum at low temperature (220°).

Fig. 2. Effect of preliminary irradiation on the kinetics of decomposition of copper oxalate in vacuum at 225°: 1 —sample not subjected to irradiation (a); sample that absorbed a dose of $2.2 \cdot 10^8$ rad (b). 2 —sample preliminarily irradiated (dose $6 \cdot 10^8$ rad). 3 —sample preliminarily irradiated (dose $1.1 \cdot 10^9$ rad). Dose rate 10^4–10 rad/sec

As follows from Fig. 2, preliminary irradiation of copper oxalate with a dose of $2.2 \cdot 10^8$ rad practically does not change the character of the kinetic curve. However, preliminary irradiation of a sample with a dose of $6 \cdot 10^8$ rad leads to a sharp shortening of the induction period (to 10 min) and to a significant increase in the rate. An even greater effect and complete disappearance of self-acceleration were observed in the decomposition of a sample preliminarily irradiated with a dose of $1 \cdot 10^9$ rad. It should be noted that, according to the kinetic data, such preliminary irradiation did not lead to the appearance of any appreciable decomposition products.

It may be thought that, under the action of the electron flux in oxalate crystals, excitation and ionization phenomena occur, accompanied by the appearance of additional charge carriers. Doubly charged oxalate ions interact with electron holes, being converted into singly charged and neutral oxalate radicals. The latter, moving through the volume (for example, by the mechanism of relay transfer of a hole (^{5})), gradually approach the external surface, where, decomposing, they are evolved in the form of carbon dioxide. Simultaneously, inside the oxalate crystal and on its surfac—

···as a result of the secondary electrons arising under the influence of radiation, cations having a double positive charge are reduced, with possible passage through the stage of formation of singly charged cations (formation of Cu_2O), to metallic atoms, followed by their aggregation into groups of atoms and crystallites.

Owing to the mobility of the electrons of the conduction band, these processes can occur at any point in the crystal where favorable conditions exist, created by electron traps (for example, anion vacancies, neutral metal atoms in interstices, etc.). Radiation defects may also be such traps. The general scheme of the process may be represented, for example, as follows:

$$\begin{array}{rcll}
C_2O_4^{2-} + \vec{e} & \longrightarrow & C_2O_4^{-}{}_{\;...p} + n & \quad Me^{++} + n \longrightarrow Me^{+} \\
C_2O_4^{-}{}_{\;...p} & \longrightarrow & C_2O_4^{-}{}_{\;...p} & \quad Me^{+} + n \longrightarrow Me \\
C_2O_4^{-}{}_{\;...p} + p & \longrightarrow & C_2O_4 & \quad kMe \longrightarrow (Me)_k \\
 & \downarrow & & \\
 & 2CO_2 & &
\end{array}$$

Here $\vec{e}$ denotes the electron flux; p and n are additional current carriers (electron hole and electron) formed upon irradiation. The rate of both electronic stages depends on the concentration of additional current carriers. Further clarification of the nature of this dependence requires experiments on the influence of dose rate on the rate of the processes under study. It should be noted that the temperature coefficient of topochemical radiation processes is apparently small (see Table 1).

The thermal topochemical process of decomposition of oxalates in vacuum can proceed by the same mechanism, the concentration of current carriers being determined by thermal motion and being a function of temperature. Since ionizing radiation is a considerably more powerful factor in increasing the concentration of current carriers in the crystal than temperature, the radiation topochemical processes of decomposition of copper and nickel oxalates take place at lower temperatures than the thermal processes (in vacuum).

An inhibiting effect of oxygen on the rate of decomposition of copper and nickel oxalates was established; this is apparently explained by oxidation of the metallic atoms being formed. Therefore the thermal decomposition of oxalates in air occurs at a higher temperature than in vacuum and leads to the formation of oxides. Let us note that, according to the proposed electronic mechanism, preliminary irradiation can create in the crystal a certain quantity of metal atoms and other centers of crystallization. This leads to an increase in the rate of subsequent decomposition and to a shortening of the duration of the induction period, evidently associated with the stage of formation of crystallites (or nuclei) of the new phase (6).

Thus, the application of ionizing radiation to the study of topochemical processes of decomposition of copper and nickel oxalates, in combination with kinetic experiments and X-ray structural analysis data, provides arguments in favor of the electronic mechanism of these processes.

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