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Fig. 1

Figure 1: Fig. 1

Abstract

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THERMAL DECOMPOSITION OF SILVER AND BARIUM AZIDES AT THE MOMENT OF X-RAY IRRADIATION

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A number of papers (1–8) propose, and by indirect methods confirm, the assumption that the rate of the process of thermal decomposition is determined by the process of excitation of electrons from the valence band into the conduction band. We believe that a direct method of testing this hypothesis may be to carry out the decomposition at the moment of irradiation. The data presented below, in our view, make it possible to draw certain conclusions about the role of the process of electron excitation in the thermal decomposition of solids.

The study of the kinetics of thermal decomposition of samples not irradiated and irradiated at the moment of decomposition was carried out by the method and on the apparatus described in (9). In the case of irradiation with ultraviolet light, a quartz reaction vessel was used. The change in electrical conductivity at the moment of irradiation with X-rays, and, in the case of silver azide, with ultraviolet light, was recorded on pressed tablets under the irradiation conditions used in the experiments on thermal decomposition.

Fig. 1. Effect of irradiation with ultraviolet light *(I)* and X-rays *(II)* at the moment of decomposition on the rate of decomposition of silver azide (*a* —unirradiated sample, *b* —sample irradiated at the moment of decomposition)

Tablets weighing 1 g were pressed under a pressure of 200 kg/cm^2 in the case of barium azide and 6000 kg/cm^2 in the case of silver azide. Graphite electrodes and a guard ring were applied to them when determining the gamma current. The tablets prepared in this way were clamped between the electrodes of a glass or quartz measuring cell. In the case of barium azide, a high voltage from a high-voltage stabilizing rectifier VS-2.5 was applied to the tablet, and the current flowing in the circuit was measured with a "Kaktus" microroentgenometer calibrated for current. The difference between the currents flowing in the circuit at the moment of irradiation of the tablet and after the irradiation was

Fig. 2. Effect of preliminary irradiation and irradiation at the moment of decomposition on the rate of thermal decomposition of barium azide.

Figure 2: Fig. 2. Effect of preliminary irradiation and irradiation at the moment of decomposition on the rate of thermal decomposition of barium azide.

stopped was taken as the value of the gamma current. The field strength in the experiments was 1650 V/cm; the current sensitivity of the measuring circuit was $1 \cdot 10^{-12}$ A. In the case of silver azide, the gamma and photocurrent was calculated from the change in the resistance of the tablet, which was measured with an F-57 teraohmmeter at a field strength of 70 V/cm. With a dark current of $1.7 \cdot 10^{-8}$ A, the current sensitivity of the measuring circuit was $0.4 \cdot 10^{-9}$ A. Measurements were carried out at a pressure in the cell of $1—2 \cdot 10^{-5}$ mm Hg. The X-ray beam was collimated to reduce the emf induced by the radiation on the electrodes.

As the source of X-rays, an industrial X-ray unit RUP-200-20-5 was used, allowing the production of

measure at the location of the sample a radiation dose rate of up to 400 r/min at quantum energies up to 200 keV. The source of the UV spectrum was a mercury lamp PRK-2500; the full spectrum was used for irradiation. In the experiments a commercial barium azide reagent of chemically pure grade was used. Silver azide was prepared by the procedure described in ([10]).

The decomposition of silver azide was carried out at a temperature of 270°; 15 mg samples were used. The experimental results are presented in Fig. 1. From these results it follows that irradiation of a silver azide sample at the moment of decomposition with x-rays or UV light does not affect the rate of its thermal decomposition. Under the irradiation conditions used in the thermal-decomposition experiments, a gamma current greater than $0.4 \cdot 10^{-9}$ A was not detected in silver azide; the photocurrent is $0.3 \cdot 10^{-8}$ A at a dark current of $1.7 \cdot 10^{-8}$ A.

Fig. 2. Effect of preliminary irradiation and irradiation at the moment of decomposition on the rate of thermal decomposition of barium azide (*a*—non-irradiated sample; *b*—preliminarily irradiated for 17 min; *v*—irradiated at the moment of decomposition during the induction period—17 min.)

The thermal decomposition of barium azide was carried out at 125° and a dose rate of 110 rad/min. The results of these experiments, presented in Fig. 2, show that irradiation of a barium azide sample at the moment of decomposition with x-rays increases the maximum decomposition rate and reduces the induction period. Moreover, irradiation at the moment of decomposition, at equal intensity and irradiation time, has a stronger effect than preliminary irradiation. The accelerating effect of short-term irradiation of the sample during decomposition can be observed if irradiation is carried out not only in the induction period, but also during the period of reaction development and even at the end of decomposition—Fig. 3. The gamma current arising at the moment of irradiation of a barium azide pellet with x-rays is $0.23 \cdot 10^{-11}$ A; this corresponds to an increase in electrical conductivity from $2.4 \cdot 10^{-15}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ without irradiation to $1.56 \cdot 10^{-14}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ at the moment of irradiation. After irradiation is stopped, the initial value of the electrical conductivity is restored after 40–60 sec.

According to (^{8}), the decomposition of silver azide includes the following elementary stages:

$$(\mathrm{N}_3^-/\square_A) \xrightarrow{k_1} (\mathrm{N}_3/\square_A) + e \tag{1}$$

$$2(\mathrm{N}_3/\square_A) \xrightarrow{k_2} 2\square_A + 3\mathrm{N}_2 \tag{2}$$

$$(\mathrm{N}_3/\square_A) + e \xrightarrow{k_3} (\mathrm{N}_3^-/\square_A) \tag{3}$$

$$\mathrm{T} + e \rightarrow \mathrm{Ag} \tag{4}$$

(Here and below the notation adopted in (^{11}) is used.)

It is asserted, moreover, in ($^{1-5,8}$) that the stage determining the rate of the entire decomposition process is stage (1), i.e., the formation of free electrons through thermal dissociation of the azide ion. As proof of this, reference is made either to the agreement observed in some cases between the activation energy of the thermal-decomposition reaction and the energy of thermal excitation of an electron from the valence band to the conduction band, calculated from Mott' s relation ($^{1-3}$), or to the fact that, in the salts under consideration, this stage is the most energy-consuming (^{8}). If this is so, then it should be expected that excitation of additional electrons into the conduction band by irradiation of the specimen with x-rays or UV light at the moment of decomposition will substantially increase the decomposition rate. Characteristic of the azide

the photoconductivity of silver ($^{1-3}$) confirms the appearance of additional free electrons under the action of ultraviolet light. In our case, with the illumination conditions observed in the thermal-decomposition experiments, the photocurrent was $0.3 \cdot 10^{-8}$ A, which corresponds to the passage of $1.88 \cdot 10^{10}$ electrons per second between the electrodes. The area of the deposit in the thermal-decomposition experiments illuminated by ultraviolet light is approximately three times smaller than the surface area of the pellet in the electrical-conductivity measurements; consequently, the number of free electrons producing the photocurrent may be estimated as $0.6 \cdot 10^{10}$ electrons per second. It should be noted that the total number of electrons excited under our conditions into the conduction band may exceed the above number by several orders of

Figure 3

Figure 3: Figure 3

magnitude, since some of the electrons from the conduction band are captured by traps or recombine with positive holes before reaching the electrode and are not registered in the photocurrent measurement.

Fig. 3. Effect of short-term (2 min) irradiation with X-rays at different stages of the process on the rate of decomposition of barium azide. (The decomposition was carried out at 135°; the irradiation time is shown by the horizontal line.)

Irradiation with X-rays also leads to the appearance of free electrons, owing to ionization produced in the material both by the primary X-radiation (photoeffect, Compton effect) and by secondary electrons possessing sufficient energy. The absence of a gamma current in our experiments may be connected with the fact that the method used does not allow changes in current smaller than $0.4 \cdot 10^{-9}$ A to be measured, while the radiation intensity was too low to produce currents of this magnitude. An attempt to estimate the number of electrons excited into the conduction band, on the basis of the radiation power and the absorption coefficient of the deposit, determined experimentally, gives $1.7 \cdot 10^{10}$ electrons per second. The absence of an effect of irradiating the deposit with X-rays and ultraviolet light at the moment of decomposition indicates that, in the case of silver azide, transfer of electrons into the conduction band is not the stage determining the rate of the process.

Carrying out arguments similar to those given in ([8]), it can be shown that, upon attainment of the stationary state,

$$d[\mathrm{N}_2]/dt = k_2[\mathrm{N}_3/\square_A]^2 = k_4[\mathrm{T}][\mathrm{e}]. \tag{5}$$

The absence of a change in $d[\mathrm{N}_2]/dt$ with change in [e] may mean that $[\mathrm{e}] \gg [\mathrm{T}]$; then, taking [e] = const, we obtain

$$d[\mathrm{N}_2]/dt = k_4'[\mathrm{T}]. \tag{6}$$

The dependence of the rate of decomposition on the concentration of traps was established in ([1],[8]). However, from (5) it follows that another limiting case is also possible, when $[\mathrm{e}] \ll [\mathrm{T}]$. Then

$$d[\mathrm{N}_2]/dt = k_4''[\mathrm{e}]. \tag{7}$$

i.e., the rate of the decomposition process, proceeding through the formation of free electrons with their subsequent capture at traps, leading to the formation of the metallic reaction product, may be determined by the concentration of free electrons, if their number is smaller than the number of traps capable of capturing electrons. Apparently, such a case we

we have in the decomposition of barium azide. From a comparison of the band-gap width in silver azide—1.88 eV, according to (1,2), and in barium azide—3.0 eV, according to (12), it follows that the concentration of electrons in the conduction band at the decomposition temperature in the case of barium azide will be smaller than in the case of silver azide.

As follows from our data, the thermal decomposition of barium azide proceeds at a much higher rate if it is carried out at the moment of irradiation. The fact that irradiation at the moment of decomposition accelerates the process considerably more strongly than preliminary irradiation with an equal dose makes it possible to suppose (if one takes into account that the accelerating action of preliminary irradiation is associated with the formation of regions of a new phase (13–16)) that the process of electron excitation is limiting also at the stage of decomposition when the reaction is catalyzed by the decomposition products. This supposition is confirmed by direct experiments on irradiation of decomposing barium azide at different stages of decomposition.

It should be noted that the mechanism proposed by Tompkins (17) for the decomposition of barium azide differs from the mechanism of decomposition of silver azide in that the principal process in the decomposition of barium azide turns out to be not the formation of free electrons, but the formation, migration, and interaction with one another of exciton states associated with the excited azide ion. Proceeding from these ideas, the absence of an effect of cyanamide-ion impurities on the decomposition of barium azide (8,18) is explained. The facts presented above make it possible to suppose that either the mechanism proposed in (17) requires additional clarification, or the mechanism of decomposition changes substantially at the moment of irradiation. This is all the more so because the fact of the existence of free electrons at the moment of irradiation is confirmed by the presence of a gamma current. In this case it should be recognized that decomposition proceeding through the formation and capture of free electrons is a more rapid process than decomposition proceeding by the exciton mechanism. The absence of an effect of additions of cyanamide ion on the decomposition of barium azide (8,18) in this case is explained not by the absence of free electrons, but by the fact that $[e] \ll [T]$ (see (17)).

Thus, from the considerations and experimental data presented above it follows that the supposition of a limiting role of the process of electron transition from the valence band to the conduction band in the process of thermal decomposition of ionic salts can be valid only for a definite relationship between the concentrations of free electrons and effective electron traps. In particular, for silver azide this supposition does not correspond to reality. In addition, the possibility has been shown of using experiments on decomposition at the moment of irradiation for direct proof of the role of electronic excitation in the process of thermal decomposition.

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