JOURNAL OF SOLID STATE CHEMISTRY **26**, 209–213 (1978)

Photothermochemical Process in Ammonium Perchlorate Crystals: I

E. JU. IVANOV, E. F. KHAIRETDINOV, AND T. V. MULINA

Institute of Physico-Chemical Principles of Processing of Mineral Raw Materials of Siberian Division of the U.S.S.R. Academy of Sciences, Novosibirsk, 630091, Derzhavina, 18, U.S.S.R.

Received January 20, 1978

It is shown that during uv irradiation of ammonium perchlorate (AP) crystals through an opaque stencil a latent photographic image of the stencil arises in their volume. This image can be developed on a crystal surface by heating at 230°C. The induction period of low-temperature decomposition (LTD) of polycrystalline AP depends linearly on the dose of preliminary uv irradiation: $\tau_{\text{LTD}} = \tau_0 - A \log (I \cdot t_{\text{irr}})$. It is suggested that the mechanism of latent image formation consists of generation in the crystal volume of the chlorine oxidic products of AP photolysis—mainly ClO_3^- ions. Based on these considerations one is able to explain in a consistent way all the experimental data obtained: τ_{LTD} dependence on dose, dependence of thermal development time on the concentration of proton-active additives, dependence of the image optical density on crystal depth, etc.

Introduction

Data about the influence of preliminary light irradiation upon the thermal decomposition of ammonium perchlorate (AP) crystals are very scarce. A slight increase in the rate of thermal decomposition of polycrystalline AP irradiated by uv light was mentioned in (*1*, *2*). In Refs. (*3*, *4*) data are presented concerning the possibility of obtaining a photographic image with AP single crystals. The influence of AP uv irradiation on its subsequent low-temperature decomposition (LTD) is discussed very briefly in the review (*5*). However, no detailed analysis of this effect has been carried out as yet. The aim of this work is to fill the indicated void by experimental investigation of AP properties.

Experimental

Twice recrystallized AP prepared from initial reagent marked "chemically pure" was used. Doping was performed by cocrystallization from an aqueous solution. Concentration of introduced proton acceptor additives was determined by standard analytical methods. The content of ClO_3^- ions was analyzed by the techniques suggested in (*6*). Irradiation was performed by a mercury quartz lamp PRK-2 with consumed power 500 W, samples being placed 20 cm from the lamp. The absorbed dose of irradiation was assumed to be proportional to the irradiation time. Spectral analysis was performed by using interference light filters.

Thermal decomposition of polycrystalline samples was performed at the automatic thermogravimetric installation in an air atmosphere at an ambient pressure of 30 to 100 Torr. The weight of the sample probe was 20 mg: the grain size in the probe was 100 to 120 μm. Thermal decomposition of monocrystals was carried out under the microscope objective as described earlier (*4*); the furnace

0022-4596/78/0263-0209$02.00/0

Printed in Great Britain

temperature in these experiments was 230 ± 0.5°C.

Results

First, the influence of preliminary irradiation on the thermal decomposition of polycrystalline AP was studied. Figure I presents the kinetic curves of decomposition of AP samples irradiated as indicated above at different times. All the curves have a characteristic S-like form. As shown in the figure the irradiation by the complete spectrum of the mercury lamp diminished AP stability, with the duration of the induction period decreasing first. The steepening part of the curve (up to ~20% decomposition) can be satisfactorily described by the formula

$$\alpha = k(t - t_0)^n \tag{1}$$

with varying parameters t_0 and n. The character of their variation as a function of irradiation time is shown in Fig. 2. Usually the t_0 decrease with increase of irradiation dose $\varphi = I \cdot t_{irr}$ is interpreted (7) as due to the photolytic increase of the size of potential decomposition nuclei, leading to a decrease in the time during which nuclei reach a critical size. The parameter n reflects the multistepped character of nucleation, its decrease after irradiation being connected with the decrease in number of nucleation steps.

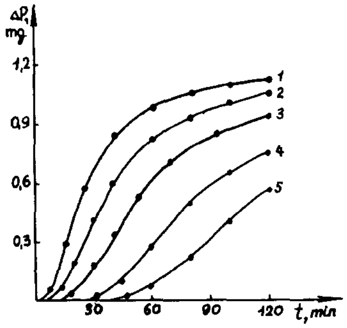

FIG. 1. Kinetic curves of AP LTD for uv-irradiated samples: 1, irradiation time, 60 min; 2, 30 min; 3, 7 min; 4, 0.5 min; 5, nonirradiated sample.

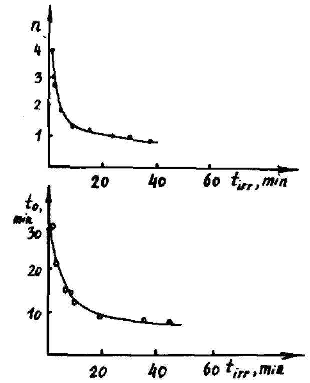

FIG. 2. t_0, n versus time of uv irradiation.

The length of the region of linear decomposition ($\alpha = K \cdot t$) on the curves of Fig. 1 changes insignificantly with the increase of the irradiation dose, while the maximum rate notably grows. This is illustrated by data of Table I.

Figure 3 presents the duration of the induction period τ_{LTD} for the decomposition of polycrystalline AP vs irradiation time. Similar to the case of preliminary radiolysis (*8–10*), the following expression can be obtained for the duration of the induction period:

$$\tau_{LTD} = \tau_0 - A \log (I \cdot t_{irr}). \tag{2}$$

The results presented suggest that a photoimage can be obtained with AP crystals. To check this suggestion an AP single crystal was irradiated through an opaque stencil—a cop-

TABLE I

DEPENDENCE OF MAXIMUM DECOMPOSITION RATE V_{max} AND TIME t_{max} OF ACHIEVING A GIVEN VALUE OF V_{max} UPON THE TIME OF PRELIMINARY IRRADIATION t_{irr}

t_{irr} (min)	$V_{max} \times 10^3$ (mg/min)	t_{max} (min)
0	9.6	90
1	11.7	55
3	16.5	35
5	18.4	27
7	22.5	25
60	25.0	15

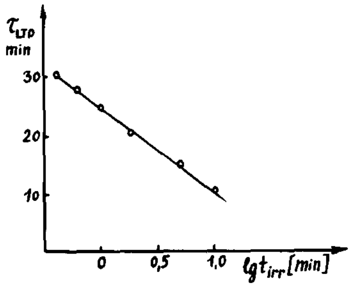

FIG. 3. Dependence of LTD induction period upon the time of preliminary uv irradiation.

per grid for the maintenance of carbon replica in an electron microscope—and after that underwent LTD. First to decompose were the exposed regions of a crystal; thus by correct choice of the LTD regime (temperature and time) a latent photoimage of the stencil could be thermally developed (Fig. 4). Analysis showed the image to be developed on the upper and lower surfaces of a transparent AP monocrystal rather than in its volume. If a preliminary irradiated single crystal is cleaved along the plane parallel to its irradiated surface and then heated, images are also developed on

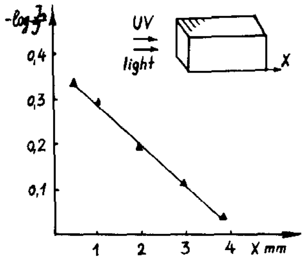

FIG. 5. Optical density of the image on cleavage planes of AP single crystal vs crystal depth.

the newly formed surface, clearly mirror-symmetric for two fresh surfaces (Fig. 4). One can make several similar cleavages on one large AP crystal and then develop them under identical conditions. Two mirror-symmetric images will correspond to each cleavage plane. The results of photometry of these images are shown in Fig. 5 in the case of one of the large AP single crystals. One can see that the optical density of an image (logarithm of the transmission coefficient) decreases linearly with increases in the distance from the upper face of the AP crystal (nearest to the uv light source during irradiation). This gives evidence

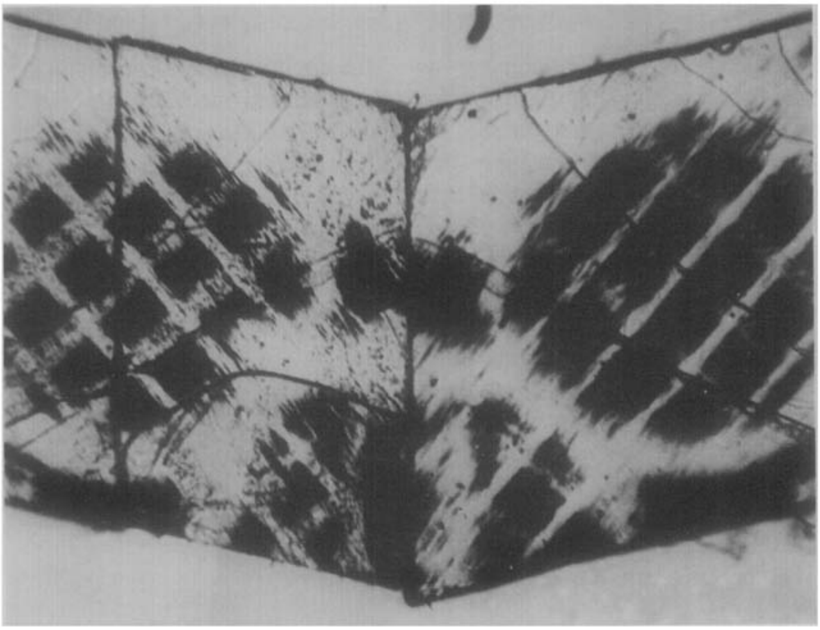

FIG. 4. Thermally developed photoimage of a stencil on the mirror-symmetric surface of a cleaved AP single crystal.

for the assertion that a hidden photoimage appears both on the surface and in the volume of the crystal, but due to the "cell effect" (steric difficulties for the reaction) it is developed only on the AP surface (more accurately, very close to its surface). Similarly, the LTD of the nonirradiated AP begins from the surface (*11–13*), i.e., in this respect photostimulated and spontaneous AP thermal decomposition proceed in identical ways.

Microscopic analysis of the structure of the developed image shows that it consists of a number of small nuclei (1 to 10 μm), i.e., uv light irradiation induces nucleation processes during AP LTD. If a crystal is "overdeveloped," nuclei begin growing as in usual thermolysis and the image loses its clearness and smears.

Spectral analysis with the aid of light filters showed that when the uv light wavelength diminishes the irradiation efficiency grows and for the filters with the smallest wavelength in the transmission region used ($\lambda = 220$ to 240 nm) achieves its maximum.

Discussion

As the influence of the preliminary uv irradiation and the radiolysis by hard irradiation (X rays, γ rays, electrons) on the AP properties is similar one can suggest that irradiation mechanisms are identical in both cases. In the opinion of the authors of (*8*, *14*) the basic factor determining the increase of the reactive ability of AP exposed to hard irradiation is formation and accumulation of ClO_3^- ions as well as dislocation generation. In fact, it turned out that after 3 min of irradiation an AP crystal gives positive reaction with *o*-tolidine, indicating that photogenerated fragments of ClO_4^- ion photolysis are produced: ClO, ClO_2, and ClO_3 molecules and the corresponding ClO^-, ClO_2^-, and ClO_3^- ions (*6*). This process can be schematically shown as

$$NH_4ClO_4 \xrightarrow{h\nu} NH_4^0 + ClO_4^0 \qquad (3)$$

$$ClO_4^0 \rightarrow ClO_x + (4-x)O \qquad (4 \geqslant x \geqslant 0) \qquad (4)$$

$$NH_4^0 + ClO_x \rightarrow NH_4^+ + ClO_x^- \qquad (5)$$

Among chlorine oxidic ions—photolysis products—the ClO_3^- ion is the most stable; thus, one can expect that its concentration will be maximum if compared to other photogenerated ions. In (*4*) the detailed mechanism of the influence of a ClO_3^- ion homophase additive upon AP nucleation during LTD has been considered: A chlorate ion accepts a proton and then decomposes with the formation of active intermediate products of thermolysis, catalyzing the following LTD process.

The mechanism of the influence of a photogenerated ClO_3^- ion is probably the same. In this connection it should be expected that additives of proton acceptors will increase the induction period of the latent photoimage development, while donors decrease it. As seen from Table II it really is so.

In (*4*) it also has been shown that the length τ_n of the induction period of nucleation depends upon the ClO_3^- ion additive concentration as follows:

$$\tau_n = \tau_0 - A \log [ClO_3^-]. \qquad (6)$$

This circumstance can explain, in the frame of the discussed mechanism presented in Fig. 3, linear dependence of the LTD induction period upon the time of uv irradiation, as $[ClO_3^-]$ and the irradiation time t_{irr} are obviously linearly connected:

$$[ClO_3^-] \sim t_{irr}. \qquad (7)$$

TABLE II

LENGTH OF INDUCTION PERIOD OF THERMAL DEVELOPMENT τ_D FOR PURE AP AND AP CONTAINING PROTON-ACTIVE ADDITIVES, $T = 230°C$, AFTER UV IRRADIATION FOR 5 MIN

Sample	τ_D (min)
Pure AP	15
AP + 5.1×10^{-2}% HSO_4^-	9
AP + 5.0×10^{-2}% $CS(NH_2)_2$	20
AP + 5.0×10^{-3}% HPO_4^{2-}	25

The linear dependence of the optical density of an image on the cleavage surface on AP crystal depth (see Fig. 5) can apparently be explained by the Bouger–Lambert–Beer law for light absorption during its penetration through an absorbing medium:

$$I = I_0 \exp(-kx). \qquad (8)$$

However, the considerations presented cannot exclude the principal possibility of another explanation of the influence of preliminary uv irradiation on the AP properties. In the opinion of the authors of (*5*, *9–13*, *15–16*) the LTD rate for AP crystals depends essentially upon the dislocation concentration. Also, one cannot exclude that during uv irradiation dislocations are produced and accumulated in AP crystals, and this very factor is decisive in the arising of a latent image. The authors plan to describe the test of this assumption in the next report.

References

1. L. L. Bircumshaw and T. R. Phillips, *J. Chem. Soc.* 4741 (1957).
2. H. Osado and E. Sakomoto, *Koguo Kaugaku Kuokaishi* **24**, 236 (1963).
3. V. V. Boldyrev, *J. Sci. Appl. Photogr. Cinemat.* **19**, 91 (1974).
4. E. F. Khairetdinov, T. V. Mulina, and V. V. Boldyrev, *J. Solid State Chem.* **17**, 213 (1976).
5. P. W. M. Jacobs and H. M. Whitehead, *Chem. Rev.* **69**, 551 (1969).
6. P. Urone and E. Bonde, *Anal. Chem.* **32**, 1666 (1960).
7. D. Yong, "Decomposition of Solids," Pergamon Press, London/New York (1966).
8. E. S. Freeman and D. A. Anderson, *J. Phys. Chem.* **65**, 1663 (1961).
9. P. J. Herley and P. W. Levy, *J. Chem. Phys.* **49**, 1443 (1968).
10. P. J. Herley and P. W. Levy, *J. Phys. Chem.* **75**, 191 (1971).
11. A. V. Raevsky, G. B. Manelis, V. V. Boldyrev, and L. A. Votinova, *Dokl. Akad. Nauk SSSR* **160**, 1136 (1965).
12. K. J. Kraeutle, *J. Phys. Chem.* **74**, 1350 (1970).
13. P. J. Herley, P. W. M. Jacobs, and P. W. Levy, *Proc. Roy. Soc. (London), Ser. A* **318**, 197 (1970).
14. V. F. Komarov, V. V. Boldrev, V. K. Zhuravlev, and G. V Ivanov, *Kinetika i Katalis* **7**, 788 (1966).
15. B. I. Kaidymov, D. P. Draganova, and M. G. Ivanova, *Kinetika i Katalis* **14**, 906 (1973).
16. J. O. Williams, J. M. Thomas, Yu. P. Savintsev and V. V. Boldyrev, *J. Chem. Soc. Ser. A* 1760 (1971).