

INFLUENCE OF PRELIMINARY UV IRRADIATION ON THE THERMAL DECOMPOSITION OF COPPER HYPOPHOSPHITE

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ABSTRACT

The effect of the influence of preliminary UV irradiation on the kinetics of the thermal decomposition of crystalline copper hypophosphite has been discovered, revealing a decrease in the induction period. Spectral dependence of the effect was determined by absorption of copper hypophosphite in the 255 nm charge transfer band. Comparison of the quantum efficiency of the disappearance of ions of bivalent copper 10^{-1} – 10^{-2} ions per quantum and the quantum output of hydrogen 10^{-4} – 10^{-5} mole per quantum as well as acid formation during photolysis shows that a proton (acid) as well as the univalent copper is the main primary product of photolysis. Formation of acid in the course of photolysis participating in the nucleation during the investigated topochemical process of thermal decomposition is the reason for the discovered effect.

INTRODUCTION

Investigation of the thermal decomposition of copper hypophosphite (CHP) $\text{Cu}(\text{H}_2\text{PO}_2)_2$ is of interest in order to study regularities in the formation and development of reaction nuclei, which determine the kinetics of topochemical transformation. One of the factors influencing the nucleation process during the thermolysis of metal salts is their preliminary irradiation by the UV light. This effect is the foundation for one method of directly regulating the kinetics of topochemical reactions [1]. Its investigation also provides a better understanding of the mechanism of the thermal decomposition itself. The main goal of the work is to find the reasons for the effect of preliminary irradiation on CHP thermal decomposition.

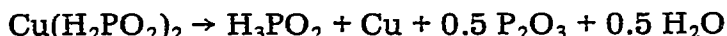
The reaction for the thermal decomposition of CHP has been studied previously [2]. It was suggested that hypophosphite ions in an active tautomeric form containing the three-coordinated phosphorus served as potential centres of nucleation. The nucleation reaction starts with the capture of a proton migrating over the substance matrix at such an ion



The reactive form of the hypophosphorus acid formed in this way interacts with a closely located bivalent copper ion. Such interaction is facilitated due to the steric peculiarity of the tautomeric form. As a result, an intermediate

univalent copper compound is produced supposedly containing CuHPO_2 and two protons. The decomposition products of this compound are the metallic copper, water and phosphorus trioxide. It is essential that two new protons (two new acid molecules) rather than one captured are produced during the decomposition, resulting in the autocatalytic growth of product nuclei.

The whole process of CHP thermal decomposition is described under the investigated conditions by the equation



EXPERIMENTAL

Synthesis of the crystalline CHP was performed by the technique described in ref. 3. The kinetics of thermal decomposition of CHP samples using small crystals with an average size 0.1 mm was investigated by the weight variation in the isothermal regime in vacuum 10^{-2} torr. An automatic thermogravimetric kinetic device was used.

Absorption spectra of CHP in UV, visible and close IR regions were obtained using SF-8 spectrophotometers using different methods of sample preparation, i.e. powder suspension in glycerine, tablets in the chloride and bromide of potassium. For kinetic experiments samples were used in the form of a thinly-ground CHP suspension in glycerine between two quartz plates with a highly polished surface.

Gas evolution during photolysis was studied in a continuously pumped out system with the help of the omegatron partial pressure gauge in vacuum 10^{-6} – 10^{-7} torr. The hydrogen sensitivity was about $5 \cdot 10^{10}$ molecules sec^{-1} . Pressed CHP tablets were used as samples.

The mercury lamp (10^{15} quanta $\text{cm}^{-2} \text{sec}^{-1}$ in the 254 nm band) and the powerful xenon lamp with a mirror monochromator were used as light sources.

RESULTS AND DISCUSSION

The kinetics of thermal decomposition for small crystalline CHP samples irradiated by a mercury lamp are presented in Fig. 1. An increase in the UV irradiation dose considerably reduced the induction period, whereas the maximum decomposition rate remained practically constant. Such characteristics of the variation of the decomposition kinetics point to the possibility that defects participating in nucleation arise during the irradiation.

Optical microscopic observations of the irradiated crystals showed that they decomposed with formation of a much larger number (compared to the case of non-irradiated crystals) of small nuclei under the crystal surface.

In the investigated spectral region two absorption bands of CHP are seen with maxima at 255 nm (Fig. 2, curve 1) and 800 nm. In compounds of the bivalent copper the first band corresponds to charge transfer from a ligand to a metal [4]. In spectra of ammonium and potassium hypophosphites as well

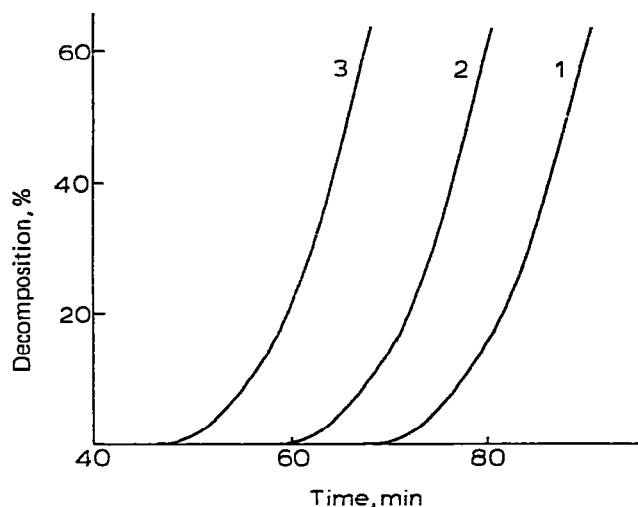


Fig. 1. Influence of preliminary irradiation on the kinetics of thermal decomposition of crystalline CHP at 50°C. 1, Non-irradiated; 2, irradiation time of 10 min; 3, irradiation time of 30 min.

as in that of the CHP structure analog — calcium hypophosphite — this band is not observed. It is evidently connected with the electron transfer from the hypophosphite ion to that of the bivalent copper. The second 800 nm band corresponds to $d-d$ transitions in the ion of the bivalent copper located in the field of ligands. CHP is not light sensitive in this region.

Figure 2 (curve 2) shows the spectral dependence of the influence of preliminary irradiation. Small crystals were irradiated with the same doses of 0.15 J cm^{-2} of the UV light with different wavelengths. The kinetics of thermal decomposition were studied by the method described above, the time of the sample decomposition by 5% was taken as a length of the induction period. The error was estimated by the reproducibility of the kinetics.

It can be seen that the spectral dependence of the effect is determined by

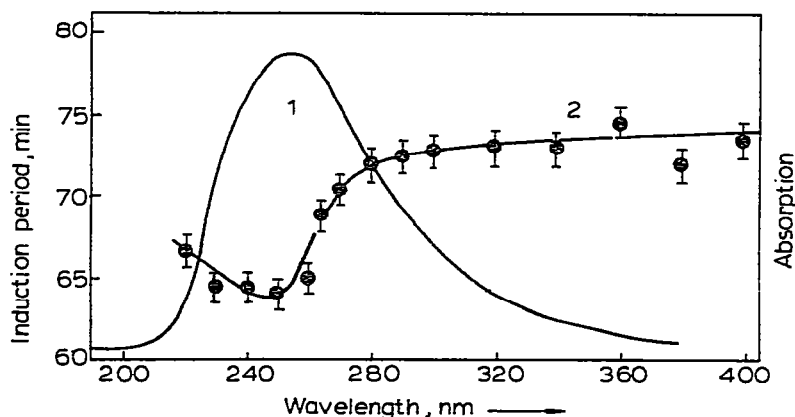


Fig. 2. Band of charge transfer in the absorption spectrum of CHP (1) and spectral dependence of the induction period during thermal decomposition of the irradiated CHP at 50°C (2).

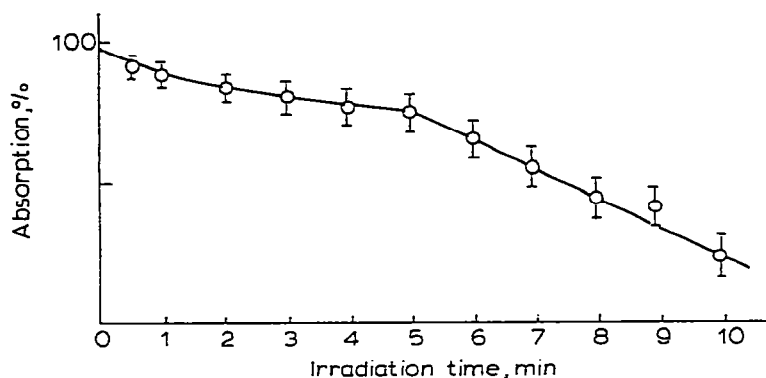


Fig. 3. Kinetics of disappearance of the 255 nm band during CHP irradiation.

the CHP absorption in the band of charge transfer. A decrease in the induction period accompanies the absorption. The minimum of the induction period corresponds to the absorption maximum.

Photochemical CHP decomposition in the course of absorption in the charge transfer band starts with the photo-transfer of the electron from the hypophosphite ion to the bivalent copper ion. In this process an ion of univalent copper is produced as well as an unstable photo-hole H_2PO_2^0 decomposing at the least energetic bond P—H. Decomposition can proceed via two ways: either with proton or hydrogen atom formation.

For quantitative comparison of the efficiency of the process in these changes, values of quantum efficiencies were estimated for the disappearance of bivalent copper ions and hydrogen appearance during the CHP irradiation.

CHP irradiation at room temperature resulted in the disappearance of the 255 nm band, the intensity of which was directly proportional to the sample, as well as the 800 nm band. The kinetics of the ion disappearance are shown in Fig. 3. The quantum efficiency of the Cu^{2+} disappearance estimated by its maximum rate at the beginning of photolysis and by the intensity of the absorbed light was about 10^{-1} – 10^{-2} ion per light quantum. The contrary flexure of the curve at large irradiation times is explained by the start of the intensive dark process of thermal decomposition.

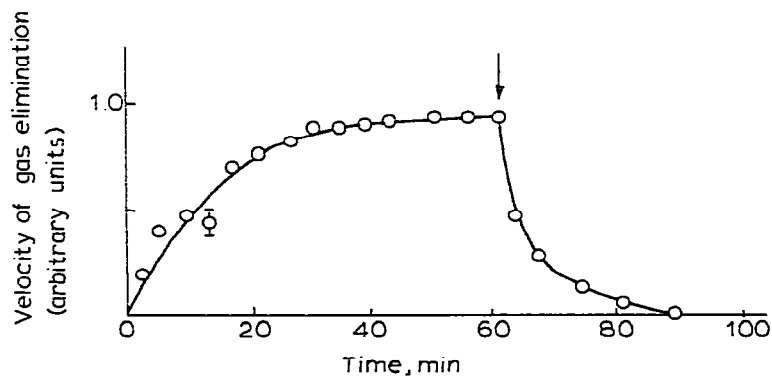
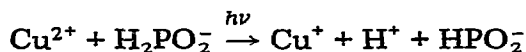


Fig. 4. Kinetics of hydrogen evolution during CHP irradiation.

The kinetics of hydrogen evolution from CHP during irradiation at room temperature are presented in Fig. 4. The start of irradiation by light of low intensity is accompanied by an increase of the gas evolution rate up to a stationary value. When irradiation stops (shown by the arrow) the gas evolution level goes down to the initial background level. An estimation of the hydrogen quantum output by the stationary rate of evolution and light intensity gives a value of about 10^{-4} – 10^{-5} molecules per light quantum.

Comparison of the quantum output of the disappearance of the Cu^{2+} ions and hydrogen formation shows that photodecomposition proceeds primarily with proton formation or, in other words, the acid.



This is in line with experimental data on the formation of the acid product during CHP photolysis as well as with literature data that HPO_2^- is the main product of hypophosphite radiolysis [5].

Taking into account the cell effect, it can be assumed that there exists the interaction of produced HPO_2^- with a closely located ion of univalent copper. This results in the formation of the intermediate product CuHPO_2 similar to that observed during the CHP thermal decomposition [2].

A spectrophotometric investigation of the products of CHP photochemical decomposition shows that at partial disappearance of the 255 nm band the absorption bands of the intermediate product at 210 and 235 nm appear similar to those for the intermediate compound during thermal decomposition. The decomposition of this intermediate compound, going at a notable rate even at room temperature, results in the following reaction products: metallic copper, water and phosphorus trioxide.

Thus, the acid is the primary product of the CHP photolysis. As noted above, the acid (proton) participates in the nucleation reaction during CHP thermal decomposition. Increase of the acid concentration in the system during irradiation results in the acceleration of nucleation and a decrease in the induction period at subsequent thermal decompositions of copper hypophosphite.

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