Thermochimica Acta, 43 (1981) 135—141
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

KINETICS AND MECHANISM OF THERMAL DECOMPOSITION OF COPPER HYPOPHOSPHITE

O.I. LOMOVSKY, Yu.I. MIKHAILOV, V.V. BOLDYREV and V.M. MASTIKHIN

Institute of Physico-Chemical Principles of Processing of Raw Minerals, Siberian Division of the U.S.S.R. Academy of Sciences, Novosibirsk 630091 (U.S.S.R.)

(Received 10 June 1980)

ABSTRACT

On the basis of an elaborate investigation of the thermal decomposition reaction for crystalline copper hypophosphite by kinetic, radiospectroscopic and optical methods, and by a study of the peculiarities of the copper hypophosphite structure and defects, it has been found possible to suggest the mechanisms by which the decomposition kinetics are regulated.

INTRODUCTION

The specificity of thermal decomposition reactions of solid inorganic substances is due first of all to their topochemical character, which means that they often proceed via the formation and growth of product nuclei. They are characterized by reaction localization at the stage of nucleation, and autolocalization at the boundary of "the initial substance-product" at the stage of reaction development. The works on the investigation of such systems are mainly devoted to the development of mathematical models describing the reaction kinetics with accounts of space characteristics. However, to control the reaction kinetics one must know the real mechanism. Copper hypophosphite (CHP), $Cu(H_2PO_2)_2$, is a convenient system for such an investigation as different methods can be used to trace the state of all atoms changing the oxidation degree in the reaction. This provides perspectives for revealing physico-chemical factors responsible for the localization and autolocalization of the reaction.

The main goal of this work is to find a mechanism of the topochemical oxidation—reduction reaction of thermal decomposition by analyzing its topochemical peculiarities and to determine methods regulating the reaction kinetics.

Methods of obtaining copper hypophosphite and general information about its thermal decomposition are given in our previous work [1]. It has been established that at temperatures above 50°C in vacuum 10^{-2} torr the copper hypophosphite decomposes according to the equation

$$Cu(H_2PO_2)_2 \rightarrow Cu + H_3PO_2 + 0.5\ H_2O + 0.5\ P_2O_3$$

Decomposition starts with the appearance of dark regions in a crystal volume-nuclei of the reaction product. Further decomposition proceeds due to growth of several nuclei which quickly occupy the whole crystal volume.

EXPERIMENTAL

Synthesis of CHP in the form of small crystals with an average size of 0.1 mm was performed according to ref. [1]. The kinetics of thermal decomposition were studied by the weight variation in the isothermal regime in vacuum 10^{-2} torr. An automatic thermogravimetric kinetic device was used.

The electroconductivity of samples was studied using the device for automatic recording of electroconductivity in Arrhenius coordinates. To obtain pressed tablets CHP crystals were carefully ground in an agate mortar and pressed into tablets to a size of 12 mm and thickness 0.3—0.5 mm in vacuum at a pressure of 10 t cm^{-2}, allowing reproducible results. Measurements were performed using silver and Aquadag electrodes both at the residual pressure 10^{-2} torr and in the atmosphere of pure helium (100 torr). Before measurements, samples were conditioned to achieve constant electroconductivity. A voltage of 1—10 V was applied. In the voltage range studied the electroconductivity was ohmic.

During the investigation of thermal e.m.f. pressed tablets 5 mm in diameter and 0.5 mm thick were used, both with and without electrodes made by the silver paste. The sample resistance at room temperature was about 10^{-14} Ω.

Admixtures were introduced into solutions out of which CHP was crystallized. Separate experiments showed that an addition really enters a crystal but not as an inclusion.

Radiospectroscopy experiments were done by means of JNM-4H-100 and EPR-20 installations. Spectra of CHP absorption in UV and visible regions were taken using an SP-8 spectrophotometer with samples in the form of thin-ground CHP suspensions in glycerine between two quartz plates with a highly polished surface.

RESULTS AND DISCUSSION

Kinetic curves of CHP thermal decomposition are presented in Fig. 1. They are typical for topochemical reactions and are characterized by the presence of the induction period, which determines to a considerable extent the duration of complete decomposition. Effective activation energies of the decomposition process are 23.8 ± 1.2 kcal $mole^{-1}$, as determined by maximum velocities, and 26.4 ± 1.3 kcal $mole^{-1}$ for the induction period determined by different methods.

Our approach to the investigation of topochemical reactions is based first of all on the considerations of peculiarities of their start and development. The main questions are: (1) where and why does the reaction start (nature of potential centres of nucleation and the reason of the reaction localization); (2) why does the reaction continue in this place (the reason of the reaction autolocalization) [2].

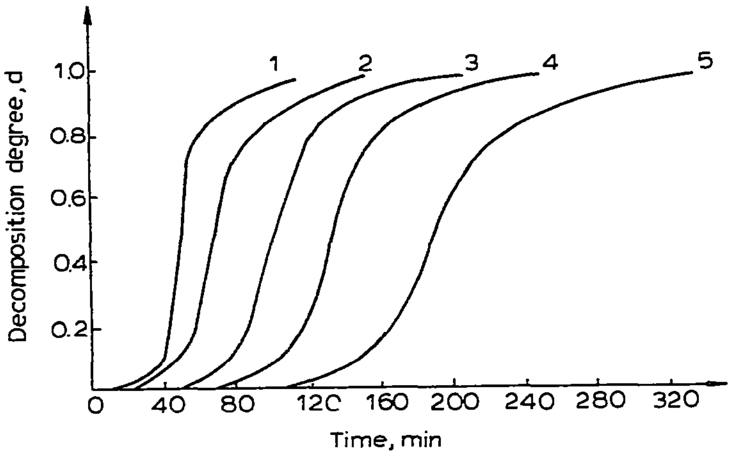


Fig. 1. Kinetic curves of CHP thermal decomposition by weight variation. Decomposition temperature in °C (1) 56; (2) 53; (3) 50; (4) 48; (5) 45.

The main peculiarity of the reduction by hypophosphites in solution is that the molecule of the hypophosphorous acid serves as an active reducing particle. The coordination number of phosphorus in form I is 4, while in form II it is equal to 3. It is form II which appears active. Its content is very low, in 1 M solution of an acid its concentration is 10^{-12} to that of form I. It is known that the rate of formation as well as concentration of the tautomeric form of an acid in solution can be regulated by proton- and electron-active additions [3].

It is natural to assume that if in a crystal similar to the solution, an acid

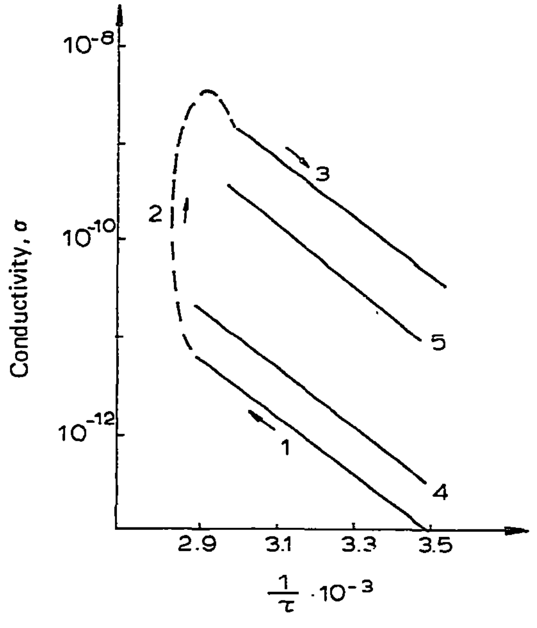


Fig. 2. (1, 2, 3) Temperature dependence of the electroconductivity of pure CHP (direction of temperature variation is indicated by arrows); (4) CHP, synthesized in presence of 0.1 mole % of HSO_4^-; (5) 0.3 mole % HSO_4^-.

molecule in the active form can be produced, then it will also be active during the reduction in a solid phase.

We believe that tautomeric hypophosphite ions cocrystallize during the CHP crystal formation. In this case they can serve potential centres of nucleation and the reaction starts at them by formation of the active molecules of acid II during protonation. The necessary condition of this is the presence of movable protons in the system. In Fig. 2 temperature dependences of the electroconductivity are presented for initial CHP, partially decomposed CHP and CHP with a special acid addition. In all cases the electroconductivity activation energies are seen to be equal. On the other hand, investigation of thermal e.m.f. leads to the conclusion that the current carrier has a positive character. These facts point to the proton character of CHP conductivity.

In this case there are necessary conditions for formation of the acid molecules in a crystal. By variation of the concentration of tautomeric ions II and protons, one can vary the nucleation rate, i.e. the length of the induction period. In fact, it appeared that introduction of the Ag^+ addition in the solution, which increased the concentration of the tautomeric ions II, diminished the length of the induction period during thermal decomposition of CHP obtained from this solution. The electron-donor addition of Fe^{2+} which lowered the concentration of tautomeric ions, results in an increase of the induction period. The addition of an acid which, first, leads to the increase of proton concentration in a matrix and, second, increases the number of tautomeric ions, results in a decrease of the induction period. The addition of alkali gives an opposite effect.

Tautomeric ions II can serve as potential centres of nucleation because for the interaction in a solid phase to occur some free space is needed for its organization. Phosphorus atoms of the hypophosphite ions in the CHP structure are closed by oxygen atoms, coordinating atoms of Cu^{2+} and hydrogen atoms. It was discovered that the PMR spectrum of broad lines of the crystalline CHP differs from that of its structure analog — calcium hypophosphite — by some asymmetry pointing to the presence of a proton signal with a chemical shift about 200 ppm besides the proton signal in usual fields (Fig. 3). Most likely, protons of at least two types exist in the CHP structure,

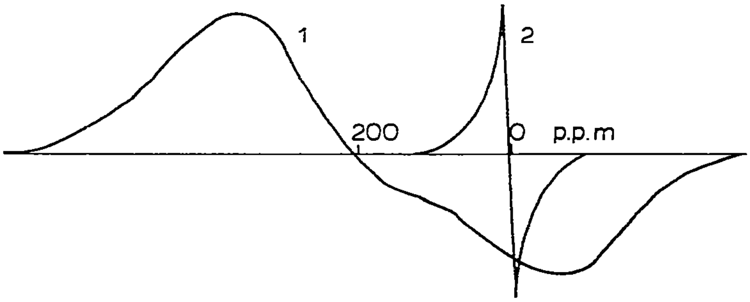


Fig. 3. PMR spectra. (1) Initial CHP (sample temperature is —120°C); (2) completely decomposed CHP at 52°C (room temperature).

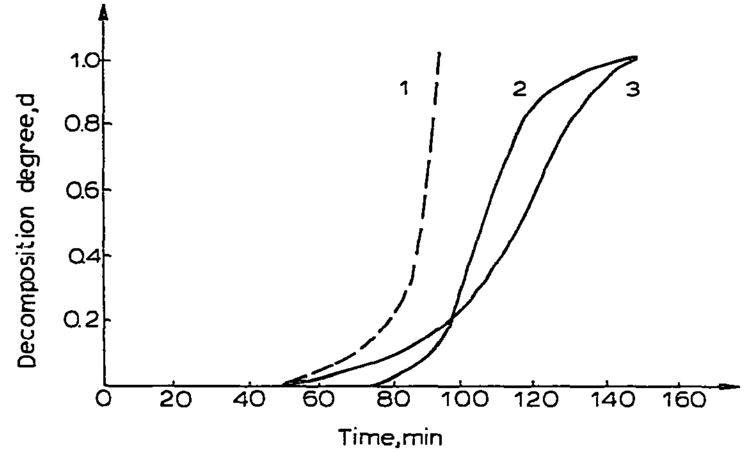


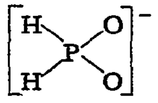
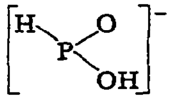
Fig. 4. Kinetic curves obtained by (1) dynamics of the variation of the standard PMR signal for experiment 2; (2) appearance of the narrow PMR signal of acid protons; (3) variation of the EPR signal of Cu^{2+}.

some of them interact stronger with Cu^{2+} ions, i.e. are closer to them than others. If the hypophosphite ion is in the tautomeric form II, then this closer hydrogen atom of the hypophosphite ion can be absent. By this the steric possibility arises of attack by the Cu^{2+} ion on the undivided pair of phosphorus electrons in a molecule of the active form of the acid. Thus, the reaction starts at the hypophosphite ion in form II by its protonation (Table 1). The steric peculiarity of the ion facilitates the interaction between the acid produced in situ and the ion of bivalent copper.

In Fig. 4 the kinetics of the Cu^{2+} ions disappearance is shown as judged by the EPR signal, as well as the kinetics of the hypophosphorous acid formation by the PMR signal of narrow lines which appears during CHP decomposition. All kinetic radiospectroscopic experiments were performed on directly decomposed samples in the device resonators in air. The coincidence of the moment when the EPR signal disappears with the beginning of the variation of standard PMR signal reflects, similar to the EPR experiments, the disappearance of the paramagnetic Cu^{2+}, and allows correct comparison of these kinetic curves. It can be seen that the formation of a notable amount of the acid in decomposition products occurs when bivalent copper has already disappeared to a considerable extent. Probably, an intermediate stage exists between the disappearance of the bivalent copper and acid appearance.

Investigation of variations in optical and UV absorption spectra of CHP shows that during decomposition the 255 nm band of initial CHP vanishes and intermediate bands at 210 and 235 nm appear. The final spectrum is characterized by the non-selective absorption of the parts due to metallic copper. As the EPR signal disappears together with the 255 nm band one can postulate that the univalent copper is produced in the course of decomposition. Taking into consideration the formation of the intermediate phase established by the Roentgen phase investigation [1], it is natural to suppose that an intermediate compound containing the univalent copper is produced in the course of decomposition.

TABLE 1
Mechanism of the thermal decomposition of $\mathrm{Cu(H_2PO_2)_2}$

Decomposition steps		Experimental result
Initial system	 $\mathrm{Cu^{2+}}$  Usual hypophosphite-ion Tautomeric ion-potential centre of nucleation	Additions increasing the active form concentration decrease the induction period.
(1) Formation of the acid in the active form	Proton migration along a matrix $\downarrow + \mathrm{H^+}$	Action of acid additions. Electrophysical experiments point to the proton CHP electroconductivity.
(2) Interaction with the active form of the acid	$\mathrm{Cu^{2+} - - - : \overset{\displaystyle H}{\underset{\displaystyle OH}{P}} - OH}$ $\downarrow$	Facilitated attack of $\mathrm{Cu^{2+}}$ ion over the undivided pair of phosphorus electrons in $\mathrm{(H_3PO_2)_{act.}}$ is a reason for localization of nucleation.
(3) Formation of the intermediate product	Complex dissociation $\left[\mathrm{Cu - \overset{\displaystyle H}{\underset{\displaystyle OH}{P}} - OH}\right]^{2+}$ $\downarrow$ $\mathrm{CuHPO_2 + 2\,H^+}$	Autolocalization of the process provided by the reproduction of two protons (instead of one) in the reaction zone. Presence of intermediate products containing $\mathrm{Cu^+}$ during decomposition.
(4) Decay of the intermediate and subsequent reactions	$\downarrow$ $\mathrm{HPO_2 + Cu}$ $\downarrow$ $\mathrm{0.5\,H_2O + 0.5\,P_2O_3}$	
(5) Development of the reaction	$\mathrm{H^+ + H_2PO_2 \rightleftharpoons H_3PO_2}$ $\downarrow$ $\mathrm{H_3PO_2}$ in the active form	Acid accumulation during the reaction
Interaction with the next $\mathrm{Cu^{2+}}$ ions [as in (2)]	$\downarrow + \mathrm{Cu^{2+}}$	

It is shown in Table 1 that $\mathrm{Cu^{2+}}$ ion interaction with a molecule of the hypophosphorous acid II leads to formation of two protons and an intermediate compound of the univalent copper with the suggested content $\mathrm{CuHPO_2}$, which further decomposes with formation of the metallic copper, phosphorus trioxide and water. Two newly-formed protons are captured by the closest hypophosphite ions and produce two molecules of the hypophosphorous acid, instead of one participating in the reaction. The acid transforms in the tautomeric form and reduces the nearest Cu^{2+} ions. Note that a tautomeric transition is facilitated as a strongly acid liquid phase is produced as a result of the reaction.

Now, discussing the reaction autolocalization at the boundary, one can state that the reason for this is formation of the increasing number of protons at the boundary during decomposition or, in other words, formation of acid.

The considered mechanism of thermal decomposition of crystalline CHP answers the man questions concerning topochemical peculiarities of the reaction, and points to the possibility of controlling the reaction kinetics by certain additions. It was observed that additions can change the decomposition kinetics from practically non-inductive to decomposition with an induction period of up to 3 h (50° C).

It is important to note that as a result of this investigation a possible role of such defects as a co-crystallized tautomeric ion has been shown for the localization of the topochemical reaction.

In the other studied topochemical reactions of decomposition with the formation of metal, the reason of autolocalization was traditionally assumed to be connected with the electron-active properties of the metal, the tradition coming from the mechanism of photochemical decomposition of silver halides by Gurney-Mott. In this system, formation of the increasing amount of acid during the decomposition appears decisive. In this respect the suggested mechanism is new and develops our conceptions of the reasons for the reaction localization in a solid phase.

REFERENCES

1 O.I. Lomovsky, Yu.I. Mikhailov and A.B. Brosalin, Proc. Sib. Branch Acad. Sci. U.S.S.R., Ser. Chem., 2 (4) (1978) 50.

2 V.V. Boldyrev, Russ. Chem. Rev., 42 (7) (1973) 1161.

3 J.R. Van Wazer, Phosphorus and Its Compounds, Vol. 1, Interscience, New York, 1958, pp. 288—290.