

BRIEF COMMUNICATIONS

Variation of the Reactivity of Solids near the Interface Reagent-Product of the Topochemical Reaction

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During the topochemical decomposition of ammonium perchlorate and copper hypophosphite an enhanced acid concentration occurs near the reagent-product interface. Concentration profiles of the acid were observed after the treatment of the partially decomposed crystals by indicator solution and by microphotometry. Profiles exhibit the diffusive characteristics. The diffusion coefficient is 10^{-10} cm²/sec for ammonium perchlorate and 10^{-9} cm²/sec for copper hypophosphite at 20°C. It is concluded that the variation of the reactivity near the interface is due to the enhanced acid concentration.

The predominant process in topochemical reactions near the reagent-product interface is thought to arise from the increase in this region of the reactivity of the initial product. For example, the formation and accumulation of a chemically active intermediate product may occur on and near the interface. It is suggested that such a situation arises in the thermal decomposition of ammonium perchlorate (1, 2), copper hypophosphite (3), and of some crystallohydrates (4). The initial decomposition of ammonium perchlorate at about 180°C results in the formation of ammonia and perchloric acid, HClO₄. The intermediate active product (a perchloric acid) oxidizes solid ammonium perchlorate, with formation of final gaseous products—nitrogen and chlorine oxides, as well as the new acid (1). Ammonium perchlorate is a proton conductor; thus, such protons can penetrate into the

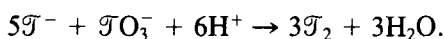
crystal by moving through the anion sublattice (5). The perchlorate ion capturing a proton becomes an acid molecule in an anion position. Such a unit on the surface may be considered as an acid center of the Brønsted type.

In the decomposition of copper hypophosphite the reduction of ions of bivalent copper occurs through hypophosphoric acid, H₃PO₂. As in the previous case, an acid molecule forms the active intermediate, which originates during the initial stages of decomposition (3). There are also indications that a copper hypophosphite is a proton conductor (6).

Additions of acids accelerate the decomposition of these compounds (1-3).

The aim of this paper is to determine whether an excess concentration of acid is formed near the interface in topochemical decompositions.

To reveal potential regions on the surface of the partially decomposed crystals where an increased acid concentration may occur, crystals were treated by a special indicator solution similar to those for quantitative determination of the Brønsted-type acid centers on the surface of solid catalysts (7, 8). These solutions were made up from potassium iodide (0.05 *M*), potassium iodate (0.01 *M*), and starch (1 *M*). During the surface treatment by a thin layer of this solution the following reaction occurred



Starch was added to increase the intensity of the reaction product color and to reduce its mobility.

To measure the optical density on the small crystal sites the following equipment was used: a microphotometer on the base of a photoelectron multiplier and an amplifier to measure small currents which permitted measurements of optical densities in the range 0–6. As a sample holder a microscope stage with a 0.003-mm micrometer screw was used. A lightguide consisting of 8- μm quartz thread was installed in the stage. The sample was in intimate contact with the end of the lightguide. Minimization of the optical path from a sample to the probe lightguide (in contrast with path lengths of dozens of centimeters in usual devices) reduces the influence of scattering and permits photometry of closely adjacent sites with strongly differing optical densities.

Crystals of ammonium perchlorate were decomposed at $180 \pm 2^\circ\text{C}$ in the air. Product nuclei form regions along the main diagonal of the rhombus *i* in the (011) plane. The decomposition of copper hypophosphite crystals at $50 \pm 1^\circ\text{C}$ in the air was characterized by the appearance of dark sites indicative of nuclei of the reaction product. Photometry was performed in the direction perpendicular to the interface.

When absorption of the decomposed

crystal was detected, after the time *t*, the crystal was treated with the indicator solution and the second photometry was carried out. Investigations of the undecomposed crystals treated with an indicator solution showed that absorption did not noticeably change. On the decomposed crystals coloring appears close to the boundary.

The logarithm of the ratio of intensities of the light passing through the region of the surface before and after treatment (\mathcal{I}_1 and \mathcal{I}) is a linear function of *n*—the concentration of the product of the indicator reaction.

Figure 1 presents the dependence of $\log \mathcal{I}_1/\mathcal{I}$ on the distance *x* along the perpendicular to the boundary for *t* = 48 hr. It can be seen that the acid concentration over the crystal surface passes through a maximum, which corresponds to the optically observed boundary. This result is consistent with the data of Ref. (9), in which it has been shown through layer-by-layer titration that the distribution of the concentration of perchloric acid has a maximum near interface. The concentration profiles ahead of the interface are well described by the Gaussian distribution

$$n(x) = n \exp\left(-\frac{x^2}{\sigma^2}\right)$$

A similar distribution is obtained by solving the diffusion equation

$$\frac{\partial^2 n}{\partial t} = \mathcal{D} \frac{\partial^2 n}{\partial x^2}$$

with the initial condition

$$n(x, t = 0) = n_0\delta(x),$$

i.e., under the assumption that protons diffuse from a very thin layer of the acid on the interface.

To check the assumption about the diffusive character of the concentration profile *n*(*x*) its broadening with time has been investigated. Figure 2 presents the *x*₀ dependence on \sqrt{t} , where *x*₀ is a distance from

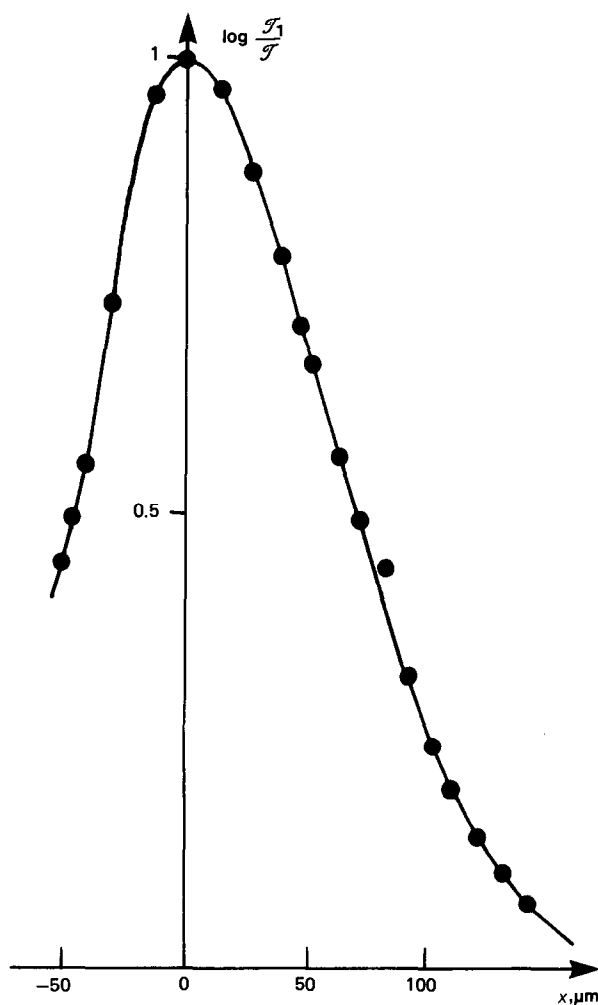


FIG. 1. Distribution of an acid near the interface (its position corresponds to $x = 0$) for ammonium perchlorate.

the interface at which $\log \mathcal{T}_1/\mathcal{T}$ decreases by a factor of 2. It can be seen that the broadening of the optical density profile proceeds according to the law

$$n(x) = n_0 \exp\left(-\frac{x^2}{4\mathcal{D}t}\right)$$

with a diffusion coefficient $\mathcal{D} = 10^{-10}$ cm²/sec.

For the thermal decomposition of copper hypophosphite the distribution of the acid near the interface has a form similar to that

of ammonium perchlorate, but with $\mathcal{D} = 10^{-9}$ cm²/sec.

Thus it has been shown that for the thermal decomposition of ammonium perchlorate and copper hypophosphite an enhanced concentration of a chemically active product—acid—exists near the reagent-product interface. The concentration profiles of an acid exhibit a diffusive character. According to our results, and taking into account existing data on the accelerating influence of acids on the decomposition,

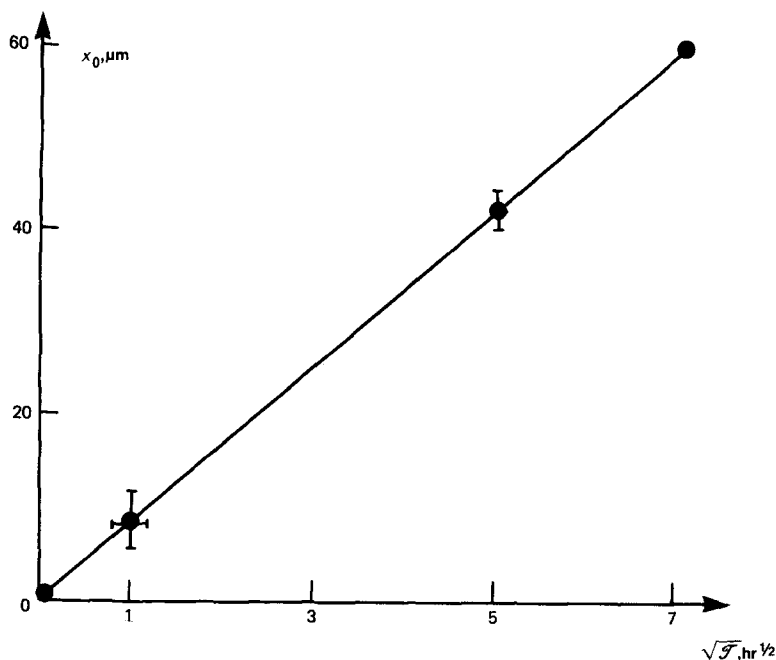


FIG. 2. Broadening of the acid concentration profile at 20°C as a function of the time beyond termination of the decomposition.

one may assume that the variation of the reactivity near the reagent-product interface is caused by the enhanced acid concentration.

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