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Thermal Disproportionation of Hypophosphorous Acid

G. T. Shechkov, I. A. Pevneva, and O. A. Meshkova

Polzunov Altai State Technical University, Barnaul, Russia

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Abstract—Thermal disproportionation of hypophosphorous acid was studied to find the reaction order, the rate constant and activation energy of the process, and also the temperature ranges in which the reaction rate is the highest.

The use of red phosphorus is based on its capability to be oxidized (manufacture of matches, getters, fire-retardants, and components of pyrotechnic formulations) [1–3]. The oxidation yields phosphorous acids (hypophosphorous H_3PO_2, phosphorous H_3PO_3, and phosphoric H_3PO_4) and phosphine PH_3. The formation of these products may result both in retrogradation of properties of phosphorous composites and in shortening of guaranteed shelf lives of articles based on red phosphorus.

However, the kinetics and temperature ranges of transformation of phosphorus acids have not been analyzed in studies devoted to phosphorus oxidation [2–4]. The main goal of the present study was to analyze the fundamental aspects of phosphine formation in disproportionation of hypophosphorous acid of varied concentration and to determine the temperature ranges and kinetic parameters of the process

$$3H_3PO_2 \rightarrow 2H_3PO_3 + PH_3. \quad (1)$$

We studied 50% hypophosphorous acid of reagent grade, TU (Technical Specification) 6-09-1462–76. The acid was diluted with twice-distilled water and concentrated by recrystallization, as described in [5].

The disproportionation was monitored by evolution of PH_3 in the temperature range (30–160) ± 1.5°C in a glass reactor connected to an AGB-67M automated gas burette.

The acid (5 g) was placed in a glass dish mounted on a quartz hook fastened to a ground tap wrench by a fiberglass thread. A sample was rapidly (10 s) introduced into the reactor with a furnace, using the tap wrench.

The sensitivity of the installation was 0.001 to 1 ml, depending on a burette volume. The error in measuring the gas volume was ±5%. A solution of calcium chloride served as a locking liquid.

Analysis for PH_3 was carried out on an LKhM-80 chromatograph by the technique described in [6]. Gas samples (1 ml) were taken from the reactor at intervals of 10–15 min through a hermetic tap made of special rubber. Polysorb-1 served as absorbent. The flow rate of the carrier gas was 24 ml min^{-1}; column temperature, 60°C; measurement error, ±3%. Phosphine for constructing a calibration plot was obtained by hydrolysis of aluminum phosphide and analyzed both chemically and chromatographically.

A thermal analysis of H_3PO_2 was carried out with 200-mg samples on an MOM Q-1500D (Hungary) derivatograph in standard ceramic crucibles at a heating rate of 10 deg min^{-1}.

We revealed low- (30–90°C) and high-temperature (110–200°C) regions of phosphine evolution in disproportionation of H_3PO_2. At low temperatures, the acid reacts with water to give hydrogen, which was detected by mass-spectrometry:

$$H_3PO_2 + H_2O \rightarrow H_3PO_3 + H_2. \quad (2)$$

At high temperatures (>110°C) the disproportionation process (1) occurs at the highest rate at 130–160°C, being complete at 190°C. The process is complicated by gas-phase oxidation of phosphine, begining at 120°C and ending in combustion of the gas mixture above 160°C.

Kinetic curves of disproportionation are S-shaped. The rate of H_3PO_2 disproportionation grows with the concentration of the acid increasing from 30 to 90%, the disproportionation being of the autocatalytic nature. This feature seems to be associated with the dependence of the rate of tautomeric regrouping of H_3PO_2 from the inactive form, containing phosphorus(V), to the active form, containing phosphorus(III). The rate constant of the regrouping is extremely low, $k = 10^{-12}\ s^{-1}$ [4]. Raising the concentration, temperature, and time presumably removes diffusion hindrances for this regrouping.

At 110 and 140°C and process duration of 40–160 min the evolution of phosphine occurs in the kinetic mode and further passes to the diffusion mode. With the temperature increasing to above 140°C, the process passes to the diffusion mode within 40–120 min. The disproportionation reaction in the kinetic mode at high temperatures (110–170°C) is first-order with rate constant $k = 1.96 \times 10^{-5}\ s^{-1}$ and activation energy of 85 ± 2 kJ mol^{-1}. The transition of the reaction of phosphine evolution from the kinetic to diffusion mode results from the accumulation of the more thermally stable products H_3PO_3 and H_3PO_4, which are formed upon PH_3 oxidation:

$$4PH_3 + 5O_2 \rightarrow 2P_2O_5 + 6H_2, \quad (3)$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4. \quad (4)$$

A pronounced endothermic effect is observed in the derivatograms at 135°C. It is determined by the equilibrium the endothermic processes of dehydration and disproportionation of H_3PO_2 and also by the exothermic oxidation of the evolving phosphine. The overall activation energy of dehydration, hydration, and disproportionation of H_3PO_2 below 100°C is 44 ± 1 kJ mol^{-1}.

According to the derivatographic data, the activation energy of H_3PO_2 disproportionation in the range 110–140°C is 69.8 ± 2 kJ mol^{-1}, in satisfactory agreement with the activation energy obtained from the kinetic data (85 ± 2 kJ mol^{-1}).

The forming H_3PO_3 disproportionates in the range 190–270°C, with simultaneous oxidation of the evolving PH_3. According to the derivatographic data, the maximum rate of PH_3 oxidation is observed in the range 280–300°C. The corresponding activation energy is 207 ± 10 kJ mol^{-1}.

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