INVESTIGATION OF THE INTERACTION OF POTASSIUM SUPERPEROXIDE WITH AMMONIA

T. P. Firsova, L. A. Mokhov, A. N. Molodkina, and P. I. Fil'chenkov

The interaction of ammonia with inorganic peroxides has practically not been studied. The literature on this question contains only a few indications. Thus, it is reported in [1] that when sodium peroxide is heated with the flame of a gas burner in an atmosphere of dry ammonia, the hydroxide, nitrogen, and partly sodium nitrite and nitrate are formed. Barium peroxide gives only the hydroxide and nitrogen under these conditions, as the same authors report. The temperature evidently was not recorded in this case. The interaction of potassium superperoxide with ammonia proceeds analogously to the latter reaction according to the data of [2].

This work was conducted in order to determine the temperature conditions and basic reaction products of potassium superperoxide with dry gaseous ammonia.

EXPERIMENTAL

The thermogram of potassium superperoxide in an atmosphere of dry ammonia was recorded on the pyrometer of the Kurnakov system (Fig. 1). The exothermic effect at the temperature 236-260°C indicates an interaction of the substances. The remaining effects pertain to potassium superperoxide [3]. The kinetics of the process, both under dynamic and under static conditions, was investigated within the indicated temperature interval. The scheme of the first apparatus is cited in Fig. 2; the second is described in [4].

The starting materials were ammonia from a cylinder and technical potassium superperoxide of the following composition (in % by weight): KO₂ 93.27; K₂O₂ 3.96; K₂CO₂ 1.41; KOH 0.77; H₂O (by difference) 0.59.

Experiments under Dynamic Conditions

The investigation of the interaction was conducted at the temperatures 240 and 300°C; the ammonia concentration in a mixture with nitrogen comprised 3.04 mg/liter or 0.4% by volume. The samples of granulated potassium superperoxide weighed 9 g, height of the layer 2 cm, dimensions of granules 2-3 mm, cross section of reactor 3.4 cm², specific velocity of the gas mixture 0.5 liter/min · cm².

The gas mixture, passing through a column with granulated potassium hydroxide 4 (see Fig. 2), passed into a vertical thermostatically controlled reactor 7, in which there was a sample of potassium superperoxide. A quantitative absorption of the unreacted ammonia occurred in two to three absorbing bottles 9 with 0.2 N H₂SO₄ solution, placed at the exit from the reactor. In monitoring the course of the process, we considered the possibility of the simultaneous occurrence of several reactions and the formation of the following compounds: the nitrate, nitrite, hydroxide, and nitrogen.
The total content of nitrogen in the solid phase was determined according to the procedure described in [5], based on the reduction of nitrogen compounds to ammonia, followed by absorption of the latter with a titrated 0.2 N solution of H$_2$SO$_4$. On the basis of preliminary experiments, in which it was established that only traces of nitrite are present in the solid phase, all the nitrogen found was counted as the nitrate. The calculation was performed according to the formula

$$KNO_3 = \frac{(a - b) \cdot 0.0202 \cdot 100}{m}, \%$$

where $a$ is the volume of the 0.2 N H$_2$SO$_4$ solution used for the absorption of ammonia, ml; $b$ is the volume of the 0.2 N sodium hydroxide solution used for back titration, ml; 0.0202 is the equivalent of KNO$_3$ corresponding to 1 ml of a 0.2-N solution; $m$ is the weight of the sample of the substance, g.

The amount of elementary nitrogen formed was found by calculation from the ammonia balance, considering the amount that passed through the reactor, that found after the reactor, and that oxidized to the nitrate. In addition, the content of total active oxygen in the solid phase was determined volumetrically, and the peroxyd oxygen by a permanganometric method. The total alkalinity in the final product, converted to K$_2$O, as well as the bound carbon dioxide, were calculated according to the change in weight during the experiment and from data on the composition of the starting material. From the sum of the analytical and calculated data, we calculated the content of the following components in the spent product: KO$_2$, K$_2$O, KNO$_3$, KOH, and K$_2$CO$_3$. The nature of the processes that occurred can be judged from the change in the ratio of potassium nitrate and hydroxide in the solid phase, as can be seen from the reactions cited below.

For the case of oxidation of ammonia to nitrate, we have

$$3NH_3 + 8KO_2 \rightarrow 3KNO_3 + 5KOH + 2H_2O$$  \hspace{1cm} (1)
$$2H_2O + 4KO_2 \rightarrow 4KOH + 3O_2$$  \hspace{1cm} (2)

summing, we obtain

$$NH_3 + 4KO_2 \rightarrow KNO_3 + 3KOH + O_2$$  \hspace{1cm} (3)

From this it followed that the molar ratio KOH : KNO$_3$ = 3 : 1. The molar ratio of active oxygen to ammonia is also 3 : 1.