Reports of the Academy of Sciences of the USSR

1962

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR

1962. Volume 146, No. 1

CHEMISTRY

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THERMAL DECOMPOSITION OF NITROSYL PERCHLORATE

(Presented by Academician I. I. Chernyaev, 5 V 1962)

According to Kruse, Huck, and Möller ([1]), solid nitrosyl perchlorate decomposes completely into gaseous substances above 120° according to the equation:

$$2NOClO_4 = N_2O_4 + Cl_2 + 3O_2.$$

In their opinion, the primary decomposition products are N_2O_5 and ClO_2, which then decompose into nitrogen dioxide, chlorine, and oxygen. Up to the present time the composition of the solid phase during the thermal decomposition of $NOClO_4$ has not been known. It was assumed that it consists entirely of nitrosyl perchlorate that has not yet decomposed ([1,2]).

The initial nitrosyl perchlorate was obtained by us by the action of N_2O_3 on an 80% solution of perchloric acid ([3]) and was freed from impurities by holding it in vacuum at 50° in the presence of P_2O_5. Results of analysis of the product obtained: NO 23.22%, Cl 27.10%, total acidity 1.995 equiv/mol; calculated: NO 23.18%, Cl 27.39, total acidity 2.000. All manipulations with nitrosyl perchlorate were carried out in a dry chamber.

The decomposition of nitrosyl perchlorate was carried out in vacuum at a residual pressure of 1 mm Hg and a temperature of $99 \pm 0.1°$. A weighed portion of the substance, previously ground in an agate mortar, was distributed in a thin layer over the flat bottom of the decomposition vessel; the evolved gases were condensed in a trap at the temperature of liquid nitrogen. Experiments were interrupted at different stages of decomposition, and a complete analysis of the solid residue and condensed gases was performed.

Fig. 1. Kinetics of decomposition of nitrosyl perchlorate at 99°. 1—$NOClO_4$, 2 —NO_2ClO_4, 3—ClO_2 and NO_2

The results of the analysis could be satisfactorily explained if it was assumed that in the solid substance, along with nitrosyl perchlorate, nitronium perchlorate,

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Fig. 2. Thermogram of the decomposition of nitrosyl perchlorate

Figure 2: Fig. 2. Thermogram of the decomposition of nitrosyl perchlorate

NO_2ClO_4, is present. To verify this assumption, the infrared spectrum of a suspension of the solid residue in Vaseline oil was recorded. In the spectrum, in addition to bands corresponding to the ClO_4^- ion, a band at 2293 cm^{-1}, corresponding to the vibration of the NO^+ ion ([4]), and a band at 1385 cm^{-1}, corresponding to the valence vibration of the linear NO_2^+ ion ([5]), were found.

The ratio of chlorine to nitrogen in the gases in all experiments proved to be close to unity. Drawing up a material balance in each experiment made it possible to conclude that chlorine and nitrogen are evolved into the gas phase in the form of the dioxides ClO_2 and NO_2. In one of the experiments, the condensed gases were dissolved in water, and the absorption spectrum in the visible region of the resulting yellow-green solution was compared with the spectrum of a solution of pure chlorine dioxide. The coincidence of the spectra showed that chlorine dioxide is one of the decomposition products of nitrosyl perchlorate. Along with ClO_2, the gases contain

Fig. 2. Thermogram of the decomposition of nitrosyl perchlorate

a considerable amount of elemental chlorine. This is apparently due to the fact that the chlorine dioxide formed decomposes in the hot zone of the apparatus into chlorine and oxygen. According to data in ([6]), this reaction proceeds at an appreciable rate already at 30-50°.

Figure 1 gives the results of a study of the decomposition products of nitrosyl perchlorate. The quantities are expressed in moles of NO_2ClO_4, ClO_2, and NO_2 formed from one mole of the initial nitrosyl perchlorate at different stages of decomposition. The accumulation curves for the final products ClO_2 and NO_2, as well as the consumption curve for $NOClO_4$, have an S-shaped form characteristic of the kinetics of thermal decomposition of solids. The amount of nitronium perchlorate at first increases, passes through a maximum, and then slowly decreases.

From the shape of curve 2 (Fig. 1) it may be concluded that, in the thermal decomposition of nitrosyl perchlorate, two consecutive reactions take place. The first is associated with the decomposition of nitrosyl perchlorate and the formation of nitronium perchlorate, and the second with the decomposition of the nitronium perchlorate formed:

$$2NOClO_4 = NO_2ClO_4 + NO_2 + ClO_2, \quad (1)$$

$$NO_2ClO_4 = NO_2 + ClO_2 + O_2. \quad (2)$$

The ratio $NO_2ClO_4 : NOClO_4$ in the solid phase increases throughout the entire process, i.e., the rate of decomposition of nitrosyl perchlorate by reaction (1) is somewhat higher than the rate of decomposition of nitronium perchlorate by reaction (2).

If nitrosyl perchlorate is decomposed under conditions of continuous temperature rise, the two stages of the process can be separated in time. Figure 2 shows a thermogram of the heating of nitrosyl perchlorate in vacuum, recorded on an N. S. Kurnakov pyrometer. The thermogram shows two clearly separated endothermic effects, the first of which, at a temperature of 100–125°, corresponds to the decomposition of nitrosyl perchlorate according to the reaction

(1), and the second, at a temperature of 165–180°, to the decomposition of the nitronium perchlorate that has accumulated, according to reaction (2).

The results of the present work make it possible to conclude that the thermal decomposition of nitrosyl perchlorate proceeds in two stages, with the intermediate formation of nitronium perchlorate, which is more stable than nitrosyl perchlorate.

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Received
24 IV 1962

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