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Abstract

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On the Products of Thermal Decomposition of Anhydrous Perchloric Acid

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The literature contains very scant information on the products formed during the thermal decomposition of anhydrous perchloric acid. It is known only that, in decomposition occurring below 100°, in addition to oxygen, lower chlorine oxides are formed, and the residue from the decomposition is perchloric acid monohydrate (^{1}-^{8}). A. E. Missan and A. M. Sukhotin (^{9}), using the method of polarization curves, established that 97% perchloric acid, partially decomposed during preparation or during storage, contains ClO_3 and ClO_2. The procedure used in the present work for decomposing perchloric acid was analogous to that described by us earlier (^{8}). Since the reproducibility of the experiments proved satisfactory, the kinetics of accumulation and consumption of the products were studied by interrupting the reaction at definite times and analyzing the entire contents of the reaction vessel. To carry out the analysis, after the end of the decomposition the reaction mixture was very slowly, and with strong cooling, diluted with water.

Preliminary analyses established that an aqueous solution of perchloric acid at various degrees of decomposition contains the ions ClO_3^-, ClO_4^-, as well as chlorine and chlorine dioxide. Since chlorine dioxide practically does not react with water in acid media, the appearance of the ClO_3^- ion in solutions can occur only as a result of the reaction of chlorine trioxide ClO_3 with water:

$$2ClO_3 + H_2O = HClO_3 + HClO_4.$$

Thus, the molecular products of the thermal decomposition of anhydrous perchloric acid, along with oxygen and the monohydrate $HClO_4 \cdot H_2O$, are ClO_3, ClO_2, and also Cl_2.

Systematic analysis of an aqueous solution of the reaction mixture in studying the kinetics of accumulation and consumption of the detected reaction products was performed as follows. By prolonged passage of air, free chlorine and chlorine dioxide from the solution of the reaction mixture were transferred into a neutral 10% KI solution. After this, the KI solution was divided into two parts. In one part, the iodine liberated was titrated with thiosulfate in a neutral medium; in the other part of the solution, in an acid medium. Using the difference in the oxidizing equivalents of Cl_2 and ClO_2 in acid and neutral media, the amounts of free chlorine and chlorine dioxide in the solution were determined by calculation ([10]). In the solution of the reaction mixture freed from chlorine and chlorine dioxide, the content of chlorate ion, formed from the interaction of chlorine trioxide with water, was determined. The chlorate ion was reduced with zinc dust in the presence of sulfuric acid to chloride ion, the content of which was determined by Volhard's method. This made it possible to calculate the amount of chlorine trioxide in the residue from the decomposition.

The content of perchlorate ion was determined by the nitron method ([11]).

In parallel with the chemical analysis, an aqueous solution of the reaction mixture was analyzed spectrophotometrically. Spectrophotometry in the visible region of the spectrum at wavelengths of 323 mμ and 360 mμ made it possible to determine the content of chlorine and chlorine dioxide. The amount of chlorine trioxide was calculated on the basis of the results of spectrophotomet—

chemical determination of chlorate by the benzidine method [(12)]. The agreement between the results of the chemical and spectrophotometric analyses was satisfactory.

The study of the reaction products of the thermal decomposition of anhydrous perchloric acid by the developed procedure for decomposition and analysis was carried out at temperatures of 60, 70, and 80°. The concentration of perchloric acid for individual series of experiments varied within the range 99.92–100.04% (a conventional designation for the composition of perchloric acid containing excess chloric anhydride). The data obtained made it possible, for each series of experiments, to construct curves for the accumulation and consumption of all products of the thermal decomposition of perchloric acid. Figure 1 presents kinetic curves for the content of chlorine trioxide, chlorine dioxide, and chlorine in the reaction mixture at 60°.

It turned out that the dynamics of accumulation and consumption of ClO_3, ClO_2, and Cl_2 are complex in character: the curves pass through two maxima. The positions of the first maxima, as well as of the minima, coincide almost in time for all three substances.

With an increase in the decomposition temperature to 80°, the character of the curves does not change. However, whereas at 70° the contents of ClO_3, ClO_2, and Cl_2 are somewhat greater than at 60°, a further rise in temperature leads to a decrease in the amount of the indicated substances in the reaction zone. This can be explained by an increase in the intensity of evaporation of the oxides into the gas phase, as well as by an increase in the degree of their decomposition in the reaction mixture.

Fig. 1. Products of the thermal decomposition of perchloric acid at 60°.
1 $-ClO_2$, 2 $-Cl_2$, 3 $-Cl_2O_6$

Earlier we advanced the proposition that the decomposition of perchloric acid proceeds through the formation and decomposition of chloric anhydride [(8)].

Fig. 1. Products of the thermal decomposition of perchloric acid at 60°. 1 $-ClO_2$, 2 $-Cl_2$, 3 $-Cl_2O_6$

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Chloric anhydride is formed as a result of the equilibrium existing in perchloric acid:

$$3HClO_4 = Cl_2O_7 + HClO_4 \cdot H_2O. \tag{1}$$

According to literature data $^{(13)}$, chloric anhydride decomposes with the formation of two radicals:

$$Cl_2O_7 \to ClO_3{}^* + ClO_4{}^*, \tag{2}$$

whereupon the ClO_3 and ClO_4 radicals subsequently undergo various transformations, the final products of which are ClO_2 and Cl_2.

In the present work it has been established that, in the decomposition of anhydrous perchloric acid, chlorine trioxide and chlorine dioxide do indeed arise. This supports the decomposition scheme proposed by us. It should be stipulated that molecular substances, which are more accessible for study than elementary processes, and whose formation and consumption were studied by us, may not reveal all the subtleties of the chemistry of the reaction. However, it was possible

an interesting phenomenon: at a certain moment of the reaction there occurs a sharp decrease in the content of ClO_3, ClO_2, and Cl_2 in the reaction mixture. Since specially conducted experiments did not show an increase of ClO_3, ClO_2, and Cl_2 in the gas phase at this time, the established fact cannot be explained by simple removal of the products from the reaction zone. Thus, the only possible cause of the obtained course of the curves may be the predominance, at this stage of the process, of the consumption of the products in secondary reactions over their formation.

In numerous experiments on the decomposition of perchloric acid, we established that at temperatures of 60-80° the yield of oxygen from 1 g of perchloric acid varies within the range 180-190 cm^3. Comparison of the oxygen yield with the results of calculation shows that the decomposition proceeds mainly according to the overall equation

$$3HClO_4 \to HClO_4 \cdot H_2O + 2ClO_2 + 1.5O_2.$$

The increase, with rising temperature, in the volume of oxygen evolved is due to the partial decomposition of chlorine dioxide into chlorine and oxygen.

Thus, the final products of the thermal decomposition of anhydrous perchloric acid under the conditions studied are oxygen, perchloric acid monohydrate, chlorine dioxide, and chlorine. The ClO_3 detected by analysis, as well as the Cl_2O_7 and ClO_4 entering into equations 1 and 2 of the proposed reaction scheme of decomposition, are intermediate decomposition products.

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