DISPROPORTIONATION OF SOME ALKALI METAL CHLORITES IN THE SOLID PHASE

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Thermal behaviours of some alkali metal chlorites were studied under dynamic and isothermal conditions and some physical data of the chlorites were also determined. It was found that these chlorites disproportionate into chlorate and chloride in the solid phase without any measurable evolution of gas. The disproportionations were strongly exothermic. The values of the activation energies for the disproportionation reactions were found to be much smaller than the dissociation energy required for the rupture of the Cl–O bond. It was concluded that the disproportionations of alkali metal chlorites take place by rearrangement inside the lattice, without formation of atomic oxygen.

During the past twenty years there has been particularly great interest in the physical and chemical properties of the salts of halogen oxyacids [1]. The main reason for this is that many of these compounds are widely used in practice as a source of oxygen. They are employed in various pyrotechnic and explosive mixtures and also used in solid propellants.

As regards the salts of the oxyacids of chlorine, the physical and chemical properties of the perchlorates and the chlorates are the most well known. Fewer data are to be found on the chlorites, although, without a knowledge of the thermal behaviours of these salts, a reliable picture cannot be obtained of the mechanisms of decomposition of the chlorates and perchlorates. The investigations to date indicate that chlorates can be demonstrated as intermediates in the decomposition of perchlorates, while chlorates are assumed to decompose via chlorites [1]. Chlorates and chlorites have the interesting property that their thermal decompositions are accompanied by parallel disproportionations in which an oxyanion of chlorine with a higher oxygen content is formed.

As a part of our research program for the better understanding of the thermal stabilities of chlorates and perchlorates, we undertook investigations of the thermal behaviours of different metal chlorites [2, 3]. We have now extended these investigations to some alkali metal, i.e. lithium, rubidium and caesium chlorites, the thermal behaviours of which are fundamentally different from those.
of the other metal chlorites. Besides kinetic investigations, we determined some important physical properties of the compounds relating to the type of bonding and the electronic structures of the substances.

Experimental

Materials

For the preparation of lithium, rubidium and caesium chlorites, the reaction:

$$\text{M}_2\text{SO}_4 + \text{Ba(ClO}_2)_2 = 2\text{MClO}_3 + \text{BaSO}_4$$

(M = Li, Rb, Cs) was used. 0.01 mole reagent grade alkali metal sulphate was dissolved in 5 ml distilled water, which was then added dropwise with constant stirring to 10 ml of solution containing 0.01 mole barium chlorite. The precipitated barium sulphate was filtered off and the solution was evaporated in vacuum up to crystallization. The chlorite salts were recrystallized twice and dried in vacuum. The products contained 99.5% chlorite. Samples were standardized by sieving, and sieve fractions with grain sizes of 80–100 μm were used. Barium chlorite was prepared by Levi's method [4].

Methods

For the thermal analysis of chlorites a Paulik-Paulik-Erdey type MOM derivatograph was used. The reference material was Al₂O₃. The disproportionation reaction under isothermal conditions was followed by chemical analysis. 50 mg samples were weighed into crucibles, which were then placed into an oven heated to the reaction temperature. After given periods the sample was dissolved in water. In the first test chlorite was determined by iodometric analysis in acetic acid solution. In the next aliquot the chlorite and chlorate contents were measured together, also by iodometric analysis, but in strong hydrochloric acid solution. In a new test the amount of chloride was measured by argentometric titration.

The refractive indices of metal chlorites were determined by the Becke line method using a Leitz microrefractometer. The low-frequency dielectric constant was measured in a Marconi RF 704 B instrument, using pellets 20 mm in diameter and 2 mm in thickness. Reflection spectra of the compounds were taken by a Unicam SP 500 instrument adapted for this purpose. Magnesium oxide served as reference material.

Results

Lithium chlorite

The TG, DTA and DTG curves of lithium chlorite are shown in Fig. 1. In the DTA curve the first exothermic peak is to be found at 215° and the second at 417°. Endothermic changes were observed at 70 and 593°. In the TG curve the weight