Thermal decomposition of tetramethylammonium pentaiodide

Irina YUSHINA, Igor KRIVTSOV, Ekaterina BARTASHEVICH
South Ural State University, Lenin avenue, 76, Chelyabinsk, 454080, Russia

Quaternary ammonium salts are widely known as effective ionic liquids, interface catalyst and bacteriostatic agents [1]. Various properties of ammonium halogenides well-investigated in order to understand the trends in Cl^-, Br^-, I^- row. Iodide derivatives take a unique place in this row as they can form not only monoiodide salts but a wide range of polyiodides R_4NI_n [1]). Their crystal structure analysis gives a great amount of information about I...I and I...cation interactions in solid state.

Paths of quaternary ammonium iodides decomposition are thoroughly investigated, though thermal properties of organic polyiodides are less studied. However, they can show a wide spectrum of thermal phenomena according to certain reasons. Foremost there is a vast variety of structural types formed with mono–, triiodide anions and molecular iodine, which can form 3d-grids and chains [1]. Also a diversity of organic cations with their unique thermal properties can drastically influence thermal stability of the corresponding salt. And finally a possible thermal structural transformation of organic cation determined by cation–polyiodide binding can happen.

Tetramethylammonium pentaiodide and triiodide are very convenient samples to study the principles and kinetics of polyiodide decomposition. Foremost, they have a simple structure with known mechanism of the corresponding monoiodide thermolysis [2], so they can be suitable for kinetic simulation since the diversity of reactions with cation are not very diverse. Furthermore, known crystalline geometry [3] gives a possibility to use quantum-chemical calculations. In order to understand the influence of cation on thermal behaviour of samples tetraethyl- and tetrabutylammonium triiodides decomposition data were also taken into account).

A thermal simulation of synthesised crystalline polyiodide samples using TG, DTG and DTA techniques was made. All thermal investigations were carried out in the range of temperature 20–700 °C at heating rate of 10 K/min. Temperature ranges of iodine mass loss were registered for all the samples. A kinetic simulation at different heating rates from 0.25 to 15 K/min was held. A sequence of thermolysis stages and its products were proposed. Two different mechanisms of thermal decomposition were observed for tetramethylammonium pentaiodide. A qualitative simulation of the competitive reactions was made. These data were combined with quantum-chemical calculations of intermolecular interactions in ion pairs within the framework of Atoms in Molecules theory [4]. Iodide...cation binding features according to this analysis were revealed.

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1) Poster presentation