

Thermal properties of substituted 8-thio- and oxyquinolinium polyiodides

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Fundamental interest to polyiodides is based on their electronic structure features and the diversity of structural types. Their spectroscopic, optical, electrochemical properties are well-investigated [1], though thermal behaviour of organic polyiodides is still a less studied field. The scope of the present investigation was focused on thermal properties of crystalline polyiodides of new tricyclic azines formed as the result of halogenocyclization process [2]. Such quinolinium derivatives are widely known as effective chelate reagents and antibiotics [3, 4]

Several powder and single crystal 8-alkenylthio- and oxyquinoline halogenocyclization products has been synthesised [5]. The main questions in this row of polyiodides with similar tricyclic cation is: do the iodide–cation interactions, polyiodide ratio and structure affect the features of thermal decomposition of organic cation? Thermal decomposition of these samples may pass through various stages including possible decyclization, loosening of iodine from anion or from R–I group in the cation, elimination of alkenyl-fragment from thioquinoline or even destruction of heterocyclic system. Dominating of one or several stages will depend on the structure of cation and I..I or «iodide – cation» interactions in solid state and after the process of melting.

A thermal analysis of polyiodide samples was performed to make clear the direction and temperature range of structural transformations. It is clear that these samples do not undergo simple decyclization as this will result in inability to hold iodine beyond its sublimation temperature. Though complexes of 8-alkenylthio- and oxyquinoline and iodine still can be formed, they exist only in solutions. It was shown that for all samples structural transformations start after the melting point. The increasing of iodine amount in the anion and substitution of hydrogen atom in the ring leads to more peaks on DTA and DTG curves. Iodine amount doesn't drastically influence the temperature of the beginning and the end of decomposition. A sample of particular interest is the one with complex polyiodide $I_3^- \cdot 0.5 I_2$. It is a suitable model to investigate the features of iodine loss and interactions inside the anion.

Obtained thermal data were combined with DFT (B3LYP) analysis of noncovalent interactions in ion pairs and crystalline state within the framework of QTAIM [5]. Observing of bond critical points between atoms help us to identify the interactions between them and estimate how it can influence decomposition path. Binding features in «iodine...cation» interactions and inside complex anion were revealed according to this analysis.

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1) **Oral presentation**