

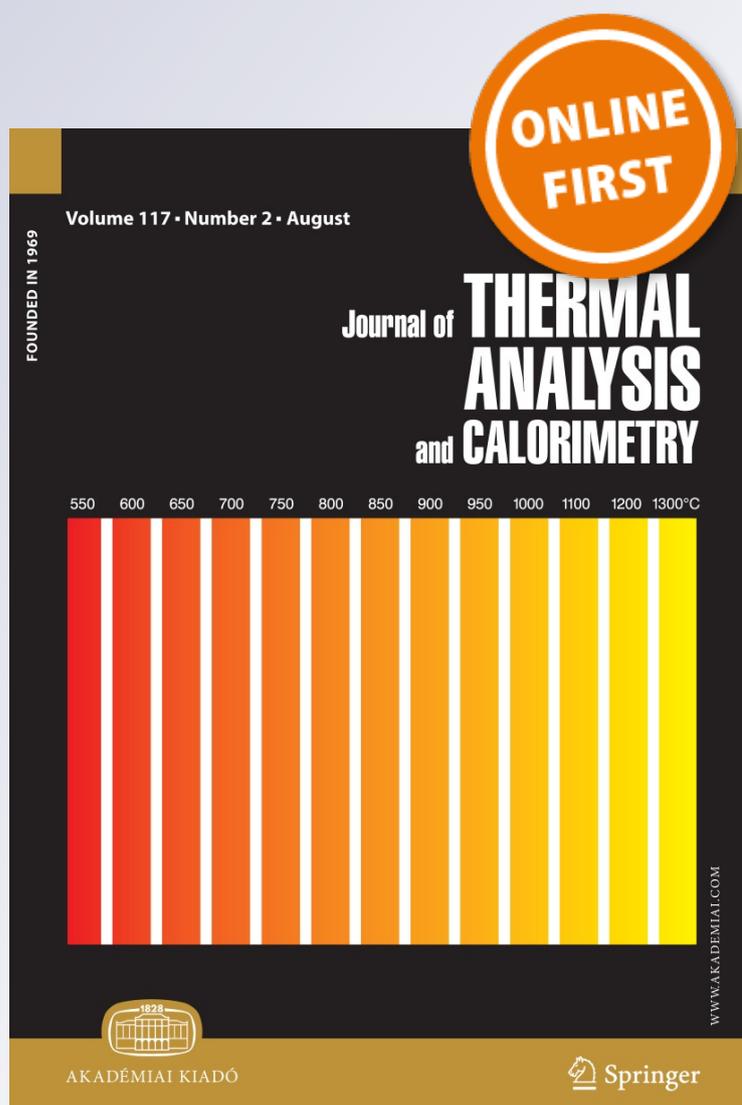
Thermal decomposition of tetraalkylammonium iodides

**Irina Yushina, Boris Rudakov, Igor
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Thermal decomposition of tetraalkylammonium iodides

Irina Yushina · Boris Rudakov · Igor Krivtsov ·
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Abstract A number of tetramethylammonium (TMA) iodides, including mono-, tri-, and penta-iodide, were synthesized. Thermal decomposition of samples was investigated by simultaneous TG–DSC analysis accompanied by gaseous IR- and mass-spectrometry analyses. Two different reaction pathways have been observed for TMA penta-iodide at different heating rates. At low heating rates ($1\text{--}5\text{ K min}^{-1}$), a gradual mass loss takes place and a stability plateau due to monoiodide formation exists on TG curve. At high heating rates ($10, 15$ and 7 K min^{-1} as the in-between stage), there are only two peaks on DTG curve (instead of three for lower heating rates) and no monoiodide formation is observed as the sample decomposes completely before $350\text{ }^{\circ}\text{C}$.

Keywords Tetraalkylammonium salts · Polyiodides · Thermal decomposition · Simultaneous thermal analysis · Evolved gas analysis

Introduction

Quaternary ammonium salts are widely known as effective ionic liquids, interface catalysts, and bacteriostatic agents [1–4]. Various properties of ammonium halides were well-investigated in order to understand the trends in Cl^- , Br^- , I^- row [5, 6]. Iodide derivatives take the unique place in this row as they can form not only monoiodide salts but also a wide range of polyiodides R_4NI_n [7]. Their crystal structure analysis gives a great amount of information about $\text{I}\cdots\text{I}$ and $\text{I}\cdots\text{H}$ in anion–cation interactions in solid state [8]. From

CCDC ver. 5.33 [9], it is known that tetramethylammonium cation can form the crystalline tri- and penta-iodide. It is not a frequent case among organic cations [10, 11]. So TMA iodides were chosen as the objects of our interest to show the influence of crystal packing, iodine quantity, and intermolecular interaction on thermal decomposition. Tetramethylammonium monoiodide decomposition was thoroughly studied [5]. It has been shown that its degradation goes in one step, volatilization starts at $300\text{ }^{\circ}\text{C}$ and ends above $350\text{ }^{\circ}\text{C}$. TMA polyiodides are still less investigated, though they can give valuable information about iodine loss features, its temperature ranges and heat effects. This information can be compared with qualitative structure analysis of crystal packing (presence of structure forming contacts, short contacts length, existence of bands, layers, stacking motifs, etc.). A synthesis of structural and thermal approaches can be the first stage for understanding the interdependency of structural features and thermal properties [12–14].

Experimental

Synthesis

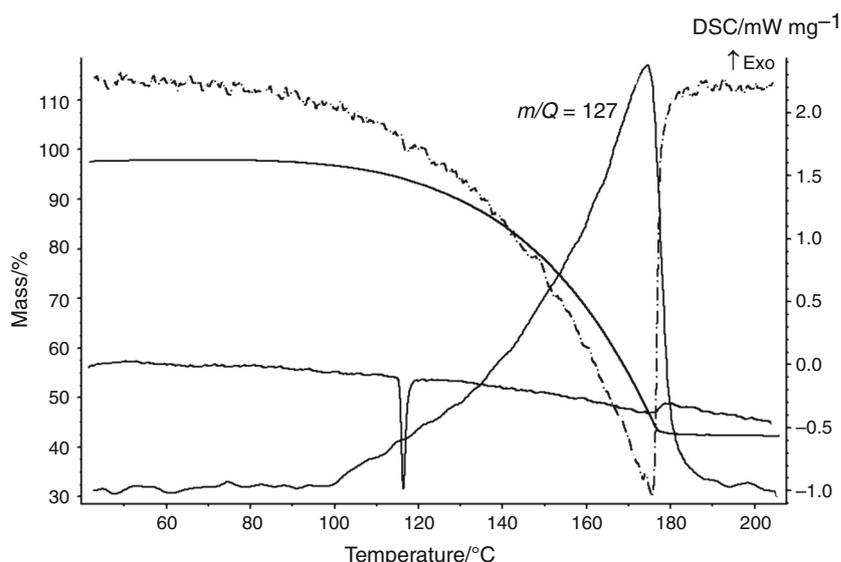
Polyiodide samples were obtained by interaction of TMA monoiodide (chemically pure, «Reachim») and iodine (1:1 for triiodide and 1:2 for penta-iodide) in ethanol solution. Polyiodide crystals were grown during slow solvent evaporation at room temperature.

Sample characterization

Tetramethylammonium monoiodide (CSD refcode QQQC VG03, P4/nmm) exists as white crystals with rather isolated iodide ion (shortest $\text{I}\cdots\text{H}$ contact 3.170 \AA) [15].

I. Yushina (✉) · B. Rudakov · I. Krivtsov · E. Bartashevich
Department of Chemistry, South Ural State University, Lenin
Avenue, 76, Chelyabinsk, Russia 454080
e-mail: idu-xda@mail.ru

Fig. 1 Thermal decomposition of $\text{TMA}^+ \text{I}_3^-$ (10 K min^{-1}) with ion current ($m/Q = 127$) curve



Tetramethylammonium triiodide (CSD refcode DULZIT01 and 03) looks like maroon needle-like crystals, capable to form polymorphs (P21/n or Pnm). Both structures consist of two triiodide anions with different bond lengths. They do not form shortened I...I contacts, so can be treated as isolated ones. Nevertheless, there are lots of rather elongated I...H contacts (the shortest is 3.132 Å) [16, 17]. Tetramethylammonium pentaiodide crystallizes as plates (C2/c), crystals have dark purple color with green refluent surface. Its structure has been proved by single-crystal X-ray diffraction; obtained data coincide with Cambridge Structural Databank structure (CSD refcode DULZOZ01) [18]. Crystal packing in this case is determined by pentaiodide 3d-organisation. Here we observe a symmetric motif with I...I contacts 3.644 Å. Tetraalkylammonium cations are located in such pentaiodide squares. Each of iodine atoms in pentaiodide anion forms I...H contacts with cation, but they all are rather elongated (3.230–3.336 Å). Due to strong I...I and I...H in anion–cation interactions in this structure a joint decomposition may be presumed.

Thermal analysis data were registered in temperature range 25–500 °C (using Netzsch STA 449C Jupiter and Netzsch STA 449F1 Jupiter) at heating rates from 1 to 15 K min⁻¹ (1, 2, 5, 7, 10, 15 K min⁻¹) in corundum crucibles in air and argon atmospheres. Evolved gas analysis was performed using the quadrupole mass-spectrometer Netzsch QMS 403C Aeolos and the FTIR- spectrometer Bruker Tensor 27. Mass-spectra of direct insert were measured on GC–MS Shimadzu 2010 Ultra in vacuum furnace with impulse heating to 350 °C at the rate 80 K min⁻¹.

Results and discussion

One can presume that iodine loss from tri- and pentaiodide anion starts at low temperatures near the melting point of

solid diiodine I₂ (113 °C) and ends soon after it, but due to different types of interactions in crystal this process might be more complicated. Generally, increasing of iodine amount in the sample causes additional decomposition stages in DTG curve: monoiodide decomposes rapidly in one step, triiodide does it in two steps with stability plateau between them, pentaiodide decomposes in two or three steps depending on the heating rate. On Fig. 1, the thermal decomposition of TMA triiodide with 1 K min⁻¹ heating rate with simultaneous evolved gas analysis is presented. The shape of DTG curve coincides with m/Q 127 signal of mass-spectrometer, mass loss on this stage corresponds to iodine loss (254 g mol⁻¹ compared to experimental 252.5 g mol⁻¹). Similar features of iodine loss were earlier observed for molecular complexes with various organic electron-donor ligands [19], though temperature range of this stage is higher for polyiodide species discussed in this work, than in neutral complexes (90–120 °C) [19]. Iodine loss process is followed by extended stability plateau due to monoiodide formed. IR-spectrum of the sample after heating to 190 °C shows good agreement with the spectra of corresponding monoiodide (940 cm⁻¹ δ H–C–I, 1,490 cm⁻¹ δ H–C–H, 3,010 cm⁻¹ ν C–H). At higher heating rates, stability plateau shifts to higher temperatures (180 °C at 1 K min⁻¹ and 250 °C at 10 K min⁻¹) and shortens. Mass loss on this stage increases up to 61 % (exceeds the part of molecular iodine in structure), that *may be* due to the start of cation degradation, though quaternary structure generally remains before monoiodide decomposition starts and provides the stability plateau existence.

Addition of another iodine molecule to the anion in TMA pentaiodide results in more significant dependence of decomposition process on the heating rate compared to triiodide (Table 1). The best agreement of mass loss and iodine ratio in the sample is observed only for low heating

Table 1 Summary of decomposition characteristics for TMA^+I_5^- for each DTG peak at different heating rates

Rate/ K min^{-1}	Peak ₁ /%	Temp ₁ /°C	Peak ₂ /%	Temp ₂ /°C	$\Sigma = \text{Peak}_1 + \text{Peak}_2$ /%	Peak ₃ /%	Temp ₃ /°C
1	33.9	100–160	39.1	160–220	73.0	28.2	290–370
2	33.6	100–180	40.8	180–250	74.4	25.5	290–380
5	35.1	100–200	50.1	200–295	85.2	15.3	295–380
10	34.4	120–230	64.1	230–320	98.5	–	–
15	32.3	120–230	65.5	230–350	97.8	–	–

Peak₁, Peak₂, Peak₃— mass losses on the 1st, 2nd, 3rd stages respectively according to DTG curve

Temp₁, Temp₂—temperature ranges, corresponding to the 1st, 2nd, 3rd peak on DTG curve respectively

Table 2 Comparative thermal stability of TMA iodides

	TMA^+I^-	TMA^+I_3^-		TMA^+I_5^-	
	10 K min^{-1}	10 K min^{-1}	1 K min^{-1}	10 K min^{-1}	1 K min^{-1}
$T_5 \%$	343 °C	178 °C	122 °C	149 °C	118 °C
T_{12}^*	–	**	180 °C	230 °C	160 °C
T_{212}^*	–	–	–	**	220 °C

* T_{12} —temperature corresponding to the end of 1 molecule of I_2 loss process, T_{212} —temperature corresponding to the end of 2 molecules of I_2 loss process

** It is impossible to separate the end of iodine loss and cation decomposition start due to simultaneous processes

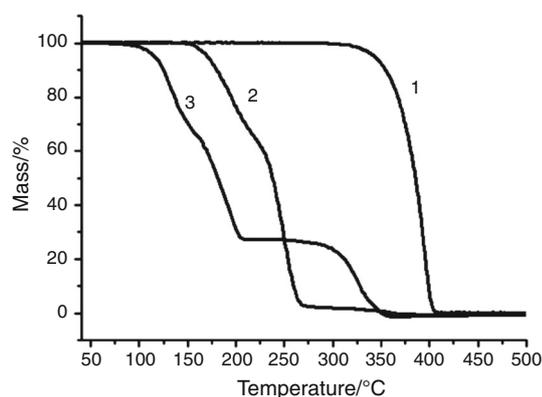


Fig. 2 Mass loss of: 1 TMAI (10 K min^{-1}), 2 TMAI_5 (10 K min^{-1}), 3 TMAI_5 (1 K min^{-1})

rates (1 K min^{-1}), when the stability plateau ($200\text{--}270 \text{ °C}$) exists and corresponding mass loss is equal to monoiodide percentage (28.3 % compared to experimental 28.2 %). Even at such low rates, two peaks of iodine loss are not clearly separated. It can be seen that mass loss on the first stage is approximately constant, though mass loss on the second stage gradually increases with the heating rate. A brief comparison of temperature ranges for different decomposition stages of TMA iodides is given in Table 2. It becomes evident that though $T_5 \%$ (temperature corresponding to 5 % mass loss) as a measure of the decomposition start decreases in a row $\text{I}^- > \text{I}_3^- > \text{I}_5^-$ for equal heating rates, temperature ranges of iodine loss for tri- and

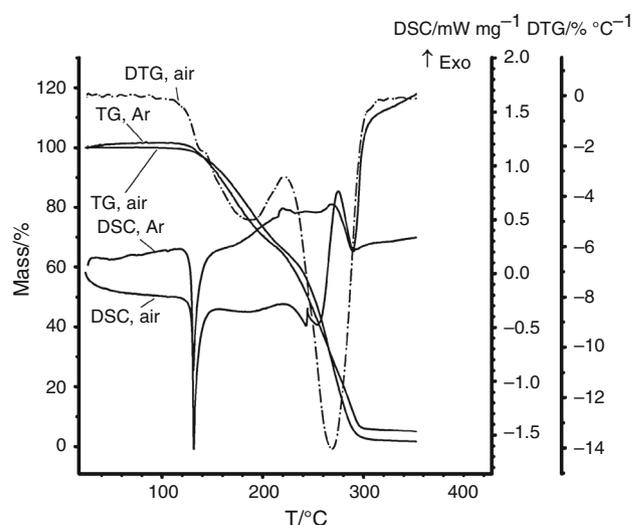
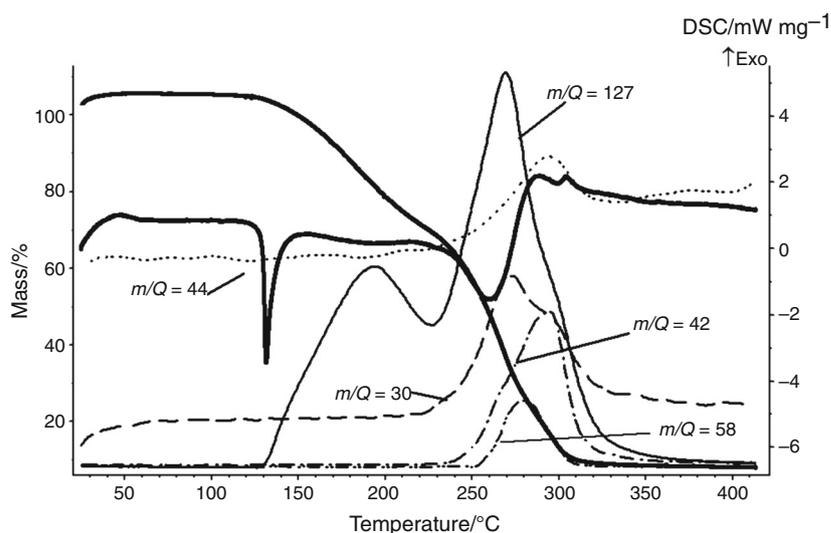


Fig. 3 Decomposition of $\text{TMA}\cdot\text{I}_5$ at 10 K min^{-1} in air and argon atmosphere

pentaiodide interconnect. So the absence of a stability plateau for TMA I_5 after molecular iodine loss (corresponds to triiodide) can be explained by overlaying temperature ranges of the end of the first peak for penta-iodide and the decomposition start for triiodide.

The loss of the second I_2 from TMA^+I_5^- starts far beyond $T_5 \%$ TMA^+I_3^- (160 °C compared to 122 °C), so it can be concluded that the stronger interactions in I_5^- nets somehow stabilize iodine in the melt compared to isolated, weakly bounded I_3^- anions.

Fig. 4 Thermal decomposition and ion current (m/Q) curves of gaseous products for TMAI_5 (10 K min^{-1})



On Fig. 2, it can be seen that TMA^+I_5 decomposition at high heating rates (curve 2) ends long before usual decomposition starts for TMA^+I^- (curve 1) and has no stability plateau of monoiodide. Decomposition of TMA^+I formed after iodine loss from TMA^+I_5^- (curve 3) starts and ends before it is observed for pure TMA^+I . This effect may be due to the difference in heating rates and the influence of iodine loss on interactions in TMA^+I^- .

On the last stage, the typical decomposition of TMA monoiodide and oxidation of organic part takes place (Fig. 3). Influence of inert atmosphere (argon, 40 mL min^{-1}) can be clearly seen on DSC curve; there is no exothermal effect corresponding to oxidation, though mass loss values and ranges are practically the same.

Additional information about the processes can be obtained from mass-spectroscopy of evolved gases (Fig. 4). Fragments with mass-to-charge ratio $m/Q = 15$ (CH_3^+), 42 ($\text{CH}_2\text{NCH}_2^+$), 58 ($\text{C}_3\text{H}_8\text{N}^+$), 127 (I^+), 142 (CH_3I^+) can be observed as the main decomposition products (Fig. 4). It is known that quaternary ammonium salts can decompose through reverse Menshutkin reaction forming tertiary amine and alkylhalide [20]. The other way of degradation is Hoffman elimination with corresponding alkene and $\text{R}_3\text{NH}^+\text{X}^-$ as products. Observing alkyl halides is an argument in favor of reverse Menshutkin reaction. At high heating rates iodine loss is registered on the first stage and then it is accompanied by simultaneous cation fragmentation ($m/Q = 42, 58$) and oxidation ($m/Q = 44, 30$).

In comparison to EGA, monoiodide decomposition detected by mass-spectra of direct insert ($350 \text{ }^\circ\text{C}$, 80 K min^{-1} , vacuum) goes very slow, observed m/Q in order of decreasing intensities: 142 (CH_3I^+), 58 ($\text{C}_3\text{H}_8\text{N}^+$), 127 (I^+), 42 ($\text{CH}_2\text{NCH}_2^+$). Triiodide under the same conditions decomposes in two stages according to total ion current (TIC) diagram: the first corresponds to

rapid iodine loss (the sharp peak on TIC diagram, $m/Q = 127, 254$) and then the typical for monoiodide acclivous peak with m/Q as mentioned above. Pentaiodide decomposition is similar to triiodide, but the first peak has relatively higher intensity, iodine loss occurs in one stage, no splitting is observed. So, gradual iodine loss for pentaiodide is possible only at low heating rates at atmospheric pressure.

Gaseous-IR spectra according to EGA (not presented), registered at $280\text{--}290 \text{ }^\circ\text{C}$ (10 K min^{-1}), when organic part decomposes, show the intensive sharp peak near $2,300 \text{ cm}^{-1}$ corresponding to CO_2 , the intensive broad peak at $2,800\text{--}2,950 \text{ cm}^{-1}$ (C–H vibrations) and several groups of peaks with low or medium intensity in the region $1,400\text{--}1,500 \text{ cm}^{-1}$ ($\delta \text{ CH}_3^-$, bending N–C–H, H–C–H). These results are in agreement with theoretical data for TMA^+I^- according to quantum-chemical calculations [5]. Intensity of all this peaks increases during heating due to accumulation of decomposition products, but the most significant product of organic part oxidation is still CO_2 .

Conclusions

A joint consideration of crystal packing features of polyiodides with different stoichiometries and their thermal properties gives a clue to deeper understanding of undergoing decomposition processes. We have demonstrated that empirical rule concerning decreasing of decomposition temperature with increasing of iodine amount in anion executes normally for high heating rates, but for low heating rates the difference in decomposition temperatures for tetramethylammonium tri- and pentaiodide is negligible. Decreasing of melting temperature in a row triiodide–pentaiodide is not observed too; moreover, it is widely known

that pentaiodide has higher m.p., than triiodide, that may be due to stronger intermolecular interactions in anion network and more numerous I...H contacts. It has been shown that increasing of iodine amount in anion complicates the processes of sample decomposition so that the number of decomposition stages for tetramethylammonium pentaiodide becomes significantly dependent on the heating rate. Iodine loss can occur independently (pentaiodide at very low heating rates, triiodide at medium heating rates) or together with organic cation decomposition (pentaiodide at medium and high heating rates). Intermolecular interactions in tetramethylammonium pentaiodide delay the loss of second iodine molecule from the I_5^- anion for at least 40 °C.

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