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THERMAL PROPERTIES OF TETRAETHYLAMMONIUM TETRACHLORO-, BROMOTRICHLORO- AND TRIBROMOCHLOROFERRATES(III)

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Thermal decomposition of tetraethylammonium tetrachloro-, bromotrichloro- and tribromochloroferrates(III), of general formula $[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4), has been studied using the TG-MS, DTA and DTG techniques. The measurements were carried out in an argon atmosphere over the temperature range 293–1073 K. Solid products of the thermal decomposition were identified by Mössbauer spectroscopy.

Keywords: *Mössbauer spectroscopy, tetrahalogenoferrates(III), thermal decomposition*

Introduction

Compounds with tetrahalogenoferrate(III) ions have inspired many research teams. Owing to the presence of the high-spin d^5 Fe(III) in their molecules, they may serve as simple models for studying physicochemical properties of biological systems involving ferro-sulfide proteins [1, 2]. Recently, much attention has been paid to designing new materials consisting of organic electron donors and tetrahalogenoferrate(III) anions exhibiting interesting electric and magnetic properties [3–8].

In recent years thermal behavior of complex compounds with transition elements has been extensively studied [9–13]. However, to the best of our knowledge, there are no reports on thermal decomposition of compounds with mixed tetrahalogenoferrate(III), $[FeBr_{4-n}Cl_n]$ (n=0–4), anions. Just this was the reason that prompted us to embark on these studies.

The recently analyzed tetrabutylammonium tetrachloroferrate(III), $[(n\text{-}C_4H_9)_4N][FeCl_4]$, has been found to be fairly stable in the molten state and its decomposition was accompanied by reduction of iron(III) to iron(II) [14]. Consequently, it seemed interesting to estimate the influence of the cation size on thermal stability of the tetrachloroferrate(III) ion as well as that of the kind of the halogen ions in the coordination sphere of Fe(III) on the composition of the thermal decomposition products of the tetrahalogenoferrates(III).

In this contribution, thermal properties of tetraethylammonium tetrachloro-, bromotrichloro- and tribromochloroferrates(III) are presented together with results of inspection of the Mössbauer spectra of their decomposition products.

Experimental

Synthesis and chemical analysis

The synthesis of tetraethylammonium tetrachloro-, bromotrichloro- and tribromochloroferrates(III) was carried out using a procedure similar to that reported for the preparation of other tetrahaloferrates(III) [15]. Identity of the compounds was confirmed by elemental analysis (C, H, N, Cl, Br and Fe). The structure of the tetrahalogenoferrate(III) ions was confirmed by Raman spectroscopy [16, 17].

Instrumental methods

The Mössbauer spectra were recorded at room temperatures on a conventional spectrometer in transmission geometry using a ^{57}Co/Rh source. A gas flow cryostat was applied for low temperature measurements. The samples were prepared in pellets with thickness of ca. 10 mg Fe cm^{-2}. The spectra were numerically analysed by the least-squares procedure assuming Lorentzian line shapes. Isomer shifts are quoted relative to α-Fe.

The TG-DTG-DTA-MS measurements in argon (Ar 5.0) were run on a Setsys 16/18 thermal analyzer (Setaram) coupled with a Thermostar quadrupole

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mass spectrometer (range 293–1073 K, corundum crucible, sample mass ca. 12–14 mg, Al_2O_3 as reference, heating rate 5 K min^{-1}, flow rate of the carrier gas 15 mL min^{-1}).

The course of the thermal analysis was broken at points corresponding to main steps of decomposition and the residues in the crucible were quickly cooled in the stream of argon. This enabled to analyze the residues at strictly pre-determined steps of decomposition. The analysis was carried out using the Mössbauer spectroscopic technique.

Results and discussion

Results of the thermal analysis of ($[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4) are compiled in Table 1, whereas the shapes of the TG curves are presented in Fig. 1.

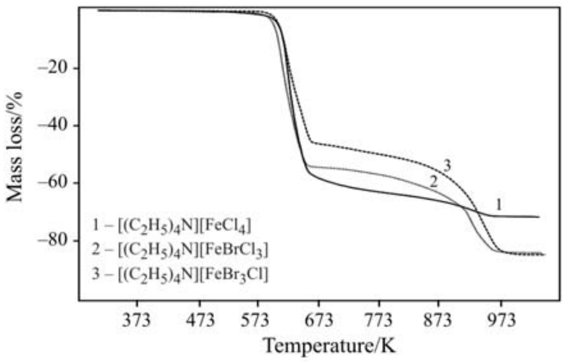

Fig. 1 TG curves of thermal decomposition of $[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4) in argon

First events in the DTA curves are seen prior to decomposition of the compounds as two endothermic peaks. The first is assigned to phase transition and the other to the melting of the sample (Fig. 2).

The phase transition preceding the melting is a characteristic feature of the compounds. The transition is likely to be due to the presence of different polymorphic forms of the compounds. Variations in ambient temperature affects spatial arrangement of the hydrocarbon chain of the organic cations resulting in transition from one polymorphic form to another. A similar behavior was noticed with methylammonium chloride, as well. Upon heating, two phase transitions were seen, whereas upon cooling only one [18].

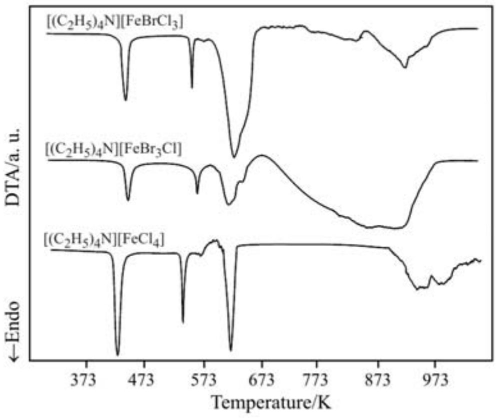

Fig. 2 DTA curves of thermal decomposition of $[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4)

The DSC measurements also revealed many phase transitions upon heating of $[(CH_3)_4N][FeCl_4]$ [19]. On the other hand, observations with optical microscope suggest a transition of the tetragonal form into the orthorhombic one upon cooling [20]. It is also worth mentioning that thermal decomposition of an analogous compound studied by us, $[(n\text{-}C_4H_9)_4N][FeCl_4]$ [14], was also preceded by phase transition at ca. 383 K while the compound melted at ca. 408 K. The compound was fairly stable when molten and its decomposition occurred at a temperature by ca. 100 K higher than its melting point.

With compounds studied herein, stabilization of the tetrahalogenoferrate(III) ions by a smaller tetraethylammonium cation has a distinct impact on stability of the compounds. For instance, the *m.p.* of $[(C_2H_5)_4N][FeCl_4]$ is by ca. 130 K higher than that of its tetrabutylammonium counterpart and occurs prior to its decomposition (at ca. 563 K; Table 1). A similar behavior is seen with the remaining compounds. Since within the series of the compounds of general formula

Table 1 Thermal characteristics of $[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4)

Formula	Range of decomposition/K	DTG	DTA			Mass loss/%
			T_σ	T_m	T_p	
$[(C_2H_5)_4N][FeCl_4]$	563–688 688–1023	617 –	427	538	623 (endo) –	59 13
$[(C_2H_5)_4N][FeBrCl_3]$	568–693 693–1023	608 –	434	554	626 (endo) –	54 30
$[(C_2H_5)_4N][FeBr_3Cl]$	586–693 693–1023	623 –	443	560	612 (endo)	50 38

T_σ – temperature of the solid-state phase transition; T_m – melting point; T_p – peak temperature – a temperature at which a maximum of the thermal effect emerges

$[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4) there is no distinct influence of the tetrahalogenoferrate(III) ion on both their decomposition temperatures and shapes of their TG curves, a conclusion can be drawn that thermal stability of the complexes is primarily dependent on the alkyl chain length of aliphatic amines incorporated in the quaternary cations. Their size also determined packing of the molecules in the crystal lattice. The tetraethylammonium compounds, such as $[(C_2H_5)_4N][FeCl_4]$ and $[(C_2H_5)_4N][FeBrCl_3]$, crystallize in the hexagonal system [21], whereas tetrabutylammonium halogenoferrates, $[(n\text{-}C_4H_9)_4N][FeCl_4]$ [22, 23] and $[(n\text{-}C_4H_9)_4][FeBrCl_3]$ [24], in the orthorhombic system.

Just these structural features are likely to affect, albeit indirectly, the differences in melting points of the compounds.

These speculations are likely to be supported by examination of the thermal behavior of tetraethylammonium tetrahalogenoferrates(III). Their thermal stability in the solid state is comparable and their melting points increase only slightly with increasing number of the bromide ligands in the coordination sphere of iron(III).

Thermal decomposition of the tetraethylammonium tetrahalogenoferrates(III) occurs in two main steps (Fig. 1). The first step is rapid and terminates at ca. 683–693 K. On the other hand, the second step is much slower and comes to an end at ca. 1023 K. During the first step, both the cation and the anion undergo decomposition in all the compounds studied. Depending on the kind of anion, the halogen ligands are released as C_2H_5X, HX and X_2 (X=Br or Cl) (Fig. 3).

The presence of Br_2 and Cl_2 among the gaseous products is probably due to concurrent reduction of Fe(III) to Fe(II). A similar behavior of the chloroferrate(III) ions has been reported for other compounds containing these ions [14, 25].

These assumptions have subsequently been supported by inspection of the Mössbauer spectra of solids left at temperatures corresponding to particular decomposition steps (Table 2).

Thus, during the first step (ca. 683–693 K), the Fe(III) ion in all the compounds studied undergoes transformations resulting in Fe(II) and Fe(III) in different coordination sphere (Fig. 4). With $[(C_2H_5)_4N][FeCl_4]$ and $[(C_2H_5)_4N][FeBrCl_3]$, two new phases emerge, namely coordination entities of Fe(II) (designated B and I) and one Fe(III) phase (designated F) with a coordination sphere differing from that in tetrahalogenoferrates(III) [15]. With $[(C_2H_5)_4N][FeBr_3Cl]$, phase I of Fe(II) during the first step of decomposition (at ca. 693 K) is missing, whereas phase B of Fe(II) and phase F of Fe(III) are present. In addition, a new phase of Fe(II) (designated C), appears.

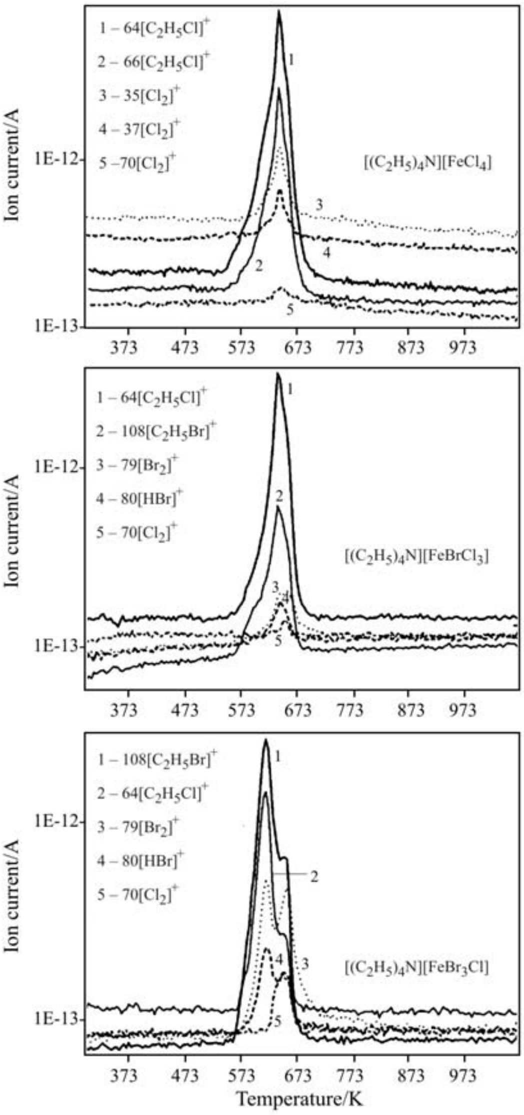

Fig. 3 Ionic current profiles recorded during TG-MS analysis of $[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4)

Iron(II) in phase B prevails in the products of the first decomposition step of all the compounds studied. It is worth mentioning here that in the previously studied compounds [14, 26], phase B of Fe(II) was also the main product of thermal decomposition of tetrachloroferrates(III). The Mössbauer parameters of a doublet assigned to phase B indicates that Fe(II) is probably involved in dihalogeno-bridged coordination entities capable of formation of larger polymeric structures [27, 28]. With increasing number of the bromide ligands in the coordination sphere of iron(III), the amount of phase B of Fe(II) in the products of the first decomposition step increases.

The number of the bromide ligands in the starting, non-heated compound, affects also both in quan-

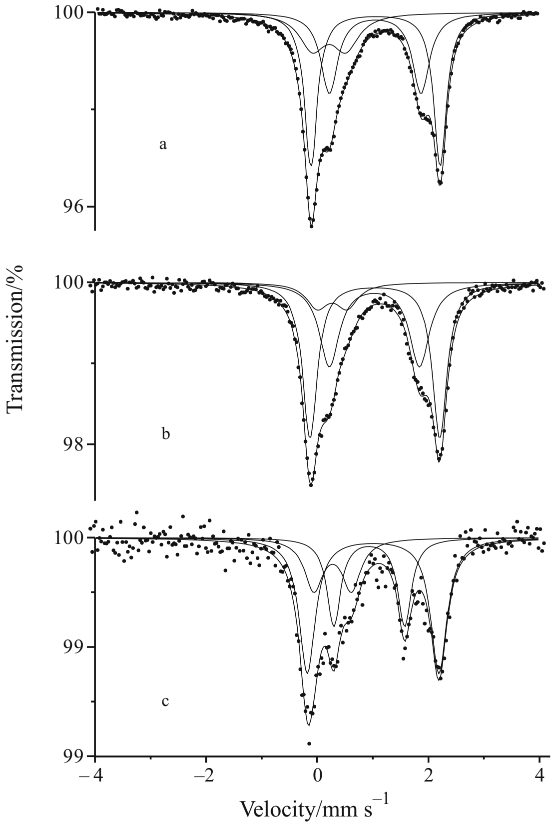

Fig. 4 Room temperature Mössbauer spectra of the products of the first decomposition step (ca. 683–693 K) of a – $[(C_2H_5)_4N][FeCl_4]$, b – $[(C_2H_5)_4N][FeBrCl_3]$ and c – $[(C_2H_5)_4N][FeBr_3Cl]$

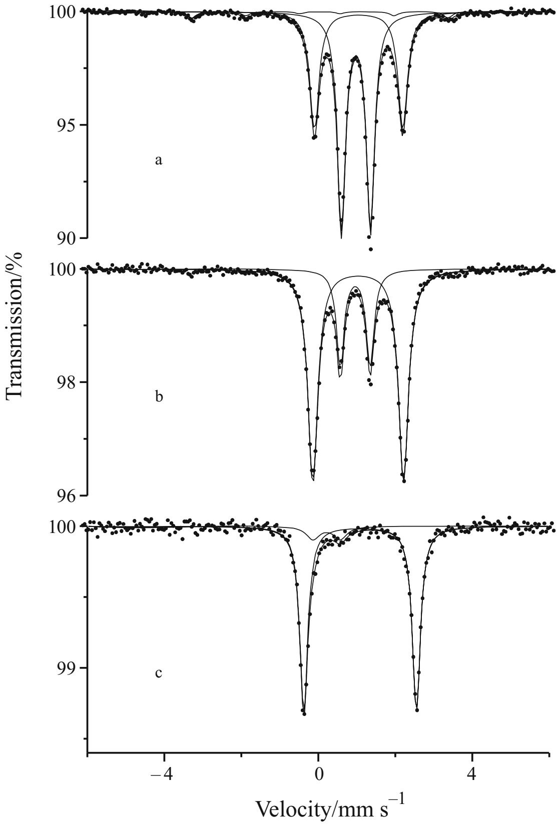

Fig. 5 Room temperature Mössbauer spectra of the products of the second decomposition step (ca. 1023 K) of a – $[(C_2H_5)_4N][FeCl_4]$, b – $[(C_2H_5)_4N][FeBrCl_3]$ and c – $[(C_2H_5)_4N][FeBr_3Cl]$

titative and qualitative terms, the composition of final products (Fig. 5).

In the Mössbauer spectra of the decomposition products of $[(C_2H_5)_4N][FeCl_4]$ and $[(C_2H_5)_4N][FeBrCl_3]$ left behind at ca. 1023 K, the doublets of phase I due to Fe(II) and that of phase F due to Fe(III) are missing, whereas a new phase of Fe(II) designated H appears. The quadrupole splitting of phase H doublet suggests

Table 2 Mössbauer parameters for $[(C_2H_5)_4N][FeBr_{4-n}Cl_n]$ (n=1, 3, 4) after decomposition in argon

Sample	Temperature/K	Phase	δ/mm s^{-1}	Δ/mm s^{-1}	Γ/mm s^{-1}	*A*/%	Species
$[(C_2H_5)_4N][FeCl_4]$	683	B	1.16 (14)	2.32 (1)	0.14	46.4 (7)	Fe^{2+}
		I	1.15 (1)	1.65 (1)	0.19	32.4 (8)	$[FeCl_5]^{3-}$
		F	0.33 (1)	0.60 (1)	0.29	21.2 (4)	Fe^{3+}
	1023	B	1.16 (1)	2.29 (1)	0.15	35.7 (2)	Fe^{2+}
		H	1.09 (1)	0.78 (1)	0.13	56.9 (2)	$[FeCl_4]^{2-}$
		G	0.15 (1)	207.1 (7)^a	0.14	7.4 (1)	Fe_3C
$[(C_2H_5)_4N][FeBrCl_3]$	693	B	1.15 (1)	2.33 (1)	0.16	50.9 (1.4)	Fe^{2+}
		I	1.14 (1)	1.62 (1)	0.22	37.5 (1.6)	$[FeCl_5]^{3-}$
		F	0.38 (2)	0.54 (3)	0.24	11.7 (6)	Fe^{3+}
	1023	B	1.15 (1)	2.35 (1)	0.16	73.4 (4)	Fe^{2+}
		H	1.07 (1)	0.78 (1)	0.12	26.6 (3)	$[FeCl_4]^{2-}$
$[(C_2H_5)_4N][FeBr_3Cl]$	693	B	1.11 (1)	2.37 (2)	0.19	56.2 (3.8)	Fe^{2+}
		C	1.20 (1)	2.91 (2)	0.10	12.0 (2.7)	Fe^{2+}
		F	0.39 (2)	0.62 (2)	0.19	31.8 (1.7)	Fe^{3+}
	1023	C	1.20 (1)	2.92 (1)	0.13	89.9 (1.3)	Fe^{2+}
		F	0.33 (3)	0.71 (5)	0.21	10.2 (1.3)	Fe^{3+}

δ – isomer shift *vs*. room temperature α-Fe, Δ – quadrupole splitting, Γ – absorber line width, *A* – relative contribution to the total spectrum. ^{a}Fixed parameter.

the presence of Fe(II) in the tetrahedral environment of the halogen ligands, whereas isomeric shift δ is slightly larger than that reported in the literature [29, 30]. In the samples examined, Fe(II) persists in a coordination state corresponding to phase B. It is, however, worthwhile to note that its quantity is about a half of that in the decomposition product of $[(C_2H_5)_4N][FeCl_4]$ than in that of $[(C_2H_5)_4N][FeBrCl_3]$. It can thus be assumed that iron(II) initially present in the coordination sphere of phase I (ca. 683–693 K; Table 2) upon raising the temperature is converted to a more stable coordination forms: phase H [Fe(II)] during decomposition of $[(C_2H_5)_4N][FeCl_4]$ and phase B [Fe(II)] during decomposition of $[(C_2H_5)_4N][FeBrCl_3]$. It is also interesting to note that during decomposition of a tetrachloroferrate(III), a small amount of Fe_3C is formed at ca. 1023 K (phase G) as indicated by a characteristic sextet in the Mössbauer spectrum (Fig. 5a).

A still more distinct influence of the bromide ligands in the coordination sphere of Fe(III) upon final products of thermal processes is seen in the Mössbauer spectra of the decomposition products of $[(C_2H_5)_4N][FeBr_3Cl]$ left behind at ca. 1023 K. In this case, Fe(II) initially present in the coordination environment corresponding to phase B (ca. 683 K) is entirely converted to a more thermally stable phase C (1023 K). Moreover, there is a small amount of phase F of iron(III).

Conclusions

Thermal decomposition of the compounds studied occurs in two main steps and is preceded by phase transition and melting. Depending on the kind of the halogen ligands, they are released as C_2H_5X, HX and X_2 (X=Br, Cl). Oxidation of the halogen ligands to X_2 is accompanied by reduction of iron(III) to iron(II).

Thermal stability of the tetrahalogenoferrate(III) ion depends primarily on the counter-ion stabilizing the structure and, in the case of quaternary amine cations, it declines with increasing number of carbon atoms in the alkyl chain.

Inspection of the Mössbauer spectra shows the kind of the tetrahalogenoferrate(III) anion to affect both quantitatively and qualitatively the composition of the thermal conversion products.

Due to non-stoichiometric progress of the decomposition reactions, as well as to concurrent complex redox processes, it is difficult to suggest an unambiguous scheme for decomposition of the compounds. This notwithstanding, it could be found that a characteristic feature of the processes is occurrence of iron(II) in a coordination form corresponding to phase B which prevails in the products of the first decomposition step (683–693 K). Upon raising the temperature, its amount decreases in the products of decomposition of $[(C_2H_5)_4N][FeCl_4]$ but increases in those of $[(C_2H_5)_4N][FeBrCl_3]$. It is interesting to note that in the Mössbauer spectrum of the final decomposition products of $[(C_2H_5)_4N][FeBr_3Cl]$ (1023 K), a doublet due to phase B is missing. In this case, unlike the two remaining compounds, the most thermally stable coordination form of iron(II) is phase C.

It is also worth emphasizing that a small amount of iron carbide, Fe_3C, could only be found in products of the final step of thermal decomposition (1023 K) of the tetrachloroferrate(III). Further study aimed at in-deep explanation of the mechanism of the thermal processes is under way.

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