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THERMAL BEHAVIOUR AND THERMOCHEMISTRY OF ETHANAMINIUM IODIDES

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Dynamic thermoanalytical methods (DTA, TG, DTG) have been applied to the investigation of the thermal features of compounds of general formula $(Et_nNH_{4-n})I$, with $n = 0$-4. The primary decomposition step of these derivatives is accompanied by the release of amine and HI to the gaseous phase. The enthalpies of this process have been evaluated on the basis of the van't Hoff equation and analytical TG curves. Values thus derived together with the available literature data were used to estimate the enthalpies of formation and the energies of the crystal lattice of the compounds. Further information regarding this latter quantity was also drawn from the Kapustinskii-Yatsimirskii formula.

Owing to the rather strong base character of alkanamines they form salt-type compounds with typical inorganic acids. The halogenide salts of such amines are one of the simplest ionic derivatives of organic compounds. Such derivatives are, thus very convenient model systems for studying the influence of the structure of cations on the features of parent molecules. In our previous note we turned our attention to the thermochemistry and thermal properties of numerous chloride salts of nitrogen organic bases [1-3]. The present note is devoted to similar studies for ammonium and ethanaminium iodides. Salts of alkanamines appear to have some industrial applications [4-5]. Nitrogen organic bases also commonly appear in biological systems. Thus, the present studies are of considerable scientific and practical importance.

Experimental

N, N, N-triethyl-ethanaminium iodide was purchased from Fluka AG and Bush SG. Other compounds studied were synthesized by mixing an aqueous solution of appropriate bases with an almost stoichiometric amount of hydroiodic acid. The resulting crystals were separated and purified by

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repeated recrystallizations from MeOH. Colorless crystals were dried in a vacuum dessicator over P_2O_5. The identity of the compounds was confirmed by C, H, N and iodine determination.

The thermal analyses were carried out on an OD-103 derivatograph placing samples weighing 50 mg on the top plate of a polyplate sample holder. Heating rate was ca. 5.5 deg/min^{-1}. All analyses were performed in a dynamic atmosphere of N_2. α-Al_2O_3 served as a reference material.

The values of temperature (T) corresponding to certain values of the extent of reaction (α) were derived in the manner previously described [1-3]. The enthalpies of dissociative volatilization (ΔH_v) of the compounds studied were evaluated on the basis of the Van't Hoff equation:

$$\ln \alpha = -(\Delta H_v/2R)(1/T) + (\Delta H_v/2R)(1/T_v) \qquad (1)$$

using the α *vs.* T sets of data thus determined (R= gas constant; T_v=volatilization temperature).

Results and discussion

The results of a typical thermoanalytical measurement are shown in Fig. 1, whereas, thermal and thermochemical characteristics for the compounds studied are compiled in Table 1. The ethanaminium iodides undergo solid phase transitions or melting before the onset of decomposition. Another interesting feature is that all the compounds examined undergo complete volatilization upon heating to ca. 800 K. Only ammonium and N, N, N-triethyl-ethanaminium iodides exhibit a simple thermal decomposition pattern. Both compounds decompose in one step accompanied by a strong endothermic effect and a release of NH_3 and HI or Et_3N and EtI, respectively, to the gaseous phase. This simple thermal decomposition course is disturbed in the case of the three remaining hydroiodides studied. Namely, at higher temperatures (i.e. ca. 550 K) some oxidative processes occur which cause strong exothermic effects in DTA curves. Such processes are feasible since enthalpy of formation of the expected reaction product, i.e. $HI_{(g)}$, is positive in ambient temperature and at 550 K ($\Delta H^{\circ}_{f,298}$ = 25.9 and $\Delta H^{\circ}_{f,550}$ = 17.8 kJ.mol^{-1} [6]). This implies that the compound can decompose spontaneously into elements. This does not actually occur at ambient temperature, which presumably results from the fact that the process requires the overcoming of an activation barrier. This barrier is easily overcome at higher temperatures causing fast decomposition of HJ to H_2 and J_2. The iodine exhibits a similar oxidative potential to gaseous oxygen (i.e. +0.536 V [6]) and thus can act as an oxidizing agent against organic fragments of molecules. The side oxidative processes are, however, observed when dissociation and volatilization are far advanced. It thus seems justifiable to assume that the primary step in decomposition of all the compounds studied is well approximated with the equation

$$(Et_nNH_{4-n})I_{(l,c)} \rightarrow Et_{n-a}NH_{3-n+a\,(g)} + (1-a)HI_{(g)} + aETI_{(g)} \qquad (2)$$

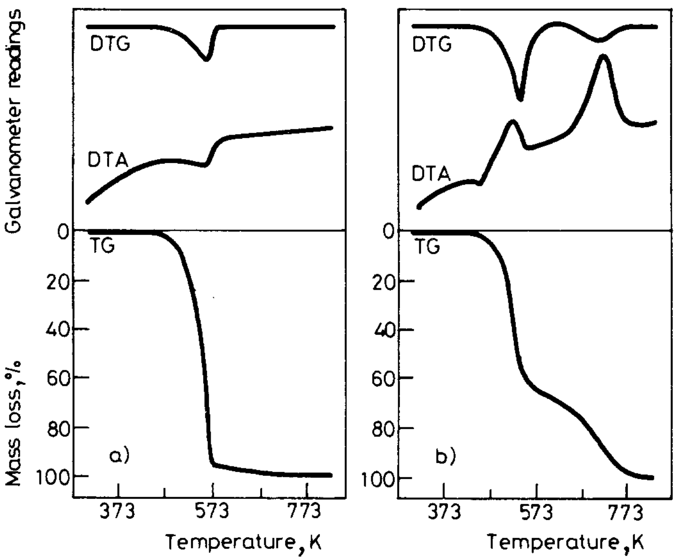

Fig. 1 Thermal curves of ammonium (a) and N, N-diethyl-ethanaminium (b) iodides

where $a = 1$ for $(Et_4N)I$ and $a = 0$ for the remaining compounds examined.

In several previous papers we have demonstrated that dynamic thermogravimetric data can be used to evaluate the enthalpy of reaction (2) on the basis of the Van't Hoff equation (Eq. (1)) [1-3]. Thus derived ΔH_v values correspond, however, to the temperature range in which the volatilization process occurs. They were modified to ambient temperature by adding a heat capacity term (assumed arbitrarily to be -7 kJ.mol^{-1} [1]). and terms resulting from phase transitions and melting [1-3]. The appropriate numeri-

Table 1 Thermal and thermochemical characteristics for ammonium and ethanaminium iodides

Compound [a]	Temperature, K					Thermochemical data, kJ $\cdot$ mol^{-1} for 298 K			
			$T\alpha = 0.01$					U° [e]	
	DTG	DTA[b]	A[c]	B[d]	T_v[d]	ΔH_v°	$\Delta H_{f,c}^{\circ}$	C	D
$(NH_4)I$	550	547	448	445	559	174	–194	624	632
		(p; endo)					–201 [13]	628 [13]	
$(EtNH_3)I$		333 (tr)	439	442	561	183	–205	573	583
		467 (m)					–234 [14]	608 [14]	640 [14]
	536	517							
		(p; exo)							
	702	702							
		(p; exo)							
$(Et_2NH_2)I$		308 372 (tr)	445	443	548	197	–244	555	562
							–263 [14]	580 [14]	624 [14]
		447 (m)							
	520	514							
		(p; exo)							
	702	702							
		(p; exo)							
$(Et_3NH)I$		456 (m)	440	443	560	177	–244	509	550
	534	524					–289 [14]	558 [14]	601 [14]
		(p; exo)							
	720	720							
		(p; exo)							
$(Et_4N)I$		472 (tr)	520	523	567	545			531
	561	561					–317 [14]		583 [14]
		(p; endo)							

[a] For names of amines see ref. [1], [b] (tr), temperature of a phase transition; (m), temperature of melting; (p), temperature of the peak, [c] obtained from thermogravimetric curves, [d] derived from Eq. (1), [e] (C), values determined from the thermochemical cycle; (D), values derived from the Kapustinskii-Yatsimirskii equation

cal values for both latter terms have been taken directly from literature [8] or were estimated by approximate procedures [1, 9, 10]. Subsequently, the enthalpies of formation of crystalline iodides and the energies of the crystal lattice of the salts were evaluated on the basis of the thermochemical cycle [1-3]. The necessary thermochemical data for these estimations have been taken from the literature [6, 7]. This procedure could not be applied to N, N, N-triethyl-ethanaminium iodide since the dissociation of the compound requires the overcoming of a noticeable activation barrier. The crystal lattice energies were also estimated from the Kapustinskii-Yatsimirskii formula [11, 12] using values of "thermochemical" radii of the anion [6] and cations [1, 7] from literature. The derived thermochemical characteristics together with some literature data are listed in Table 1. As can be noticed the derived values of $\Delta H^{0}_{f,c}$ and U^{0} are always lower than the values of those quantities determined on the basis of calorimetric measurements [13, 14]. The discrepancy is particularly pronounced in the case of N, N-diethyl-ethanaminium iodide. One possible source of such discrepancies might be that dissociation products interact and do not volatilize as kinetically free fragments. On the other hand, the agreement may be considered to be quite good, taking into account that both sets of data were drawn from independent and totally different experiments. It is also worth mentioning that "thermochemical" radii are the additive quantities for halogenide salts of alkanamines. This results from the fact that the crystal lattice energies evaluated from the Kapustinskii-Yatsimirskii formula compare well with those derived from the thermochemical cycle.

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Zusammenfassung — Unter Anwendung dynamischer thermoanalytischer Methoden (DTA, TG, DTG) wurden die thermischen Eigenschaften von Verbindungen der allgemeinen Formel $(Et_nNH_{4-n})I$ mit $n = 0$-4 untersucht. Im ersten Schritt der Zersetzung werden Amin und HI freigesetzt und gehen in die Gasphase über. Die Enthalpien dieses Prozesses wurden auf der Grundlage der Van't Hoffschen Gleichung und analytischer TG-Kurven ermittelt. Experimentell ermittelte Werte sowie zugängliche Literaturangaben wurden benutzt, um die Bildungsenthalpie und die Kristallgitterenergie dieser Verbindung zu schätzen. Weitere Informationen bezüglich letzterer Größe wurden auch über die Kapustinskij-Yatsimirskij-Formel erhalten.