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Thermal features and thermochemistry of hexachlorozirconates of aliphatic and aromatic mono-amines—stability of hexahalogenozirconates

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Abstract

Thermal behaviour of the hexachlorozirconates of several alkanamines and aromatic mono-amines was examined using dynamic and quasi-isothermal–isobaric thermoanalytical methods. Decomposition of the compounds upon an increase in temperature is accompanied by partial volatilization. The residue contains ZrO_2 and is sometimes contaminated with traces of carbonization products. It is believed that the primary process, which can be summarized with the equation

$$(A_pNH_{4-p})_2ZrCl_{6(s)} \rightarrow 2aHCl_{(g)} + 2(1-a)ACl_{(g)} + 2A_{p-s}NH_{3-p+s(g)} + ZrCl_{4(cond)}$$

(where A denotes an alkyl or aryl substituent ($p=1$–4; $a=0$ and $s=1$ for quaternary, and $a=1$ and $s=0$ for other compounds studied)) is followed by instantaneous oxidation of zirconium tetrachloride remaining in the condensed phase (cond). An insight into the thermodynamics of the compounds became possible on employing the van't Hoff equation to the non-isothermal thermogravimetric curves. This enabled evaluation of the enthalpies of the thermal decomposition and consequently the enthalpies of formation and the crystal lattice energies of the salts. The latter quantity was further examined using the Kapustinskii–Yatsimirskii method. Geometries, energies and other physicochemical properties of simple aliphatic and aromatic amines and their protonated forms were determined by AM1 and PM3 methods in order to reveal which of these correlate with the proton affinity of amines and the thermal behaviour and thermochemical characteristics of hexachlorozirconates. In addition, the influence of dimensions of ions on the thermodynamic stability of hexahalogenozirconates, with respect to dissociation and oxidation processes, was studied.

Keywords: Thermal features; Thermochemistry; Stability; Hexahalogenozirconates

1. Introduction

Zirconium tetrahalides are one of the best known derivatives of tetravalent Zr [1–3]. Owing to the distinct electron acceptor ability, the compounds easily coordinate halogen ions forming complex anions [1–4]. Highly symmetrical octahedral ZrX_6^{2-} species which are the main constituents of a large group of salt-like derivatives are the best known of these ions [1–4]. Such salts are very convenient objects for studying general features of chemical entities since they are relatively simple, easy obtainable and easy to handle. Tetrachlorides of alkali metal hexachlorozirconates can play the role of intermediates in the production of the pure metal or in its separation from other group IVA elements [1,5–8]. Furthermore, zirconium tetrahalides and particularly tetrachlorides, as well as hexachlorozirconate salts have found some other applications [9,10]. These reasons constituted a premise for undertaking study on the thermochemistry of hexachlorozirconates of nitrogen aromatic bases [3]. Recently, a theoretical examination of the structure, thermochemistry and features of ZrX_6^{2-} [11], as well as thermochemistry and lattice energetics of numerous hexahalogenozirconates [11,12] has also been conducted. This paper completes the study on hexachlorozirconates. This group of compounds was chosen to enable direct comparison of their behaviour with that of hexachlorostannates (Zr and Sn are both fifth row elements) investigated in detail in the past [13–19]. Moreover, examination of salts containing the same $ZrCl_6^{2-}$ ion enables relations between their various features and those constituting these amines, either in neutral or in protonated forms to be revealed. Lastly, as the compounds border on inorganic

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and organic matter a knowledge of their features and behaviour is of crucial importance in understanding the basic rules of chemistry.

2. Materials and methods

2.1. Syntheses

All reagents were the best grades available and were purified, where necessary, using standard methods. All hexachlorozirconates with the exception of quaternary salts were prepared by mixing a solution of $ZrCl_4$ saturated with HCl (Aldrich) in absolute methyl(ethyl)alcohol, with stoichiometric amounts of amines dissolved in the same solvent [1,20,21]. Quaternary salts were prepared by mixing solutions containing stoichiometric amounts of quaternary chlorides and $ZrCl_4$ in $SOCl_2$ (sometimes small amounts of acetic anhydride were added to initiate crystallization) [1,21,22]. The precipitates formed upon cooling were filtered off, carefully washed with anhydrous tetrahydrofuran, and dried in a vacuum desiccator over P_2O_5. The stoichiometry of the compounds was revealed by determination of the contents of Cl (mercurometric titration of chloride ions) and C, H, N (using a Carlo–Erba elemental analyzer, model 1108).

2.2. Measurements

The dynamic thermal analyses were carried out on an OD-103 derivatograph (Monicon), with α-Al_2O_3 as reference, in a dynamic nitrogen atmosphere. The samples, weighing 50 mg, were placed in a shallow platinum crucible (cf. Ref. [23]; Appendix 3, crucible 2). Other operating conditions were as follows: heating rate ≈ 5 K min^{-1}, sensitivities of DTG, DTA and TG galvanometers 1/10, 1/1–1/5 and 50 mg respectively.

Thermogravimetric analyses under quasi isothermal–isobaric conditions (Q-mode) [24] were performed on a Q-1500 derivatograph (Monicon) with 50 mg samples placed in a special platinum labyrinth type crucible. The samples were heated at a rate of about 6 K min^{-1}. The rate of mass loss was adjusted to 2 mg min^{-1}.

Powder diffraction analyses of residues after dynamic and quasi isothermal–isobaric thermal analyses were carried out on an HZG4-A diffractometer (Carl Zeiss, Jena).

The procedure described previously [25] was applied to identify the gaseous products of decomposition of hexachlorozirconates in the presence and absence of oxygen. For this purpose, the sample was placed in a quartz reactor and heated at a constant temperature in a stream of air or argon. Some organic substances were trapped inside the reactor on a cold finger, whereas volatile products were carried out of the reactor and absorbed in cyclohexane, an acidified solution of KI or water. All phases were checked for the presence of organic substances, chlorine and HCl.

From TG curves, such as those shown in Fig. 1, values of the temperature (T) corresponding to certain values of the apparent extent of reaction (α^*) were derived in the manner described in Ref. [26] (α^* is a fraction of a substrate decomposed, reflected by a ratio of a measured mass loss to the initial mass of a sample). For each compound, a set of α^* vs. T data points was determined on the basis of at least three replicate measurements. An example is given in Table 1.

2.3. MO calculations

The geometries of neutral (Am) and protonated (AmH^+) amines were optimized by the semiempirical AM1 [27] and PM3 [28] methods, incorporated in MOPAC 93 [29] and SPARTAN version 2.1 [30] program packages. The standard routines of both programs were used to evaluate heats of formation, energies of LUMO and HOMO, energies of non-bonded orbitals, net atomic charges on nitrogen atoms arising either from natural [18,31] or Mulliken [32] population analysis, the lone-pair densities of electrons [33], as well as N–H bond lengths and orders.

Calculations were carried out on a PC-486 and Hewlett–Packard model 730 Apollo workstation.

3. Results and discussion

3.1. Remarks on syntheses of hexachlorozirconates

It was the original intention to synthesize primary, secondary, tertiary and quaternary hexachlorozirconates of unbranched alkanamines containing up to 4 C atoms in the substituent, as well as relevant salts of neat benzenamine and benzenemethanamine and their methyl, phenyl or benzyl derivatives. Actually, the chemical composition of only 10 hexachlorozirconates confirmed the desired stoichiometry (i.e. those listed in Table 2), although in several more cases solid products were isolated. Furthermore, we were unable to obtain any compound in the monocrystalline phase adequate for complete X-ray analysis. Failures in syntheses of more hexachlorozirconates may result from the similar solubility of these and relevant chloride salts (the composition of solid products often suggested precipitation of mixtures of both salts). Furthermore, hexachlorozirconates may undergo hydrolysis, oxidation, reaction with amines or even self-transformation towards less chlorine-containing derivatives [1–3,20]. Therefore, inadequate choice of conditions for syntheses could lead to undesired products. The above discussion ex-

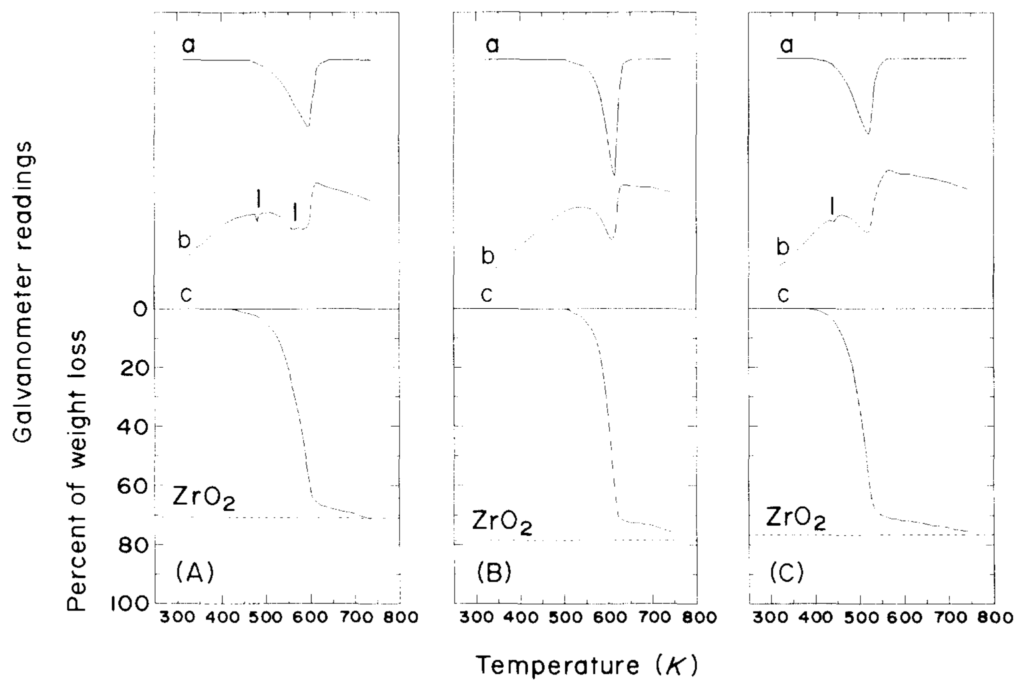

Fig. 1. Thermal analyses of N,N-dimethylmethanaminium (A), N,N, N-triethylethanaminium (B) and N-methylbenzenaminium (C) hexachlorozirconates carried out in dynamic conditions; (a) differential thermogravimetry (DTG); (b) differential thermal analysis (DTA); (c) thermogravimetry (TG). (|) indicates the solid state phase transition. At thermogravimetric curves expected amount of ZrO_2 in the residue is indicated.

Table 1
α^* vs. T for the thermal decomposition of N,N-dimethylmethanaminium (A), N,N,N-triethylethanaminium (B) and N-methylbenzenaminium (C) hexachlororozirconates

$\alpha^{*\,a}$	T (K)		
	A	B	C
0.08	521	567	457
0.16	543	585	476
0.24	555	596	490
0.32	566	603	499
0.40	576	608	507
0.48	584	614	515
0.56	593	619	522
0.64		624	528

[a] Mass loss relative to the initial mass of the sample.

plains why hexachlorozirconates are much less recognized than relevant hexachlorostannates [1–4,13]—compounds related to each other by the fact that Sn and Zr are both 5th row elements belonging to the main and sub-group IV respectively.

3.2. *Thermal features of hexachlorozirconates*

Examples of the results of dynamic and quasi isothermal–isobaric thermoanalytical investigations are shown in Figs. 1 and 2, while Table 2 compiles characteristic parameters either derived from the thermal analysis curves or evaluated by approximation of thermogravimetric data with van't Hoff's equation. In contrast to the chlorides [34,35,37] and the majority of hexachlorostannates [13–15] constituted of aliphatic and aromatic mono-amines, none of the hexachlorozirconates studied decomposed with complete volatilization. Solid residues always remained after dynamic (white or slightly grey in colour) and quasi isothermal–isobaric (black) measurements. The amount of solid products in dynamic experiments either exactly corresponded to ZrO_2 or was slightly higher. The presence of the latter compound was confirmed by powder diffraction analysis. A possible explanation of this finding is that the oxygen always present in small amounts in the derivatograph oven reacts with the primarily released $ZrCl_4$, forming ZrO_2. It was estimated in our previous paper that the amount of oxygen needed to complete the transfer from $ZrCl_4$ to ZrO_2 is of the order of a few cm^3 [3]. This amount of O_2 may be available in the reaction zone since the inner part of the derivatograph oven remains in contact with the natural atmosphere. Surprisingly, ZrO_2 was also found in residues after Q-analyses. The amount of this was usually lower than the stoichiometric one since only oxygen in air kept in covered labyrinth-type crucibles is available to released $ZrCl_4$. The colour of the residues is most probably due to carbonization products formed as a result of side effects. These may be facilitated by the formation of non-volatile ZrO_2 which covers the surface of the analyzed material impeding transfer of organic molecules released upon primary dissociation to the gaseous

Table 2
Thermal characteristics of hexachlorozirconates of aliphatic and aromatic amines

No.	Substance [a]	Peak temperature [b] (K)				Temperature [b] (K)			
		DTG	DTA			$T_{0.01}$ [g]		$T_{0.1}$ [g]	
			T_p	T_σ	T_m	A	B	A	B
1	$[(CH_3)_2NH_2]_2ZrCl_6$				506 [d]	458	462	532	531
2	$[(CH_3)_3NH]_2ZrCl_6$	595	594	477 [c]; 483 [d] 543 [d]; 558(d) [e]	603 [d]	458	461	526	527
3	$[(CH_3)_4N]_2ZrCl_6$	638	635		595(d) [f]	530	530	585	586
4	$[(C_2H_5)_2NH_2]_2ZrCl_6$			407 [c]	535–538(d) [e] 547 [d]	451	454	521	520
5	$[(C_2H_5)_3NH]_2ZrCl_6$	591	588	355 [c]	579 [d]	443	445	516	516
6	$[(C_2H_5)_4N]_2ZrCl_6$	620	616			522	521	573	573
7	$[(n\text{-}C_4H_9)NH_3]_2ZrCl_6$	596	596		543–548(d) [e] 545(d) [c]	449	450	516	516
8	$[(n\text{-}C_4H_9)_3NH]_2ZrCl_6$	571	571			454	456	516	515
9	$[(n\text{-}C_4H_9)_4N]_2ZrCl_6$	586	585	436 [c]	548–553(d) [e] 553(d) [d]	504	502	548	546
10	$[(C_6H_5NH_2(CH_3)]_2ZrCl_6$	522	521	440 [c]	523–525(d) [e]	403	402	464	462

[a] For names of amines (cations), see Refs. [34,35].

[b] The symbols are taken from Ref. [36]. T_p, temperature of the peak; T_σ, temperature of the solid state phase transition; T_m, melting temperature; T_α, temperature at which the fraction reacted is equal to α^*.

[c] T_σ or T_m determined from DTA curves; (d), decomposition.

[d] Ref. [20].

[e] T_m determined by the standard capillary method; (d), decomposition.

[f] Ref. [21].

[g] A, determined directly from TG curves; B, predicted by approximation of experimental α^* vs. T dependencies with Eq. (3).

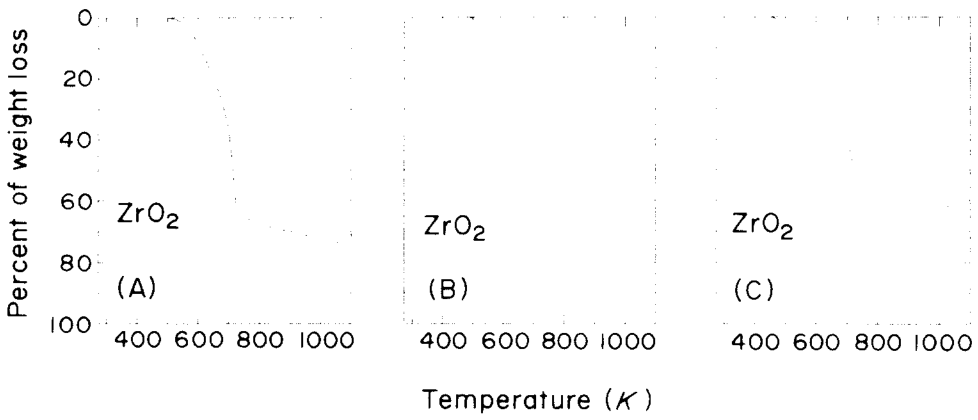

Fig. 2. Quasi isothermal–isobaric analyses of N,N-dimethylmethanaminium (A), N,N,N-triethylethanaminium (B) and N-methylbenzenaminium (C) hexachlorozirconates.

phase. Occurrence of carbonization products is even more likely in quasi isothermal–isobaric measurements where initiation of the decomposition takes place at relatively higher temperatures, thus creating favourable conditions for the destruction of organic fragments of the compounds.

All thermoanalytical curves exhibit a smooth shape (see, for example, Fig. 1) over the major part of the process, typical for the simple decomposition pattern. Only at higher temperatures, when volatilization is far advanced, do side processes come to light. It may thus be assumed that this major part of the dynamic thermoanalytical curves reflects primary dissociation of the compounds studied into HCl, chloroalkanes (in the case of quaternary salts), amines and $ZrCl_4$, accompanied with subsequent oxidation leading to ZrO_2. Thermogravimetric dependencies relevant to the initial stage of the process can, therefore, be used for the evaluation of the enthalpy of decomposition.

As data in Table 2 demonstrate, decomposition of compounds 4, 5 and 9 is preceded by phase transitions. Compounds 2 and 10 undergo phase transitions, and 1–5, 7, 9 and 10 melting, in all cases simultaneously with decomposition. Effects which accompany melting were, however, reflected only on DTA curves of compounds 7 and 9. In other cases they were most probably masked by strong effects accompanying decomposition. Temperatures characterizing thermal dissociation, i.e. peak maxima on DTA and DTG curves, as well as $T_{0.01}$ and $T_{0.1}$ are similar to those for hexachlorostannates [13–15], but are much higher than those for chlorides [34,35,37] of aliphatic and aromatic amines. Such behaviour is most probably the consequence of the formally higher thermodynamic stability of $ZrCl_6^{2-}$ [3,12] and $SnCl_6^{2-}$ [13–17] containing salts over that of chlorides [34,35,37], as well as the much lower volatility of products of decomposition of both former groups of compounds, i.e. $ZrCl_4$ and $SnCl_4$. The characteristic temperatures of the decomposition depend somewhat on the nature and length of substituents at the nitrogen atom. It is difficult, however, to reveal general relations since a set of the compounds studied is incomplete. Nevertheless, the relatively high temperatures of decomposition of quaternary salts, as well as relatively low temperatures of dissociation of salts of aromatic amines can be noted.

3.3. *Nature of the thermal processes*

Hexachlorozirconates of aliphatic and aromatic monoamines behave as typical salt-like derivatives [1–3,20,22]. Such compounds exist in crystal lattices predominantly due to the strong electrostatic interactions between ionic fragments [11]. It must therefore be that before decomposition and release of products to the gaseous phase the compounds undergo rearrangement accompanied by proton transfer from a position closer to the basic site to one closer to the acidic site and by changes in the structure of acidic and basic constituents such as to facilitate the process. More details regarding the possible mechanism of the thermal decomposition of hexachlorozirconates can be found in our previous paper [3]. Taking into account these and other considerations concerning this matter [13,37], the primary process can be summarized with the equation

$$(A_pNH_{4-p})_2ZrCl_{6(s)} \longrightarrow 2aHCl_{(g)} + 2(1-a)ACl_{(g)} + 2A_{p-s}NH_{3-p-s(g)} + ZrCl_{4(cond)} \qquad (1)$$

where A denotes an alkyl or aryl group ($p = 1$–4; $a = 0$ and $s = 1$ for quaternary and $a = 1$ and $s = 0$ for other compounds studied), g or s indicates gaseous or solid state, while cond indicates $ZrCl_4$ remaining in the condensed phase. Proton transfer which precedes decomposition should not cause substantial changes in the structure of the solid phase and, therefore, should necessitate only the overcoming of the thermodynamic barrier. Our previous studies seem to indicate that rearrangement within protonated amines and $ZrCl_6^{2-}$ accompanying decomposition of primary, secondary and tertiary salts also requires that only the thermodynamic barrier be overcome. This can not generally be said about quaternary salts which decompose only when a kinetic barrier, higher than the thermodynamic one is passed [14,34]. This is actually reflected in higher values of the characteristic temperatures of decomposition of the latter compounds (Table 2). As the result of decomposition of quaternary salts, tertiary amines and chloroalkanes are released instead of amines and HCl being the products of thermolysis of all other compounds studied [14,34].

HCl, chloroalkanes and amines released in the primary process tend to evolve into the gaseous phase, since their volatilization temperatures are lower than those of decomposition of relevant hexachlorozirconates. $ZrCl_4$ is much less volatile (the sublimation temperature reported in the literature is 604 K [3]) and should remain in the crucible. The compound would thus volatilize at higher temperatures in oxygen free conditions. The results of this work reveal, however, that $ZrCl_4$ reacts with oxygen, present in small amounts in the reaction zone, which can be summarized with Eq. (1)

$$ZrCl_{4(cond)} + O_{2(g)} \longrightarrow ZrO_{2(s)} + 2Cl_{2(g)} \qquad (2)$$

The process is exothermic by 227 or 116 kJ mol^{-1} if the substance is gaseous or crystalline [3] respectively, although it requires the overcoming of an activation barrier equal to 101 kJ mol^{-1} [1]. This barrier is apparently passed since stoichiometric amounts of Zr are kept in solid reaction products. If oxidation ends with the reaction in Eq. (2), then in a stream of gas leaving the reaction zone stoichiometric (to $ZrCl_4$) amounts of Cl_2 should be present. Experiments carried out in a quartz reactor confirmed the presence of chlorine only upon decomposition of quaternary salts in air, whereas HCl was always identified in the gas stream. As stoichiometric amounts of amine hydrochlorides are trapped on the cold finger of the reactor, therefore the presence of HCl must be a consequence of secondary chlorination processes. Moreover, new organic compounds were detected after decomposition. This implies that the major part of Cl_2 reacts with organic molecules. A similar effect has been noted upon decomposition of hexachlorozirconates of mononitrogen aromatic bases [3] and hexachloroplumbates containing various organic bases [25,38].

A few words should be said about the behaviour of volatile products in the gaseous phase. As results of quantum mechanical calculations reported in our previous paper [3] reveal, amine and HCl molecules evolved to the gaseous phase should exist predominantly as kinetically free species.

3.4. Enthalpy of volatilization of hexachlorozirconates

If, as mentioned, primary dissociation of all hexachlorozirconates, with the exception of quaternary, studied requires the overcoming of the thermodynamic energy barrier only, then the system should reach equilibrium simultaneously with decomposition. This equilibrium is actually accomplished within the species involved in the primary process and thus may be regarded as corresponding to the reaction in Eq. (1). Subsequent oxidation (reaction in Eq. (2)) will necessitate substantial structural rearrangements within the $ZrCl_4\cdots O_2$ activated complex and will require, as mentioned, the overcoming of a certain kinetic activation barrier, despite the fact that the overall process is exothermic. It may thus be assumed that secondary oxidation does not influence the equilibrium created upon primary decomposition. Taking into account the above considerations, it may be assumed that the actual extent of decomposition (α) is equal to $P/P^\ominus$, where P is the equilibrium vapour pressure at a given temperature and $P^\ominus$ is the reference (atmospheric) pressure. Using this extent of reaction, the enthalpy of decomposition ($\Delta_d H^\ominus$) can be evaluated on the basis of the van't Hoff equation [3]

$$\ln \alpha = -\frac{\Delta_d H^\ominus}{4R}\frac{1}{T} + \frac{\Delta_d H^\ominus}{4R}\frac{1}{T_c} \tag{3}$$

where R is the gas constant, the multiplicator 4 accounts for the fact that primary dissociation of 1 mol of $(A_p NH_{4-p})_2ZrCl_6$ yields 4 mol of gaseous products (Eq. (1)) and T_c represents the temperature of the completion of dissociation, i.e. the temperature at which P attains $P^\ominus$. Originally, values of the apparent extent of decomposition (α^*) were determined (Table 1). As decomposition of the compounds studied ended with nearly stoichiometric amounts of ZrO_2, all α^* values had to be modified according to [3]

$$\alpha = \alpha^*/\{1 - M[ZrO_2]/M[(A_pNH_{4-p})_2ZrCl_6]\} \tag{4}$$

that afforded values corresponding to the complete volatilization.

The values of $\Delta_d H^\ominus$ resulting from Eq. (3), listed in Table 3, are relevant to the reaction in Eq. (1), i.e. the state where $ZrCl_4$ remains in a condensed phase. In order to change these to more convenient standard enthalpies of volatilization ($\Delta_{v,298}H^\ominus$), reflecting the complete transfer of substances to the gaseous phase, the $\Delta_d H^\ominus$ were increased by the standard enthalpy of sublimation of $ZrCl_4$ ($\Delta\sigma H^\ominus$), equal to 110.8 kJ mol^{-1} [3]. Furthermore, since the $\Delta_d H^\ominus$ values refer to the temperature range in which the compounds actually decompose, they were modified so as to refer to 298 K. The overall modification was, therefore

$$\Delta_{v,298}\mathrm{H}^\ominus = \Delta_d H^\ominus + \Delta_s H^\ominus + \Delta_{fus}H^\ominus + \Sigma\Delta_\sigma H^\ominus - \int_{298}^{T} \Delta C_p^\ominus \, dT \tag{5}$$

where $\Delta_{fus}H^\ominus$ is the enthalpy of fusion, the term $\Sigma\Delta_\sigma H^\ominus$ arises from any polymorphic transitions which compounds may undergo between 298 K and the onset of the fusion or decomposition process, and $\int_{298}^{T} C_p{}^\ominus\, dT$ accounts for the change in enthalpy resulting from changes in the heat capacities of the reactants. Values of $\Delta_{fus}H^\ominus$ and $\Delta_\sigma H^\ominus$ were estimated by comparison of the areas of the DTA peaks relevant to phase transitions with those resulting from the volatilization process and assuming that the latter areas correspond to the $\Delta_d H^\ominus$ values listed in Table 3 (the estimated quantities are given in Table 3). The values of the heat capacity term were, finally, estimated assuming that $\Delta C_p{}^\ominus$ increases due to the increase of possibilities of the storage of energy in translational and rotational degrees of freedom of molecules released to the gaseous phase and that these molecules behave perfectly. Modified values of $\Delta_{v,298}H^\ominus$ are given in Table 3.

3.5. Thermochemical characteristics of hexachlorozirconates

Various relations between the thermochemical quantities characterizing hexachlorozirconates can be presented in the form of a thermochemical cycle (see for example Ref. 3, Scheme 1), from which the following relationships result

$$\begin{aligned}
&\Delta_{f,298}H^\ominus[(A_pNH_{4-p})_2ZrCl_{6(s)}] \\
&\quad = 2a\Delta_{f,298}H^\ominus[HCl_{(g)}] + 2(1-a)\Delta_{f,298}H^\ominus[ACl_{(g)}] \\
&\qquad + 2\Delta_{f,298}H^\ominus[A_{p-s}NH_{3-p-s(g)}] \\
&\qquad + \Delta_{f,298}H^\ominus[ZrCl_{4(g)}] \\
&\qquad - \Delta_{v,298}H^\ominus[(A_pNH_{4-p})_2ZrCl_{6(s)}]
\end{aligned} \tag{6}$$

$$\begin{aligned}
&{}_{298}E_c{}^\ominus[(A_pNH_{4-p})_2ZrCl_{6(s)}] \\
&\quad = 2\Delta_{f,298}H^\ominus[A_{p-s}NH^+_{4-p-s(g)}] + \Delta_{f,298}H^\ominus[ZrCl^{2-}_{6(g)}] \\
&\qquad - \Delta_{f,298}H^\ominus[(A_pNH_{4-p})_2ZrCl_{6(s)}] - 3RT
\end{aligned} \tag{7}$$

and

$$\begin{aligned}
&\Delta_{f,298}H^\ominus[A_{p-s}NH^+_{4-p-s(g)}] \\
&\qquad - \Delta_{f,298}H^\ominus[A_{p-s}NH_{3-p-s(g)}] \\
&\qquad + \Delta_{f,298}H^\ominus[H^+_{(g)}] - {}_{298}PA^\ominus[A_{p-s}NH_{3-p-s(g)}]
\end{aligned} \tag{8}$$

where $\Delta_{f,298}H^\ominus$ denotes the enthalpy of formation of an entity given in square brackets; ${}_{298}E_c{}^\ominus + 3RT$ is the lattice enthalpy and ${}_{298}E_c{}^\ominus$ represents the lattice energy; and ${}_{298}PA^\ominus$ denotes the proton affinity of the amine (all values in Eqs. (6)–(8) refer to the standard conditions, i.e. 298 K and 1 atm).

Table 3
Thermochemical characteristics for hexachlorozirconates at 298 K

Compound No.	Thermochemical data					
	$\Delta_d H^\ominus$ [a] (kJ mol^{-1})	$\Delta_{v,298} H^\ominus$ [b] (kJ mol^{-1})	T_c (K)	$\Delta_{f,298} H^\ominus$ [b] (kJ mol^{-1})	$E_c^\ominus$ (kJ mol^{-1})	
					From the thermochemical cycle [b]	From Eq. (9) [c]
1	275	362	606	−1454	1085	1288 (0.179*) 1277 (0.184**)
2	281 (8^{+}) (3^{+})	380	600	−1482	1071	1248 (0.199*) 1094 (0.290**)
3	420	502 (313)	646	(−1394)	(943)	1219 (0.214*) 1030 (0.336**)
4	275 (15^{+})	378	594	−1578	1063	1269 (0.188*) 1085 (0.296**)
5	246 (19^{+})	354	601	−1595	988	1249 (0.198*) 986 (0.372**)
6	438	521 (289)	629	(−1569)	(849)	1217 (0.215*) 878 (0.476**)
7	268 (11^{++})	368	591	−1607	1102	1307 (0.170*) 1210 (0.219**)
8	303	392	584	−1891	996	1160 (0.248*) 932 (0.421**)
9	474 (24^{+}) (20^{++})	604 (339)	594	(−1962)	(863)	1137 (0.262*) 812 (0.554**)
10	235 (3^{+})	332	533	−1206	1079	1311 (0.168*) 1205 (0.222**)

[a] Heats of phase transitions (+) or melting (++) are given in parentheses.

[b] Values obtained by extrapolation are given in parentheses.

[c] In parentheses r_C values are given (in nm). Values with asterisk (*) originate from crystal lattice energies of chloride salts [34,35,38] (assuming r_{Cl^-} equal to 0.181 nm [2,39,40] and with two asterisks (**) hexachlorostannate salts [13–15] (assuming $r_{SnCl_6^{2-}}$ equal to 0.37 nm [14]).

The enthalpies of formation and the crystal lattice energies of hexachlorozirconates, which are shown in Table 3, were determined using values of the enthalpies of formation of amines [40,42,44–46] (Table 4) and their protonated forms [15,35,38] (Table 4) available in the literature, values of $\Delta_{v,298}H^\ominus$ [$(A_p NH_{4-p})_2ZrCl_{6(s)}$] determined here (Table 3), and the following values of the enthalpies of formation of $HCl_{(g)}$ [39,40,47], $ZrCl_{4(g)}$ [4] and $ZrCl_6{}^{2-}{}_{(g)}$ [4,11,12] (in kJ mol^{-1}): −92.3, −870.3 and −1530 respectively.

Enthalpies of volatilization of quaternary salts originating from thermogravimetric data are much higher than those for other compounds studied (Table 3). Such behaviour, also observed upon examination of quaternary chlorides [34] and hexachlorostannates [14], can be ascribed to the existence of a substantial kinetic activation barrier for the decomposition process. In such cases, enthalpies of formation and lattice energies can be estimated by assuming that both quantities follow additivity rules, i.e. are linearly dependent on the number of a given alkyl substituent at the nitrogen atom (similar correlation has been revealed in the case of other salts, see for example Refs. 14 and 34 and references cited therein). This procedure afforded values $\Delta_{f,298}H^\ominus$ and $298E_c{}^\ominus$ shown in parentheses in Table 3. Moreover, subsequent extraction of $\Delta_{v,298}H^\ominus$ from Eq. (6) enabled us to reveal the expected values of the enthalpies of volatilization of quaternary salts (shown in parentheses in Table 3) by substituting the enthalpies of formation of relevant chloroalkanes [40,42] instead of the enthalpy of formation of HCl. The estimated $\Delta_{v,298}H^\ominus$ values fit reasonably well to those for primary, secondary and tertiary salts.

Further insight into the crystal lattice energy problems was possible by invoking an approximate method developed originally by Kapustinskii [48] and Yatsimirskii [49]. Following the authors, the crystal lattice energy of ionic compounds can be expressed by the equation

$$E_c\ (\mathrm{kJ\ mol^{-1}}) = 120.2\,\frac{(\Sigma n)Z_A Z_C}{r_C + r_A} \times \left[1 - \frac{0.0345}{r_C + r_A} + 0.087(r_C + r_A)\right] \qquad (9)$$

Table 4
Energetic, structural and physicochemical features of aliphatic and aromatic amines (Am) and their protonated forms (AmH^+) determined theoretically

Compound, Am	Quantum chemistry method used	Am								AmH^+						
		Enthalpy of formation $\Delta_f H$ (kJ mol^{-1})	Proton affinity PA (kJ mol^{-1})	Energy (eV)		Energy of non-bonded orbital (eV)	Lone pair electron density^{i}	Net charge at N^{j}	Mulliken net charge at N^{k}	Enthalpy of formation $\Delta_f H$ (kJ mol^{-1})	Energy (eV)		Net charge at N^{j}	Mulliken net charge at N^{k}	N–H bond length	N–H bond order
				LUMO	HOMO^{h}						LUMO	HOMO				
NH_3	AM1	−45.9^{a}	860^{f}		−10.16*					630^{f}						
		−30.5	874.8	4.22	−10.42	−14.93	1.000	−0.396	−0.528	630.9	−4.81	−24.78	−0.094	−0.345	1.025	0.918
		30.6^{b}	875.9^{b}							630.3^{b}						
	PM3	−12.8	879.6	3.33	−9.70	−12.08	1.000	0.007	−0.081	643.8	−5.44	−24.24	0.998	0.918	0.999	1.000
CH_3NH_2	AM1	−22.7^{a}	909^{f}		−8.97*					605^{f}						
		−30.9	882.0	3.81	−9.76	−15.20	0.989	−0.352	−0.470	623.3	−4.60	−19.02	−0.059	−0.289	1.027	0.913
		−31.0^{b}	883.5^{b}							622.3^{b}						
	PM3	−21.7	872.0	3.18	−9.40	−12.34	0.993	−0.029	−0.104	642.5	−5.19	−19.50	0.880	0.798	1.001	0.991
$(CH_3)_2NH$	AM1	−18.6^{a}	934^{a}		−8.25*					584^{f}						
		−23.6	887.4	3.48	−9.39	−15.47	0.979	−0.308	−0.409	625.2	−4.43	−18.54	−0.027	−0.233	1.028	0.907
		−23.4^{b}	882.6^{b}							630.7^{b}						
	PM3	−33.1	863.9	2.91	−9.22	−12.56	0.987	−0.055	−0.107	639.2	−4.99	−19.10	0.778	0.702	1.003	0.983
$(CH_3)_3N$	AM1	−23.7^{a}	950^{f}		−7.82*					563^{f}						
		−7.2	892.1	3.19	−9.12	−15.69	0.971	−0.267	−0.347	636.9	−4.30	−18.18	0.003	−0.179	1.030	0.901
		−7.1^{b}	893.5^{b}							636.1^{b}						
	PM3	−45.5	858.3	2.73	−9.07	−12.69	0.981	−0.072	−0.092	632.4	−4.80	−18.70	0.692	0.632	1.005	0.977
$C_2H_5NH_2$	AM1	−47.5^{a}	921^{f}		−8.86*					568^{f}						
		−56.6	898.4	3.65	−9.68	−15.23	0.990	−0.349	−0.464	581.2	−4.41	−17.12	−0.070	−0.293	1.026	0.914
		−63.2^{b}	893.1^{b}							580.5^{b}						
	PM3	−46.7	885.0	3.04	−9.37	−12.29	0.993	−0.038	−0.112	604.5	−5.02	−17.48	0.832	0.748	1.002	0.988
$(C_2H_5)_2NH$	AM1	−72.5^{a}	953^{f}		−8.01*					511^{f}						
		−71.5	917.2	3.27	−9.30	−15.50	0.981	−0.303	−0.397	547.5	−4.13	−16.65	−0.042	−0.237	1.027	0.907
	PM3	−79.2	888.9	2.77	−9.19	−12.44	0.986	−0.066	−0.116	568.1	−4.70	−17.00	0.698	0.622	1.006	0.977
$(C_2H_5)_3N$	AM1	−92.8^{a}	978^{f}		−7.50*					465^{f}						
		−68.4	939.3	2.96	−8.95	−15.77	0.974	−0.256	−0.325	528.5	−3.93	−16.39	−0.014	−0.180	1.029	0.900
	PM3	−111.3	893.3	2.56	−9.01	−12.49	0.980	−0.082	−0.098	531.6	−4.43	−16.64	0.596	0.536	1.008	0.968
n-$C_3H_7NH_2$	AM1	−70.2^{a}	926^{f}		−8.78*					540^{f}						
		−85.3	900.6	3.59	−9.68	−15.24	0.990	−0.349	−0.464	550.3	−4.34	−15.90	−0.067	−0.291	1.026	0.914
		−92.5^{b}	896.8^{b}							547.4^{b}						
	PM3	−69.2	886.6	2.99	−9.38	−12.30	0.993	−0.036	−0.110	580.4	−4.96	−16.13	0.844	0.761	1.002	0.988
(n-$C_3H_7)_2NH$	AM1	−116.2^{a}	961^{f}		−7.84*					459^{f}						
		−128.7	921.0	3.23	−9.30	−15.50	0.981	−0.303	−0.397	486.5	−4.02	−15.63	−0.037	−0.233	1.027	0.908
	PM3	−124.2	891.4	2.71	−9.21	−12.46	0.986	−0.063	−0.113	520.6	−4.61	−15.88	0.719	0.644	1.006	0.977

$(n\text{-}C_3H_7)_3N$	AM1	-161.0^{a}	988^{f}							387^{f}						
		-153.1	942.9	2.93	-8.95	-15.74	0.974	-0.255	-0.324	440.2	-3.79	-15.43	-0.008	-0.175	1.029	0.900
	PM3	-180.8	896.4	2.50	-9.04	-12.53	0.980	-0.077	-0.094	459.0	-4.31	-15.62	0.622	0.564	1.008	0.968
$n\text{-}C_4H_9NH_2$	AM1	92.0^{a}	928^{f}		-8.71*					516^{f}						
		-113.8	901.9	3.53	-9.68	-15.24	0.990	-0.349	-0.464	520.5	-4.31	-14.98	-0.067	-0.291	1.025	0.914
		-120.9^{b}	896.8^{b}							518.9^{b}						
	PM3	-91.8	887.5	2.96	-9.38	-12.31	0.993	-0.036	-0.110	556.9	-4.94	-15.16	0.842	0.760	1.002	0.988
$(n\text{-}C_4H_9)_2NH$	AM1	-156.6^{a}	966^{b}		-7.69*					414^{f}						
		-185.8	923.2	3.19	-9.30	-15.50	0.981	-0.302	-0.396	427.2	-3.98	-14.80	-0.037	-0.233	1.027	0.907
	PM3	-169.4	893.0	2.68	-9.22	-12.46	0.986	-0.062	-0.112	473.8	-4.57	-15.00	0.717	0.642	1.006	0.977
$(n\text{-}C_4H_9)_3N$	AM1	-222^{a}	993^{f}		-7.40*					321^{f}						
		-238.8	945.8	2.89	-8.95	-15.78	0.974	-0.254	-0.323	351.6	-3.74	-14.67	-0.008	-0.175	1.029	0.900
	PM3	-248.7	898.6	2.46	-9.04	-12.53	0.980	-0.077	-0.093	388.9	-4.26	-14.88	0.621	0.563	1.008	0.968
$C_6H_5NH_2$	AM1	87.3^{a}	889^{g}		-7.72*					734^{g}						
		85.9	882.4	0.64	-8.52	-14.73	0.950	-0.327	-0.462	739.7	-4.39	-14.09	-0.005	-0.228	1.027	0.908
		86.6^{b}	884.7^{b}							738.7^{b}						
	PM3	89.2	891.9	0.42	-8.61	-12.42	0.956	0.071	-0.006	733.5	-4.73	-14.24	0.968	0.900	1.000	0.984
$C_6H_5NH(CH_3)$	AM1	90.4^{c}	922^{g}		-7.33*					705^{g}						
		101.5	890.4	0.66	-8.41	-14.80	0.940	-0.287	-0.403	747.3	-4.26	-13.96	0.026	-0.174	1.028	0.905
	PM3	86.6	885.9	0.43	-8.53	-12.54	0.953	0.039	-0.014	736.9	-4.60	-14.13	0.869	0.806	1.002	0.981
$C_6H_5N(CH_3)_2$	AM1	100.5^{a}	945^{g}		-7.12*					692^{g}						
		130.3	900.3	0.59	-8.50	-15.25	0.946	-0.244	-0.331	766.2	-4.10	-13.85	0.055	-0.121	1.032	0.899
	PM3	88.0	883.9	0.34	-8.75	-12.58	0.967	-0.005	-0.023	740.3	-4.44	-14.02	0.786	0.739	1.005	0.974
$(C_6H_5)_2NH$	AM1	219.3^{a,d}			-7.16*											
		236.8	896.6	0.20	-8.27	-14.21	0.916	-0.259	-0.381	876.4	-4.07	-13.64	0.076	-0.119	1.029	0.902
	PM3	212.8	905.7	0.14	-8.56	-12.54	0.941	0.108	-0.061	843.3	-4.38	-13.83	0.951	0.900	1.001	0.978
$(C_6H_5)_2N(CH_3)$	AM1	271.8	904.1	0.25	-8.26	-14.36	0.919	-0.224	-0.318	903.9	-3.92	-13.52	0.104	-0.067	1.033	0.897
	PM3	219.3	895.6	0.12	-8.47	-12.45	0.946	0.074	0.058	859.9	-4.21	-13.72	0.876	0.838	1.004	0.971
$(C_6H_5)_3N$	AM1	326.8^{d}	910^{g}							953^{g}						
		412.3	913.7	0.18	-7.96	-12.07	0.873	-0.211	-0.318	1034.8	-3.66	-13.28	0.150	-0.015	1.035	0.894
	PM3	354.0	915.7	0.09	-8.35	-12.19	0.929	0.148	0.136	974.5	-3.96	-13.54	0.949	0.921	1.004	0.970
$C_6H_5CH_2NH_2$	AM1	87.8^{a,e}	918^{g}		-8.64*					706^{g}						
		71.6	903.0	0.34	-9.56	-15.69	0.988	-0.333	-0.447	704.8	-4.29	-13.36	-0.073	-0.293	1.023	0.915
	PM3	83.6	894.4	0.14	-9.45	-12.43	0.992	-0.034	-0.108	725.4	-4.75	-13.49	0.810	0.726	1.001	0.990
$(C_6H_5CH_2)_2NH$	AM1	205.5	940.8	0.43	-9.33	-15.67	0.981	-0.302	-0.397	800.9	-3.99	-13.06	-0.044	-0.235	1.028	0.905
	PM3	198.4	918.2	0.26	-9.23	-12.50	0.986	-0.057	-0.109	816.4	-4.33	-13.21	0.675	0.598	1.008	0.974
$(C_6H_5CH_2)_3N$	AM1	340.6	952.1	0.34	-9.25	-15.96	0.971	-0.252	-0.323	924.7	-3.77	-12.86	-0.010	-0.172	1.031	0.899
	PM3	298.8	919.9	0.13	-9.09	-12.51	0.978	-0.066	-0.083	915.1	-4.04	-13.02	0.591	0.532	1.009	0.967

[a] Mean values from those given in Refs. [40–42]. [b] Values determined by AM1 from Ref. [43]. [c] Value from Ref. [44]. [d] Values from Ref. [45]. [e] Value from Ref. [46]. [f] Values from Ref. [38]. [g] Values from Refs. [15,35]. [h] (*), negative values of an ionization potential from Ref. [40]. [i] For details see Ref. [33]. [j] For details see e.g. Refs. [18,31]. [k] From Mulliken population analysis (Ref. [32]).

where (Σn) is the total number of ions in the simplest stoichiometric unit of the compound, Z_C and Z_A denote the numerical values of the charges of cation and anion respectively, and r_C and r_A are the thermochemical ionic radii (in nm). For $r_{ZrCl_6^{2-}}$ a value equal to 0.373 nm was assumed [12], while relevant radii of cations are given in Table 3. The lattice energies evaluated by the Kapustinskii–Yatsimirskii approach are listed in the last column of Table 3.

In general, lattice energies obtained by the Kapustinskii–Yatsimirskii method conform reasonably with those arising from the thermochemical cycle only if thermochemical radii of cations originate from relevant hexachlorostannate salts.

3.6. Structure, energetics and physicochemical features of amines

As protonated amines are the cationic constituents of compounds studied, it is now interesting how far features of these influence the behaviour of hexachlorozirconates. Unfortunately, structural, thermochemical and charge distribution data of amines are reported in different sources and are fragmentary. To complete these we employed semiempirical quantum chemistry methods (AM1 and PM3). The results are compiled in Table 4.

It is generally recognized that salts containing amines are formed as the result of hydrogen bonding interactions ($>$N–H$\cdots$(A)). Such interactions should, in some way, be dependent on their proton affinities (*PA*s). For these reasons, the main emphasis in the discussion below is concentrated on the relationships between *PA*s and various features of the base molecules.

Generally speaking, AM1 method provides values of physicochemical features which conform better with experimental ones (Table 4). For these reasons, mainly data originating from this method are considered in further discussion. As reveal both AM1 and experimental data, *PA*s increase with an increase of the number and size of substituents at nitrogen atom. Proton affinities of amines, which reflect their thermochemical ability for proton attachment, are surprisingly inversely related to the excess of a negative charge imparted to the nitrogen atom [50]. The excess of a negative charge diminishes upon gradual substitution and protonation (PM3 predicts even deficiency of a charge at nitrogen). The energies of LUMO (lowest unoccupied molecular orbitals) and non-bonded orbitals of neutral amines both decrease with an increase of the number and size of substituents at N and thus are, as can be expected, inversely related to proton affinities. Energies of HOMO (highest occupied molecular orbitals) are directly related to *PA*s and increase upon the increase of the number and size of substituents at nitrogen. Protonation lowers energies of LUMO and HOMO and causes that values of both quantities are directly related to *PA*s (all increase with an increase of the number and size of substituents at the nitrogen atom). Lone pair electron density only weakly depends on the constitution of amines. Nevertheless, unexpected gradual decrease in value of this quantity with the number and size of substituents can be noted. This implies that the proton affinity is inversely related to the lone pair electron density. Finally, proton affinities are directly related to N–H bond lengths and inversely related to N–H bond orders. Values of both latter characteristics increase and decrease respectively, with an increase of the number of substituents at the nitrogen atom, while they are only slightly affected by the size of these.

3.7. Influence of features of amines on the behaviour of hexachlorozirconates

Combination of Eqs. (6) and (8) reveals that enthalpies of volatilization of hexachlorozirconates should increase with the increase of proton affinities of amines, while the combination of Eqs. (7) and (8) reveals that enthalpies of formation of the salts should decrease with the increase of *PA* values. These trends are generally observed when examining data in Tables 3 and 4.

Crystal lattice energies show a downward trend when moving towards more voluminous cations. This finding conforms with several empirical rules [51] and may be linked to the fact that an increase in dimensions of cationic fragments causes a decrease of energy of cohesion.

Simple quantitative description of the influence of dimensions of ions on the crystal lattice energy is provided by the Kapustinskii–Yatsimirskii formula. Lattice energies obtained using this equation and thermochemical radii of cations originating from lattice energies of hexachlorostannates compare well with those evaluated through the thermochemical cycle. Conformity was poor when thermochemical radii of cations arose from the lattice energies of chloride salts. This implies that the Kapustinskii–Yatsimirskii approach applies well only to compounds similar in the chemical and structural sense. On the other hand, thermochemical radii, being, in fact, quantities characterizing protonated nitrogen bases, do not correlate, in general, with their structural and physicochemical features.

4. Stability of hexahalogenozirconates

The measure of the thermodynamic stability of the compound can be either its free enthalpy of formation or the free enthalpy change accompanying any process in which it may participate. In general, the lower the free enthalpy of formation, the higher the stability of the compound and vice-versa. On the other hand, the compound decomposes into smaller fragments if the free enthalpy change for such a process is negative. The stability of hexahalogenozirconates containing mono- (K′) and divalent (K″) cations was examined, in this latter sense, considering their dissociation towards relevant zirconium tetrahalides and halides holding cationic fragments of the salts:

$$\mathrm{K'_2(or\ K'')ZrX_{6(s)}} \longrightarrow \mathrm{2K'X(or\ K''X_2)_{(s)} + ZrX_{4(s)}}(\Delta_{\mathrm{dis}}H) \quad (10)$$

or decomposition accompanied with oxidation:

$$\mathrm{K'_2(or\ K'')ZrX_{6(s)} + O_2} \longrightarrow \mathrm{2K'X\ (or\ K''X_2)_{(s)} + ZrO_{2(s)} + 2X_{2(g,l,s)}}(\Delta_{\mathrm{ox}}H) \quad (11)$$

The latter process is ready to occur if the reaction given in Eq. (1) takes place in air [1]. Considerations in this work were restricted to the enthalpy term owing to the inability to quantitatively evaluate the entropy changes.

Between parameters affecting stability of hexahalogenozirconates and thus ability to participate in processes denoted by Eqs. (10) and (11) of particular importance are dimensions of ions constituting these salts. These dimensions can, in the first approximation, be reflected by the thermochemical radii to be found in the Kapustinskii–Yatsimirskii formula (Eq. (9)). Such an assumption seems to be particularly sound in the case of monoatomic ions [39,40,48,49,52], where thermochemical radii correspond to the crystallographic ones. To reveal relations between $\Delta_{\mathrm{dis}}H$ and $\Delta_{\mathrm{ox}}H$ and thermochemical radii of cations we combined simple dependencies resulting from a relevant thermochemical cycle:

$$\Delta_{\mathrm{dis}}H[\mathrm{K'_2(or\ K'')ZrX_{6(s)}}] = \mathrm{E_c}[\mathrm{K'_2(or\ K'')ZrX_{6(s)}}] - 2E_{\mathrm{c}}[\mathrm{K'X_{(s)}}](\mathrm{or\ E_c[M''X_{2(s)}]}) - HIA[\mathrm{ZrX_{4(s)}}] \quad (12)$$

$$\Delta_{\mathrm{ox}}H[\mathrm{K'_2(or\ K'')ZrX_{6(s)}}] = \Delta_{\mathrm{dis}}H[\mathrm{K'_2(or\ K'')ZrX_{6(s)}}] + \Delta_{\mathrm{o}}H[\mathrm{ZrX_{4(s)}}] \quad (13)$$

with the Kapustinskii–Yatsimirskii equation [48,49] enabling evaluation of E_{c} of all the salts. In Eqs. (12) and (13) *HIA* $[\mathrm{ZrX_{4(s)}}]$ denotes halide ion affinity of species given in square brackets [4], i.e. enthalpy change for the reaction:

$$\mathrm{ZrX_{4(s)} + 2X^-_{(g)}} \longrightarrow \mathrm{ZrX^{2-}_{6(g)}} \quad (14)$$

and $\Delta_{\mathrm{o}}H[\mathrm{ZrX_{4(s)}}]$ – enthalpy change for the oxidation of solid zirconium tetrahalides:

$$\mathrm{ZrX_{4(s)} + O_{2(g)}} \longrightarrow \mathrm{ZrO_{2(s)} + 2X_{2(g,l,s)}} \quad (15)$$

Ancillary data necessary to disclose $\Delta_{\mathrm{dis}}H$ and $\Delta_{\mathrm{ox}}H$ vs. r_{C} dependencies are compiled in Table 5.

Hexafluoro-, hexachloro-, hexabromo- and hexaiodozirconates consisting of monovalent cations are predicted to be stable with respect to dissociation (reaction in Eq. (10)) if r_{C} exceeds 0.075, 0.086, 0.156 and 0.128 nm respectively (Fig. 3(A)). The approach applied reveals that between hexahalogenozirconates of divalent cations only fluoro- and chloro- compounds in which $r_{\mathrm{C}} > 0.193$ and 0.220 nm respectively (Fig. 4(A)) should be stable in the latter meaning. The ability to undergo oxidation (reaction in Eq. (11)) changes drastically when moving from fluoro- to chloro-, bromo- and iodo-derivatives. Hexafluorozirconates of both mono- and divalent cations should be resistant to oxidation ($\Delta_{\mathrm{ox}}H$ are highly positive) (Figs. 3(B) and 4(B)). All other hexahalogenozirconates with the exception of some hexachlorozirconates of monovalent cations should be susceptible to such process. Data for the $\mathrm{K_2'ZrX_6}$ type salts reveal that resistant to oxidation should be chloroderivatives containing large cations ($r_{\mathrm{C}} > 0.166$) (Fig. 3(B)). With two exceptions (Cs and Fr) the monoatomic cations do not fulfil this condition [2,12,39,40]. However, thermochemical radii of cations of numerous nitrogen organic bases exceed the above mentioned value [12,52].

The entropy term for both reactions in Eqs. (10) and (11) should be positive since the number of product molecules is greater than the number of substrate molecules. This would mean that $\Delta_{\mathrm{dis}}G$ and $\Delta_{\mathrm{ox}}G$ would be lower than the relevant $\Delta_{\mathrm{dis}}H$ and $\Delta_{\mathrm{ox}}H$ values, and that hexahalogenozirconates would be even less thermodynamically stable than results from the enthalpy change evaluations.

Concluding, it may be said that the most stable of the compounds examined appear to be hexafluorozirconates. Indeed, numerous such salts are known and for many of them crystal phase structures have been refined [11]. The instability towards decomposition predicted for $\mathrm{M''ZrF_6}$ salts (Fig. 4(A)) is not observed in reality and is most probably due to the qualitative character of the approach applied. Hexachloro-, hexabromo- and hexaiodozirconates of divalent cations are not known most probably because of their high ability to oxidate. Between $\mathrm{K_2'ZrX_6}$ type salts (X = Cl, Br and I) only hexachlorozirconates containing relatively large cations (e.g. nitrogen organic base cations [12]) should be resistant to oxidation. The results of this and our previous work [3] conform completely with these findings. Hexabromo- and hexaiodozirconates consisting of monovalent cations could be stable only if an adequately high kinetic barrier for the oxidation would exist, otherwise thermodynamic force would move the system towards oxidation products. This is presumably the reason why only few such compounds are known [11]. It should also be mentioned that $\mathrm{K_2'ZrX_6}$ salts become stable in oxygen free conditions if dimensions of cationic fragments exceed certain values. The above described findings account for all known experimental facts and

Table 5
Ancillary data for determination of $\Delta_{dis}H$ and $\Delta_{ox}H$ vs. r_C dependencies [a]

X	r_C		$\Delta_{f,298}H^{\ominus}$			$HIA[ZrX_{4(s)}]$	$\Delta_oH[ZrX_{4(s)}]$ [g]
	X^- [b,c,d]	ZrX_6^{2-} [e]	$X_{(g)}^-$ [b,c,f]	$ZrX_{4(s)}$ [b,d]	$ZrX_6{}^{2-}{}_{(g)}$ [e]		
F	0.133	0.281	−257	−1912	−2503	−77	811
Cl	0.181	0.373	−233	−981	−1542	−95	−120
Br	0.197	0.387	−219	−761	−1163	36	−340
I	0.220	0.403	−196	−483	−829	46	−618

[a] $\Delta_{f,298}H^{\ominus}$, HIA and Δ_oH values in kJ mol^{-1}; r_A values in nm.
[b] Ref. [2].
[c] Ref. [39].
[d] Ref. [40].
[e] Ref. [11].
[f] Ref. [47].
[g] $\Delta_{f,298}H^{\ominus}[ZrO_{2(s)}]$ was assumed to be −1101 kJ mol^{-1} (Ref. [40]).

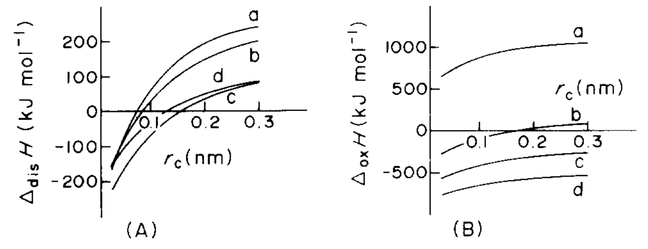

Fig. 3. Enthalpy of dissociation ($\Delta_{dis}H$) (A) and enthalpy change upon oxidation ($\Delta_{ox}H$) (B) of (a) hexafluoro-, (b) hexachloro-, (c) hexabromo- and (d) hexaiodo- zirconates vs. radii of cations (r_C) for $M_2'ZrX_{6(s)}$ type salts.

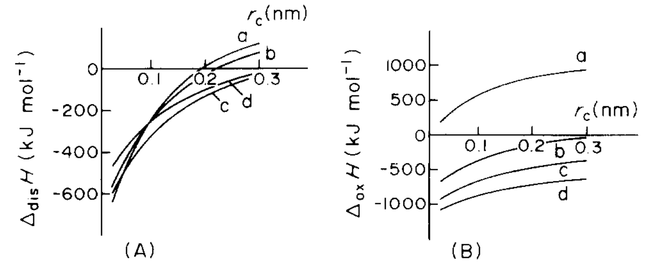

Fig. 4. Enthalpy of dissociation ($\Delta_{dis}H$) (A) and enthalpy change upon oxidation ($\Delta_{ox}H$) (B) of (a) hexafluoro-, (b) hexachloro-, (c) hexabromo- and (d) hexaiodo- zirconates vs. radii of cations (r_C) for $M''ZrX_{6(s)}$ type salts.

shed new light on features and behaviour of this group of compounds.

5. Conclusions

Several known and previously unknown hexachlorozirconates containing aliphatic or aromatic amines were synthesized and examined by thermoanalytical methods. These studies, except for revealing the general thermal behaviour, also enabled determination of basic thermochemical quantities such as enthalpies of formation and crystal lattice energies of the compounds. Numerous such characteristics have not so far been available.

Enthalpies of formation and lattice energies of alkanamine salts follow additivity rules, i.e. are linearly dependent on the number of alkyl substituents at the nitrogen atom. It was also revealed that crystal lattice energies of hexachlorozirconates and hexachlorostannates [13–15] of relevant amines reproduce each other quite well by the Kapustinskii–Yatsimirskii equation. This implies that lattice energies can be considered as additive quantities with respect to thermochemical radii of ions.

Numerous features of amines, such as net negative charge at the nitrogen atom, lone pair electron density, and energies of LUMO, HOMO and non-bonded orbitals are qualitatively related to proton affinities of these, as well as to the enthalpies of volatilization and volatilization temperatures. This implies that properties of cationic constituents of the salts have some impact on their features and behaviour.

Crystal lattice energies of hexachlorozirconates are inversely related to the dimensions of ions, which is qualitatively revealed by the Kapustinskii–Yatsimirskii [48,49] equation and other empirical dependencies [51]. The combination of the former equation with certain thermochemical data enables prediction of stability or reactivity of the compounds, in the thermochemical sense, with respect to geometric parameters constituting these fragments. As was found, this phenomenological approach accounts qualitatively for the ability of hexachlorozirconates to undergo thermal dissociation or oxidation. The latter approach seems to be quite general in revealing features and behaviour of chemical systems of an ionic constitution.

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