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THERMAL FEATURES AND THERMOCHEMISTRY OF HEXACHLOROHAFNATES OF NITROGEN AROMATIC BASES

Theoretical studies on the geometry and thermochemistry of $HfCl_6^{2-}$

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Abstract

Hexachlorohafnates of pyridine and its three methyl-substituted derivatives were synthesized and examined by the thermoanalytical methods. The van't Hoff equation employed for the thermogravimetric α *vs.* T dependencies enabled evaluation of the heats of the thermal dissociation and subsequently enthalpies of formation and crystal lattice energies of the salts. Geometry and energy of formation of $HfCl_6^{2-}$ was determined at the ab initio Hartree-Fock SCF level, using all electron MINI basis set augmented with standard polarization functions (MINI*). Electron correlation was considered at the MP2 level. Thermodynamic characteristics for the latter species were also obtained combining ab initio results with those of statistical thermodynamics. The usefulness of theoretical methods in examination of solid state energetics is briefly discussed.

Keywords: hexachlorohafnate ion, organic hexachlorohafnates, theoretical calculations, thermoanalytical studies

Introduction

Hafnium tetrachloride and hexachlorohafnates originating from it are one of the simplest and best known derivatives of hafnium [1, 2]. They are attractive model compounds for examining features of chemical entities, due to their high symmetry. These reasons prompted us to undertake theoretical studies on hexahalogenohafnates and HfX_6^{2-} ions [3, 4]. This paper summarized results of thermoanalytical investigations on selected hexachlorohafnates of nitrogen organic bases and provides theoretically obtained thermochemical and structural data for $HfCl_6^{2-}$.

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Materials and methods

Hexachlorohafnates were synthesized by mixing a solution of $HfCl_4$ in ethyl alcohol acidified with HCl with stoichiometric amounts of hydrochlorides of organic bases dissolved in the same medium [5, 6].

Dynamic thermoanalytical measurements were carried out on an OD-103 derivatograph (Monikon), analogously as described elsewhere [6].

Bond length and energies of $HfCl_6^{2-}$ at constrained O_h symmetry were determined at the Hartree-Fock level (*HF*) employing Baker's optimization procedure [7] together with an all electron *MINI* basis set augmented with standard polarization functions (*MINI**) [8]. The energies of formation of $HfCl_6^{2-}$ ($\Delta_f E$) were obtained following Hess's Law, i.e., subtracting from the energy of gaseous $HfCl_6^{2-}$ the energies of gaseous Cl_2 (three times) and Hf in the lowest electronic state (the geometry and energy of Cl_2 and energy of Hf were determined similarly to the geometry and energy of $HfCl_6^{2-}$ [3]). To improve the quality of ab initio calculations with respect to energy, the *HF* results were supplemented with the second order Moller-Plesset (*MP2*) electron correlation correction [9] calculated at the geometry optimal for the *MINI** basis set (relevant information is referred to as *MP2/MINI*||HF/MINI**, where '||' means 'at the geometry of'). All the quantum mechanical calculations were carried out on a Hewlett-Packard 730 Apollo workstation employing the GAMESS (General Atomic and Molecular Electronic Structure System) program package [10]. The enthalpies ($\Delta_{f,298}H^0$) and free enthalpies ($\Delta_{f,298}G^0$) of formation of $HfCl_6^{2-}$ were evaluated analogously as in the case of $\Delta_f E$, [3], using entropies ($_{298}S^0$), as well as enthalpies and free enthalpies of species relative to their ab initio energies determined previously [3].

Results and discussion

Figure 1 demonstrates examples of the results of dynamic thermoanalytical measurements, while Table 1 summarizes thermal characteristics for all the compounds studied. Hexachlorohafnates of nitrogen bases, similar to relevant hexachlorozirconates [6], do not decompose with complete volatilization. Solid residues (white or slightly grey in colour) corresponded to stoichiometric amounts of HfO_2. Formation of the latter species was confirmed by powder diffraction analysis.

The results of thermoanalytical studies can best be explained assuming that primary decomposition of hexachlorohafnates of nitrogen organic bases (B), which follows Eq. (1) by analogy to hexachlorozirconate salts [6],

$$(BH)_2HfCl_{6(c)} \rightleftarrows 2HCl_{(g)} + 2B_{(g)} + HfCl_{4(ads)} \tag{1}$$

is accompanied by oxidation leading to HfO_2 (Eq. (2))

$$HfCl_{4(ads)} + O_{2(g)} \rightarrow 2Cl_{2(g)} + HfO_{2(c)} \tag{2}$$

The presence of Cl_2 between the gaseous products was not, however, confirmed since it is most probably consumed in instantaneous chlorination of organic bases [6]. It may be thought that process (1) maintains the system in the equi-

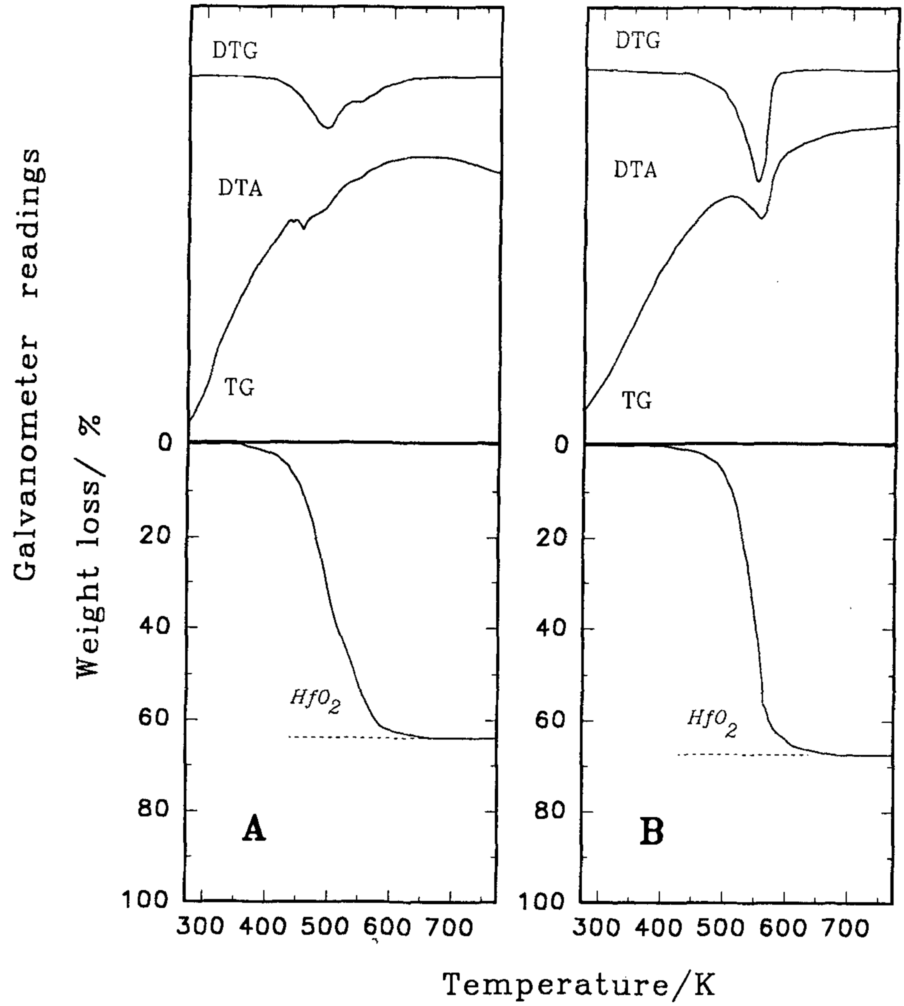

Fig. 1 Thermal analyses of 4-methylpyridinium (A) and 2,3,4-trimethylpyridinium (B) hexachlorohafnates

Table 1 Thermal characteristics of hexachlorohafnates of nitrogen bases

No.	Substance[a]	Peak remperature[b] /K				Temperature[b] /K				
		DTG		DTA		$T^c_{0.01}$		$T^c_{0.1}$		T^c_c
		T_p	T_p	T_σ	T_m	A	B	A	B	
1	Pyridine (Py)	504	506				394	458	456	521
2	4–Methylpyridine (4–MePy)	490	488	447 (d)[d]	464 (d)[d] 441–446 (d)[e]		400	454	454	511
3	2,4–Dimethylpyridine (2,4–DiMePy)	508	510			409	413	469	468	525
4	2,4,6–Trimethylpyridine (2,4,6–TriMePy)	536	537			431	433	492	490	549

[a] Name of organic base

[b] T_p, temperature of the peak; T_σ, temperature of the solid state phase transition; T_m, temperature of melting; T_α , temperature at which the fraction reacted in equal to α^*; T_c, temperature of the completion of decomposition (Eq. (3)).

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

[d] Determined from DTA curves; (d), decomposition.

[e] Determined by standard capillary method; (d), decomposition.

librium state at any temperature which justifies the use of the van't Hoff equation to determine the enthalpy of decomposition ($\Delta_d H^0$ (Eq. (3))

$$\ln\alpha = -\frac{\Delta_d H^0}{4R}\frac{1}{T} + \frac{\Delta_d H^0}{4R}\frac{1}{T_c} \tag{3}$$

where R is the gas constant, the multiplier 4 accounts for the fact that primary dissociation of 1 mol of $(BH)_2HfCl_6$ yields 4 moles of gaseous products, T_c represents the temperature of the completion of decomposition and α is the actual extent of decomposition – related to the apparent extent of decomposition α^* (obtained originally from the TG curves) through Eq. (4) [6]

$$\alpha = \alpha^*/\{1-M\,[HfO_2]/M\,[(BH)_2\,HfCl_6]\} \tag{4}$$

(M represents the molar mass of the species given in parentheses). To obtain the standard enthalpies of volatilization ($\Delta_{v,298}H^0$), the $\Delta_d H^0$ values were increased by the standard enthalpy of sublimation of $HfCl_4$ (equal to 99 kJ·mol^{-1} [1]) and modified as previously described [6] (heats of phase transition and fusion for compound 2 were assumed to be, in kJ·mol^{-1}, 8 and 10, respectively, i.e. the same as for the relevant hexachlorozirconate salt [6]). Values of both $\Delta_d H^0$ and $\Delta_{v,298}H^0$ are shown in Table 2.

Table 2 Thermodynamic characteristics of hexachlorohafnates (in kJ·mol^{-1})

Compound	$\Delta_d H^0$	$\Delta_{v,298}H^0$	$\Delta_{f,298}H^0$	${}_{298}E_c^0$ Thermochemical cycle	Kapustinskii-Yatsimirskii method
$(PyH)_2HfCl_6$	223	310	–1103	953	1146
$(4\text{–}MePyH)_2HfCl_6$	253	357	–1222	976	1155
$(2,4\text{–}DiMePyH)_2HfCl_6$	270	355	–1301	951	1137
$(2,4,6\text{–}TriMePyH)_2HfCl_6$	286	368	–1352	934	1120

Following relations resulting from the thermochemical cycle [6], the evaluated $\Delta_{v,298}H^0$ values were combined with other thermochemical data to afford the enthalpies of formation ($\Delta_{f,298}H^0$) and crystal lattice energies (${}_{298}E_c^0$ of the salts [4, 6] (these are listed in Table 2). In these latter calculations a value equal to –1641 kJ·mol^{-1} was assumed for the enthalpy of formation of $HfCl_6^{2-}$ (Table 3) and other data were taken from Refs [4, 6]. The crystal lattice energies were also estimated employing the Kapustinskii–Yatsimirskii method [11, 12] and using 'thermochemical' radii of cations and $HfCl_6^{2-}$ reported in Refs [4, 13], respectively (relevant values are given in the last column in Table 2). Thermal and thermochemical characteristics reveal that stability of hexachlorohafnates increases upon increase of the number of methyl substituents in the pyridine aromatic system. The discrepancies between lattice energies obtained from thermochemical cycle and those from the Kapustinskii–Yatsimirskii approach (Table 2) can be ascribed to both difficulties in determination of 'thermochemical' radii of cations [6, 13] (which influence values from the latter method), as well as uncertainties imparted to heats of volatilization of the salts (which affect values originating from he thermochemical cycle). These factors also account, most probably, for discrepancies in E_c values for relevant haxachlorozirconates [6].

Table 3 Thermochemical and structural characteristics of $HfCl_6^{2-}$ determinated theoretically

Basis set || geometry	$\Delta_f E$ / kJ·mol^{-1}	$\Delta_{f,298}H^{0a}$ / kJ·mol^{-1}	$\Delta_{f,298}G^{0}$ / kJ·mol^{-1}	Hf–Cl bond length	
				This work	Lit.
HF /MINI||HF /MINI**	–2070	–1453	–1385	2.518	2.526 [3] 2.548 [3] 2.574 [14]
MP2 /MINI||HF /MINI**	–2258	–1641	–1573		

[a] Literature values of the enthalpy of formation (in kJ·mol^{-1}) are: –1593 [3] (theoretical), as well as –1626 [4] and –1640 [15] (from the thermochemical cycle).

The theoretically determined geometry of $HfCl_6^{2-}$ (Table 3) compares quite well with that established in the solid phase [14] or found by using other basis sets [3]. The most valuable information which theory provides is, however, the standard enthalpy of formation of $HfCl_6^{2-}$. The value determined here fits excellently to those reported in the literature and is reliable enough to be used in the evaluation of crystal lattice energies of the compounds examined.

Conclusions

Thermoanalytical investigations afforded new information on the thermal behaviour of hexachlorohafnates containing organic cations compounds which border on the inorganic and organic matter.

Determination of the enthalpies of volatilization on the basis of experimental thermogravimetric data, enabled evaluation of two important thermochemical characteristics, namely enthalpies of formation and crystal lattice energies of the salts. The values of the latter characteristic could be obtained since the enthalpy of formation of $HfCl_6^{2-}$ was determined theoretically. This proves that ab initio methods are very useful in evaluating the thermochemical characteristics for such complex ions and opens the way for theoretical determination of heats of formation of crystalline compounds for which lattice energies can be obtained theoretically [3].

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Zusammenfassung — Es wurden Pyridin-hexachlorohafnate und deren trimethylsubstituierten Derivate hergestellt und mittels thermoanalytischen Methoden untersucht. Die Anwendung der van't Hoff'schen Gleichung auf die Abhängigkeit des thermogravimetrischen von der Temperatur ermöglichte die Ableitung der thermischen Dissoziationswärme und anschließend der Bildungsenthalpie und der Kristallgitterenergie der Salze. Auf dem ab initio Hartree-Fock SCF Level wurden Geometrie und Bildung von $HfCl_6^{2-}$ bestimmt, wobei alle durch Standard-Polarisationsfunktionen (MINI*) verstärkte Elektronen-Mini-Basis-Sets verwendet wurden. Die Elektronenkorrelation wurde auf dem MP2 Level berücksichtigt. Die thermodynamischen Charakteristika für letztere wurden auch durch eine Kombination aus ab initio Ergebnissen und statistischer Thermodynamik erhalten. Die Nützlichkeit theoretischer Methoden bei der Untersuchung der Energetik von Feststoffen wird kurz diskutiert.