Chemistry Research Journal, 2016, 1(6):1-3

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Gaseous phase ionic formation enthalpy for 3-cyanopyridinecoordination compounds by modified forms of Kapustinskii equation

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Abstract In the present work, it is shown that modified forms of Kapustinskii equation can be successfully employed to calculate the gaseous phase ionic formation enthalpy for coordination compounds, considering the reaction: $M_{(g)}^{2+} + 2Br^-_{(g)} + n3\text{-cyanopy}_{(g)} \rightarrow [MBr_2(3\text{-cyanopy})_n]_{(g)}$; cyanopy = cyanopyridine. The calculated ionic formation enthalpy ($\Delta_{fl}H^0$) values are compared with experimental (calorimetric) values from literature. The derived equation is as follows: $\mathbf{\Delta_{fl}H^0 = [N\ (Z^+Z^-)\ 2\varepsilon/d+\sigma][1-(34.5/d+\sigma)]k}$, where ε is the electrostatic charge on the coordinative nitrogen atom and σ is the radius of the coordinative nitrogen atom, as calculated from its exposed area. Both, ε (-0.743) and σ (74.5 pm) values were obtained by molecular modelling calculations (Hartree-Fock, 3-21G, vacuum). The calculated $\Delta_{fl}H^0$ values agree very well with the experimental ones.

Keywords Kapustinskii equation; coordination compounds; 3-cyanopyridine; ionic gaseous formation enthalpy; molecular modelling

Introduction

As is well known, Kapustinskii equation [1] can be successfully employed to calculate the energy/enthalpy of ionic salts.

Due to its simplicity and reliability, Kapustinskii equation has been, along the last years, usedto obtain some "modified" equations, allowing the lattice energy/enthalpy calculations of multiple ions crystals [2], for example. Previously, it was shown that modified forms of Kapustinskii equation can be successfully employed to calculate the lattice enthalpy of coordination compounds of zinc and cadmium halides with a series of sixteen different ligands [3]. In that work, some empirical constants, related with donor power and steric factors (specifics values for each ligand), were empirically obtained.

It has been shown that there are intimate relationships among ionic lattice energies, formula unit, volume and thermochemical radii for a series of MX_2 and M_2X salts [4] and that, even for complex ionic solids, reliable lattice energy calculations can be performed [5].

In this connection/context, in the present work, it is shown that modified forms of kapustinskii equation can be successfully employed to calculate the gaseous phase ionic formation enthalpy ($\Delta_{fl}H^0$) for coordination compounds, considering the reaction: $M_{(g)}^{2+} + 2Br^-_{(g)} + n3\text{-cyanopy}_{(g)} \rightarrow [MBr_2(3\text{-cyanopy})_n]_{(g)}$. The calculated ionic formation enthalpy values are compared with experimental (calorimetric) values from literature [6].

Methodology

All computational chemistry calculations for 3-cyanopyridinewere performed usingSpartan´14 (version 1.1.8) [7], by Hartree-Fock(3-21G, vacuum) method.

The calculated data were employed to propose a modified form of Kapustinkii equation, which was then employed to calculate the ionic formation enthalpy ($\Delta_{fl}H^{\theta}$) for a series of coordination compounds. The calculated $\Delta_{fl}H^{\theta}$ values were compared with experimental (calorimetric) values from literature [6].

Results and Discussion

The electrostatic charge on the nitrogen heterocyclic atom for 3-cyanopywas calculated as -0.743. It is worth noting that this is the electrostatic charge on the nitrogen heterocyclic atom employed as coordination site, as verified by experimental spectroscopic data [6].

The nitrogen radius (74.5 pm) was obtained by using the calculated nitrogen exposed area (6.975 quadratic Angstorns)

The "pure" Kapustinskii equation was employed in the form:

$$\mathbf{\Delta_L H^0 = [N (Z^+Z^-)/d][1-(34.5/d)]k} \quad (1)$$

where N is the number of ions per unit formula, Z^+ and Z^- the charges (integer numbers) for the cation and anion, respectively, d is the sum of the cation and anion radius and k = 1.21 x 10^5 kJ pm mol^{-1}.

The modified equation obtained here to calculate the gaseous phase ionic formation enthalpy for coordination compounds, considering the reaction: $M_{(g)}^{2+} + 2Br^-_{(g)} + n(3\text{-cyanopy})_{(g)} \rightarrow [MBr_2(3\text{-cyanopy})_n]_{(g)}$ is as follows:

$$\mathbf{\Delta_{fl}H^0 = [N (Z^+Z^-)2\varepsilon/d+\sigma)][1-(34.5/d+\sigma)]k} \quad (2)$$

Where ε^+ is the electrostatic charge on the coordinative nitrogen atom and σ is the radius of the coordinative nitrogen atom, as calculated from its exposed area. Both, electrostatic charges and radius were obtained here by quantum chemical calculations.

The experimental and calculated $\Delta_{fl}H^{\theta}_{(g)}$ values are shown in Table 1. The employed ionic radii (pm) are as follows [8]: Mn^{2+} (83), Fe^{2+} (61), Co^{2+} (65), Ni^{2+} (69), Cu^{2+} (73) and Zn^{2+} (74). The radius were employed taking into account the coordination number of the considered cation, as proposed based on UV-Vis experimental data [6], that is, pseudo-octahedral structures, coordination number 6. The ionic radius of Br^- was taken as 196 pm [8].

Table 1: Experimental and calculated $\Delta_{fl}H^{\theta}$ values ($kJmol^{-1}$).

Compound	$\Delta_{fl}H^0$ (exp.)	$\Delta_{fl}H^0$ (calc.)	Δ%*
$[MnBr_2(3\text{-cyanopy})_{4(g)}$	-2701 ± 27	-2754	+2.0
$[FeBr_2(3\text{-cyanopy})_{4(g)}$	-3052 ± 30	-2196	-4.5
$[CoBr_2(3\text{-cyanopy})_{4(g)}$	-2913 ± 27	-2885	-1.0
$[NiBr_2(3\text{-cyanopy})_{4(g)}$	-3011 ± 31	-2855	-5.2
$[CuBr_2(3\text{-cyanopy})_{2(g)}$	-2846 ± 20	-2825	-0.6
$[ZnBr_2(3\text{-cyanopy})_{2(g)}$	-2774 ± 21	-2818	+1.6

*Disregarding the uncertainty in the experimental values.

As can be verified, the calculated $\Delta_{fl}H^{\theta}_{(g)}$ values agree very well with the experimental ones. At this point, for the derived equation, two facts remain unsolved:

a) Why the $\Delta_{fl}H^{\theta}_{(g)}$ values are not dependant on the number of ligands molecules (the number of ligand is not included in the equation, which works very well for compounds with 2 and 4 ligand molecules);
b) What it is the physical meaning of the constant "2" in the equation?

It was thought that is not only a coincidence that R/4 = 8.314/4 = 2.0785. That is, the constant "2" is the gas constant divided by four. Since in the reaction investigated, all reactants and products are in gaseous phase, seems natural that the gas constant could be involved. However, the first question remains and the second has a new form: what is the physical meaning of "4"?

It is possible to suppose that "4" is the Z value, that is, the number of formula units per unit cell [4]. So, it is supposed here that for both, compounds with two or four ligand molecules, the number of formula units per unit cell is the same, and this is the reason why $\Delta_{fl}H^{\theta}$ values are independent of the number of ligands.

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