



Thermochemistry of Platinum Fluorides: A Computational Study

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Abstract In the present work, thermochemical parameters for platinum fluorides: PtF_2 , PtF_4 , PtF_5 and PtF_6 were calculated by quantum chemical Semi-Empirical (PM6), method and the results compared with (when available) experimental data from literature. Lattice energies are calculated by using Kapustinskii and the generalized Glasser-Jenkins equations. It was concluded that, in gaseous phase, all platinum fluorides are diamagnetic.

Keywords Platinum fluorides, Thermochemistry, Semi-Empirical, molecular modelling

Introduction

There are relatively few thermochemical data available in the literature for platinum fluorides, probably due to their chemical instability (they are highly reactive) and high volatility [1-3], making them difficult compounds to be studied by traditional thermochemical techniques, such as calorimetry.

Hence, there are a few experimental thermochemical data available in the literature about this class of compounds, most of them obtained by Knudsen-cell mass spectrometry with no other measurements (by another techniques) to be compared with.

For such kind of compounds, the so-called computational thermochemistry could have an important contribution to make. It was proposed, for example, that platinum fluorides with Pt(VIII) are nonviable (from a thermodynamic point of view) compounds [4].

In the present work, thermochemical parameters for platinum fluorides: PtF_2 , PtF_4 , PtF_5 and PtF_6 were investigated by quantum chemical calculations (Semi-Empirical/PM6 method) and the results compared with (when available) experimental data from literature. Furthermore, lattice energies are calculated by using Kapustinskii and the generalized Glasser-Jenkins equations.

Computational and Calculations Details

All computations were performed by using Spartan'16 [5]. Thermochemical calculations were performed by Semi-Empirical (PM6) method.

Platinum hexafluoride, PtF_5 and PtF_4 have octahedral environments (CN = 6), and so, were modelled with such environments. Platinum pentafluoride is a tetramer [6], and so, was modelled as a tetramer. Since PtF_5 disproportionates to PtF_4 and PtF_6 , PtF_4 was modelled as a trimer and platinum hexafluoride was modelled as a monomer. Platinum (II) fluoride was modelled as dimer.

The lattice energy values ($\Delta_{\text{latt}} H^\theta$) were calculated by using Kapustinskii [7] and the generalized (with a ionic strength-like term) Glasser-Jenkins [8] equations. When using Kapustinskii equation, the following Shannon-Prewitt crystal radius (pm) were employed: Pt(II) 94; Pt(IV) = 76.5; Pt(V) = 71 and F^- = 119. The radius to Pt(VI) was obtained by extrapolation, as 62.3 pm.



When using Glasser-Jenkins equations, Z (the number of formulas per unit cell) = 8 for PtF_5 . To PtF_4 , $Z=6$ and to PtF_6 , $Z=2$. The unit cell parameters necessary to use Glasser-Jenkins equation are experimental values from literature [9-18].

The SE-PM6 approach was chosen since, as previously shown, it is effective to the thermochemistry of platinum fluorides [19].

Results and Discussion

The calculated and experimental [9-18] values to the thermochemical parameters for platinum fluorides are summarized in Table 1. As comparison, another calculated values [20-21] to PtF_6 by using a DFT approach, are also shown. As can be verified, the SE-PM6 approach provides results with better relation with experimental values.

From Table 1 data can be verified that the calculated values agree well with the (when available) experimental ones.

Table 1: Calculated thermochemical data to platinum fluorides. Experimental values are between () and calculated values from literature are between [].

	PtF_2	PtF_4	PtF_5	PtF_6
$\Delta_f H^\circ_{(g)}/\text{kJmol}^{-1}$	-85.93 ¹⁹ (-105.2) ¹⁶	-528.43 ²¹ (-518.2 \pm 6.2) ¹⁴	-755.43 ¹⁸ (-663.35) ²⁰	-669.47 ⁴ [-529.19; -553.01] ¹⁷ (-676 \pm 28) ⁵ (-672.0 \pm 6.3) ¹⁴
$\Delta_f H^\circ_{(s)}/\text{kJmol}^{-1}$	—	-594.51 (-679.5 \pm 6.0) ¹⁴	-787.40	(-714 \pm 28) ^{2,5} (-722 \pm 28) ^{1,5}
$C_v/\text{JK}^{-1}\text{mol}^{-1}$	99.27 ¹⁹	106.61	109.51 ¹⁸	114.59
$C_{p(c)}/\text{JK}^{-1}\text{mol}^{-1}$	107.58	114.93	117.82	122.90 (122.7) ¹³
ZPE/ kJmol^{-1}	25.76 ¹⁹	26.92 ²¹	35.12 ¹⁸	34.71
$G^\circ/\text{kJmol}^{-1}$	-163.70 ¹⁹	-634.38	-770.48 ¹⁸	-742.22
$H^\circ/\text{kJmol}^{-1}$	-40.47 ¹⁹	-467.13	-703.22 ¹⁸	-612.20
$S^\circ/\text{JK}^{-1}\text{mol}^{-1}$	415.99 ¹⁹	291.89	225.58 ¹⁸	436.10
$\Delta_c H^\circ/\text{kJmol}^{-1}$	—	66.08	5.89	4.42 (4.514) ⁶ (29.512) ^{3,6}
$\Delta_l H^\circ/\text{kJmol}^{-1}$	—	—	26.51	—
$\Delta_c H^\circ/\text{kJmol}^{-1}$	—	(161.3 \pm 1.4) ⁸ (207 \pm 16) ⁹	32.4	—
$\Delta_{\text{latt}} H^\circ/\text{kJmol}^{-1}$	2856 ¹⁰	7880 ¹⁰ 7502 ¹¹	15636 ¹⁰ 12919 ¹¹	22697 ¹⁰ 15354 ^{1,11} , 17979 ^{2,11}
EA/eV	6.85 ¹⁹	(5.20 \pm 0.16) ¹⁵	6.7 ¹⁸	7.6 [7.09] ¹⁷ (7 \pm 0.35) ⁷
IE/eV	(11.85 \pm 0.25) ¹²	(12.83 \pm 0.28) ¹⁵	—	—

¹orthorhombic form; ²cubic form; ³At the boiling point; ⁴SE (PM-6; Ref. 20); ⁵(Ref.10); ⁶(Ref.11); ⁷(Ref.12), ⁸(Ref.13); ⁹(Ref. 14); ¹⁰Using Kapustinskii equation; ¹¹Using the generalized Glasser-Jenkins equation; ¹²(Ref. 15); ¹³(Ref. 16); ¹⁴(Ref. 17); ¹⁵(Ref. 18); ¹⁶Using experimental data from Ref. 10 and 17; ¹⁷(Ref. 19); ¹⁸The value obtained to the tetramer divided by four; ¹⁹Obtained to the dimeric structure shown in Figure 1; ²⁰Calculated using the experimental $\Delta_f H^\circ_{(s)}$ for PtF_4 , the experimental $\Delta_f H^\circ_{(g)}$ for PtF_6 and the enthalpy for the reaction $\text{PtF}_{4(s)} + \text{PtF}_{6(g)} \rightarrow \text{Pt}_2\text{F}_{10(g)} = 28.8 \pm 0.6 \text{ kJmol}^{-1}$ (Ref.13); ²¹The value obtained to the trimer divided by three.



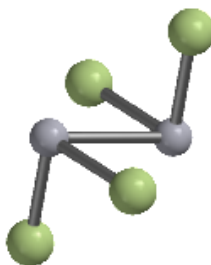


Figure 1: Modelled dimmeric structure for gas phase PtF_2 .

As a general behaviour, there is a good agreement between the lattice energy values calculated from Kapustinskii and the generalized Glasser-Jenkins equations. To PtF_6 the Kapustinskii values are very higher than Glasser-Jenkins ones. Since Kapustinskii equation works well only for ionic compounds, whereas the generalized Glasser-Jenkins equation works very well even for complex solids with high covalence, such as silicates and double salts²¹, I believe that the Glasser-Jenkins values are more trustable, in this case.

As previously reported [19], the gaseous phase formation enthalpy for PtF_6 obtained by PM6 calculations agrees very well with the experimental value only if PtF_6 is modelled as diamagnetic (zero unpaired electrons, because a relativistic effect) and such gaseous compound exhibits a structure with C_1 symmetry in contrast with the octahedral solid compound. Platinum (IV) fluoride was also modelled as diamagnetic.

Platinum difluoride was also modelled as diamagnetic with a dimmeric structure, as shown in Figure 1. For such structure (point group C_{2h}), bond distances are as follows: Pt-Pt= 239.9 pm and Pt-Cl= 196.2 pm. To PtF_2 a ring structure, with no Pt-Pt bond and with bridged fluorine atoms was also modelled. For such structure the obtained gas phase energy (65.87 kJmol^{-1}) is very far from the experimental value. So, such structure was discharged.

It is worth to reinforce that all platinum fluorides were modelled with zero unpaired electrons. When unpaired electrons are considered in the modelled structure, the formation enthalpy values are in large disagreement with the experimental ones. So, is concluded that, in gaseous phase, all platinum fluorides are diamagnetic.

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