



The first calculation of triosmium dodecacarbonyl lattice energy by using Glasser-Jenkins VBT approach

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Abstract. By using a semi-empirical (PM6) approach, the gas phase formation enthalpy for triosmium dodecacarbonyl is calculated as $-1592.50 \text{ kJmol}^{-1}$. By using sublimation enthalpy values from literature, solid phase formation enthalpy values of $-1697.10/-1726.9 \text{ kJmol}^{-1}$ are calculated, in very good agreement with previously reported data. Furthermore, it is shown that, by using formal charges, and applying the Glasser-Jenkins VBT equations, the lattice energy for such compound can be calculated as $19176.81 \text{ kJmol}^{-1}$.

Keywords: Triosmium dodecacarbonyl, thermochemistry; formation enthalpy; lattice energy

INTRODUCTION

Triosmium dodecacarbonyl [*cyclo*-tris(tetracarbonylosmium)(3 Os—Os)], $\text{Os}_3(\text{CO})_{12}$ (Figure 1) is a yellow-colored metal carbonyl cluster and important precursor to organo-osmium compounds, with its derivatives promoting advances in cluster chemistry investigations [1].

However, to the best of the author's knowledge, the thermochemistry of this compound has been (proportionally) little studied. The main objective of the present work is precisely to fill this gap, providing greater insight into the thermochemistry of Triosmium dodecacarbonyl. To this end, a theoretical (molecular modelling) study is carried out.

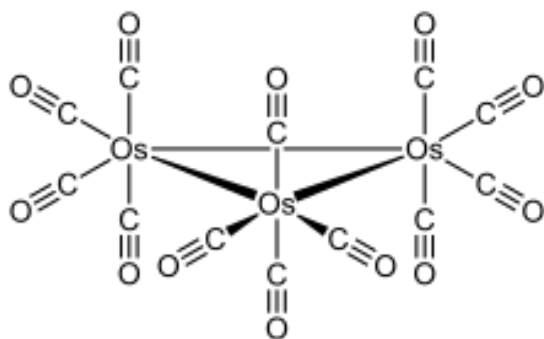


Figure 1. Structural formulae to $\text{Os}_3(\text{CO})_{12}$

Furthermore, by using the Glasser-Jenkins volume-based thermodynamics (VBT) equations [2] the lattice energy of this compound is calculated for the first time.

METHODOLOGY

The quantum chemical calculations were performed by using Spartan [3]. The SE-PM6 approach was chosen, taking into account its minor computation time consuming and its reliability for calculations involving inorganic systems, as verified for PtF_6 [4] and Ag and Hg fulminates [5] as well as Pb, Ag and Cu azides [6].

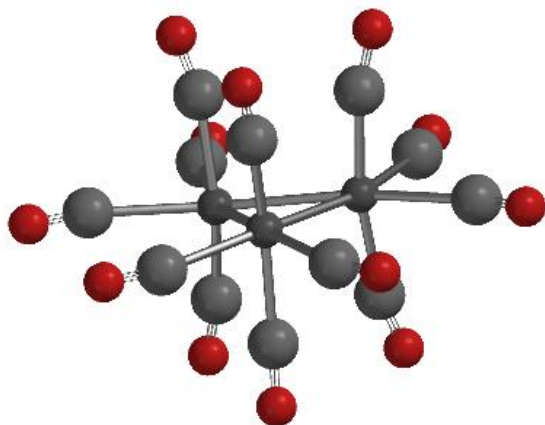


Figure 2. SE-PM6 Modelled Triosmium dodecacarbonyl.

The molecular modelling of triosmium dodecacarbonyl was made taking into account its experimentally obtained X-ray structure [7]: “The molecular unit of approximately D_{3h} symmetry consists of an equilateral triangular array of osmium atoms with four terminal carbonyls attached to each osmium: two of the carbonyls are approximately perpendicular to the plane of the osmium atoms while other two are essentially in the same plane. The three $\text{Os}(\text{CO})_4$ fragments are linked to one another by “bent” metal-metal bonds; the average Os-Os distance is 2.88 Å”.

The modelled structure (this work) is shown in Figure 2. The Os-Os bond distance obtained in the modelled structure is 2.73 Å.

RESULTS AND DISCUSSIONS

The calculated thermochemical data are summarized in Table 1. The ΔH_f (g) calculated value (kJmol^{-1}) was -1592.50, in very good agreement (-3.13%) with the previously reported value [8]: -1644 ± 26 (this value is quoted as a private communication by Martinho Simões, J.A.; it is not clear whether the value is theoretical or experimental). A value of -1644 ± 28 is also available in the literature [1].

By using the calculated gas phase formation enthalpy value (this work) and the sublimation enthalpy ($104.6 \pm 20 \text{ kJmol}^{-1}$) [9] a solid phase enthalpy (kJmol^{-1}) of -1697.10 was calculated, in very good agreement (-2.97%) with the previously reported value of -1749 ± 17 [8]. By using the most recent sublimation enthalpy value provided by Chandra et al [10], that is, $134.4 \pm 0.4 \text{ kJmol}^{-1}$, a solid phase formation enthalpy value of -1726.9 kJmol^{-1} is calculated, in a better agreement (-1.26%) with the NIST value [8].

Table 1. Calculated thermochemical data to Triosmium dodecacarbonyl.

ΔH_f (g)/ kJmol^{-1}	-1592.50
ΔH_f (cr)/ kJmol^{-1}	-1697.10/-1726.9
C_p	365.29
$C_v/\text{JK}^{-1}\text{mol}^{-1}$	356.98

Volume-based thermodynamics (VBT) equations, such as proposed by Glasser-Jenkins [2] was successfully applied, for example, to calculate the lattice energies of unusual chlorides such as NaCl_3 and NaCl_7 [11], study the thermochemistry of metal fulminates [5] as well as to establish relationships between absolute hardness, hydration

enthalpies and nuclear effective charges [12]. Furthermore, since we have here a trinuclear compound, to use Kupustinskii equation is not a good choice, since we have not a simple “cation-anion distance” to put into the equation. Hence, VBT approach is the right choice.

By using experimental X-ray data, the unit cell volume can be calculated as [2]:

$$V_m = [abc (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cos\alpha \cos\beta \cos\gamma)^{1/2}] / Z \quad (1)$$

To triosmium dodecacarbonyl, with a monoclinic unit cell [7] $a = 0.81$ nm, $b = 1.479$ nm, $c = 1.464$ nm, $\beta = 110.27^\circ$. In this case, Eq. (1) reduces to [2]:

$$V_m = abc \sin \eta / Z \quad (2)$$

where η is the unique oblique angle.

Applying, in Eq. (2) the X-ray experimental data to triosmium dodecacarbonyl [7], and using $Z = 4$, we calculate $V_m = 0.411$ nm³ in very good agreement with the molecular modelling value of 0.378 nm³ (this work).

The lattice energy (U_{POT}) can be calculated by [2]:

$$U_{\text{POT}} = AI / V_{\text{norm}}^{1/3} \quad (3)$$

where $V_{\text{norm}} = V_m / 2I$ and $2I = \sum n_i z_i^2$, an ionic strength-like term.

Hence, in order to calculate U_{POT} to triosmium dodecacarbonyl we need to calculate $2I$. However, there is a problem here: we have not (such as In NaCl, CaF₂, etc.), ions to which attribute a charge, based on their oxidation states. To overcome this impasse, it seemed appropriate to employ the so-called formal charges. To triosmium dodecacarbonyl the formal charges to osmium atoms can be calculated as -4, to carbon 0 (zero) and to oxygen +1. Hence, the summation of charges is $12 \times 1 + 3 \times (-4) + 12 \times 0 = 0$, as expected, to a neutral compound. For those who consider it strange that to osmium is assigned a value of -4, we remind you that formal charges and oxidation state are not the same thing (concept).

By using this formal charges, $2I = 60$ to triosmium dodecacarbonyl. $A = 121.4$ kJmol⁻¹ nm [2], and so, applying Eq. (3), we calculate $U_{\text{POT}} = 19176.81$ kJmol⁻¹.

Thus, as far as the author is aware, we have calculated, for the first time, the lattice energy to

triosmium dodecacarbonyl. However, precisely because this is the first time that such a parameter has been calculated for this compound, how do we know if the calculated value is absolutely right, or absolutely wrong? Fortunately, in the same work [2] the Glasser-Jenkins VBT approach provided another equation:

$$\rho = (10^{21} M_m / N_A 2I^4) (U_{\text{POT}} / A)^3 \quad (4)$$

where ρ is density (gcm⁻³), M_m is the molar mass (to triosmium dodecacarbonyl, 906.81 g mol⁻¹). Hence, applying the previous calculated U_{POT} value in Eq. (4), we calculate, to triosmium dodecacarbonyl a density of 3.67 gcm⁻³, in very good agreement with the experimental value of 3.48 gcm³ [7]. Taking into account the uncertainty (standard deviations) that there are in the experimental X-ray data [7], is an excellent result, indeed.

Therefore, the results obtained also attest that the procedure (for non-ionic compounds) of employing formal charges is adequate, from a theoretical/practical point of view.

Obviously, the compound under study here was used only as an example, and the same approach can be used to calculate the lattice energy of other organometallic and similar compounds. Thus, we believe we have pointed out a path that could lead to interesting correlations between thermochemical data and the solubility and reactivity of this class of compounds.

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