



Molecular modelling of tantalum penta-halides during hydrolysis and oxidation reactions



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ABSTRACT

The transition metals tantalum (Ta) and niobium (Nb), which are usually found together in nature, have similar chemical and physical properties, making their separation challenging. There are various methods available for the separation of these two metals, including reduction, fluorination, chlorination and solvent extraction (SX) (Ayanda and Adekola, 2011). In a recent study investigating the suitability of SX for the separation of Ta and Nb, it was shown that speciation data would be required to help explain the distribution data obtained. Since traditional speciation techniques cannot be readily applied for Ta and Nb, it was decided to determine the suitability of molecular modelling for this purpose. To investigate the suitability of modelling for this application a case study was selected where it was hypothesised that when TaF₅ is dissolved in water, it could react stepwise with water to finally form tantalum pentahydroxide (Ta(OH)₅) and other oxyfluoride species including TaOF₃. Due to the fact that literature on TaF₅ reactions with water is limited, TaCl₅ and its reactions was used to develop the model (method). As part of the model development and verification, DFT was used to calculate the energy needed for these reactions, comparing different functionals and basis sets. The validated model was then applied to TaF₅ as a case study. From the results it was confirmed that the reaction of TaX₅ (X = Cl or F) with water to form Ta(OH)₅ and Ta₂O₅ is an endothermic reaction, while the formation of Ta(H₂O)F₅ and TaF₄OH was exothermic.

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1. Introduction

While several techniques have been proposed for separation and purification of various metals [1], solvent extraction (SX) is widely used for amongst others copper (Cu), nickel (Ni), iron (Fe), platinum group metals (PGMs), zirconium (Zr), hafnium (Hf), tantalum (Ta) and niobium (Nb). Ta and Nb are valuable metals with various high-end uses, where Ta is used in the nuclear industry as cladding material, as capacitors, as high power resistors and to make high strength corrosion resistant alloys, while Nb is used in super alloys for jet engines and heat resistant equipment. Ta and Nb, which co-occur in mineral deposits, have near identical properties making their separation challenging.

In a recent study Ungerer et al. [2] studied the SX based separation of Ta and Nb, using alternative and safer chemicals while investigating the suitability of membrane-based solvent extraction (MBSX). While partial separation of Ta and Nb was achieved, it was not possible to predict extraction behaviour prior to experimental testing, due to the current absence of speciation data for Ta and Nb.

Speciation data for Ta and Nb is not available, possibly due to their insolubility in most aqueous liquids [3,4] and because they are UV inactive making the detection and identification of the aqueous species difficult. An alternative method that could however be suitable for predicting the speciation and hence extraction of Ta and Nb is molecular modelling [5]. Applying molecular modelling to SX could for example entail a step-by-step analysis of the extraction process on a molecular level, thereby determining the molecular properties as well as the system reactions occurring during SX.

According to the previously published data [2], the SX process of Ta and Nb can be divided into three parts: (1) the aqueous phase containing water soluble tantalum (V) penta-fluoride (TaF₅), (2) the organic phase containing the extractant and diluent and (3) the interface where these two phases make contact. For the modelling of the first step (TaF₅ in an aqueous environment), the molecular structure of TaF₅ is required. Since single crystals of TaF₅ do not form readily, they exist as oligomeric penta-fluorides with three possible structure types [6], neither the experimentally determined molecular structure of TaF₅ is well known, nor have these properties been modelled. However, for TaCl₅ both the molecular structure [7] as well as its interaction in an aqueous environment have been modelled [8,9]. If it is assumed that TaF₅

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has a similar symmetrical structure and behaviour in water than TaCl₅, (an assumption that will be evaluated in this paper), then TaCl₅ could be used to validate the novel modelling approach before applying the modelling to a compound of which the structure and behaviour is unknown.

According to Agulyansky [7] TaCl₅ has a trigonal bipyramidal structure, assuming above mentioned similarity, TaF₅ would have a similar trigonal bipyramidal structure. The differences between TaF₅ and TaCl₅ will be discussed further in Section 3.

Using the above information, it is the aim of this paper to develop a molecular modelling approach to validate the structure of TaF₅ while determining the possible hydrolysis and subsequent oxidation reactions thereof in an aqueous environment. However, as stated above limited experimental or modelling data is available for the reactions of TaF₅ to verify the suitability of the newly developed model. Hence, the paper was subdivided into two sections. Firstly, the model will be verified in terms of the structure of TaCl₅ as well as its possible hydrolysis and oxidation reactions. Once the correlation of the modelled and literature data has been demonstrated for TaCl₅, a case study is presented where the verified model will be used to confirm the structure of TaF₅ as well as to calculate its possible hydrolysis and oxidation reactions. In a final step a brief section is presented discussing the possible transition states found during the most likely hydrolysis reaction of TaF₅ to TaF₄(OH).

2. Computational methods

2.1. Model verification (TaCl₅)

For the molecular modelling of TaCl₅ and its reactions with H₂O in an aqueous environment, the DMol³ module of the Biovia Materials Studio 6.1 software from Dassault Systems (previously Accelrys) [10] was used in conjunction with the DFT semi-empirical dispersion interaction correction module (DFT-SEDC). For comparison five different combinations of functional and basis sets were used to determine the structure of the TaCl₅ molecule (geometry optimisation [11,12]), as well as its hydrolysis and oxidation reactions.

- (1) Generalised-gradient approximation (GGA) with Perdew–Wang correlation functional (PW91) [11] and DND (double-numeric polarisation plus d-functions) basis set with basis file 4.4 and OBS dispersion correction. (DND is comparable with the Gaussian 6-31G* basis set.)
- (2) GGA PW91 functional with basis set DNP (double-numeric polarisation functions), with basis file 4.4 and OBS dispersion correction. (DNP is comparable with the Gaussian 6-31G** basis set.)
- (3) GGA PW91 functional with basis set DNP+ (double numerical plus polarisation, with addition of diffuse functions) with basis file 4.4 and OBS dispersion correction. (DNP+ is more accurate than a Gaussian basis set (Gaussian 6-31G**) of the same size.)

- (4) GGA with Perdew–Burke–Ernzerhof (PBE) [13] correlation, with basis set DNP+ and basis file 4.4.
- (5) Becke exchange plus Lee–Yang–Parr correlation (B3LYP) [14,15] hybrid exchange–correlations energy functional, with basis set DNP and basis file 4.4.

For the calculations done with PBE(DNP+) and B3LYP(DNP), no dispersion correction was added. Only Tkatchenko–Scheffler (TS) [16] and Grimme [17] dispersion corrections were available in these settings and in both TS and Grimme the element coverage for Ta was unavailable. Under the electronic properties, smearing of 0.005 Hartree (Ha) was chosen for all the calculations [18]. Furthermore, the conductor-like screening model (COSMO) [19] was used to simulate the molecules within a solvent. In this case the solvent was water, with a dielectric constant of 78.54.

After the geometry optimisation process, single point energy calculations were done to calculate various electronic properties with the same settings that were used for the geometry optimisations. The calculations were done at 0 K and an energy correction term was added to give Gibbs free energy values at 298.15 K. The zero-point vibrational energy (ZPVE) was included in all calculations. Frequency calculations were used to confirm optimised structures (minimum energy) and transition states (one imaginary frequency).

2.2. Case study (TaF₅)

For the molecular modelling of TaF₅ and its hydrolysis and oxidation reactions, the DMol³ module of the Biovia Materials Studio 6.1 software from Dassault Systems (previously Accelrys) [10] was used with the GGA PBE functional [13]. The basis set used was DNP+ with basis file 4.4, which includes diffuse functions. Under the electronic properties, smearing of 0.005 Hartree (Ha) was chosen [18]. The single point energy calculations were done as described in Section 2.1. A potential energy surface (PES) scan was done by a stepwise shortening of the distance between the Ta atom of TaF₅ and the O atom of one of the surrounding H₂O to determine the energy and geometry change during the formation of Ta(H₂O)F₅.

3. Results and discussion

3.1. Model verification (TaCl₅)

3.1.1. Geometry optimisation of TaCl₅

The TaCl₅ molecule was geometrically optimised with the five functional and basis set settings (Section 2.1). The bond lengths and bond angles between the Ta and the five Cl atoms were measured and compared to experimental literature as shown in Table 1.

From Table 1 it can be seen that according to the modelled values the two Ax Cl atoms (Cl3 and Cl4) have longer bond lengths than the three Eq Cl atoms (Cl1, Cl5 and Cl6), which correlates with various literature sources [6,20,21]. This implies that the three

Table 1
Calculated and experimental literature values of bond lengths and bond angles of TaCl₅.

Bond/angle	Literature [6]	PW91 (DND)	PW91 (DNP)	PW91 (DNP+)	PBE (DNP+)	B3LYP (DNP)
Ta–Cl1 (Å)	2.284	2.327	2.327	2.327	2.321	2.331
Ta–Cl3 (Å)	2.426	2.381	2.381	2.379	2.379	2.385
Ta–Cl4 (Å)	2.426	2.381	2.381	2.379	2.380	2.385
Ta–Cl5 (Å)	2.284	2.317	2.317	2.317	2.321	2.314
Ta–Cl6 (Å)	2.284	2.317	2.317	2.317	2.322	2.321
Cl1–Ta–Cl6 (°)	120.00	120.61	120.61	120.80	119.96	122.40
Cl1–Ta–Cl5 (°)	120.00	120.61	120.61	120.80	120.13	121.16
Cl1–Ta–Cl3 (°)	90.00	89.28	89.28	89.54	89.99	88.94
Cl1–Ta–Cl4 (°)	90.00	89.28	89.28	89.54	90.00	89.94

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