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Quantum Chemical Prediction of Standard Formation Enthalpies of Uranyl Nitrates and Its Degradation Products

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Abstract : All spent nuclear fuel reprocessing plants use the PUREX process (Plutonium Uranium Refining by Extraction), which is a liquid-liquid extraction method. The organic extracting solvent is a mixture of tri-n-butyl phosphate (TBP) and hydrocarbon solvent such as hydrogenated tetra-propylene (TPH). By chemical complexation, uranium and plutonium (from spent fuel dissolved in nitric acid solution), are separated from fission products and minor actinides. During a normal extraction operation, uranium is extracted in the organic phase as the $UO_2(NO_3)_2(TBP)_2$ complex. The TBP solvent can form an explosive mixture called red oil when it comes in contact with nitric acid. The formation of this unstable organic phase originates from the reaction between TBP and its degradation products on the one hand, and nitric acid, its derivatives and heavy metal nitrate complexes on the other hand. The decomposition of the red oil can lead to violent explosive thermal runaway. These hazards are at the origin of several accidents such as the two in the United States in 1953 and 1975 (Savannah River) and, more recently, the one in Russia in 1993 (Tomsk). This raises the question of the exothermicity of reactions that involve TBP and all other degradation products, and calls for a better knowledge of the underlying chemical phenomena. A simulation tool (Alambic) is currently being developed at IRSN that integrates thermal and kinetic functions related to the deterioration of uranyl nitrates in organic and aqueous phases, but not of the n-butyl phosphate. To include them in the modeling scheme, there is an urgent need to obtain the thermodynamic and kinetic functions governing the deterioration processes in liquid phase. However, little is known about the thermodynamic properties, like standard enthalpies of formation, of the n-butyl phosphate molecules and of the $UO_2(NO_3)_2(TBP)_2$ $UO_2(NO_3)_2(HDBP)(TBP)$ and $UO_2(NO_3)_2(HDBP)_2$ complexes. In this work, we propose to estimate the thermodynamic properties with Quantum Methods (QM). Thus, in the first part of our project, we focused on the mono, di, and tri-butyl complexes. Quantum chemical calculations have been performed to study several reactions leading to the formation of mono-(H_2MBP), di-(HDBP), and TBP in gas and liquid phases. In the gas phase, the optimal structures of all species were optimized using the B3LYP density functional. Triple-ζ def2-TZVP basis sets were used for all atoms. All geometries were optimized in the gas-phase, and the corresponding harmonic frequencies were used without scaling to compute the vibrational partition functions at 298.15 K and 0.1 Mpa. Accurate single point energies were calculated using the efficient localized LCCSD(T) method to the complete basis set limit. Whenever species in the liquid phase are considered, solvent effects are included with the COSMO-RS continuum model. The standard enthalpies of formation of TBP, HDBP, and H2MBP are finally predicted with an uncertainty of about 15 kJ mol^{-1}. In the second part of this project, we have investigated the fundamental properties of three organic species that mostly contribute to the thermal runaway: $UO_2(NO_3)_2(TBP)_2$, $UO_2(NO_3)_2(HDBP)(TBP)$, and $UO_2(NO_3)_2(HDBP)_2$ using the same quantum chemical methods that were used for TBP and its derivatives in both the gas and the liquid phase. We will discuss the structures and thermodynamic properties of all these species.

Keywords : PUREX process, red oils, quantum chemical methods, hydrolysis

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