

Theoretical study of Cr (III) hydrolysis in aqueous solution by means of Density-functional method

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ABSTRACT

Cr(III) hydrolysis in aqueous solution has been studied theoretically by means of density-functional method (DFT). All possible structures arising from different tautomers have been determined. The solvation energy has been calculated using the UAHF-PCM method. The hydrolysis reaction free energies have been calculated and compared with the available experimental data. The different hydrolysis species have distinct geometries and electronic structures. Improvement of theory level in calculating the electronic energy does not necessarily improve the calculated free energies in aqueous solution since the UAHF-PCM is a simple method that neglects specific interactions with the solvent. Therefore, it is important to have the correct balance between theory level used in the electronic properties calculation especially in the UAHF-PCM method. The PBE/TZVP/UAHF-PCM method has been found to calculate correctly the hydrolysis energies of Cr(III), deviating about 2.7 kcal/mol from experimental values.

Key words: Theoretical study, Cr(III) hydrolysis, UAHF-PCM method.

INTRODUCTION

Hydration and hydrolysis of metal ions in aqueous solution play a fundamental role in the reactivity and mobility of these species in aquatic environment¹ and biological² systems. Despite the progress in the recent years, current instrumental methods are still far from being able to determine microstructures and stoichiometry of different species arising from hydration and hydrolysis of metal ions. The study of these species at the molecular level is the first step to understanding the chemical, biological, and surface reactivity of metal ions³.

Cr(III) is one of these metal ions that are important in many different processes related to biology and environment⁴. Trivalent chromium is required in trace amounts for sugar metabolism in humans (Glucose Tolerance Factor) and its deficiency may cause a disease called chromium deficiency. In plasma, absorbed chromium(III) is bound mostly to transferrin and to other plasma proteins, which are responsible for its transport in the body. Long-term storage occurs particularly in the liver, spleen, bones and other organs⁴.

Formation of different species by hydrolysis gives rise to a complex equilibrium in

solution as pH increases. $[\text{Cr}(\text{OH})_x(\text{H}_2\text{O})_m]^{3-x}$ species are formed; however, the favorable geometries, isomers, and conformations are difficult to be determined. The number of water molecules in the first sphere of solvation has to be determined. These factors must be taken into account for the understanding of the Cr(III) adsorption mechanism on the mineral and its mobility in the environment. Therefore, a theoretical investigation of Cr(III) hydrolysis can be helpful to improve our knowledge on Cr(III) species in aqueous solutions.

Density-functional theory (DFT) calculations have been successfully applied to study metal ions in solution⁵⁻⁷. Most of the theoretical studies in this field are based on hydrated ions^{5,6}, and only a little attention has been given to the hydrolyzed species⁷ which are much more complex. In the present work, we have studied all conformations, isomers, and geometries of the $[\text{Cr}(\text{OH})_x(\text{H}_2\text{O})_m]^{3-x}$ ($x = 0-4$) species and their low lying excited states through DFT calculations. The stepwise hydrolysis equilibrium constants have been estimated and compared with the available experimental values.

Computational methods

Density-Functional Calculations

All calculations were performed using the density-functional method (DFT) implemented in the Gaussian 03 program package. The following generalized gradient approximations (GGA) for the exchange and correlation (XC) functional have been used: BP86 scheme with the Becke⁸ expression for exchange and Perdew⁹ expression for correlation, and PBE scheme with Perdew, Burke, and Ernzerhof¹⁰ expression for exchange and correlation. We have used the DZVP and TZVP basis sets optimized explicitly for DFT by Godbout *et al.*¹¹ and the Ahlrichs basis sets (A-PVTZ)¹²⁻¹⁵. Harmonic frequency calculations have been performed. The thermodynamic properties at gas phase have been evaluated using the canonical formalism¹⁶ at 298 K.

Solvation Model

Nonspecific solvent effects have been estimated using the united atoms Hartree-Fock/polarizable continuum model (UAHF/PCM)¹⁷⁻¹⁸. As described by Saracino *et al.*,^{19,20}, we have used

for all calculations the UAHF radii obtained by single point calculations at the HF/6-31G(d,p) level of theory using DFT optimized structures in gas phase. In the UAHF/PCM approach the solute is placed in a polarizable cavity formed of spheres centered in the atomic groups. Inside the cavity, the dielectric constant is the same in a vacuum, and outside it takes the solvent value ($\epsilon = 78.4$ for water).

Initial species

The Cr(III) hydrolysis products, $[\text{Cr}(\text{OH})_x(\text{H}_2\text{O})_m]^{3-x}$ ($x = 0-4$) complexes, have been investigated in an attempt to contribute to the understanding of Cr(III) speciation in aqueous solution at a molecular level. Pappalardo and co-workers²¹ showed that DFT can yield reasonable aqueous Cr(III) ground-state structures and also the excited-state properties. It is possible to simulate the distribution of the species with respect to pH; however, information about their geometries and electronic structures are difficult to be gathered on the sole basis of experimental studies. In the present work, the Cr(III) first sphere of coordination was filled with water molecules in such a way that all structures used as starting geometries for the optimization had coordination number 6, as shown in Fig. 1.

RESULTS AND DISCUSSION

Structural Properties

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

Hexaaquachromium(III) has been theoretically and experimentally studied quite extensively²¹⁻²². The octahedral geometry with weak-field water ligands leads, according to ligand field theory, to the break of degeneracy of the d shell. The Cr-O distances experimentally determined by different methods are in the range of 1.97-2.05 Å^{36,40}. Ohtaki and Radnai discuss in their review²³ a number of experiments and concluded that the Cr-O distance lies in the range of 2.01-2.05 Å. The optimized geometry of the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is shown in Figure 2a. The predicted structural parameters are in good agreement with the previously published results^{21, 22, 24-26}. Camaniti and co-workers have predicted the Cr-O distances to be about 2.07 Å using the BPW91/A-PVTZ level of theory which should be compared with our results of 2.067 Å for PBE/TZVP. This result supports the observation that

in such systems in which the electronic correlation effects are important, the Cr-O bond distances can differ by about 0.02 Å depending on the XC scheme used. The UMP2/A-PVTZ Cr-O bond distance is predicted to be 2.06 Å, 0.007 Å smaller than our DFT value.

$[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$

The $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ optimized structure is shown in Figure 2b. The Cr-OH bond distance is predicted to be 1.764 Å and Cr-OH₂ bond distances are predicted to be in the range of 2.100-2.162 Å. Read and coworkers²⁷, using the B3LYP/6-31G*

hybrid functional, found the Cr-OH distance equal to 1.760 Å and Cr-OH₂ distances lengthening to 2.103-2.150 Å, which are in very good agreement with our results. Another work done by Bertini *et al.*²⁹ have studied this hydroxo species with one and two solvent coordination shells using the BP86/TZVP method. The Cr-OH distance in the solvated system was predicted to be equal to 1.787 Å, which is in agreement with the values found in our work. It is important to note the influence exerted by the water molecules of the second coordination shell which leads to the increase of the Cr-O bond distances.

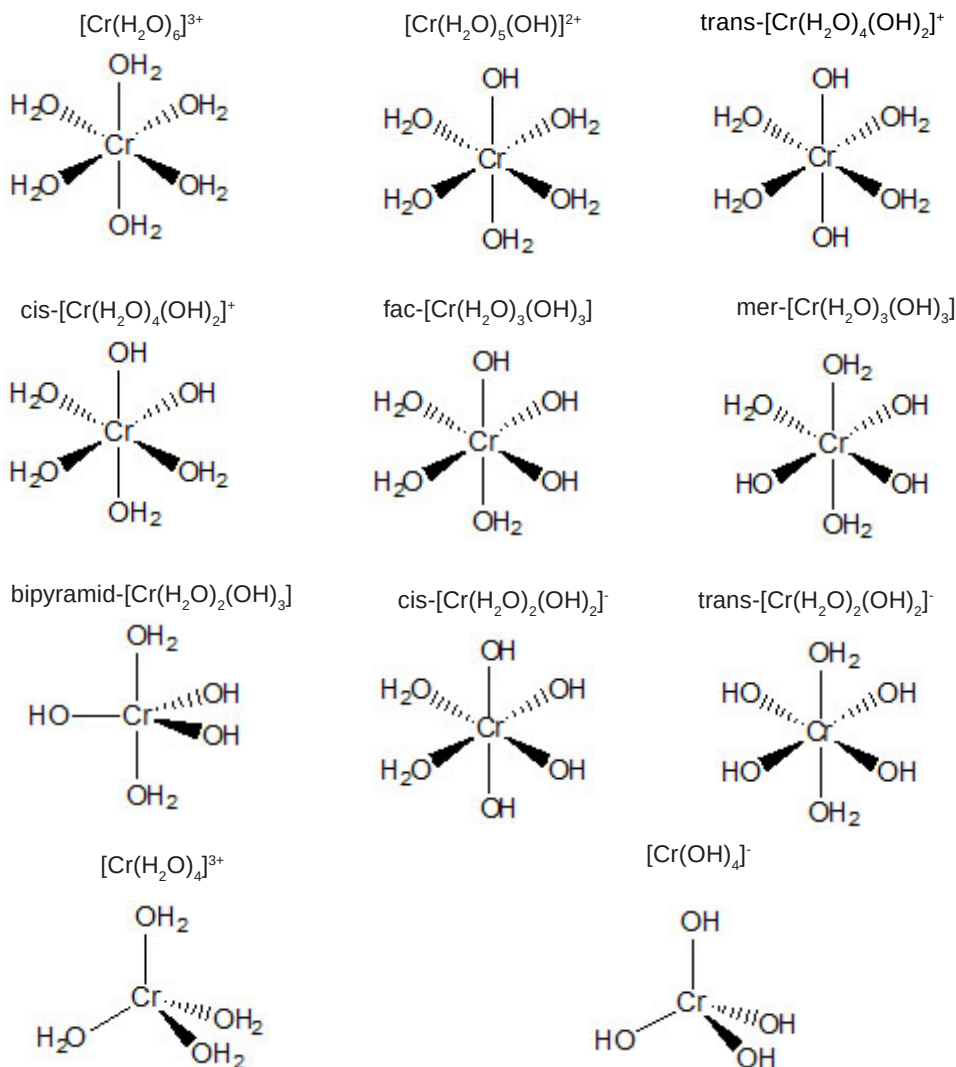


Fig. 1: Initial structures used to perform geometry optimization

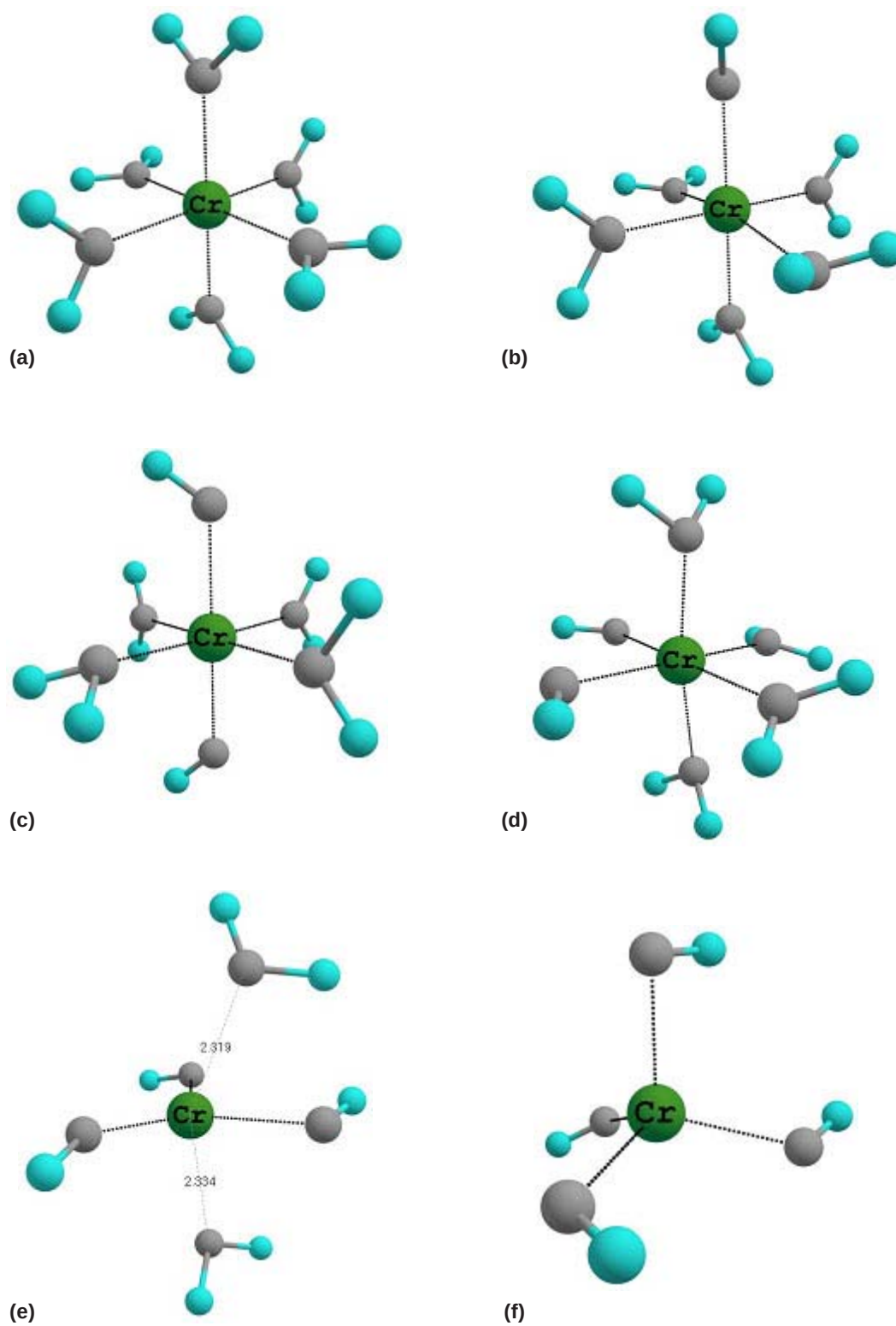


Fig. 2: The most stable structures arising from the hydrolysis of Cr(III)

[Cr(OH)₂(H₂O)₄]⁺

The second deprotonation process produces two different species the *trans*- and *cis*-[Cr(OH)₂(H₂O)₄]⁺. The *cis* isomer is the most stable species being about 5 kcal/mol lower in energy than the *trans* isomer. The replacement of water ligands to weaker-field ligands OH⁻ breaks the octahedral symmetry, and consequently, different states as quartet can become more stable. The *cis*-[Cr(OH)₂(H₂O)₄]⁺ species is shown in Figure 2d, which presents Cr-OH and Cr-OH₂ bond distances predicted to be 1.794 and 2.054-2.315 Å, respectively. Bleuzen and Foglia [28] have also

studied this species. He found a stable octahedral species only when using a supermolecule model with 10 water molecules surrounding the solvated complex. Their Cr-OH and Cr-OH₂ bond distances are predicted to be 1.80 and 2.11 Å, respectively, using ab initio QM/MM-MD method. Even though he has performed this study with a second solvation shell, it is important to note that his results support our Cr³⁺ hydrolysis model.

Concerning the *trans* isomer (Figure 2c), it is interesting to note the presence of the *trans* effect evidenced by the lengthening of the Cr-OH

Table 1: Reaction free energies of the Cr(III) hydrolysis using different levels of theory ^{a,b}

Reactions	Basis sets	ΔE _e	ΔG ^{T c}	ΔG ^{solv}	ΔG ^{tot d}	-log β
[Cr(H ₂ O) ₆] ³⁺ + H ₂ O ↔ [Cr(H ₂ O) ₅ (OH)] ²⁺ + H ₃ O ⁺	BP86/DZVP	-151.4	4.8	143.6	-5.3	-3.9
	BP86/A-PVTZ	-145.7		144.4	1.2	0.9
	BP86/TZVP	-145.0		152.5	9.9	7.2
	PBE/DZVP	-150.0		146.3	-1.3	-0.9
	PBE/A-PVTZ	-145.5		147.0	3.9	2.9
	PBE/TZVP	-147.8		147.0	1.6	1.2
	exptl				3.0	2.2
[Cr(H ₂ O) ₆] ³⁺ + 2H ₂ O ↔ [Cr(H ₂ O) ₄ (OH) ₂] ⁺ + 2H ₃ O ⁺	BP86/DZVP	-190.1	15.4	174.3	-5.2	-3.8
	BP86/A-PVTZ	-173.5		181.0	18.2	13.3
	BP86/TZVP	-174.7		178.1	14.0	10.3
	PBE/DZVP	-187.6		179.5	2.5	1.9
	PBE/A-PVTZ	-172.8		177.4	15.3	11.2
	PBE/TZVP	-184.9		179.3	5.0	3.7
	exptl				7.8	5.7
[Cr(H ₂ O) ₆] ³⁺ + 2H ₂ O ↔ [Cr(H ₂ O) ₂ (OH) ₃] ⁺ + 3H ₃ O ⁺	BP86/DZVP	-114.3	8.0	113.1	2.0	1.4
	BP86/A-PVTZ	-101.3		122.4	24.3	17.8
	BP86/TZVP	-105.0		124.3	22.5	16.5
	PBE/DZVP	-112.4		123.3	14.2	10.4
	PBE/A-PVTZ	-98.8		124.8	29.2	21.4
	PBE/TZVP	-110.1		123.6	16.8	12.3
	exptl				18.5	13.6
[Cr(H ₂ O) ₆] ³⁺ + 2H ₂ O ↔ [Cr(OH) ₄] ⁺ + 4H ₃ O ⁺	BP86/DZVP	55.9	5.9	-38.6	18.5	13.6
	BP86/A-PVTZ	69.1		-29.2	41.0	30.1
	BP86/TZVP	61.7		-27.6	35.3	25.8
	PBE/DZVP	56.6		-28.9	28.8	21.1
	PBE/A-PVTZ	73.9		-27.4	47.6	34.9
	PBE/TZVP	58.7		-28.1	31.8	23.3
	exptl				29.5	21.6

^aAll energies are in kcal mol⁻¹. ^bMedium used in PCM model is water (^a = 78.4). ^cThermal contribution at 298 K. The zero-point energy is included. ^dΔG_{tot} = ΔE_e + ΔG^T + ΔG^{solv}

bonds which are predicted to be 1.843 Å. One can compare these distances with that present in the $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ species, that is about 0.079 Å shorter. Two different works^{28, 29} show the same Cr-OH bond distances equal to 1.851 Å. That is in very good agreement with our results.

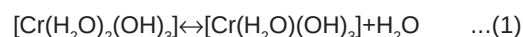
Using 10 water molecules in a supermolecule model, Best [30] found a difference between the isomeric species equal to 4.8 kcal/mol, in good agreement with our results. However, it is important to note that, in the supermolecule model, water molecules are added forming a second solvation shell which can lead to artifacts since the dynamical behavior of the solvent is not included in such a model. The water molecule or hydroxyl ion bound to the Cr center can be rich or deficient of hydrogen bonding depending how water molecules of the second shell are placed, and, consequently, the Cr-O bond distances can increase or decrease.

$[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_2]$

The *fac*- $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3]$ and *mer*- $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3]$ species are not minima in the potential-energy surface. The optimized structure is pentacoordinated presenting trigonal bipyramid geometry. The remaining water molecule is not bonded to the Cr atom. The OH⁻ ligands prefer to stay in the equatorial positions, and H₂O ligands

are bonded at axial positions. It is important to note that the axial axis is distorted presenting an angle of 75.3° with respect to the equatorial plane formed by the OH⁻ groups (Figure 2e). According to previous data obtained by Best³⁰, considering the second shell of solvation with eight water molecules, the average value for the Cr-OH distances is equal to 1.89 Å, which may be compared to our average value of 1.86 Å.

Other possible structures can be envisaged for the $[\text{Cr}(\text{OH})_3]$ complex in aqueous solution. The tetrahedral geometry, with one water ligand bonded to the chromium center, is also possible. To determine which species is the preferred one in aqueous medium, we have calculated the reaction free energy described at



At the BP86/DZVP level of theory, the ΔE^{elec} , ΔG^{therm} , and ΔG^{solv} are estimated to be 5.7, 16.1, and -9.3 kcal/mol, respectively, leading to $\Delta G^{\text{tot}}_{(\text{aq})}$ equal to 12.5 kcal/mol. This means that the pentacoordinated bipyramid structure is favored in aqueous solution.

$[\text{Cr}(\text{OH})_4]^-$

The *cis*- and *trans*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{OH})_4]^-$ are

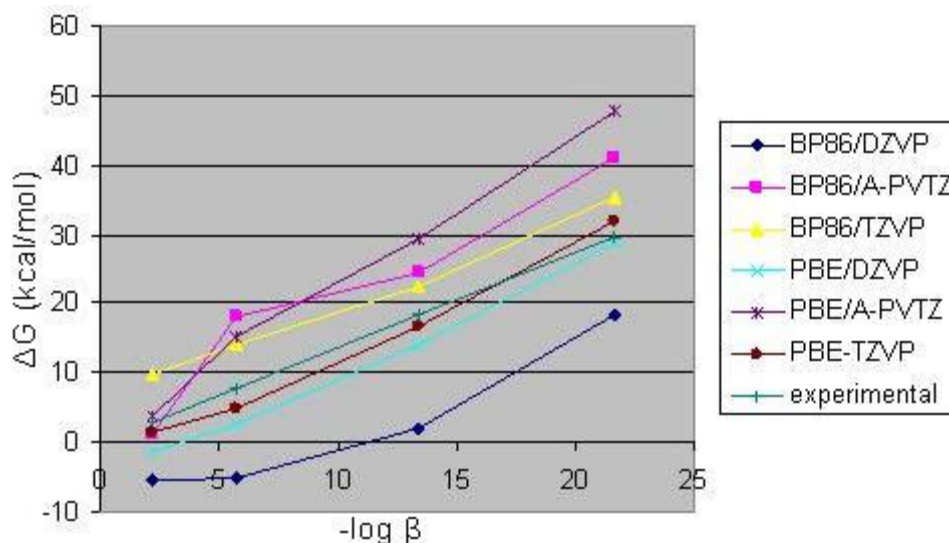


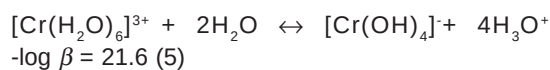
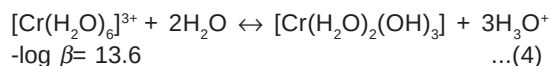
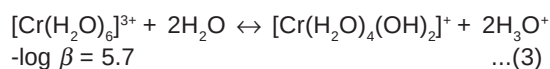
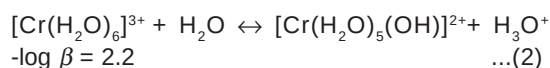
Fig. 3: Comparison between the theoretically estimated Gibbs free energy of Cr(III) hydrolysis and the respective experimental value

also not minima in the potential energy surface, and both converged to the tetrahedral form $[\text{Cr}(\text{OH})_4]^-$ (Figure 2f). In contrast to octahedral species predicted by hydrolysis data³¹, we found a tetrahedral form to be the most stable species. We can compare our geometrical parameters with those calculated early by Best³⁰ that studied a very similar species, $[\text{Cr}(\text{H}_2\text{O})_2(\text{OH})_4]^-$, being the water molecules in the first solvation shell and having specific interactions with the OH⁻ groups. In this way he found the medium distances Cr-OH to be equal to 1.88 Å. Our values are again longer than those by less than 0.02 Å, and this deviance is probably due to both the XC scheme used and the specific interactions considered by Best in his work.

pKa Estimate

Hexaaquachromium(III) is an acid which deprotonates according to the solution pH. The many hydrolysis species formed in the medium are the blocks to form the polynuclear hydroxylated species of chromium(III). The pKa values of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ allow us to simulate the species distribution with respect to the pH; however, information concerning electronic and geometrical structure of these species is difficult to investigate. It has been shown that theoretically estimated reaction energies of the deprotonation process follow the correct trends and correlate with the equilibrium constants reasonably well. It is important to correctly determine the predominant species and their solvation energies. The treatment of the proton solvation is still a challenge, even though the simple H_3O^+ model seems to work reasonably well^{32,33}. Most of the theoretical pKa estimates have been performed for closed shell systems as carboxylic acids, and other organic systems^{32,34,35}. Despite this effort, it is still necessary to show the reliability of this method for open shell systems. The pKa estimate of -4.0 deviated significantly from the experimental value of 2.2. Rustad and co-workers [36] showed that DFT calculated hydrolysis energies have good correlation with the observed first pKa of aqueous trivalent ions. Best³⁰ extended the study to the successive pKa values showing that correlations of deprotonation energies with observed pKa values follow the expected

behavior for individual Al^{3+} , Cr^{3+} , and Si^{4+} cations. However, the linear free energy relationship for Cr(III) hydrolysis leads to a slope that corresponds to 481 K, which is too high. This corresponds to an error of 50 kcal/mol in the fourth hydrolysis constant ($-\log \hat{a} = 21.6$). He pointed out four factors for this disagreement: inadequate method, model structures which do not reflect the aqueous Cr(III) species, Cr(III) complexes in solution, or uncertainties in the $\log \hat{a}$ for Cr(III) hydrolysis [30]. The energetics is adequately described using the following equations:



It is worthwhile to separate the reaction free energies in each contribution according to eq 6.

$$\Delta G_{(\text{aq})}^{\text{tot}} = \Delta E_{(\text{g})}^{\text{elect}} + \Delta G^{\text{therm}} + \Delta G^{\text{solv}} \quad \dots(6)$$

All energy estimates and the respective equilibrium constants are shown in Table 1. The estimate of equilibrium constants of reactions in condensed medium is a very difficult task. It has been pointed out by De Abreu et al [32] that DFT calculated thermal contribution is insensitive to the choice of XC functional and basis sets. They showed that the difference is not larger than 1 kcal/mol. Therefore, we decided to calculate this contribution at the level of BP86/DZVP. The UAHF/PCM method has limitations as any other method based in the continuum models for estimating solvation energy. Specific interaction of the solvent with the solute is not taken into account in this type of model. However, in the literature there are enough evidences that these specific interactions are canceled when the reaction involves similar reactants and products³⁴. In fact it is not easy to

establish a manner to improve the results in order to estimate experimental equilibrium constants and free reaction energies in aqueous solution. However, it has been speculated that a great part of the success of estimating equilibrium constant values is due to a good synergism between level of theory, basis sets, and the continuum method leading to error compensation³². For open shell systems, it is important to ensure that the converged electronic density is free of spin contamination, since this can significantly interfere in the solvation energy estimated by the UAHF/PCM. Therefore we have used the restricted open shell Hartree-Fock (ROHF) method for calculating the open-shell systems.

According to Table 1, the solvation energy has the same magnitude as the electronic energy. Hence, it is an important contribution that can favor or not a specific reaction. Therefore, the good balance between the theoretical method that calculates the electronic energy and the UAHF/PCM model for solvation energy is important. It is observed that slight differences in the geometry can change the solvation energy estimates up to 10 kcal/mol. This is particularly true when the DZVP and TZVP basis sets results are compared. The compacted A-PVTZ basis sets do not follow the same trends as the other basis sets with respect to the electronic energy. For all reactions studied, the PBE XC functional performs much better compared to the BP86 scheme. PBE results are closer to the experimental values. It is important to note that PBE describes better weak interactions such as those related to the hydrolysis of Cr(III) species.

In Figure 3, the experimental $-\log \beta$ is plotted against the estimated hydrolysis free energies. The successive reaction energies must lie in a straight line according to the thermodynamics. The BP86/DZVP does not follow a line as it is expected. However, the other methods follow the same tendency having different shifts with respect to the experimental values. It can be observed that the PBE/TZVP provides the results that are closest to the experimental line with error bars about 2.7 kcal/mol. It is important to note that we are neglecting the ionic strength of the solution,

and also that the error bar of the experimental free energies quoted from the experimental hydrolysis constants are normally about 1 logarithmic unit, that is, about 1.4 kcal/mol.

CONCLUSION

The geometrical, electronic, and thermodynamic properties of Cr(III) species arising from its hydrolysis in aqueous solution have been reported. The solvation energy estimate is very important since it accounts roughly for a half of the reaction energy. However, continuum methods as the UAHF-PCM are based in simple models and cannot be improved easily. Therefore, the use of such an approach has to be combined with a method for the electronic calculations that provides the best results. Simply increasing the level of theory does not ensure that one is improving the reaction free energy in solution. While the gas-phase reaction free energy can be improved, in the aqueous solution one has to face the challenge of calculating the solvation energy of the reactants. In our approach, the PBE/TZVP/UAHF-PCM provided the best results for all hydrolysis reactions studied following the expected behavior. The PBE/TZVP/UAHF-PCM estimated hydrolysis reaction energies are about 2.7 kcal/mol different from the respective experimental values. It is important to mention that electronic and geometrical parameters of these species in solution are crucial for understanding many reactions and processes related to the environment. Our approach can provide important insights about systems of increasing complexity as those related to the adsorption on minerals, complexation and nucleation modeling, and the pKa determination of mineral surfaces.

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