A Theoretical Study of the Structure of Tricarbonatodioxouranate

Laura Gagliardi,*,† Ingmar Grenthe,‡ and Björn O. Roos§

Dipartimento di Chimica G. Ciamician, Università di Bologna, Via F. Selmi 2, 40126, Bologna, Italy, Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden, and Department of Theoretical Chemistry, Chemical Center, P.O.B. 124, S-221 00 Lund, Sweden

The results of a study on the ground states of tricarbonato complexes of dioxouranate using multiconfigurational second-order perturbation theory (CASSCF/CASPT2) are presented. The equilibrium geometries of the complexes corresponding to uranium in the formal oxidation states VI and V, $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$ have been fully optimized in D_{3h} symmetry at second-order perturbation theory (MBPT2) level of theory in the presence of an aqueous environment modeled by a reaction field Hamiltonian with a spherical cavity. The uranyl fragment has also been optimized at CASSCF/CASPT2, to obtain an estimate of the MBPT2 error. Finally, the effect of distorting the D_{3h} symmetry to C_3 has been investigated. This study shows that only minor geometrical rearrangements occur in the one-electron reduction of $[UO_2(CO_3)_3]^{4-}$ to $[UO_2(CO_3)_3]^{5-}$ confirming the reversibility of this reduction.

1. Introduction

The use of computational chemistry on actinide systems is an emerging area with many applications. This holds both for the development of theoretical methods and their use to describe structures, chemical bonding, and chemical reactivity.

In this paper we present the results of a theoretical study on the carbonate system of dioxouranyl(VI) and -(V), $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$. Both solid-state structures and EXAFS information are available for complexes of this type. It is well-known that the $MO_2{}^{2+}/MO_2{}^+$ (M = metal) redox couple is reversible, (see ref 1 and references cited therein). Standard emf methods show that the $[UO_2(CO_3)_3]^{4-}/[UO_2(CO_3)_3]^{5-}$ couple provides a fast, stable, and reproducible equilibrium potential with a Nernst response, a strong criterion for reversibility in the thermodynamic sense. A chronopotentiometric study by Caja and Pradvic[2] comes to the same conclusion, as does cyclic voltammetry studies of the chemical analogous Np(VI)/Np(V) couple. On the other hand, Docrat et al.[3] claim from their cyclic voltammetry study that the U(VI)/U(V) couple is not reversible. A similar observation has previously been made by Riglet.[4] The fact that the potential peak separation in cyclic voltammetry changes with the scan rate is not surprising, it simply indicates that there are some step in the electron-transfer reaction that has a rate similar to the scan rate. There is no information in the literature on whether the homogeneous electron exchange between $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$ takes place by an inner-sphere or outer-sphere mechanism. There is also no information on the rate-determining step for the heterogeneous electron-transfer step at an inert electrode. The scan rate dependence might indicate that this is where one may find the rate-determining step.

We expect that a theoretical study, calibrated against known structure information on solids and solutions, will provide precise data on the geometry and that electron distribution in the two carbonate complexes may shed light on the redox mechanism, in particular, if there is a substantial conformation change between the two carbonate complexes as suggested by the paper by Docrat et al.[3] Such a change could arise from a twist about the U−C direction which moves the coordinated O atoms out of the equatorial plane, as has been observed in the solid state for $[UO_2(CO_3)_3]^{4-}$ compounds.[5-7]

The structure of $[UO_2(CO_3)_3]^{4-}$ has previously been studied by Pyykkö et al.[8] with theoretical methods. The authors calculated the uranium−oxygen uranyl and equatorial bond distances at the HF level of theory.

We initially optimized the geometry of the two compounds at second-order perturbation level of theory (MBPT2 and CASPT2) by imposing D_{3h} symmetry. We then relaxed the symmetry of the U(V) compound toward a twisted structure, as suggested in ref 3, and investigated if this implied extra-stabilization.

Negative ions are rarely stable in gas phase, while they are stabilized by the interaction with a surrounding medium, for example, a polar solvent such as water. In quantum chemistry one often uses a solvent model. In this study the aqueous environment has been modeled with a reaction field Hamiltonian throughout all the calculations (See section 2).

In section 2 the theoretical methods and computational details are described. Section 3 reports the results of the calculations, and finally in section 4 some conclusions are presented.

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* To whom correspondence should be addressed. E-mail: laura.g@ciam.unibo.it.
† Università di Bologna.
‡ The Royal Institute of Technology.
§ Chemical Center.

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2. Theoretical Methods and Computational Details

The calculations have been performed at the Hartree−Fock (HF) and complete active space (CAS) SCF[9] level of theory, with dynamic electron correlation added using second-order perturbation theory, MBPT2 and CASPT2,[10,11] respectively. The presence of an aqueous environment has been taken into account by a reaction field Hamiltonian with a spherical cavity. The size of the spherical cavity has been optimized pointwise for the two structures, and it has a radius of 4.99 Å for the U(VI) compound and of 5.08 Å for the U(V) compound.

The relativistic effects due to the high atomic number of the uranium atom are taken into account implicitly through the use of effective core potentials (ECPs) derived from high accuracy relativistic calculations on atoms. The energy-adjusted uranium ECPs of Küchle et al. were used for this purpose.[12] The accompanying basis sets of the uranium ECPs were used to describe the valence electron density.[13] On the carbon and oxygen atoms, the atomic natural orbital, ANO-S, 4s3p2d basis sets[14] were used. The basis set effects on the CASPT2 results for uranium compounds have been investigated in a previous study,[15] showing that the use of the atomic natural orbital, ANO-L, 4s3p2d1f basis sets[16] on oxygen instead of ANO-S and of two g-type functions in the uranium valence basis decreases the uranyl bond distance 0.016 Å for the uranyl ion in the gas phase. This effect will be considered in the final discussion of the structure.

We initially performed MBPT2 calculations on $[UO_2(CO_3)_3]^{4-}$ for a closed-shell HF reference wave function, and MBPT2 calculations on $[UO_2(CO_3)_3]^{5-}$ for an open restricted HF wave function, corresponding to one electron in a uranium 5φ orbital. We then performed CASSCF calculations with dynamic electron correlation added using second-order perturbation theory, CASPT2 on $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$ with the assumption that the most important orbitals would be the uranyl O 2p orbitals and the strongly correlated orbitals of the same symmetry centered on uranium. This gives an active space of 12 electrons in 12 active orbitals (12/12) for $[UO_2(CO_3)_3]^{4-}$ and 13 active electrons in 13 active orbitals (13/13) for $[UO_2(CO_3)_3]^{5-}$.

Geometry optimizations with 5 degrees of freedom were performed at the MBPT2 level of theory, using a two-dimensional grid (22 points distributed on a sphere with a radius of 0.05 au). The U−O uranyl bond distance, R_{UO1}, the U−O carbonate bond distance, R_{UO2}, the two typical carbon oxygen bond distances, R_{CO2} and R_{CO3}, and the equatorial O2−U−O2 angle were optimized (see Figure 1 for the numbering of the atoms). The calculations with the large active space were performed at the optimized geometries, and only the bond distance in the uranyl moiety was reoptimized.

MBPT2 followed by CASSCF/CASPT2 12/12 and 13/13 calculations were performed also on UO_2^{2+} and UO_2^+ without the complex, to investigate the effect of the active space on the isolated cations. Comparative calculations were also performed in the gas phase at the MBPT2 level of theory, for $[UO_2(CO_3)_3]^{4-}$. Such calculation could not be performed on $[UO_2(CO_3)_3]^{5-}$ which is unstable in the gas phase.

All calculations were performed with a prerelease of the MOLCAS-5 quantum chemistry software.[17]

Spin−orbit effects were not treated explicitly in this work. They should be more relevant in the 5− compound, corresponding to the
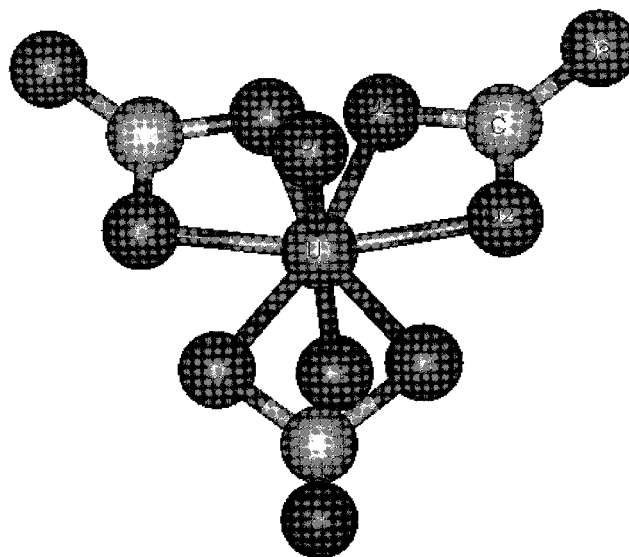

Figure 1. $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$ structures.

doublet U(V), than in the 4− compound, corresponding to the singlet U(VI). However, considering the primarily atomic nature of these effects, it is reasonable to believe that they will have little influence on bond lengths, while they would affect more substantially energetics, which were not considered in this study.

3. Results and Discussion

In Table 1 the typical U−O uranyl, U−O carbonate, and C−O bond distances obtained at the different levels of theory are reported, together with the equatorial O−U−O and O−C−O angles for the 4− and 5− compounds.

MBPT2 on $[UO_2(CO_3)]^{4-}$ gives a uranyl bond distance of 1.881 Å and a U−O carbonate bond distance of 2.407 Å. The corresponding experimental values are 1.80 and 2.43 ± 0.02 Å, respectively. The U−O carbonate distance is thus within the experimental range, while the uranyl distance is larger than experiment. This can be explained by considering the nature of the two bonds. The uranyl bond is strongly covalent, while the U−O carbonate bond has a more ionic character. MBPT2 is more appropriate to describe the ionic bond, while the uranyl description suffers from limitations in the active space. The uranyl bond distance was reoptimized at the 12/12 CASSCF/CASPT2 level, and a value of 1.845 Å was obtained, which is closer to experiment. A comparison with the gas-phase results shows that the typical U−O bond distances of $[UO_2(CO_3)]^{4-}$ are shorter in the presence of the reaction field Hamiltonian than in the gas phase. The typical C−O bond distances in gas are similar to those of the isolated carbonate case, as expected.

The MBPT2 U−O uranyl and U−O carbonate bonds are respectively 1.933 and 2.529 Å in $[UO_2(CO_3)]^{5-}$, where the experiment gives 1.90 and 2.50 ± 2 Å. Unlikely in the (4−) compound, the MBPT2 U−O uranyl bond value is already very close to the experimental value, indicating that the presence of the extra negative charge makes the uranyl bond less covalent than in the (4−) case and a MBPT2 treatment is already

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Table 1. Typical Bond Distances, Å, in $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$ (see Figure 1 for atom numbering). All Results Obtained in the Presence of the Reaction Field Hamiltonian, Except the MBPT2 Gas Phase Results for $[UO_2(CO_3)_3]^{4-}$

system	R_{UO1}	R_{UO2}	R_{CO2}	R_{CO3}	R_{UC}	R_{UO3}
$[UO_2(CO_3)_3]^{4-}$						
MBPT2	1.881	2.407	1.377	1.164	2.841	4.111
(MBPT2 gas)	1.894	2.426	1.321	1.297	2.893	4.790
CASPT2 (12/12)	1.845					
HF[8]	1.75	2.55				
exp.[3]	1.80 ± 0.02	2.43 ± 0.02			2.89 ± 0.04	4.13 ± 0.04
$[UO_2(CO_3)_3]^{5-}$						
MBPT2	1.933	2.529	1.310	1.296	2.947	4.243
CASPT2 (13/13)	1.929					
exp.[3]	1.90 ± 0.02	2.50 ± 0.02			2.94 ± 0.04	4.23 ± 0.04

Table 2. U–O Bond Distance in UO_2^{2+} and UO_2^{+}, Å, at MBPT2 Level and CASSCF/CASPT2 Level with a 12/12 and 13/13 Active Space, Respectively, in the Presence of the Reaction Field Hamiltonian

method	UO_2^{2+}	UO_2^{+}
MBPT2	1.747	1.772
CASPT2	1.707	1.758

adequate. The 13/13 CASSCF/CASPT2 treatment also has a minor effect, reducing the U–O uranyl bond to 1.929 Å.

A simple Mulliken population analysis confirms these qualitative observations. The extra electron in going from the (4−) to the (5−) compound is mainly located on the uranium atom, with some delocalization on the uranyl oxygens, which increase their total charge by ca. 0.2 electron each; the equatorial oxygens on the other hand increase their charge only by 0.03 electron each. In the (5−) compound the uranyl bond has a more ionic character than in the (4−) compound, due to the fact that uranium is less positively charged and as a consequence the oxygen charge is less delocalized toward uranium.

A similar trend was observed on the isolated cations (see Table 2). In going from MBPT2 to (12/12)/(13/13) CASSCF/CASPT2, the bond reduces by ca. 0.04 Å in UO_2^{2+} and 0.01 Å in UO_2^{+}. The bond length reduction due to the active space is larger in the isolated cations than in the complexes, indicating that the presence of the anions modify the U–O uranyl bond.

The basis set effect should also be considered in the discussion. As already mentioned in section 2, the uranyl bond distance in the gas phase reduces by 0.016 Å in going from ANO-S to ANO-L on oxygen and adding two g-type functions on uranium. A similar effect can be expected in the present compounds. A reduction of the uranyl bond of 0.016 Å would give a final value which is in agreement with experiment for both the U(VI) and U(V) compounds. The U–O carbonate distance, on the other hand, would be less affected by the basis set, because of its ionic character, as discussed above.

In Table 1 the carbonate bond distances are also reported. The CO2 and CO3 bond distances are 1.377 and 1.164 Å, respectively, in the U(VI) compound and 1.310 and 1.296 Å in the (V) compound. A CASPT2 calculation on the isolated CO_3^{3-} fragment in the presence of the reaction field gives a C–O bond distance of 1.312 Å. The carbonate is thus distorted in the U(VI) complex due to the strong interaction with the uranyl. The CO2 bond pointing toward the uranium atom is longer than in the isolated carbonate, while the CO3 bond becomes shorter. At the same time the carbonate angles distort from 120° and ∠O2CO2 becomes 108°. The distortion is less evident in the U(V) compound, where the carbonate has a weaker interaction

with the uranyl. The two C–O distances are similar to the isolated carbonate typical distance and the angles are close to 120°. All distances from uranium to the ligand atoms have been reported in the EXAFS experiment.[3] The theoretical distances are in agreement with these experimental data.

The (5−) compound was successively distorted from D_{3h} symmetry to a C_3 twisted structure, in which the two carbonate oxygens pointing toward uranium are lifted one up and one down with respect to the equatorial plane. A slight distortion of ca. 5° from planarity produces a structure which is ca. 6 kcal mol^{-1} higher in energy than the D_{3h} structure. This indicates that the D_{3h} structure is a real minimum on the energy surface.

In agreement with experiment, the reduction of $[UO_2(CO_3)]^{4-}$ to $[UO_2(CO_3)]^{5-}$ causes a U–O equatorial increase of ca. 0.12 Å and a U–O uranyl increase of ca. 0.08 Å, while no substantial rearrangement of the structure occurs.

4. Conclusions

The structures of $[UO_2(CO_3)]^{4-}$ and $[UO_2(CO_3)]^{5-}$ have been studied using multiconfigurational second-order perturbation theory. The geometries of the two compounds have been fully optimized in D_{3h} symmetry at the MBPT2 level of theory. This level of theory predicts a too long uranyl bond distance in both compounds, while the U–O carbonate bond distances are in agreement with experiment. A CASSCF/CASPT2 treatment with the uranyl oxygen 2p orbitals and the uranium orbitals forming the uranyl bonds included in the active spacs gives a uranyl bond distance in better agreement with experiment. A twisting of the carbonate oxygen gives a less stable (5−) structure. This study indicates that the difference in structure between $[UO_2(CO_3)]^{4-}$ and $[UO_2(CO_3)]^{5-}$ is not a probable explanation for the observed nonreversible behavior of the $[UO_2(CO_3)]^{4-}$/ $[UO_2(CO_3)]^{5-}$ redox couple. The close similarity in structures is instead one of the prerequisites for reversibility. The electron exchange at the electrode involves a number of different steps, one of which is diffusion of the redox pair to the electrode surface. If the sweep-rate in the Coulombic experiment is faster than the rate of diffusion, a nonreversible behavior may be observed.