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Articles

Determination of the In-Solution Molecular Structure of Reactive Osmium Compounds Involved in the Synthesis of Vicinal Diols

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Extended X-ray absorption fine structure spectroscopy, EXAFS, has been used to determine the in-solution structure of the two principal reactive components involved in the production of vicinal diols by olefin dihydroxylation using osmium tetroxide. These components are osmium tetroxide (OsO_4) and the corresponding diester osmium glycolate complex. The results show that initially the osmium tetroxide molecules are found free and unbound in the investigated solvent (6:1 tertiary butanol in water), with a molecular structure close to that found in the solid state. On addition of an excess of 2,3-dimethyl-2-butene, a compound of formula $OsO(O_2C_6H_{12})_2$, a monomeric diester of osmium tetroxide, is formed. The structural refinement of this compound indicates that the osmium center is surrounded by five oxygen atoms, one located at a shorter distance than the other four (1.69 and 1.90 Å, respectively). The same structure has been found for the osmium complex formed as the result of the slow reaction of osmium tetroxide with an excess of ethylene glycol in solution, $OsO(O_2C_2H_4)_2$. This last complex is compared with the known solid state structure.

Introduction

Arguably the most powerful means to produce vicinal diols is the dihydroxylation of olefins by osmium tetroxide (OsO_4). The key aspect of this reaction that makes it so useful is the degree of product enantioselectivity that can be achieved under appropriate conditions.[1] The dihydroxylation reaction can proceed either by a stoichiometric pathway[2,3] with a large consumption of OsO_4 or via a catalytic route[4,5] in which the osmium compound is reduced and then regenerated by a less expensive secondary oxidant. Although the catalytic route is more efficient in its use of OsO_4 and is thus more cost-effective, the yield of diol products is generally higher in the stoichiometric version of the reaction.[6] In addition, for the case of tetra- and trisubstituted alkenes, the stoichiometric route is preferred, as the rate for the oxidative hydrolysis is very slow. This is thought to be probably due to internal steric considerations. In both routes the identification and characterization of the species involved in these sorts of reactions is crucial for understanding the mechanisms. In the past few years several efforts have been made to obtain their structures, mainly as pure compounds in the solid or liquid states, using techniques such as X-ray diffraction,[7−9] Raman,[10−13] or IR spectroscopy.[12,13] The transferability of these results to understanding the active reaction system is not always trivial, as solvent effects are often significant. Furthermore, assumptions that solid and in-solution state structures are interchangeable are also not always valid. An example of these kinds of discrepancy has been found in a related osmium system. A comparative IR study performed on an associated species of an oxo-osmium ester complex with quinuclidine[14] has shown clear differences between the structures found in-solution and in the solid state. In the solid, dimeric complexes of osmium have been detected, but only monomeric species have been identified in carbon tetrachloride or diethyl ether solutions. To date, the in-

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solution studies of these kinds of complexes by ^{1}H NMR[15,16] and IR[15,17] spectroscopic techniques have not been able to provide a detailed structural picture of the reactive complex or of the product.

In this study we present the structure of the two osmium species involved in the reaction of OsO_4 with 2,3-dimethyl-2-butene, i.e., the structure of OsO_4 itself and the structure of oxobis(tetramethylethane-1,2-diolato)osmium(VI), a monomeric diester of formula $OsO(O_2C_6H_{12})_2$ in which an OsO_4 unit bonds to the C=C double bond of two olefins. For comparison, the structure of oxobis(ethane-1,2-diolato)osmium(VI), the osmium complex of formula $OsO(O_2C_2H_4)_2$, formed in the reaction between OsO_4 and ethylene glycol, was also determined. All of these structures have been measured as a dissolved species in a 6:1 mixture of tertiary butanol in water. This solvent was chosen as it is commonly used in the catalyzed asymmetric dihydroxylation of olefins, which is the most widely used version of the reaction.[18] The ratio of the two components reproduces the same solvent stoichiometry as found in the reaction's organic phase, and thus, in contrast with earlier investigations, the structures of the osmium species are determined under the same conditions as found in the reaction itself, i.e., in a coordinating solvent mixture.

The experimental technique we have utilized for this study is extended X-ray absorption fine structure (EXAFS) spectroscopy. This technique is local structure sensitive and element selective and thus allows us to investigate the local environment of the reaction complexes from the viewpoint of the osmium atomic site, out to a distance of ~4 Å. Many previous studies have proven this technique to be very suitable for the study of metal-containing molecular systems in solution.[19,20] The local structure focus of the method in combination with its element specificity make data interpretation far simpler than diffraction-based studies of similar systems.

Experimental Section

(a) Sample Preparation. For the measurements reported here, three solutions were prepared: (1) A 0.05 *m* solution of osmium tetroxide (Sigma-Aldrich 99.999% purity) made up by dissolving the corresponding amount in a 6:1 mixture of *tert*-butanol (Sigma Aldrich 99.99% purity) and distilled deionized water and stabilized with *tert*-butyl hydroperoxide. (2) A 1:1 solution by volume of a 1.0 *m* solution of 2,3-dimethyl-2-butene (Sigma-Aldrich 99.999% purity) in 6:1 *tert*-butanol−water, and a *tert*-butyl hydroperoxide stabilized 0.1 *m* solution of osmium tetroxide in 6:1 *tert*-butanol−water. (3) A 0.1 *m* solution of osmium tetroxide in 6:1 *tert*-butanol−water, stabilized with *tert*-butyl hydroperoxide, with ethylene glycol added to an excess of 10 times the osmium concentration.

The concentrations selected for this study in the cases of solutions 2 and 3 ensured that complete complexation of the osmium had taken place, as the alkene and the ethylene glycol were present in large excess. This allowed us to avoid having to make any corrections for mixtures of more than one species involving osmium atoms. The *tert*-butyl hydroperoxide added to stabilize the OsO_4−alcohol−water mixture is known to be an oxidizing agent[21] and thus ensures the clean production of the appropriate diesters.

All the samples were prepared in a well-ventilated fume hood due to the high toxicity of the OsO_4. The solutions were measured immediately after preparation. Several spectra per sample were measured over a period of up to 3 h, and no change in the measured spectra was observed during this time. This indicates that if the ester complexes formed in the case of solutions 2 and 3 suffer any hydrolysis, only a very small proportion of the diol is likely to have been created on the time scale of the experiment.

(b) Measurements and EXAFS Data Analysis. The EXAFS spectra of the species involved in the reaction were collected at beamline BM29, at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The spectra were collected at the Os L_{III} edge (10.871 keV), using a double crystal monochromator fitted with a pair of flat Si(311) crystals detuned to 50% fwhm of the maximum transmission, for the suppression of higher energy harmonics. The X-ray beam profile was defined to be 0.2 mm (v) by 10 mm (h), providing conditions under which an energy resolution of ~0.5 eV was obtained. This can be compared with the natural width of the Os L_{III} absorption edge of 5.16 eV.

All measurements were made at room temperature (293 K) in transmission mode. The samples were contained in a PTFE cell equipped with two 25 μm Kapton foil windows that constrained the X-ray path length to 4 mm, i.e., optimized for the concentrations studied. Beam intensity was measured using gas-filled ionization chambers, optimized for 30% absorption of the incident beam and 70% of the transmitted beam, at the energy of the Os L_{III} edge.

The background corrections required to obtain the EXAFS functions $\chi(k)$ from the measured X-ray absorption spectra were performed using the AUTOBK code from the University of Washington.[22] E_0 was defined as the maximum of the first derivative of the absorption edge.

To analyze the EXAFS spectra of the three solutions, the theoretical phases and amplitudes were calculated using the FEFF 7.00 code.[23,24] The fit to the experimental data was performed using the FEFFIT program (version 2.54).[22]

Results and Discussion

In Figure 1 we show the experimental data and model fits to the $k\chi(k)$ EXAFS spectrum and associated Fourier transform obtained for solution 1. The analysis of this spectrum is consistent with a tetrahedral structure, and the results are summarized in Table 1. The best fit is obtained considering four oxygen atoms equally distributed at 1.714 Å around the metal center. Though it is difficult to rule out a nontetrahedral, square planar geometry for this molecule, the absence of any multiple scattering components in the spectrum (which would be evident at longer distances in the Fourier transform) lends support to the assumption of the former molecular geometry.

The structure of OsO_4 has been extensively studied, in the solid as well as in the liquid state. Over the years, several X-ray diffraction,[7,25,26] Raman,[10,11,13,17] IR,[13,17,27]

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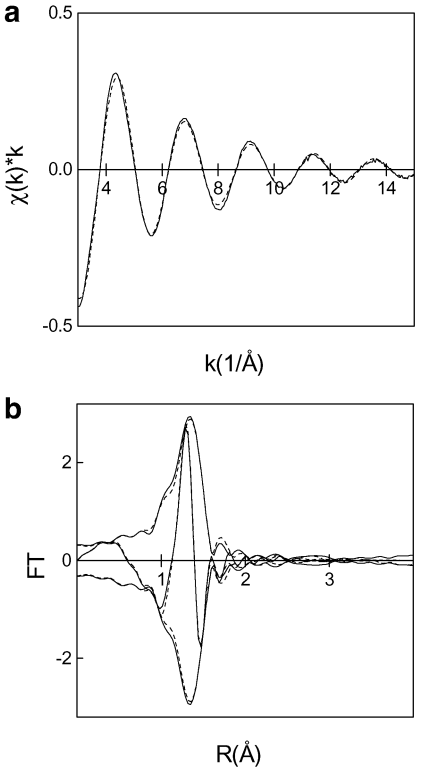

Figure 1. (a) Raw EXAFS data, *k*-weighted, of the osmium tetraoxide solution in a 6:1 *tert*-butanol–water mixture: experimental function (solid line) and best fit obtained with the parameters included in Table 1 (dashed line). (b) Magnitude and imaginary part of the Fourier transform of the EXAFS spectra included in part a.

electron diffraction,[28] and theoretical studies[29,30] have been published. The majority of these studies have shown that the osmium center is surrounded by four oxygen atoms in a slighly distorted tetrahedral environment. All the crystallographic studies have shown that two of the four oxygen atoms are nearer than the other two, though this difference in the two Os–O distances is small, ~0.03 Å. The symmetric result obtained by EXAFS could be due to the lack of crystallographic constraints present in the solid, leading to a more symmetric structure. However, as the differences in the two possible distances are at the detection limit of the technique, it is not possible in this study to rule out the possibility of a small distortion.

It is important to highlight the simple form of the EXAFS function measured for this species in solution. The presence of a single-frequency component in the measured spectrum indicates an absence of neighbors at longer distances, as seen in the Fourier transform. This finding suggests that the solvent molecules, water and/or *tert*-butanol, are found far from the osmium atom and that the osmium tetroxide is present in the solution as a free, i.e., unbound molecule.

The results obtained from the EXAFS analysis of this system are thus consistent with the most recent XRD published data,[7] including the asymmetry mentioned above, and compare well with recent theoretical investigations of the OsO_4 molecule, where complete symmetry has been assumed.[29,30]

Figure 2 shows the measured EXAFS spectrum and best fit, together with the corresponding Fourier transforms for solution 2. The slight increase in noise over the spectrum obtained for solution 1 is due to the large background absorption induced by the presence of the 10-fold excess of alkene, which, as mentioned above, ensures the complete complexation of the osmium tetroxide.

What is immediately seen on examination of Figure 2 is the more complicated form of the EXAFS function when compared to the previous case. This indicates that the local environment around the osmium has changed considerably from that of the free molecule. The corresponding Fourier transform clearly shows a splitting of the distances in the first oxygen shell, and features at larger distance (between 2 and 3 Å) highlight the formation of the diester complex.

The parameters obtained from the best fit to this spectrum are included in Table 1 and correspond to a 5-fold coordinated osmium environment, with two main distances in the first shell of oxygen atoms. The first feature in the Fourier transform corresponds to one oxygen atom at 1.69 Å from the osmium atom. This distance is associated with an Os=O double bond as confirmed by comparison with the distance Os=O found for the free osmium tetroxide. The second very intense peak in the figure corresponds to four oxygen atoms at 1.90 Å from the osmium atom and which by virtue of their increased length over the short bond we assign to four single Os–O bonds.

Beyond this first neighbor environment, a third feature in the Fourier transform at longer distances can be observed. This third peak is best modeled by four carbon atoms at 2.85 Å from the metal center. The fit is thus consistent with the model structure shown in Figure 3 and, as mentioned, supports the formation of a five-coordinate cyclic diester in this solution.[15]

The parameters obtained from the fit are found to be in good agreement with the crystallographic parameters obtained for the parent compound oxobis(ethane-1,2-diolato)osmium(VI), of formula $OsO(O_2C_2H_4)_2$.[8] However, in the solid state structure a splitting in the distances of the four oxygen neighbors and the four carbon contributions is found. A second fit of the EXAFS data taking as a model the nonsymmetric compound found by the crystallographic measurements has been performed, but the improvements of the fit do not justify the inclusion of an extra four fitting parameters. However, the average distances found in the present study are within 0.05 Å of the average distances of the parent compound crystallographic determination. Crystallographic data for oxobis(tetramethylethane-1,2-diolato)osmium(VI), the complex formed in solution 2, is not available due to the difficulty of obtaining crystals of sufficient quality.[31]

To perform a more direct comparison with the crystallographic data, the spectrum corresponding to the mixture solution of osmium tetroxide with ethylene

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Table 1. Best Fit Parameters Obtained from the Analysis of the EXAFS Spectra of the Three Osmium Species Indicated in the Text[a]

	osmium tetraoxide	osmium diester (from olefin)	osmium diester (from ethylene glycol)
ΔE_0 (eV)	6.7 ± 0.7	6.7 ± 1.1	6.6 ± 0.9
N_{coord} Os−O (fixed)	4	1 (Os−O$_1$) 4 (Os−O$_2$)	1 (Os−O$_1$) 4 (Os−O$_2$)
N_{coord} Os−C (fixed)		4	4
d(Os−O) (Å)	1.714 ± 0.003	1.69 ± 0.02 1.90 ± 0.03	1.69 ± 0.02 1.90 ± 0.03
d(Os−C) (Å)		2.85 ± 0.08	2.82 ± 0.05
σ^2(Os−O) (Å^2)	0.0006 ± 0.0002	0.0015 ± 0.001 0.0017 ± 0.0004	0.0012 ± 0.0009 0.0017 ± 0.0003
σ^2(Os−C) (Å^2)		0.003 ± 0.002	0.004 ± 0.002
R factor	0.002	0.034	0.023

[a] ΔE_0 is inner potential correction; N_{coord} is coordination numbers; σ^2 is Debye−Waller factors; d is coordination distances; R is goodness of fit parameter. Osmium tetraoxide: $\Delta k = 2-15.5$ Å^{-1}; k^2. Osmium diester (from olefin): $\Delta k = 3-15$ Å^{-1}; k^2. Osmium diester (from ethylene glycol): $\Delta k = 3-16$ Å^{-1}; k^2.

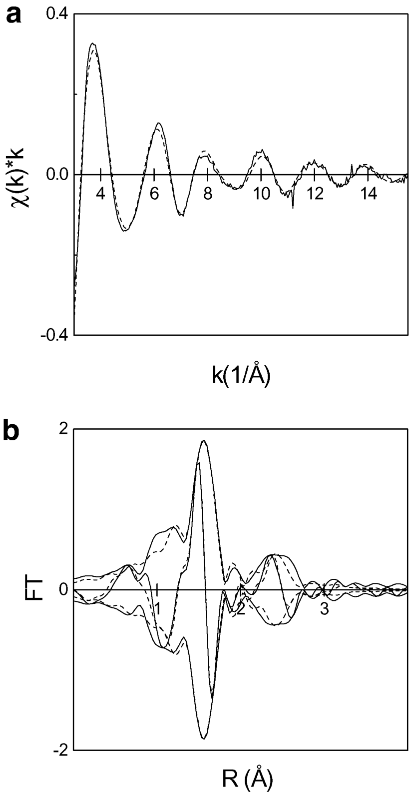

Figure 2. (a) Raw EXAFS data, k-weighted, for OsO($O_2C_6H_{12}$)$_2$ in a 6:1 *tert*-butanol−water mixture: experimental function (solid line) and best fit obtained with the parameters included in Table 1 (dashed line). (b) Magnitude and imaginary part of the Fourier transform of the EXAFS spectra included in part a.

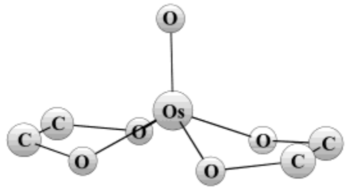

Figure 3. Schematic diagram of the local environment of osmium in a symmetric five-coordinate cyclic diester.

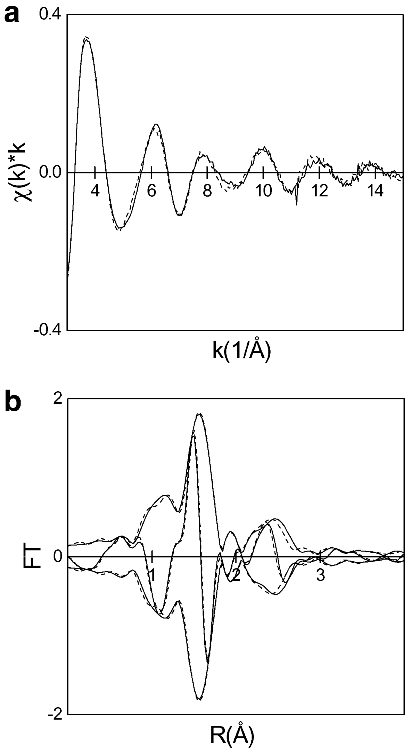

Figure 4. (a) Raw EXAFS data, k-weighted, for OsO($O_2C_6H_{12}$)$_2$ in a 6:1 *tert*-butanol−water mixture (solid line) and for OsO($O_2C_2H_4$)$_2$ in the same mixture (broken line) and produced by reaction of osmium tetroxide with ethylene glycol. (b) Magnitude and imaginary part of the Fourier transform of the EXAFS spectra included in part a.

glycol, solution 3, was measured. If this solution is left for several weeks, the solid compound is formed. Its crystalline structure has been determined by XRD[8] and found to be the monomeric diester oxobis(ethane-1,2-diolato)osmium(VI), of formula OsO($O_2C_2H_4$)$_2$. This compound is believed to be the same complex as that obtained by direct reaction of ethylene with osmium tetroxide following results obtained by Raman spectroscopy[15] and ^{1}H NMR studies.[16] The data corresponding to solution 3 are shown in Figure 4, together with their corresponding Fourier transform. For comparison, the data corresponding to the monomeric diester of formula OsO$_2$($O_2C_4H_{12}$)$_2$, formed in the solution 2, is also shown. The striking similarity between these functions is graphic proof that the local environment around the osmium center is the same in both complexes, corroborating the conclusions drawn from the earlier results.[15,16] In addition, these two spectra show that the local environment around the osmium atoms is not affected by the degree of substitution of the organic reactant used. The parameters corresponding to the best fit obtained for system 3 are also included in Table 1. Within the errors, these are the same as those obtained for the dimeric monoester present in solution 2.

The absence of any longer distance contributions in the Fourier transform of either of the two diester compounds investigated correlates with the absence of obvious multiple scattering components in the measured spectra. This fact suggests that the osmium center within the complex is not in the same plane as the four singly bonded oxygen atoms. If this were the case, we would expect to see spectral components corresponding to strong linear scattering paths associated with the in-plane O−Os−O linkage.

Conclusions

In conclusion, we have presented a detailed investigation of the local atomic environment of osmium as a solvated but free osmium tetroxide molecule and also when forming two different monomeric diester complexes. Both these structures are important for developing a baseline understanding of the commercially important dihydroxylation reaction.

In the case of an osmium tetroxide−*tert*-butanol−water solution, the molecule is found to be free in the solvent media. The distances obtained agree with the crystallographic data and thus indicate that the local structure around the osmium metal is not affected by the molecules of the solvent. We can also conclude that the solvent molecules are not located closer than 4 Å from the central metal.

In the case of the diester compounds, the structure obtained is in agreement with a symmetric monomeric diester. The splitting of the distances of the four further oxygen atoms, as well as the carbon atoms, detected in the solid structure is not detectable in the solution. However, the average distances are in perfect agreement with the crystallographic average distances, thus showing that the presence of coordinating solvents such as water or *tert*-butyl alcohol do not affect the local structure of the complex.

Finally, the comparison of the two diester systems studied, $OsO(O_2C_4H_{12})_2$ and $OsO(O_2C_2H_4)_2$, allows us to conclude that the local environment around the osmium atom is not affected by the degree of substitution of the organic reactant.

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