



	Experiment title: A time-resolved study of the dihydroxylation of olefins by osmium tetroxide	Experiment number: CH-867
Beamline:	Date of experiment: from: 26/01/00 to: 31/01/00	Date of report: 1/03/00
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Report:

During the beam time allocated for the experiment CH-867 we have successfully started an investigation of the dynamics of the dihydroxylation of olefins by osmium tetroxide. Two different reaction pathways have been proposed, (1) a concerted [3+2] cycloaddition, or (2) a [2+2]-like insertion with subsequent structural rearrangement.

To elucidate the reaction pathway we performed a time resolved X-ray absorption spectroscopy experiment at the Os L_{III} edge (10.871 keV). The experimental set up consisted of a stopped flow injector coupled via specially developed trigger electronics to a CCD-based position sensitive detector. With this system, the acquisition of series of up to 15 spectra with a per-spectrum time resolution of 100 μ s is possible.

The experimental programme started with the study of the simple direct dihydroxylation of 2,3-dimethyl-2-octene by the osmium tetraoxide. It was not possible to study the dynamics of this reaction before beam time (i.e. with UV-Vis), so significant time was spent finding the right time frame.

Several successful series of spectra were taken, which clearly show the reaction dynamics. A series with a time resolution of 100ms per spectra is seen in the figure below. By comparison with a static EXAFS-spectra, the first spectra of this series is identified as OsO₄. Similarly, the last spectrum is identified as the second possible intermediate state shown in the figure. We see a shift in the position of the edge as well as changes in the XANES and the EXAFS regions. After a preliminary data analysis, no evidence for the first

intermediate state — which would provide proof of the [2+2]-like insertion as the favoured reaction pathway — could be found.

These data show that the mechanism of the dihydroxylation of olefins by osmium tetroxide occurs via a concerted [3+2] cycloaddition. However, our data do not dismiss the possibility of the existence of a shorter-lived intermediate.

