

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: ELUCIDATION OF THE ACTIVE SPECIES IN THE OXIDATION REACTION OF $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ HOMOGENEOUSLY CATALYSED BY CH_3ReO_3/H_2O_2

Experiment number:
CH1944

| | | |
|------------------|--|--------------------------|
| Beamline: | Date of experiment: from: 29/06/05 to: 5/07/05 | Date of report: |
| Shifts: | Local contact(s): Gemma Guilera | <i>Received at ESRF:</i> |

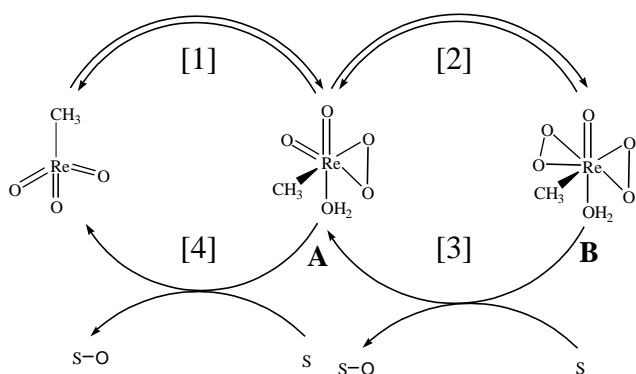
Names and affiliations of applicants (* indicates experimentalists):

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Dr Moniek Tromp* Dept. Chemistry, University of Southampton, UK

Report:

In this experiment we planned to investigate the mechanism of the oxidation of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ ($CoSR^{2+}$) by the catalyst CH_3ReO_3/H_2O_2 at room temperature (see Fig.1). This oxidation reaction may lead to a convenient synthesis of organic sulfoxides, disulfides, or sulfonic acids.¹ Although this reaction has been studied by electronic spectroscopy to obtain kinetic data, no structural information on the reactive intermediates could be extracted.² In order to be able to attain such information we performed the experiment by means of complementary techniques (stopped-flow/UV-Vis/Dispersive-EXAFS (EDE)) synchronised at the millisecond range.



Reaction path of the substrate under study:

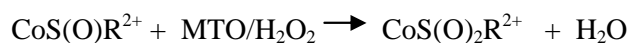
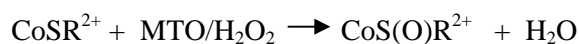


Figure1. Reaction under study.

Acetonitrile solutions of CH_3ReO_3 and CoSR^{2+} were prepared off-line. Final mixtures in the stopped-flow cuvette contained 20mM of Re. EDE measures were monitored on the Re L_{III} -edge (10.535 KeV). During this experiment we improved the normalisation method of the spectra by doing a tailored modification in the software, which allowed us to obtain the I_0 as the solvent in exactly the same spot where data was taken for the sample. This normalisation method improved significantly the quality of the data, and we could get reliable information down to 8mM of Re.

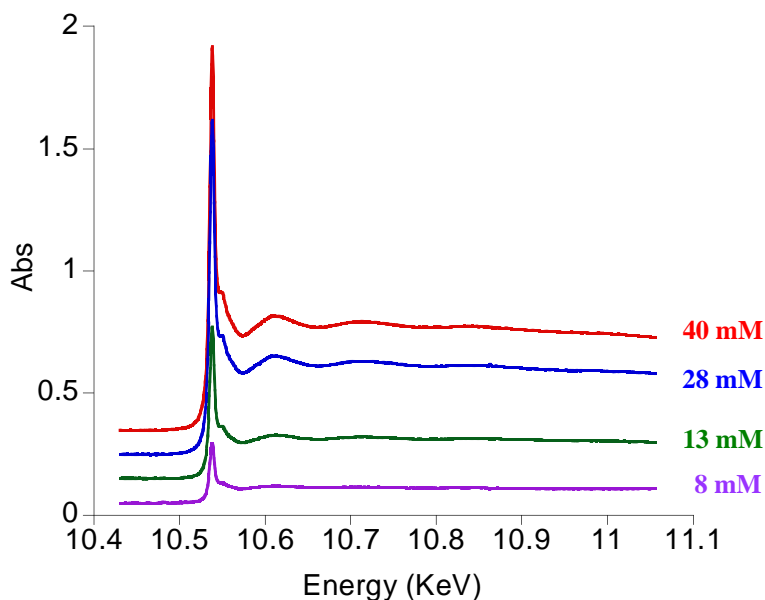
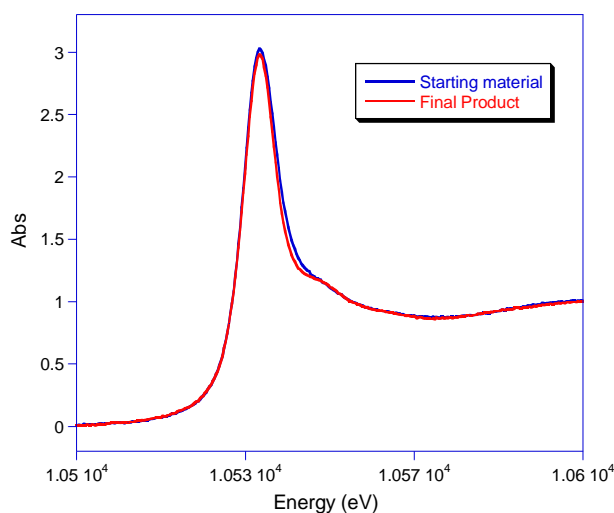


Figure 1. EDE raw spectra of CH_3ReO_3 in acetonitrile at different concentrations illustrating the quality of the data.

The first reaction monitored was the CH_3ReO_3 with H_2O_2 . This was extremely problematic because of bubble formation induced by the beam. This made this reaction impossible to follow by means of EDE experiments. As such, we decided to monitor another related reaction: the deactivation of CH_3ReO_3 by competing pathways in basic acetonitrile solutions, in particular NaOH .³ The time resolution of this experiment was 600 ms. Small but consistent changes in the XANES region could be observed. This could be attributed, in average, to a change in the type of Re-O bonding. We are planning to apply in the near future a fitting routine for the XANES region (MXAN program) to obtain quantitative structural information and compare it with FEFF8.2 simulations.



During the last day of the experiment we changed energy to the Co K-edge (7.709 KeV) so we could obtain static spectra of all different reactants of the original reaction. In this case we tested new cuvettes (capillary with diameter of 1.5mm) in collaboration with ID02. These gave positive results and consequently these cuvettes are going to be used to study the soft edges on ID24, such as Cr, Mn and Fe, with this stopped-flow/UV-Vis/EDE facility.

1. Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293.
2. Romao, C. C.; Kuhn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197.
3. Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966.

