Time-Resolved X-Ray Absorption Spectroscopy Data for the Study of Chemical Reaction Intermediate States

Sofia Diaz Moreno¹, Daniel T. Bowron² and John Evans³

¹*Diamond Light Source, Chilton, Didcot, OX11 0DE, UK;* ²*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK;* ³*School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.*

Abstract. Energy-dispersive X-ray absorption spectroscopy is an increasingly powerful tool for the investigation of kinetic processes in chemical systems as an element-specific local structure and electronic-state probe. In this paper we present a study of the structural evolution of the inner-sphere electron transfer reaction between $[\text{IrCl}_6]^{2-}$ and $[\text{Co}(\text{CN})_5]^{3-}$. The experimental requirements necessary for the extraction of maximal structural and electronic information are discussed.

Keywords: Energy Dispersive EXAFS, EDXAS, Time Resolved, Chemical Reactions

PACS: 61.10.Ht; 61.66.Fn

INTRODUCTION

Advances in synchrotron radiation sources and detector technology are pushing the time resolution of techniques such as Energy Dispersive X-ray absorption spectroscopy (EDXAS) to ever shorter time periods. The resolution of this technique currently stands at milliseconds to microseconds and equally with the ability of the new synchrotron sources to provide data of exceptional quality, it has recently been possible to show that it is now a realistic proposition to identify the structural and electronic motifs that are characteristic of the intermediate states in chemical processes [1]. Electron transfer reactions occur when one or more electrons are transferred from one chemical species, called the reductant, to another, called the oxidant. If the transfer of the electrons occurs via the formation of an intermediate species where two metal centres are joined through one of the ligands that form the coordination sphere of one of the metals, the reaction is called an inner sphere process, and the reaction intermediate, a bridged activated complex [2]. In this paper we report the application of x-ray absorption spectroscopy in its energy dispersive variant to the study of the reaction between $[\text{IrCl}_6]^{2-}$ and $[\text{Co}(\text{CN})_5]^{3-}$.

EXPERIMENTAL SECTION

All the x-ray absorption spectroscopy data reported here were taken at the European Synchrotron Radiation Facility, Grenoble, (France). The synchrotron was operating at a ring energy of 6GeV

with ring current of 250mA. Investigations of the chemical reactants were performed at both the Co K-edge (7709eV) and Ir L_{III}-edge (11215eV) to provide structural insight from the viewpoint of each of the participating chemical species.

The absorption spectra of the initial and the final states for both the cobalt and the iridium centres were measured at beamline BM29 [3], using a Si(111) double crystal monochromator, detuned to 50% intensity for harmonic rejection. The measurements were performed at room temperature in transmission mode using ionization chambers as detectors, filled with the appropriate mixture of gases to absorb 20% of the intensity of the beam in I_0 and 70% in I_t . The samples were measured in solution in PTFE cells with kapton windows. The solutions measured as the initial states were 0.08M of $[\text{IrCl}_6]^{2-}$ for the iridium species and 0.08M of $[\text{Co}(\text{CN})_5]^{3-}$ for the cobalt species. The final state was measured as the product of the reaction present in the reaction mixture after some time: $\sim 0.04\text{M}$ in $[\text{IrCl}_6]^{3-}$ and $\sim 0.04\text{M}$ in $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$. The spectral energy scale was calibrated by the simultaneous measurement of cobalt and platinum foils as reference samples.

The time resolved data were collected at beamline ID24 [4] using a bent Si(111) crystal in the Bragg configuration as the energy dispersive polychromator. A masked, Peltier cooled, Princeton CCD was used as a position sensitive detector. The energy calibration of the spectrometer was established by comparison with spectra measured using Co and Pt foils for the cobalt and iridium energy ranges used in the experiment.

To initiate the reaction, a Biologic stopped-flow apparatus was integrated into the beamline. Due to the air sensitive nature of the cobalt species it was necessary to house the stopped-flow cell in a nitrogen filled glove box, integrated into the beamline. The operation of the stopped flow cell was synchronized with the detector and a fast shutter. The shutter was placed in front of the cell to protect the sample from radiation damage. An ultraviolet-visible spectrometer was simultaneously connected to the stopped-flow reaction cell to provide additional kinetic information.

The iridium solution was prepared by dissolving a pre-weighed amount of the commercially available sodium salt of the complex in the corresponding amount of water. The cobalt complex was prepared in solution by adding sodium cyanide to a basic aqueous solution of cobalt(II) nitrate hexahydrate under inert atmosphere [5]. The solution was kept under argon to avoid oxidation of the cobalt complex by the air, and then transferred to the stopped-flow cell placed in the nitrogen filled glove box.

An equal volume of a 0.08 M solution of $[\text{IrCl}_6]^{2-}$ was mixed with a 0.08 M solution of $[\text{Co}(\text{CN})_5]^{3-}$ in the stopped-flow apparatus at 18 °C. A series of 32 EXAFS spectra were collected in 200ms time slices from the moment the reactants were mixed. The total study thus covers a total reaction time of 6.4s and corresponds to the time required for the reaction to go to completion at this reactant concentration and temperature.

RESULTS AND DISCUSSION

The result of the EXAFS analysis of the static measurements collected for the initial and final states for the iridium complexes show that, in both cases, the iridium is an octahedral complex surrounded by six chlorine ligands [6]. The main difference between the two states is the Ir-Cl distance. This was found to be $\sim 0.03\text{\AA}$ longer in the final state than in the initial state. The energy position of the edge feature for the two species shows a clear shift to lower energies for the final state complex compared to the initial state, consistent with the lower formal oxidation state of the iridium centre following the electron transfer process.

The extracted EXAFS functions for the 32 spectra collected during the time resolved study at the Ir L_{III} edge are shown in Figure 1. The first feature to note is the very good signal to noise ratio of the spectra despite the fact that only 200ms were employed in recording each frame. Due to the high quality of the data, small changes can be observed across the series and in particular small differences are visible at low k values [6]. The analysis of the XAS time series together with the additional kinetic information obtained using the uv-vis data that was recorded

simultaneously during the experiment allowed the determination of the structure of the long lived intermediate produced during the reaction [6]. This intermediate was found to be a binuclear complex with a chlorine ligand acting as a bridging bond between the cobalt and iridium metal centres. In the kinetic data, the position of the absorption edge was found to remain fixed at a constant energy value throughout the reaction and indicates that the electron transfer had already occurred before the intermediate state, followed in this investigation, begins its decomposition.

FIGURE 1. Series of 32 spectra showing the reaction from the iridium point of view.

The analysis of the static spectra collected for the initial and final states of the cobalt complexes in principle allows us to obtain the complementary view of the electron transfer reaction. The static study again showed that there is a change of the oxidation state of the metal centre. This conclusion is obtained from the shift to higher energies that the absorption spectra display, in agreement with a change of the formal oxidation state of the cobalt from +2 to +3. The analysis of the extracted EXAFS function for the initial state reveals a cobalt centre surrounded by five cyanide ligands. The Fourier transform shows two main peaks corresponding to the C and the N ligand, as can be observed in Figure 2. The abnormally high amplitude of this second peak can be explained by the focusing effect of the linear configuration of the CN ligand. In the case of the final state, a good fit to the data can be obtained with the same five CN ligands around the metal centre, but with slightly smaller distances. The inclusion of a water molecule as a ligand on the sixth coordination position does not significantly improve the fit.

The extracted EXAFS functions corresponding to the 32 spectra of the series for the cobalt edge are shown in Figure 3. As can be seen in the figure, there

are no appreciable structural changes during the reaction when observed from the cobalt point of view.

There are several reasons that explain this apparently contradictory result with respect to the findings of iridium study.

FIGURE 2. Fourier transform corresponding to the EXAFS spectrum of $[\text{Co}(\text{CN})_5]^{3-}$ (—) and the best fit (---) showing the two main contribution to the spectrum, Co-C 1.898(8)Å and Co-N 3.08(1)Å.

First, the k range of the spectra measured in the time series is very limited corresponding to a spectral energy range of 300eV. This restriction is imposed by the low energy capabilities of an energy dispersive spectrometer and only allows the first three oscillations in each spectrum to be observed. The limitation results from the size of the curved crystal polychromator necessary for the energy dispersive configuration [7] and in the case of ID24, is further exacerbated by the narrow bandpass of the undulator harmonic.

FIGURE 3. Series of 32 spectra showing the reaction from the cobalt point of view.

Second the quality of data shown in Figure 3 is limited and distinctly worse than data taken at the iridium L_{III} edge. This is due to (a) the large background absorption at the cobalt edge energy

caused by the heavy element chemical species present in the sample and (b) the requirement for the use of non-optimal pyrolytic carbon for the X-ray windows of the stopped flow observation cuvette. Ideally the window materials have to be both very rigid and very smooth. For experiments at the relatively low cobalt X-ray energy the choice of window material is severely limited and pyrolytic carbon was chosen despite the difficulty in machining a high quality surface finish on the material.

Finally the strong multiple scattering from the five CN linear ligands mask any comparatively weak structural contribution that would come from the additional ligand in the sphere of the cobalt when in the bridged intermediate.

CONCLUSIONS

In this paper we have shown that though EDXAS can be of great relevance for the structural study of reaction intermediates, the application of the technique is often limited by sometimes unexpected challenges. The results presented in this paper reveal the need for very high quality data over an extended energy range, particularly if the structure of a very minor component in the reaction mixture is to be determined. We have illustrated that beyond the basic performance of the EDXAS beamline, the quality of the data is largely limited by the background absorption in the sample and the materials used as windows for the reaction cuvette.

ACKNOWLEDGMENTS

We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities and for beam time allocated under experiment proposal CH-1369. We thank T. Mairs for his help in optimizing the performance of the ID24 beamline for time-resolved in-solution chemistry.

REFERENCES

1. D. T. Bowron and S. Diaz Moreno, *Anal. Chem.* **77**, 6445-6452 (2005)
2. H. Taube and H. Myers, *J. Am. Chem. Soc.* **76**, 2103-2111 (1954)
3. A. Filipponi, M. Borowski, D. T. Bowron, S. Ansell, A. Di Cicco, S. De Panfilis, J.-P. Itié, *Rev. Sci. Instr.*, **71**, 2422-2432 (2000)
4. M. Hagelstein, A. SanMiguel, A. Fontain, J. Goulon, *J. Phys. IV*, **7**, 303-308 (1997)
5. B. Grossman and A. Haim, *J. Am. Chem. Soc.*, **92**, 4835-4840 (1970)
6. S. Diaz Moreno, D. T. Bowron and J. Evans, *Dalton Transactions*, 3814-3817 (2005)
7. H. Tolentino, E. Dartyge, A. Fontaine and G. Tourillon, *J. Appl. Cryst.*, **21**, p. 15-26 (1988)