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The design of a thin layer, infrared-transparent electrochemical cell and its use in the study of cluster species

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Abstract

The design of a thin layer, infrared-transparent electrochemical cell is described, and its application to the study of the IR spectra of some air sensitive reduced cluster species is demonstrated.

Introduction

Although the use of a simple thin-layer optically transparent electrochemical cell is well established as a technique for studying the changes in optical spectra that occur upon oxidizing or reducing inorganic compounds [1], analogous equipment for studying such species by infrared spectroscopy is not a common-place piece of equipment for the inorganic electrochemist. A number of sophisticated designs for a thin-layer infrared transparent electrochemical cell based upon reflectance IR techniques have been reported [2], but these are unsuitable for general purpose use. Cell designs based upon transmission infrared spectroscopy have appeared in the literature [3], but if the cells are to have optimal electrochemical properties the designs must be relatively sophisticated, and hence expensive and difficult to construct. We report here the construction of a simple thin layer, IR-transparent electrolysis cell (TIRTEC) which gives excellent results when used to study air sensitive compounds generated by the two electron reduction of some medium and high nuclearity osmium carbonyl clusters.

Experimental, research and discussion

The glass top (Fig. 1) was constructed by Cambridge Glassblowing Ltd. A typical rectangular NaCl IR solution cell was fitted with a 1 mm or 0.5 mm Teflon spacer with the top edge cut away. A small piece of Pt mesh (working electrode) was placed between the plates with the attached wire emerging through the central port of the glass top. Similarly a small coil of fine Pt wire formed the auxiliary electrode and a

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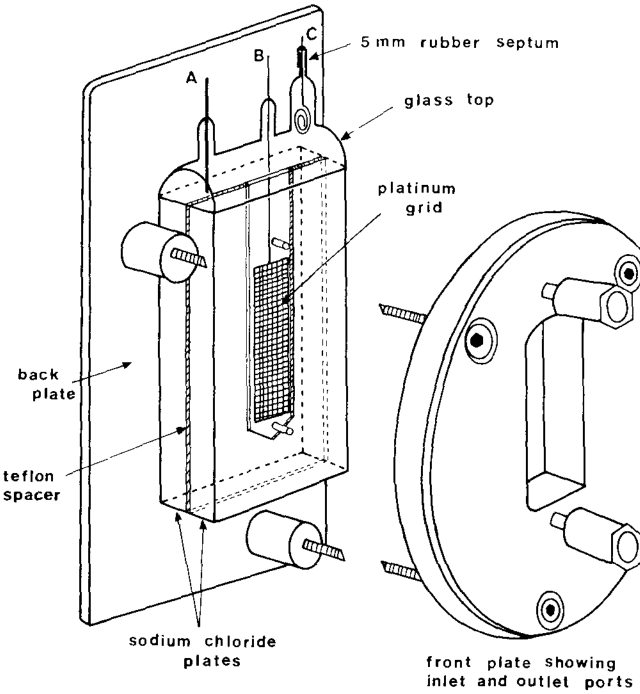

Fig. 1. Design of the thin-layer infrared transparent electrolysis cell (TIRTEC). Electrodes: A. Reference, short length of 1 mm diameter silver wire; B. Working, platinum grid electrode; C. Auxiliary, coil of fine platinum wire.

short piece of 1 mm Ag wire formed the pseudo-reference. These wires emerged through the second and third ports of the glass top. In each case the wire was either sealed into the glass top or led through a rubber septum (auxiliary electrode in Fig. 1) which ensured that the cell was air tight. The top was then secured to the NaCl plates using epoxy-resin.

When in use the cell could be filled and emptied anaerobically through the usual ports in the NaCl plates using the following procedure. The cell would be connected to a vacuum/Ar manifold via a male luer lock to male luer lock stopcock (Aldrich Chemical Co.) screwed onto the upper cell inlet port. Freeze-thaw degassed solutions could then be introduced via a syringe, equipped with a luer lock, which was screwed onto the lower inlet port. This allowed the solution to be injected into the cell under a positive pressure of argon.

A typical experiment was carried out as follows. A solution of 0.4 *M* tetrabutylammonium fluoride (TBAF) [4*] in CH_2Cl_2 is made up and freeze-thaw degassed. A sample of this solution is then placed in the cell and a background spectrum stored on the FTIR spectrometer (Perkin–Elmer, Model 1710). The compound to be studied is added to the degassed electrolyte solution and the solution (about 1–1.5 ml) is then anaerobically transferred to the IR cell as described above. The IR spectrum may be obtained and stored for subsequent data-handling operations. The

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* Reference numbers with asterisks indicate notes in the list of references.

thin-layer electrolysis cell is then connected to a PAR 170 potentiostat and the solution electrolysed. The time for complete electrolysis is 5–20 min, depending upon the concentration of the sample, the potential chosen for the electrolysis, the concentration of the electrolyte, and the electron transfer characteristics of the redox process. We have established that the use of a conventional electrolyte concentration (usually about 0.1 *M*) causes a high uncompensated solution resistance due to the non-ideal cell geometry and this means that high overpotentials (0.6–1.0 V) are required to complete the electrolyses. Hence in the later experiments we increased the electrolyte concentration to 0.4 or 0.5 *M* and this gave improved currents and the electrolyses required much lower overpotentials (typically 0.2–0.4 V). Many of the cluster compounds we wished to study have a large number of carbonyl ligands that give intense IR absorptions and this limits the concentration of cluster (to about 10^{-3} *M*) that can be used in a 1 mm thin layer electrolysis cell. Such concentrations are less than ideal for efficient electrolyses, so in later experiments we decreased the thickness of the spacer between the NaCl plates to 0.5 mm to allow the concentration of the cluster to be raised.

The electrolysis of acetylferrocene (reversible oxidation at about +0.8 V [5]) was carried out as an initial test reaction. The electrolyte concentration for this experiment was too low (about 0.1 *M*), and a substantial overpotential was required to complete the electrolysis. However, after about 30 min at +1.4 V complete electrolyses was obtained, with quantitative conversion to the cation. It was noticed that the 1 mm thick cell portion was deep blue but the solution above the NaCl plates was still orange. This demonstrated that even with prolonged electrolysis times, and the relatively long cell pathlength, diffusion from the top compartment down between the NaCl plates was slow enough not be to a problem.

Next $[Os_6(CO)_{18}]$ was electrochemically reduced to $[Os_6(CO)_{18}]^{2-}$. The cyclic voltammogram of $[Os_6(CO)_{18}]$ shows a chemically reversible process ($E_{1/2} = 0.04$ V) with slow heterogeneous charge transfer believed to be associated with a change in structure from a bicapped tetrahedron to an octahedron upon reduction [6]. Electrolysis of $[Os_6(CO)_{18}]$ in 0.1 *M* TBAF/CH_2Cl_2 at −1.0 V in the thin layer electrolysis cell demonstrated that the IR bands of this compound [7] steadily decreased in intensity, with concomitant growth of the bands of $[Os_6(CO)_{18}]^{2-}$, showing clean conversion to the dianion [8]. If the spectrum of $[Os_6(CO)_{18}]$ recorded before electrolysis was absorbance-subtracted from spectra recorded during electrolysis, only bands due to the dianion were observed, showing that no intermediate was present in the solution. The absorbance-subtraction also allows the concentration of $[Os_6(CO)_{18}]$ as a percentage of its initial concentration to be monitored. Changing the potential to +1.0 V allowed the regeneration of $[Os_6(CO)_{18}]$ in quantitative yield, as judged by a comparison of the intensities of the CO stretching modes, before and after the experiment.

The reduction of $[Os_6(CO)_{18}]$ can be easily carried out, either in a bulk electrolysis cell [6], or by chemical reduction [9], and the product solution transfered to an IR cell, so that the use of a thin layer electrolysis cell confers no obvious advantage. However, in our recent studies of the electrochemistry of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) [10] it was found that the two-electron-reduced species ($[Os_{10}C(CO)_{24}]^{4-}$ (**2**)) was extremely air sensitive, and it was impossible to obtain high quality IR spectra of **2** by conventional techniques, or to investigate the generation of intermediates during this reduction. In this instance, and in others where electrochemically-reduced products are very air sensitive, the use of a thin layer electrochemical cell allowing IR spectra to be obtained in situ is invaluable.

We have reported upon the electrochemistry of **1** [10–12]. In CH_2Cl_2/0.1 *M* TBAF a two electron reduction at −1.2 V is observed to split at low temperatures into a reversible one electron reduction (generation of $[Os_{10}C(CO)_{24}]^{3-}$ (**3**)), and this is followed by a further electrochemically irreversible one-electron reduction at more negative potentials (generation of $[Os_{10}C(CO)_{24}]^{4-}$ (**2**)). The second reduction showed slow heterogeneous charge transfer and was assumed to be associated with a structural change [10]. Using the techniques outlined above, a solution of CH_2Cl_2/0.5 *M* TBAF **1** (approx. 10^{-3} *M*) was made up and the original spectrum stored in one of the memories of the FTIR spectrometer (Fig. 2a) [13*]. The solution was then electrolysed at −1.2 V for ca. 10 min and the resulting spectrum was that of a mixture of products **1**, $[Os_{10}C(CO)_{24}]^{3-}$ (**3**) and $[Os_{10}C(CO)_{24}]^{4-}$ (**2**)) [10]. Using the absorbance-subtraction facility of the spectrometer the IR of **1** was

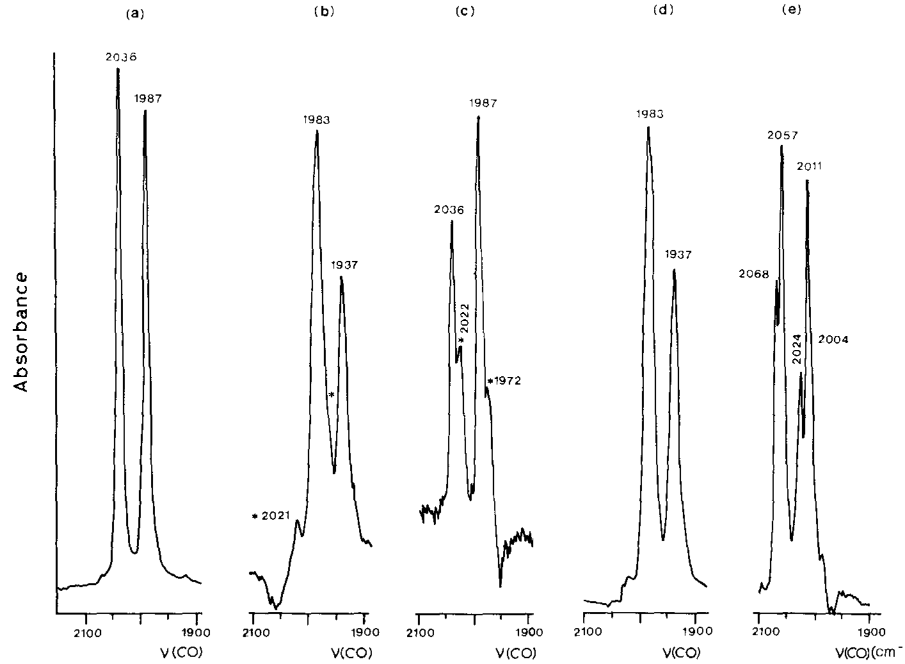

Fig. 2. IR spectra obtained from the electrochemical reduction and oxidation of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) in the TIRTEC; (a) to (d) inclusive are in CH_2Cl_2/0.5 *M* TBAF, while (e) is obtained in THF/0.4 *M* TBAF. Features marked with * in spectra (b) and (c) are due to $[Os_{10}C(CO)_{24}]^{3-}$ (**3**) generated as an intermediate at low concentration during the reduction of **1** to $[Os_{10}C(CO)_{24}]^{4-}$ (**2**). (a) Spectrum of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**). (b) Spectrum of product solution generated by electrolysing **1** at −1.2 V for five minutes and then absorbance subtracting out the spectrum of the residual **1**. Principle absorptions due to **2**. (c) Spectrum of product solution after reducing > 95% of the original **1** and then absorbance subtracting out the spectrum of the electrochemically generated **2**. Principle absorptions are due to residual **1**. (d) Spectrum of **2** generated by the exhaustive electrolysis of **1** at −1.6 V for 10 minutes. (e) Spectrum of the product solution after oxidising **1** in THF at +1.2 V for 15 minutes and then absorbance subtracting the spectrum of residual **1**. The main absorptions at 2057 and 2011 cm^{-1} are due to $[Os_{10}C(CO)_{24}]^{-}$ (**4**), while the weaker peaks at 2068 and 2024 cm^{-1} are due to $[Os_{10}C(CO)_{24}]$ (**5**).

subtracted out, to leave a spectrum consistent with a mixture of **2** with a small proportion of the trianion **3** (Fig. 2b). Alternatively the reduction can be continued until about 95% of **1** has been reduced, whereupon the spectrum of **2** can be subtracted out leaving a spectrum of a small percentage of **1** with the trianion **3** (Fig. 2c). This shows that upon reduction of **1**, a small concentration of trianion **3** is present as an intermediate at room temperature during the reduction to the tetraanion. However the amount of trianion present is never more than a few percent, and it was not possible to obtain high quality IR spectra of the trianion from this source. Electrolysis at −1.6 V for about 10 min generated a clean spectrum of $[Os_{10}C(CO)_{24}]^{4-}$ (**2**) (Fig. 2d). When the potential was adjusted to 0.0 V, the starting species **1** was generated in > 95% yield, showing that the reduction to **2** was chemically reversible.

Raising the potential to +1.0 V for about 10 min gave an IR spectrum that was consistent with the generation of the previously reported monoanion $[Os_{10}C(CO)_{24}]^-$ (**4**) [12]. Electrolysis at higher potentials caused the formation of some $[Os_{10}C(CO)_{24}]$ (**5**) [12], but this oxidized mixture could not be quantitatively reduced back to the starting material. This, and the lack of a clear spectrum of **5**, suggests that this product either decomposes or precipitates out onto the electrode as it is electrochemically generated.

Repeating the experiment using THF/0.4 *M* TBAF produced similar results on the reductive electrolyses. In this solvent no oxidation of **1** was observed until a potential of about +1.2 V was reached, and then a mixture of **4** and **5** was generated [12]. Subtraction of the spectrum of the residual **1** gave a good spectrum (Fig. 2e) of these mixed products. Raising the potential to +1.6 V did not drive all the cluster to the oxidized state, presumably because the potential was too close to the solvent background limit. However, in this solvent, reduction at 0.0 V did regenerate all the original cluster **1**, suggesting that oxidation to **5** was chemically reversible.

The similarity of the spectrum of $[Os_{10}C(CO)_{24}]^{4-}$ (**2**) to those of the other species mentioned here shows that upon reducing **1** by two electrons there is no great change in the tetrahedral symmetry. Certainly there is no change in geometry comparable to that in the reduction of $[Os_6(CO)_{18}]$ to the octahedral dianion [6], but close inspection of the IR spectrum of **2** does give some evidence for a slight change in structure upon reduction. The peaks for **1** and $[Os_{10}C(CO)_{24}]^-$ (**4**) show a consistent peak width at half maximum absorbance (fwhm) of 9–11 cm^{-1}. For $[Os_{10}C(CO)_{24}]^{4-}$ (**2**) this pattern is broken. The high frequency peak shows fwhm = 20 cm^{-1}, with some asymmetry on the low frequency side, while the low frequency peak shows a fwhm of 16 cm^{-1}. The two line spectrum of **1** is due to the highly symmetrical tetrahedral structure of this cluster [14]. The broadening of the absorptions in the spectrum of **2** are consistent with a fine splitting of these two principal absorptions. The extra peaks are poorly resolved owing to the highly polar solvent electrolyte mixtures required for the electrochemistry.

In continuation of our studies of large and medium sized osmium clusters containing interstitial atoms we have studied the electrochemistry of a hexaosmium interstitial phosphido cluster $[Os_6(CO)_{18}(P)]^-$ (**6**) [15] and several of its derivatives. The detailed electrochemistry will be described elsewhere [16] but these clusters generally show a two electron reduction with slow heterogeneous charge transfer to generate extremely air sensitive anionic products. Thus the conventional bulk

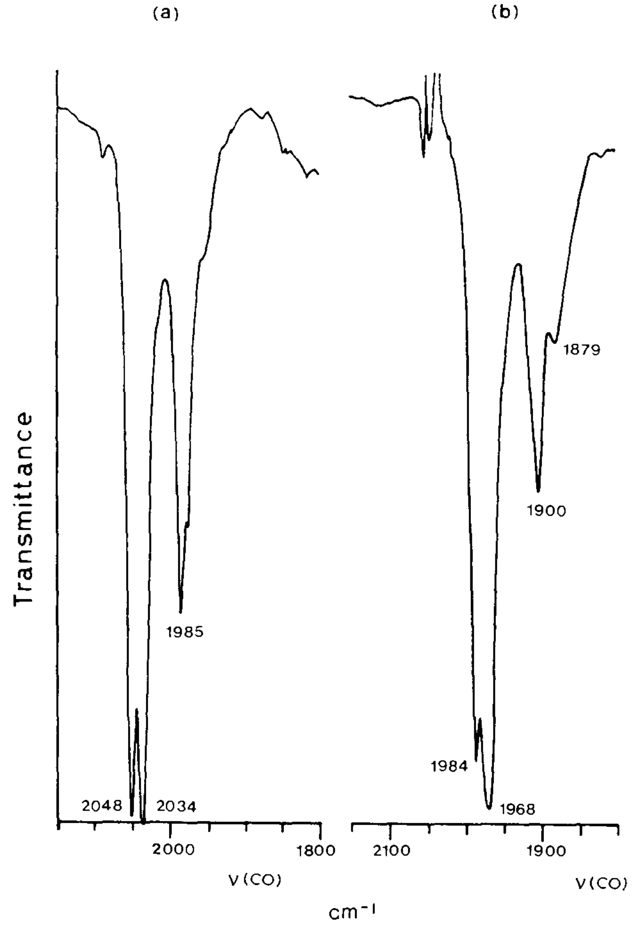

Fig. 3. IR spectra in transmittance mode in CH_2Cl_2/0.4 *M* TBAF of $[Os_6(CO)_{18}(P)]^-$ (**6**) and the reduced form $[Os_6(CO)_{18}(P)]^{3-}$ (**7**). (a) Spectrum of **6** before electrolysis. (b) Spectrum of **7** after electrolysis of **6** at −1.6 V and absorbance subtraction of the spectrum of the residual **6**. The noise between 2030 and 2050 cm^{-1} in this spectrum is an artifact of the absorbance subtraction process. The spectrum of **6** was regenerated after oxidation of this solution at 0.0 V.

reduction of $[Os_6(CO)_{18}(P)]^-$ (**6**) (IR spectrum Fig. 3a) at about −1.4 V generated $(Os_6(CO)_{18}(P)]^{3-}$ (**7**), the IR spectrum of which could not be obtained due to its air sensitivity. However electrochemical reduction of a sample of **6** in CH_2Cl_2/0.4 *M* TBAF at −1.6 V in the thin layer electrolysis cell gave the reduced species **7** together with a small proportion of starting material **6**. The spectrum of the residual **6** could be subtracted out to give a high quality spectrum of $[Os_6(CO)_{18}(P)]^{3-}$ (**7**) (Fig. 3b). The spectrum of the reduced species is surprisingly similar to that of the starting material although it is shifted about 65 cm^{-1} to lower frequency, consistent with the increased electron density upon the cluster. The dominant carbonyl stretching bands at 2048(s) and 2034(vs) cm^{-1} in the spectrum of the monoanion **6** have been assigned [16] to the *a″* mode of the axial carbonyls and an *e′* mode of the radial carbonyls respectively [15]. In the spectrum of trianion **7** (Fig. 3b), the *e′*

mode is not split, suggesting that the three-fold axis of the trigonal prism is still present, and the two bands have moved to low frequency by similar amounts. This, in turn, suggests that the two added electrons are highly delocalized over the cluster framework. Hence despite the electrochemically irreversible reduction for this interstitial phosphido cluster, there is no major change in structure upon reduction.

The cheap and easy-to-construct thin layer electrochemical cell described here can be of great value for the characterization by IR of air-sensitive reduced products generated electrochemically. It can also be used for the detection of intermediates generated during an electrochemical process.

Acknowledgements

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References

1 (a) W.R. Heineman, J. Chem. Educ., 60 (1983) 305; (b) R.W. Murray, W.R. Heineman and G.W. Dom, Analytical Chem., 39 (1967) 1666; (c) W.R. Heineman, T. Kuwana, and C.R. Hartzed, Biochem. Biophys. Res. Commun., 50 (1973) 892; (d) W.R. Heineman, Anal. Chem., 50 (1978) 390A; (e) D. Lancon and K.M. Kadish, J. Am. Chem. Soc., 105 (1983) 5610.

2 Southampton Electrochemistry Group, Instrumental Methods in Electrochemistry, Ellis Horwood, Chichester/England, 1985; Section 10.2.1 and references therein.

3 W.R. Heineman, J.N. Burnett, and R.W. Murray, Analytical Chem., 40 (1968) 1074.

4 The preparation of materials and the use of the equipment to run electrochemical experiments has been previously reported: see ref. 11. All potentials quoted are against a silver wire pseudoreference (potential approximately 0.3 V vs. standard hydrogen electrode under these experimental conditions) unless otherwise indicated. SCE, saturated calomel electrode; potential 0.24 V vs. standard hydrogen electrode.

5 C. LeVanda, K. Bechgaard, D.O. Cowan and M.D. Rausch, J. Am. Chem. Soc., 99 (1977) 2964.

6 B. Tulyathon, and W.E. Geiger, J. Am. Chem. Soc., 107 (1985) 5960.

7 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., 37 (1972) C39.

8 C.R. Eady, B.F.G. Johnson, J. Lewis, M.C. Malatesta, P. Machin and M. McPartlin, J. Chem. Soc. Chem. Commun., (1976) 945.

9 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun., (1976) 302.

10 M.H. Barley, S.R. Drake, B.F.G. Johnson, and J. Lewis, J. Chem. Soc. Chem. Commun., submitted.

11 S.R. Drake, M.H. Barley, B.F.G. Johnson, and J. Lewis, Organometallics, submitted.

12 S.R. Drake, B.F.G. Johnson, J. Lewis, and R.C.S. McQueen, J. Chem. Soc. Dalton Trans., (1987) 1051.

13 ν(CO) (in cm^{-1}) in CH_2Cl_2/0.5 *M* TBAF: (**1**) 2036, 1987; (**2**) 1983, 1937; (**3**) 2022, 1972; (**6**) 2048(s), 2034(vs), 1985(m), 1975(w); (7) 1984(s), 1968(vs), 1900(m), 1879(w); ν(CO) (in cm^{-1}) in THF/0.4 *M* TBAF: (**4**) 2057, 2011; (**5**) 2068, 2024. Some of these values may disagree with those previously reported because of the high electrolyte concentration used.

14 P.F. Jackson, B.F.G. Johnson, and J. Lewis, M. McPartlin, and W.J.H. Nelson, J. Chem. Soc. Chem. Commun., (1980) 224.

15 S.B. Colbran, C.M. Hay, B.F.G. Johnson, F.L. Lahoz, J. Lewis and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1986) 1766.

16 M.H. Barley, S.B. Colbran, C.E. Anson, B.F.G. Johnson and J. Lewis, to be published.