Inorganica Chimica Acta, *145* (1988) 141–147

Infrared Spectroscopic Studies of Aqueous Solutions of Dioxouranium(VI) and its Hydrolysed Products and of *in situ* Electro-generated Dioxouranium(V)

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(Received September 29, 1987)

Abstract

Aqueous solutions of dioxouranium(VI) (pH range 0 to 4) give rise to bands at 954 and 938 cm^{-1} attributable to the $\nu_3(MO_2)$ stretching modes of the UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ cations, respectively. A shoulder at 916 cm^{-1} is assigned to the $\nu_3(MO_2)$ mode of hydrolysed dioxouranium(VI) species of higher nuclearity. Infrared spectro-electrochemical studies using a thin-layer reflection-absorption cell have facilitated the study of the reduction of aqueous solutions of dioxouranium(VI) to yield dioxouranium(V) which may be further reduced to uranium(IV). The electrogeneration of dioxouranium(V) is monitored by following the increase in intensity of a band at 914 cm^{-1} which is present in the spectra at potentials between −0.2 and −0.8 V. The dioxouranium(V) species is predominantly in the form UO_2^+, which may be in solution or incorporated into an insoluble phase of uranium oxides which deposit onto the working electrode. The U^V–O bond length is estimated to be 1.76 Å, 0.03 Å longer than the U^{VI}–O bond in aqueous solution. The maximum concentration of UO_2^+ able to be achieved is highly dependent on the pH and is optimum at pH 3.4. Changes in the pH of the solution under study can be monitored by infrared spectroscopy during the course of the reduction by determining the relative concentrations of hydrolysed dioxouranium(VI) species.

Introduction

The richness of the aqueous chemistry of the actinides results from their having a wide range of accessible oxidation states each with a tendency to undergo hydrolysis. The chemistry of uranium is typical of this behaviour with oxidation states III to VI having been identified in aqueous solutions [1]. Indeed, under appropriate conditions of potential and pH, U^{VI} (yellow), U^{IV} (green), and U^{III} (red) are stable and predominant [2]. The U^V species forms only transiently during the reduction of dioxouranium(VI) and is likely to be in the form of a dioxo cation [3]. Uranium(V) is unstable partly because of its tendency to disproportionate at low pH [4–10] and partly from its desire to form polynuclear ions and polymers at high pH in the absence of strongly coordinating anions [5]. For these reasons, uranium(V) is the least defined state of uranium in terms of its chemistry and spectroscopy [11].

The ease of hydrolysis of uranium cations is found to decrease with decrease in the effective nuclear charge of the cation, *i.e.* in the order, $U^{4+} > UO_2^{2+} > U^{3+} > UO_2^+$ (unless otherwise specified solvent molecules occupy the coordination sites on the cations referred to in this paper). Specifically, dioxouranium(VI) is hydrolysed in aqueous solution to yield a complex mixture of mononuclear and polynuclear species whose relative abundance is highly dependent on the pH and the uranium(VI) concentration [12–14]. Therefore a necessary aspect of this study is the identification of the $\nu_3(MO_2)$ modes of the most important hydrolysed species of dioxouranium(VI) present in solution under the conditions of our experiments.

The existence of U^V was first deduced by Herasymenko [15] in the course of a polarographic study on the reduction of UO_2^{2+}; numerous such studies during the period 1940–50 have demonstrated the reversibility of the UO_2^{2+}/UO_2^+ couple and the disproportionation of UO_2^+. Kraus, Nelson, and Johnson [6] prepared millimolar solutions of UO_2^+ and demonstrated the reversibility of the disproportionation reaction as a function of pH and measured the visible spectrum of UO_2^+ between 300 and 1000 nm. The visible spectrum of UO_2^+ has been recorded in dimethylsulphoxide [16], in molten salt solutions [17], and in acidified saturated aqueous solutions of KCl and LiCl [18]. At higher pH (11–12) and in the presence of 1 to 3 M carbonate, the Raman [19] and visible [18] spectra of U^V have been recorded. Under these conditions the visible spectrum of dioxouranium(V) is different from that recorded for concentrated chloride media and is

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likely to be associated with complexed $\mathrm{UO_2^+}$ species. Consequently there are no reliable vibrational data for the $\mathrm{UO_2^+}$ species, and no vibrational data for any $\mathrm{U^V}$ species in aqueous solution in the absence of strongly coordinating anions. The aim of this report is to present infrared spectra of the $\mathrm{U^V}$ species formed from the electrochemical reduction of acidic solutions of dioxouranium(VI). Owing to the instability of $\mathrm{U^V}$ thus produced it has been necessary to study *in situ* electrogenerated species. Infrared spectroscopy has been chosen as the most appropriate technique since the band arising from the $\nu_3(\mathrm{MO_2})$ mode (asymmetric O–U–O stretch) is strong, and its wavenumber is known to be sensitive to the U–O bond strength [20, 21] and hence to the oxidation state and the nature of the inner coordination sphere of the metal atom.

Experimental

Solutions of dioxouranium(VI) were prepared by dissolving $\mathrm{UO_2(NO_3)_2 \cdot 6H_2O}$ (BDH) in water and adjusting the pH using nitric acid (15 M) or solid KOH (BDH). The pH measurements were performed using a standard combination pH electrode (Russell) which had been standardised using a pH 4.00 buffer (BDH). Solutions to be studied by infrared spectroscopy were degassed and prepared using $\mathrm{D_2O}$ (99.8% isotopic purity, Aldrich), water of crystallisation being removed by repeated solvent exchange (three times). Both $\mathrm{UO_2(NO_3)_2 \cdot 6H_2O}$ and KOH were used without further purification.

Voltammetric studies were carried out with a Metrohm E506 potentiostat utilising a three electrode geometry. Unless otherwise stated the platinum electrodes were constructed from the high purity metal (99.9% Johnson Matthey) either in the form of wire or foil (0.5 mm thick). In each case a saturated calomel electrode (Metrohm 6.0702.100) was used as the reference electrode. All potentials quoted were measured relative to this reference. Voltammograms recorded with a conventional electrochemical cell (Metrohm E505) also employed a platinum wire working electrode (Metrohm EA285) and a glassy carbon auxiliary electrode (Metrohm EA276/2), while those conducted with the spectroelectrochemical cell utilised a platinum disc working electrode (5 mm diameter) and a platinum wire auxiliary electrode. Cyclic voltammetric measurements also employed a Metrohm E612 VA scanner and a Tektronix 5D10 waveform digitiser.

Infrared spectra were recorded using a Bruker IFS 113V Fourier transform spectrometer, employing a cooled (78 K) mercury cadmium telluride detector and a germanium-coated potassium bromide beamsplitter. Solution spectra were recorded on thin films (*ca.* 1–5 μm) supported between sheets of low density polyethylene. For the infrared spectroelectrochemical experiments a modified infrared reflection-absorption spectroscopic (IRRAS) cell was used (Fig. 1). This cell differs from the usual design [22] in the following ways: (i) the working electrode is maintained in an horizontal disposition, (ii) the cell body and electrode sheath is constructed from teflon, (iii) the thickness of the thin film can be accurately and reproducibly adjusted using a micrometer, and (iv) the infrared transmitting window is easily demountable. The infrared beam was focused onto the working electrode and was collected using a modified specular reflectance attachment (Specac P/N 19.170) which enabled the infrared beam to be refocused onto the detector without altering the internal optics of the spectrometer. The potential of the working electrode relative to the reference electrode was controlled by a Metrohm E506 potentiostat. The platinum wire auxiliary electrode was looped around the teflon sheath holding the working electrode in order to minimise inhomogeneities of the potential across the working electrode. For each of the experiments the thickness of the film contained between the working electrode and the front window was adjusted to obtain a satisfactory balance between the solvent absorption and the intensities of the infrared-active bands being monitored. The films thus produced were *ca.* 0.5 to 2 μm thick. A potassium bromide window covered by a film of high density polyethylene provided a satisfactory method of containing the solution whilst maintaining a high throughput over the spectral region of interest.

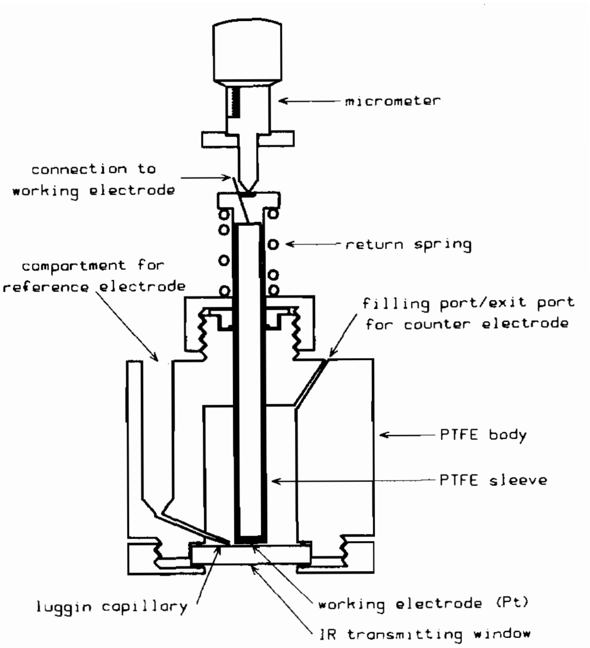

Fig. 1. Schematic diagram of the thin layer reflection/absorption cell for spectro-electrochemistry.

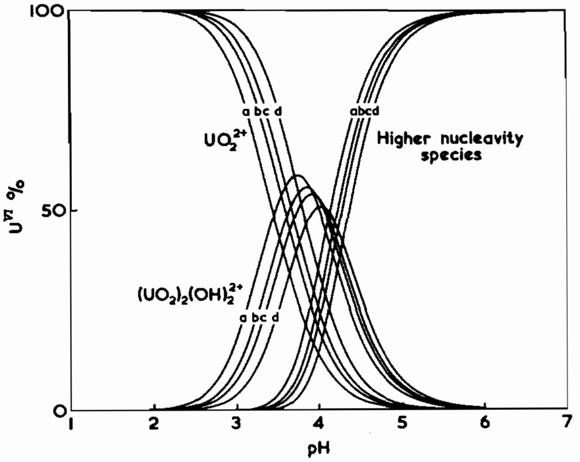

Fig. 2. Equilibrium distribution of dioxouranium(VI) as a function of pH and $[U^{VI}]_{total}$ based on the three-species model of Baes and Mesmer [14]. The equilibrium quotients for $(UO_2)_2(OH)_2^{2+}$ and higher nuclearity species are 8.83 × 10^{-7} and 1.56 × 10^{-17}, respectively. $[U^{VI}]_{total}$ are: (a) 0.30 (b) 0.15, (c) 0.10, and (d) 0.05 mol dm^{-3}.

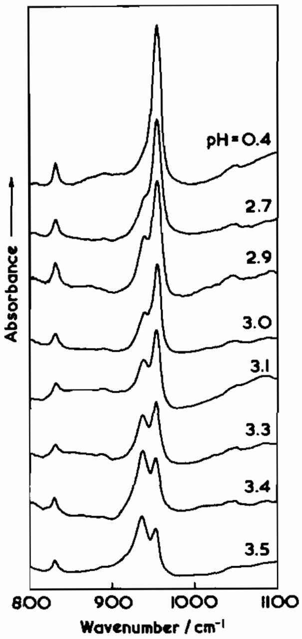

Fig. 3. FTIR spectra of aqueous solutions of dioxouranium(VI) (0.3 mol dm^{-3}).

Results and Discussion

(a) Dioxouranium(VI) Speciation at pH 0–4

The hydrolysis of dioxouranium(VI) is complex, with a recent potentiometric study requiring the existence of six species, *viz.* UO_2^{2+}, $(UO_2)(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_4(OH)_7^+$, to account adequately for the results under the conditions used [12]. For more concentrated uranium(VI) solutions (>0.1 M) the experimental data are adequately described by models with fewer species. Toth and Begun [13] accounted for their Raman data on the hydrolysis of dioxouranium(VI) using a three-species model based on the work of Baes and Mesmer [14]; however a more recent study supports the presence of other tri- and tetranuclear UO_2^{2+} species [12]. For clarity of presentation we will adopt the simpler three-species model for the analysis of the hydrolysis of dioxouranium(VI), *viz.* UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ where, instead of the $(UO_2)_3(OH)_5^+$ label, we use the term 'higher nuclearity species' since their form has not been reliably defined. The speciation calculated from the equilibrium quotients for dioxouranium(VI) over the appropriate concentration range is given in Fig. 2.

While the speciation of dioxouranium(VI) is most simple at low pH (<2) this is inappropriate for the study of U^V species since the disproportionation reaction, which has a pH dependent rate, is rapid under these conditions. The optimum pH range for the study is 2.8 to 3.4 since the disproportionation reaction is thereby inhibited, the presence of dioxouranium(VI) is detectable by infrared spectroscopy, and the speciation is relatively simple and is dominated by UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$.

The changes in the infrared spectrum as a result of changes in the speciation of dioxouranium(VI) are evident in the infrared spectra of deuteriated aqueous solutions of dioxouranium(VI) over the pH range 0 to 4 (Fig. 3). For pH less than two only UO_2^{2+} is expected to be present in solution in observable quantities (Fig. 2). A single band is observed at 954 cm^{-1}, in poor agreement with a previous solution study [23] (965 cm^{-1}); it is assigned to the $\nu_3(MO_2)$ mode of UO_2^{2+}. The discrepancy of 11 cm^{-1} is attributed to the different experimental conditions of the earlier study ($[UO_2^{2+}] = 1$ M, $[HClO_4] = 4$ M). As the pH of the solution is increased to 3.3 the band at 954 cm^{-1} decreases in intensity while a new feature grows into the spectrum at 938 cm^{-1}. The changes in the relative intensities of these two bands are in close agreement with the expected increase in the concentration of $(UO_2)_2(OH)_2^{2+}$ relative to that of UO_2^{2+} (Fig. 2). This leads us to assign the band at 938 cm^{-1} to the $\nu_2(MO_2)$ mode of the $(UO_2)_2(OH)_2^{2+}$ cation. Infrared spectra of the highest pH solutions (>3.3) exhibit a shoulder at 916 cm^{-1}. For pH greater than three a significant proportion of dioxouranium(VI) is expected to be in the form of higher nuclearity dioxouranium(VI) species (Fig. 2), bands from which should contribute to the spectrum. Accordingly the 916 cm^{-1} band is assigned to the $\nu_3(MO_2)$ mode of higher nuclearity dioxouranium(VI) species. The only other possible assignment of this band is to a mode of solid dioxouranium(VI) suspended in the solution; however this is unlikely since, on standing, hydrated dioxouranium(VI) precipitates from solutions of pH 3.4 and 3.5, and the spectra of such precipitates yield broad bands with no distinct maxima near 916 cm^{-1}. The likelihood that more than one species is responsible for this band is supported by its large full width at half height (fwhh) compared to that of the 938 and 954 cm^{-1} bands.

The above interpretation of the infrared spectra is supported by the close agreement of the speciation inferred from the spectra and that calculated from the equilibrium products (Fig. 2) at each pH. Furthermore the effect of hydrolysis of UO_2^{2+} on the ν_1-(MO_2) (symmetric O–M–O stretch) [13] and the $\nu_3(MO_2)$ modes is similar. The shifts of the ν_1 and $\nu_3(MO_2)$ modes of UO_2^{2+} on formation of $(UO_2)_2(OH)_2^{2+}$ are 18 and 16 cm^{-1}, respectively, and on formation of higher nuclearity species are 33 and 38 cm^{-1}, respectively. Therefore the different hydrolysed products of dioxouranium(VI), particularly UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$, can be distinguished by infrared spectroscopy. Since the speciation is particularly sensitive in the pH range 2 to 4, the pH of the solution can be monitored by the use of infrared spectroscopy provided that spectra are recorded after the solutions have attained equilibrium. The $UO_2^{2+}/(UO_2)_2(OH)_2^{2+}$ equilibrium is reported to be established rapidly [14], having a second-order rate constant for dimerisation of *ca.* 100 M^{-1} s^{-1}. The approach to equilibrium of even a complex reversible reaction is first order provided that the perturbation is small. For the experimental conditions of $[U^{VI}]_{total} = 0.3$ M, pH = 3.2, and ionic strength = 1.9, the first-order rate constant for the return to equilibrium is calculated to be *ca.* 10^3 s^{-1}, according to the procedure outlined in ref. 24. This corresponds to a half-life in the millisecond region. Since the acquisition time of a single interferogram is 0.8 s, and each spectrum is calculated from ten co-added interferograms, equilibrium concentrations of UO_2^{2+} relative to $(UO_2)_2(OH)_2^{2+}$ can be inferred from the spectra. Therefore the pH of the thin film of solution can be reliably deduced from the infrared spectra.

(b) FTIR Spectro-Electrochemisty

The pH sensitivity of the chemistry of dioxouranium(VI) is relevant to the thin-layer electrochemical experiment since changes in the pH of the aqueous thin layer may occur as the potential of the working electrode is changed. Furthermore, given the conditions of pH and U^{VI} concentration which are optimal for the stabilisation of dioxouranium(V), a small change in pH will have a significant effect on the speciation. Under the conditions of our experiments the stabilisation of U^V by the formation of U^{VI}–U^V dimers may be important [8, 10] so it is desirable to identify the electroactive species, UO_2^{2+} and/or $(UO_2)_2(OH)_2^{2+}$, which foreshadow a stable U^V cation. The resolution of these aspects of the U^{VI}/U^V couple require that the pH of the thin layer of solution in contact with the working electrode is known accurately; this is possible (see above) in the infrared spectro-electrochemical experiment.

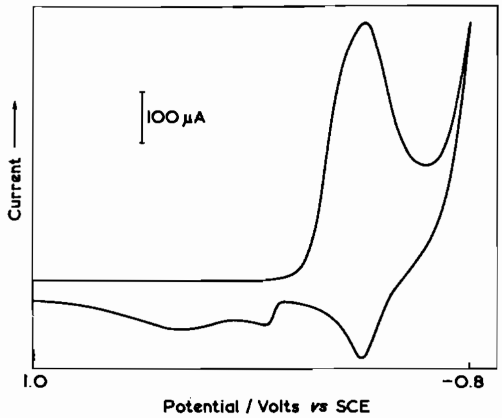

Fig. 4. Cyclic voltammogram of the reduction of dioxouranium(VI). Conditions: concentration 0.3 mol dm^{-3}, KNO_3 supporting electrolyte (2 mol dm^{-3}), pH 3.4, Pt working and saturated calomel reference electrodes, sweep speed 100 mV s^{-1}.

Cyclic voltammograms of dioxouranium(VI) (0.3 M, pH 3.4) on a platinum working electrode indicate highly irreversible behaviour (Fig. 4). The one-electron reduction wave (−0.37 V) is clearly asymmetric, probably as a result of the presence of significant concentrations of both UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ in the solution. Two return waves which are broad and weak are observed for this reduction, at 0.04 and 0.39 V. Their form is sensitive to whether or not the switching potential is sufficiently cathodic to drive the second reduction. The anodic peak at −0.36 V occurs only when the switching potential is more negative than −0.6 V. In addition to the observation of highly irreversible voltammograms, we find that repeated sweeping of the potential results in a loss of current response. This passivation of the electrode may result from the deposition of a solid phase on the electrode surface. The nature of the solid phase cannot be easily inferred from the cyclic voltammetric results, but the potential of the second reduction (*ca.* −1 V) is close to that observed for the U^V/U^{IV} couple on mercury (−0.92 V) [25] and may therefore indicate that some form of U^V is present either in solution or incorporated into the solid phase.

The IRRAS spectra of a thin film of a deuteriated dioxouranium(VI) solution (0.3 M, pH 3.3) were recorded as a function of applied potential. Spectra were recorded at 300 s intervals after the potential was stepped by −0.2 V from an initial potential of

1.0 V. Little change is evident in the spectra until the potential is reduced to −0.2 V whereupon the dioxouranium(VI) features at 938 and 954 cm^{-1} are diminished while a new band at 914 cm^{-1} grows into the spectrum. Further reduction in the potential, to −0.6 V, results in the complete removal of the 938 and 954 cm^{-1} bands. Yet further reduction in the potential (−0.8 to −1.0 V) leads to the removal of the band at 914 cm^{-1}.

In these experiments we find that the intensity of the 914 cm^{-1} band is sensitive to the condition of the electrode. When a freshly polished electrode is used only a modest increase in absorption at 914 cm^{-1} is observed on reduction of dioxouranium(VI), whereas repeat experiments lead to a much more pronounced feature at this wavenumber. These observations are in keeping with the cyclic voltammetry where highly irreversible electrochemical behaviour is observed at a platinum electrode. Initial sweeping of the electrode to potentials more cathodic than −0.4 V leads to the formation of a uranium–oxide-modified platinum electrode at which the stability of the one-electron reduced form of UO_2^{2+} is evidently greater.

The assignment of the 914 cm^{-1} band to some species which involves U^V is strongly implied by the coincidence between the potential and pH range over which U^V is likely to be stable [2] and the intensity of the 914 cm^{-1} band in the spectrum. Since this is a region expected for dioxo-species the 914 cm^{-1} band is assigned to the $\nu_3(MO_2)$ mode of dioxouranium(V) either in solution or in a solid phase deposited onto the electrode. The only alternative assignment of the band is to extensively hydrolysed dioxouranium(VI); however, this would be unreasonable since it would require a massive increase in the pH of the thin layer on stepping the potential from 0.0 to −0.2 V. No such increase in the pH is indicated by the relative intensities of the 938 and 954 cm^{-1} bands; indeed, if anything, the pH of the thin film is lowered with this potential step. Such a decrease in the pH is expected and results from the electrode polarising the solution. The assignment of the 914 cm^{-1} band to the $\nu_3(MO_2)$ mode of dioxouranium(V) is supported by a similar experiment using a dioxouranium(VI) solution of lower pH (1.0). Under these conditions the disproportionation reaction is sufficiently rapid as to preclude the observation of dioxouranium(V). The potential of the UO_2^{2+}/UO_2^{+} couple is insensitive to pH and occurs at −0.18 V. In this experiment the removal of UO_2^{2+} occurred at −0.2 V, this time without the appearance of the 914 cm^{-1} band.

Both the wavenumber and the fwhh of the 914 cm^{-1} band merit further comment. Neptunium and americium form reasonably stable penta- and hexavalent dioxo ions, MO_2^{n+}, which have been studied by infrared spectroscopy [23]. The $\nu_3(MO_2)$ mode of NpO_2^{+} occurs 145 cm^{-1} to lower wavenumber than the corresponding mode of NpO_2^{2+}. For americium the corresponding difference is 107 cm^{-1}. Our results indicate a relatively modest difference of 40 cm^{-1} for uranium. The fwhh of the 914 cm^{-1} band is *ca.* 3 times that of the band arising from the $\nu_3(MO_2)$ mode of UO_2^{2+}. This may be interpreted: (i) as the normal bandwidth of the $\nu_3(MO_2)$ mode of UO_2^{+}, (ii) to be a consequence of there being a range of species in solution, or (iii) to result from the incorporation of UO_2^{+} into a solid phase. We note that the first possibility cannot be dismissed since the $\nu_3(MO_2)$ bands of AmO_2^{+} and NpO_2^{+} are similarly broad compared to those of AmO_2^{2+} and NpO_2^{2+}, respectively [23]. Since the pK_a of UO_2^{+} is much higher than that of UO_2^{2+} (estimated by comparison with those of dioxoions of Am and Np [6]) the presence of hydrolysed UO_2^{+} species is ruled out under the conditions of these experiments; therefore the species referred to in (ii) must be of a mixed valence type, e.g. $(UO_2)_2^{3+}$.

In order better to characterise the chemistry accompanying the electrochemical reduction and to determine the form of the electrogenerated dioxouranium(V), a series of time-resolved experiments was performed at an electrode surface modified by stepping the potential to −0.6 V for *ca.* 30 s then returning the potential to +0.4 V. The thin film of solution was then flushed several times whereupon spectra were recorded at 16 s intervals. After collection of the first spectrum the potential was stepped to −0.4 V. Two such experiments were conducted on dioxouranium(VI) solutions (0.3 M) of different pH (3.2 and 3.4) and are shown in Fig. 5. The rate of reduction of dioxouranium(VI) was found to be faster for solutions of higher pH. In each case the potential step is accompanied by a reduction in the pH of the thin film. The maximum achievable concentration of dioxouranium(V) is extremely sensitive to the pH and in none of the experiments was there quantitative conversion of dioxouranium(VI) to dioxouranium(V). Owing to the rapid equilibration of UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$, even after allowing for differential rates of depletion of the species at the electrode surface, no comment can be made regarding the relative importance of UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ in generating a stable dioxouranium(V) species. These spectra suggest that the band at 914 cm^{-1} does not arise from $(UO_2)_2^{3+}$ since the form of the band does not change in the course of the reduction, even on exhaustive depletion of dioxouranium(VI). The ease of reduction of $(UO_2)_2^{3+}$ to dioxouranium(V) is demonstrated by stopped flow studies of the reduction of UO_2^{2+} by stoichiometric quantities of Eu^{2+} [8, 10], experiments in which UO_2^{2+} is quantitatively reduced. If only half the quantity of Eu^{2+} is used, the $(UO_2)_2^{3+}$ species is formed. Therefore the potential applied

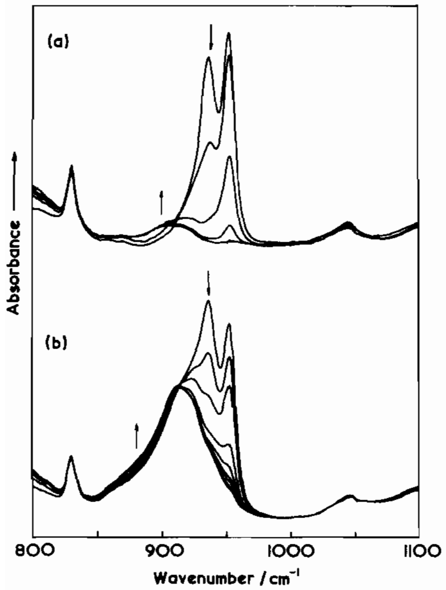

Fig. 5. Time-resolved infrared spectra of the reduction of dioxouranium(VI) solutions of pH 3.2 (a) and 3.4 (b). Initial potential 0.2 V, step potential −0.6 V. Time between spectra *ca.* 16 s.

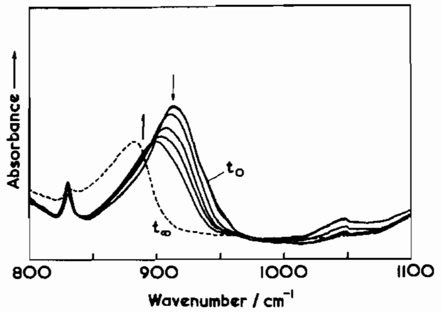

Fig. 6. Time-resolved infrared spectra of the reduction of dioxouranium(V) (same solution as for Fig. 5b). Initial potential at $t_0 = -0.6$ V, final potential = −1.0 V. Time between spectra *ca.* 30 s. The spectrum at t_∞ was recorded after the potential was stepped from −0.6 to −1.0 V.

to the working electrode is sufficient to reduce any $(UO_2)_2^{3+}$ formed and, were the 914 cm^{-1} band to arise from that species, changes in its band wavenumber and profile would be observable as the dioxouranium(VI) is completely reduced. The time-resolved spectra of the reduction of UO_2^+ (−1.2 V) are shown in Fig. 6. The time between the spectra is 30 s.

While the reduction of UO_2^{2+} to UO_2^+ is expected to be faster than that of UO_2^+ to U^{4+}, on account of the greater structural change which accompanies the second reduction, the slow rate of reduction results from passivation of the electrode by the deposition of a solid film of uranium oxides. This conclusion is supported by the similarly slow rate of reoxidation of UO_2^+. It is unclear from these results whether the UO_2^+ produced resides in solution or is incorporated into the solid film. Reduction of UO_2^{2+} at a freshly cleaned platinum electrode results in the deposition of a film of uranium oxides with the formation of, at best, only small quantities of UO_2^+, but reduction of a fresh solution of UO_2^{2+} at the modified electrode leads to the formation of measurable quantities of UO_2^+. The reduction of the uranyl species at a potential of −1 V leads to a general increase in absorption below 900 cm^{-1}, often with a feature at 883 cm^{-1}. The general increase in absorption is consistent with the deposition of a solid phase of uranium oxide (probably UO_2). The feature at 883 cm^{-1} may suggest the presence of dioxouranium(IV) species incorporated into the solid film, but such an assignment would be speculative at this stage. The similarity of the half-widths of the features at 883 and 914 cm^{-1} suggests that the dioxouranium(V) species may similarly be incorporated into a solid phase.

Conclusion

The highly irreversible reduction of UO_2^{2+} at a platinum electrode results from the rapid decomposition of the electrogenerated dioxouranium(V) species which leads to the deposition of an insoluble film of uranium oxides. Subsequent to this modification of the electrode surface, dioxouranium(VI) is reduced to UO_2^+. We are unable to establish whether the unstable UO_2^+ species resides in solution or is incorporated into the oxide film.

The wavenumber of the $\nu_3(MO_2)$ mode of UO_2^+ (914 cm^{-1}) is significantly higher than those reported for AmO_2^+ (832 cm^{-1}) and NpO_2^+ (824 cm^{-1}). The U^V–O bond length is estimated to be 1.76 Å based on the empirical relation given in eqn. (1) [20, 21]. Under the same conditions the U^{VI}–O bond length

$$R_{U-O} = 81.2\nu_3^{-2/3}(MO_2) + 0.895 \qquad (1)$$

is estimated to be 1.73 Å, indicating a 0.03 Å lengthening of the bond on reduction. No evidence for the formation of significant concentrations of $(UO_2)_2^{3+}$ were obtained from our studies.

This study demonstrates the advantages of *in situ* spectro-electochemical techniques in identifying unstable chemical species which are not able to be isolated from solution. It is clear that the application of spectroscopic techniques, particularly vibrational spectroscopic ones, to electrochemistry is of particular importance owing to the variety of chromophores on show and their ease of identification.

Acknowledgements

S.P.B. gratefully acknowledges the Ramsay Memorial Fellowships Trust for the award of a fellowship. R.P.C. is indebted to the University of Newcastle (Australia) for the study leave during which this work was started.

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