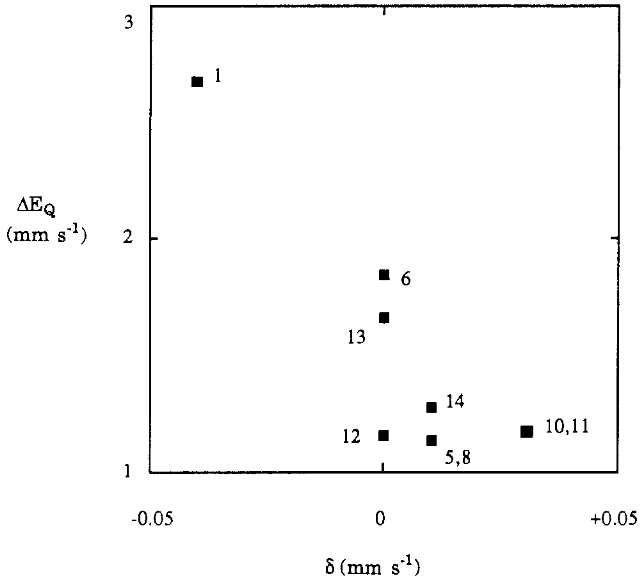

Figure 2. Plot of isomer shift vs quadrupole splitting at 77 K for μ-carbido iron(IV) phthalocyanine complexes.

to each other about each $Fe^{IV}Pc$ macrocyclic moiety. The precise ordering and separations of the single-ion energy levels appropriate to a $[(CN)Fe^{IV}(Pc)C]$ fragment are very difficult to obtain experimentally but are likely to be different from those generated by fragments such as $[pyFe^{IV}(Pc)C]$, $[(thf)Fe^{IV}(Pc)C]$, and $[FFe^{IV}(Pc)C]$ found in **5**, **6**, and **8**.

One of the interesting observations to emerge from the present δ and ΔE_Q values is their close similarity to those determined for the Fe^{IV} forms of iron proteins such as horseradish peroxidase, chloroperoxidase, etc. (**15–18**).[7,8,11,14,15] It is now reasonably well established[16] that compounds I and II of these proteins contain oxoiron(IV) porphyrin centers of the kinds $OFe^{IV}(P^{\bullet+})$ and $OFe^{IV}(P)$, respectively, each bonded to the protein via a sixth axial "ligand".[7,8,11] $P^{\bullet+}$ represents the π cation radical form of the heme group, the same oxidation level as that found in the present Pc(1−) complexes **12–14**. There are a small number of synthetic model porphyrin–Fe^{IV} compounds available to compare with these high-valent iron enzymes, the best known being the complexes $[OFe^{IV}(TPP)(N\text{-Meimd})]$[17,18] and $[(MeO)_2Fe^{IV}(TMP)]$,[11] which contain the normal dinegatively charged porphyrin ligand, and $[OFe^{IV}(TMP^{\bullet+})]$, which contains the π cation radical form of the sterically hindered tetramesitylporphyrin ligand.[19] Binuclear μ-nitrido and μ-carbido iron(IV) porphyrins have also been studied in some detail.[8,20]

The IR and visible spectra and the electrochemical properties of complexes **12–14** clearly show that they contain the Pc(1−) (i.e. $(Pc^{\bullet+})$) π cation radical form of the phthalocyanine ligand.[10] Further confirmation of ligand-centered oxidation is evident in the Mössbauer data in Table I, where it can be seen that the δ and ΔE_Q values are very similar to those of the $Fe^{IV}Pc(2-)$ species.

Lang et al. have recently shown, by means of applied-field Mössbauer studies and a crystal-field ($S = 1$ spin Hamiltonian) model for the low-spin Fe^{IV} centers in the heme enzymes and porphyrin models, that a rather uniform relationship between δ and ΔE_Q values exists.[11,19] This, in turn, was proposed to be related to differences in d_{z^2}-bonding electron density (where z is the Fe═O direction). The present zero-field Mössbauer data generally seem to fit into this interpretation although a plot of δ vs ΔE_Q, while reasonably linear (Figure 2), shows a steeper slope than does the analogous iron porphyrin plot presented in ref 11b. This may be a result of comparing OFe(porph)L with CFe(Pc)L. The values for **1**, for instance, would suggest that the $Fe^{IV}(Pc(2-))C$ core produces very small d_{z^2}-bonding density and the electric field gradient at Fe arises essentially from contributions by the valence electrons alone.[11] The other axially ligated complexes show increased d_{z^2}-bonding electron density. The cyano complex, **9**, does not fit this model, possibly because of CN^- π-bonding effects and/or a markedly different overall crystal-field splitting, alluded to earlier.

Acknowledgment. We wish to thank Associate Professor J. D. Cashion (Department of Physics, Monash University) for access to Mössbauer facilities and fitting programs. K.S.M. acknowledges financial support from the Australian Research Grants Scheme and Monash University Special Research Grants.

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(24) A reviewer suggested that some of the $Fe^{IV}Pc$ fragments in these binuclear species might have spin-paired, $S = 0$, spin states. While this is possible, it is unlikely in view of the $S = 1$ states displayed by Fe(IV) porphyrins and the nonzero μ_{Fe} values observed. Ongoing applied-field Mössbauer and variable-temperature susceptibility studies should help clarify matters.

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Electrochemical Oxidation of Ruthenium(IV) at Platinum Rotating Disk Electrodes: Preparation and Characterization of a Tetrameric Ruthenium(4.25) Species

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Received May 27, 1987

Ruthenium(IV) exists in noncomplexing acid media, e.g. perchloric acid solutions, as a tetrameric ion formulated as $Ru_4(OH)_{12}{}^{4+}$.[1,2] The evidence for the existence of this species and its redox chemistry have been reviewed recently.[3] The electrochemical reduction of $Ru_4(OH)_{12}{}^{4+}$ on noble metal electrodes[1,4] and mercury electrodes[5,6] has been investigated in detail and is now fairly well understood. However, much less work has been performed on the anodic oxidation of ruthenium(IV), despite the fact that several literature reports suggest the existence of a ruthenium(4.25) species.[7-11] Wehner and Hindman[7] observed

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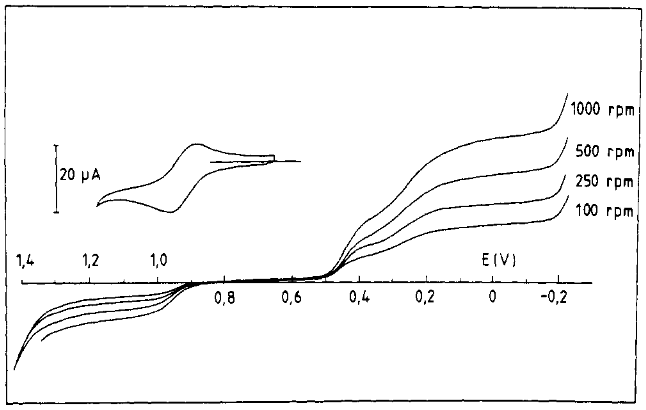

Figure 1. Reduction/oxidation of $Ru_4(OH)_{12}^{4+}$ in 1.0 M $HClO_4$ solution at a platinum rotating disk electrode (also shown is a cyclic voltammogram started from 0.650 V vs SCE to more positive potentials). The analytical concentration of ruthenium(IV) is 5×10^{-3} M.

a sharp potential break during the electrolytic reduction of RuO_4 in perchloric acid solutions at platinum electrodes after passing 3.7–3.8 F/mol of ruthenium, thus indicating the formation of a species with valence of 4.2–4.3. Cady[8] observed valences of 4.2, 4.25, 4.28, and 4.38 upon the cerimetric oxidation of ruthenium(IV) in perchloric and trifluoroacetic acids. Avdeev et al.[9,10] obtained a black hydrous oxide (claimed to be $Ru_2O_5 \cdot mH_2O$) by the electrolytic reduction of RuO_4 in 0.5 M sulfuric acid solutions on platinum electrodes: this solid phase is insoluble in water and in sulfuric acid solutions but reacts with ruthenium(IV) in sulfuric acid solutions to form a solute species with an average valence of 4.2 ± 0.1. Maya[11] studied the electrochemical oxidation of ruthenium(IV) in nitric acid solutions and calculated the valence of the oxidation product as 4.38 from his cyclic voltammetric data. As argued by Rard[3] in his review, these valences are uncertain by about 0.1 unit and all these data probably point to the existence of the same species with valence 4.25, this value being the most plausible since ruthenium(IV) exists as a tetrameric ion.

This paper reports the results of a voltammetric study of the anodic oxidation of $Ru_4(OH)_{12}^{4+}$ at the platinum rotating disk electrode. Evidence is presented that the product is a tetrameric ruthenium(4.25) ion, formulated as $Ru_4(OH)_{12}^{5+}$, at least in the more acidic solutions. Furthermore, this species was prepared by controlled-potential coulometry and characterized by absorption spectrometry.

Experimental Section

Ruthenium(IV) in $HClO_4/NaClO_4$ solutions of constant ionic strength (μ = 1.0 M) was prepared and analyzed as described previously.[4]

Voltammetric experiments were performed in a conventional three-compartment cell with a Tacussel Model EDI (0–5000 rpm) platinum rotating disk electrode (the same electrode was used in the nonrotating mode for cyclic voltammetry). The solutions were desoxygenated with a stream of purified argon (presaturated with water). A small electrolytic cell (volume of the working electrode compartment: 2–4 cm^3) with a platinum-gauze working electrode was used for controlled-potential coulometry and potentiometric experiments; a larger cell with a 5 × 5 cm^2 platinum electrode was used for the electrolytic preparation of larger volumes of ruthenium(4.25) used for voltammetric experiments. The reference electrode is a NaCl-saturated calomel electrode (the standard potential of this electrode ($E^{\circ\prime} + E_j$) is 0.236 V vs NHE[12]): unless indicated otherwise, all the potentials in this paper, including the values taken from the literature, are expressed against this common reference electrode for the sake of comparison. The counter electrode (a coiled platinum wire in a $HClO_4/NaClO_4$ solution) was separated from the solution by a fritted-glass disk. The electrochemical instrumentation consisted of a PAR Model 173/179 potentiostat/digital coulometer, a PAR Model 175 function generator, and a Houston Model 2000 XY-recorder. All experiments were performed at 25 ± 1 °C.

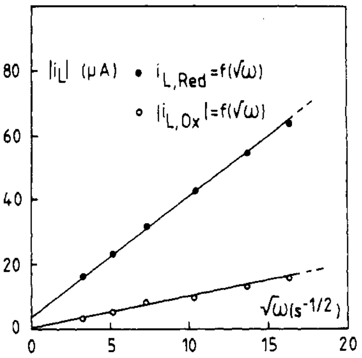

Figure 2. Plots of $i_{L,red}$ (the sum of the limiting currents of both reduction waves) and $|i_{L,ox}|$ vs $\omega^{1/2}$ for the reduction/oxidation of $Ru_4(OH)_{12}^{4+}$ in 1.0 M $HClO_4$ solution at a platinum rotating disk electrode. The analytical concentration of ruthenium(IV) is 5×10^{-3} M.

Absorption spectra were recorded on a Pye Unicam Model 8800 UV/VIS spectrophotometer using 1 cm quartz cells against a reference of the appropriate $HClO_4/NaClO_4$ solution. Irradiation experiments were carried out with a low-pressure mercury arc (98% radiation at 254 nm).

Results and Discussion

A series of voltammograms for the reduction/oxidation of $Ru_4(OH)_{12}^{4+}$ in 1.0 M $HClO_4$ at the platinum rotating disk electrode is shown in Figure 1 (also shown is a cyclic voltammogram started from 0.650 V vs SCE to more positive potentials). The voltammograms exhibit two reversible waves for the reduction steps Ru(IV) → Ru(3.5) → Ru(III) as described previously[4] (each wave is the sum of two one-electron processes and involves the formation of tetrameric ruthenium(3.75) and ruthenium(3.25) as intermediate species). Furthermore, the voltammograms exhibit a smaller but well-defined oxidation wave with a half-wave potential $E_{1/2}$ of ±0.950–0.960 V vs SCE (100 rpm; the half-wave potentials shift slightly to more positive values with increasing rotation rate). Oxygen evolution in 1.0 M $HClO_4$ solution starts at about 1.500 V vs SCE, but this potential is some 0.250–0.300 V less positive in solutions containing ruthenium(IV). Lowering of the oxygen overvoltage on platinum electrodes in the presence of ruthenium salts has been reported previously by Burke et al.[13,14] The value of the half-wave potential of the anodic wave is in good agreement with the values reported by Avdeev et al.[9] and Maya[11] for the oxidation of ruthenium(IV) in sulfuric and nitric acid solutions, respectively. Thus, Avdeev et al.[9] observed an oxidation wave with half-wave potential $E_{1/2}$ = 0.945 V vs SCE for the oxidation of ruthenium(IV) in 0.5 M H_2SO_4 solutions at platinum electrodes (the half-wave potential of the corresponding reduction wave was reported as $E_{1/2}$ = 0.855 V). These workers concluded that this wave is irreversible and involves one electron per ruthenium atom, but the electrode reaction was attributed to a ruthenium(V)/ruthenium(IV) redox couple involving a solid hydrous ruthenium(V) oxide and a monomeric ruthenyl ion ($Ru_2O_5 + 6H^+ + 2e^- \rightarrow 2RuO^{2+} + 3H_2O$). Maya[11] observed a redox process at 0.920 V vs SCE in the cyclic voltammogram of ruthenium(IV) in 0.1 M HNO_3/0.9 $NaNO_3$ solutions, in addition to redox reactions at 0.330 and 0.150 V, which must correspond with the redox couples ruthenium(IV)/ruthenium(3.5) and ruthenium(3.5)/ruthenium(III).[4] The number of electrons involved in the electrode reaction at 0.920 V vs SCE was calculated from the peak currents as 0.38 electron/ruthenium atom, but no further information was obtained about the nature of the oxidation

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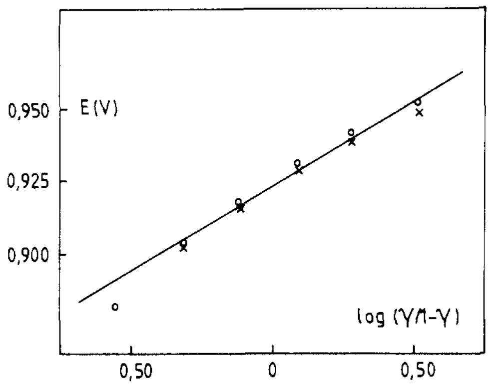

Figure 3. Plot of the equilibrium potential E vs log [ruthenium(4.25)]/[ruthenium(IV)] (actually shown in the abscissa is log ($\gamma/(1 - \gamma)$), with $\gamma = Q/Q_\infty$ where Q and Q_∞ respectively are the charge passed and the charge needed for the complete oxidation of a $Ru_4(OH)_{12}^{4+}$ solution.

product.[15] The limiting current at the rotating disk electrode is given by the Levich equation[16]

$$|i_L| = 0.620\ nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C \qquad (1)$$

where all the symbols have their usual meaning (by convention a reduction current is positive and an oxidation current is negative). Plots of $i_{L,red}$ (the sum of the limiting currents of both reduction waves) and $|i_{L,ox}|$ vs $\omega^{1/2}$ are shown in Figure 2. The limiting currents increase linearly with $\omega^{1/2}$ as expected from eq 1 and also depend linearly on the concentration of ruthenium(IV) over the range investigated (5×10^{-3} to 10^{-4} M, analytical concentrations). The value of the diffusion coefficient of ruthenium(IV) was calculated as $D = 2.48 \times 10^{-6}$ cm^2/s from the data of Figure 2 (the value reported in a previous paper[4] ($D = 4.1 \times 10^{-6}$ cm^2/s) is too high due to a computational error). The ratio of the slopes $(|i_{L,ox}|/\omega^{1/2})/(i_{L,red}/\omega^{1/2}) = n_{ox}/n_{red} = 0.26 \pm 0.01$. This result shows that the oxidation wave involves 1 electron/$Ru_4(OH)_{12}^{4+}$ ion (0.25 electron/ruthenium atom) and thus strongly suggests the formation of a ruthenium(4.25) species. This conclusion was confirmed directly by controlled potential coulometry (1.150 V vs SCE). A plot of log $|i|$ vs time is linear as is expected for a simple electron-transfer reaction without any complications by chemical reactions:[17] the charge involved in the oxidation reaction was calculated after a slight background correction as 0.25 ± 0.02 electron/ruthenium atom, thus confirming the results of the voltammetric experiments and indicating that the oxidation product is a rather stable species, at least on the time scale of the controlled-potential coulometry experiments.[18]

Direct evidence that the oxidation product is indeed a tetrameric ruthenium(4.25) ion was obtained from potentiometric measurements during the coulometric titration of a ruthenium(IV) solution. Thus, a plot of the equilibrium potential E vs log ($\gamma/(1 - \gamma)$), with $\gamma = Q/Q_\infty$ (Q and Q_∞ are respectively the charge passed during coulometry and the charge needed for complete oxidation) is linear with a slope of 0.059 ± 0.002 V/decade as is shown in Figure 3 (theoretical value of the slope for a one-electron process is 0.059 V/decade). This behavior is expected for a simple one-electron-redox reaction that does not involve a change in the degree of polymerization of the oxidized and the reduced species. The same conclusion can be reached from the fact that the half-wave potential of the oxidation wave is independent of the analytical ruthenium(IV) concentration.[19]

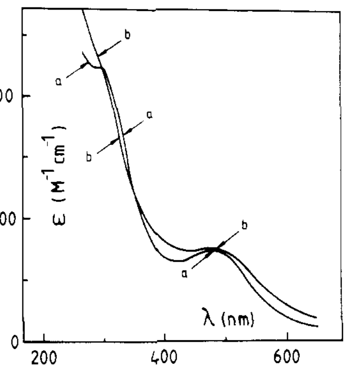

Figure 4. UV–visible absorption spectrum of ruthenium(IV) (a) and of ruthenium(4.25) (b) in 1.0 M $HClO_4$ solution (spectrum b was recorded after exhaustive electrolysis of a $Ru_4(OH)_{12}^{4+}$ solution (1.150 V vs SCE)).

Furthermore, the half-wave potential of the oxidation wave is almost independent of the solution acidity: thus, at constant rotation rate, the experimentally measured half-wave potentials decrease by ~0.020 V with increasing solution acidity over the range $1 \le pcH \le 0$, but for the larger part this decrease can be accounted for by the variation of the liquid-junction potential with the acid concentration (the liquid-junction potential between a 1.0 M $HClO_4$ solution and the saturated calomel electrode is estimated as 0.017 V[20] but this value decreases rapidly with decreasing solution acidity). Therefore, the oxidation product is a tetrameric ruthenium(4.25) species formulated as $Ru_4(OH)_{12}^{5+}$, at least in the more acidic solutions, and the electrode reaction for the ruthenium(4.25)/ruthenium(IV) redox couple can simply be written as

$$Ru_4(OH)_{12}^{5+} + e^- \rightleftharpoons Ru_4(OH)_{12}^{4+} \qquad (2)$$

The formal standard potential of this redox couple in 1.0 M $HClO_4$ solutions is determined from the potentiometric measurements in Figure 3 as $E^{\circ\prime} = 0.925 \pm 0.005$ V vs SCE; therefore, the standard potential of the ruthenium(4.25)/ruthenium(IV) couple is estimated as 1.160 ± 0.010 V vs NHE.

It must be noted that ruthenium(IV) is usually formulated as $Ru_4(OH)_{12}^{4+}$, but there are indications that more hydrolyzed

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[15] Actually, Maya[11] calculated his value of 0.38 electron/ruthenium atom by assuming a reversible electrode process and a value of $D = 10^{-5}$ cm^2/s for the diffusion coefficient of ruthenium(IV); the number of electrons involved in the redox process at 0.330 V was then calculated as 0.24 electron/ruthenium atom, a value that obviously is much too low. If the calculation is repeated with the correct value of the diffusion coefficient, $D = 2.5 \times 10^{-6}$ cm^2/s as reported in this paper, then the number of electrons per ruthenium atom is 0.50 as expected for the redox couple ruthenium(IV)/ruthenium(3.5). However, the number of electrons involved in the electrode reaction at 0.920 V is then calculated as 0.75, and even this value is probably too low since the reaction is irreversible. There is no ready explanation for this result at present, and more work in nitric acid solutions is needed to clarify this point.

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[18] Maya[11] tried to prepare his ruthenium(4.38) (?) species by anodic oxidation of a ruthenium(IV) solution in 0.1 M HNO_3/0.9 M $NaNO_3$ at 1.050 V vs SCE. He reported that the current was low and so close to the background that it prevented an accurate coulometric estimate of the number of electrons involved in the reaction (the electrolysis was continued for 120 h!). Electrolysis of ruthenium(IV) in 1.0 M HNO_3 did not produce any measurable amount of oxidized species at all. As stated already, it seems worthwhile to repeat some of Maya's experiments in nitric acid solutions.

[19] The half-wave potentials of the oxidation wave shift slightly to more positive values with increasing rotation rates, thus indicating a slow electron transfer. The kinetics of the electron-transfer process was investigated by using the well-known general equation for the current–potential curve for a one-electron process at the rotating disk electrode,[20] yielding $k^\circ = 5 \times 10^{-4}$ cm/s and $\alpha = 0.50 \pm 0.05$ (k°, standard heterogeneous rate constant; α, transfer coefficient); the same order of magnitude of the value of k° was obtained by analysis of the cyclic voltammetric data. Therefore, the half-wave potentials do not have a strict thermodynamic meaning as is the case for a reversible electrode reaction, and consequently, the argument as presented in the text is strictly speaking not really valid. However, at low rotation rates (e.g. 100 rpm) the half-wave potentials are shifted positive of the formal standard potential by only ~0.020 V and the process is still under mixed mass-transfer and electron-transfer control. For this reason it still seems possible to draw meaningful conclusions from the fact that the half-wave potentials are independent of the analytical concentrations of ruthenium(IV) and of the solutions acidity.

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species exist in less acid solutions, pcH ≥ 1;[4] obviously, more hydrolyzed forms of ruthenium(4.25) can also exist in the same range of acidity since the formal standard potential of the couple ruthenium(4.25)/ruthenium(IV) is independent of the solution acidity. Furthermore, the high charge on these ions most probably is reduced by perchlorate complex or ion-pair formation.

The absorption spectrum of ruthenium(4.25) in 1.0 M $HClO_4$ solution is shown in Figure 4 (this spectrum was recorded immediately after the end of an exhaustive electrolysis of a ruthenium(IV) solution at 1.150 V vs SCE). The spectrum of ruthenium(IV), also shown in Figure 4, is in agreement with earlier literature reports[1,7] ($\epsilon_{486} = 710 \pm 5$). After electrolysis, the absorption maximum in the visible is shifted slightly to longer wavelengths and exhibits a slight increase in absorptivity ($\epsilon_{490} = 730 \pm 5$), in good agreement with the spectrum reported by Avdeev et al.,[10] whereas the shoulder in the ultraviolet has disappeared. Evidently, the spectral changes are rather minimal, and thus absorption spectroscopy certainly is not the most suitable method to measure the presence of small quantities of ruthenium(4.25) in ruthenium(IV) solutions, or vice versa.

Solutions of ruthenium(4.25) in 1.0 M $HClO_4$, stored under "normal" conditions (i.e. in a closed glass container on a lab bench) slowly transformed to ruthenium(IV) (it took several days to obtain 50% conversion). This transformation was ascertained by monitoring the spectral changes and by a series of voltammetric experiments. Thus, the RDE voltammogram of a freshly prepared solution of ruthenium(4.25) in 1 M $HClO_4$ exhibits a wave at 0.800 V vs SCE for the reduction to ruthenium(IV) (of course, the waves for the further reduction of this species are also present in the voltammogram). However, when the solution is allowed to stand, the height of this reduction wave slowly decreases and the height of the oxidation wave at 0.950 V vs SCE slowly increases, thus indicating the formation of ruthenium(IV) (the sum of the heights of both the reduction and oxidation waves remains constant).

Obviously, the only component present in the system that possibly can be oxidized by ruthenium(4.25) is water, but the thermodynamics of this reaction is not favorable. Therefore, it was decided to check qualitatively whether the reaction of ruthenium(4.25) and water is a photochemical process. Indeed, it was found that solutions of ruthenium(4.25) in 1.0 M $HClO_4$ are stable if stored in the dark (the observation period lasted for about 3 weeks, i.e. much longer than the time needed to observe conversion under normal daylight conditions). However, if the solution was irradiated with 254-nm light, transformation of ruthenium(4.25) to ruthenium(IV) was complete in 4–5 h. Thus, while these experiments confirmed qualitatively that the reduction of ruthenium(4.25) to ruthenium(IV) is indeed a photochemical reaction, more work is needed to clarify the photochemistry of this system and the nature of the excited state involved in the reaction.

In solutions of lower acidity, ruthenium(4.25) is quickly transformed to ruthenium(IV), even if the solution is stored in the dark: thus, at pcH = 2, the conversion is complete in a couple of hours. Apparently then, under these conditions, ruthenium(4.25) can react directly with water, but the kinetics of this process has not been investigated in detail.

Conclusions

The results of this study confirm the existence of a ruthenium(4.25) species that can be formulated as $Ru_4(OH)_{12}^{5+}$, at least in the more acidic solutions (it is probable that more hydrolyzed species exist in less acidic solutions, pcH ≥ 1). The formal standard potential of the ruthenium(4.25)/ruthenium(IV) redox couple was estimated as 1.160 V vs NHE. The redox reaction is independent of the solution acidity and it seems unlikely therefore that the process involves the oxidation of hydroxyl ligands as has been suggested previously.[11] However, any discussion of the bonding in the series of tetrameric ruthenium ions seems premature since the structure of these species in solution remains at present unknown. In 1.0 M $HClO_4$ solution, ruthenium(4.25) can be reduced by water to ruthenium(IV) in a photochemical reaction, but more work is needed to clarify the photochemistry of the process and the nature of the excited state involved in the reaction. In solutions of lower acidity, ruthenium(4.25) is not stable and reacts directly with water (thus, at pcH ≥ 2, conversion to ruthenium(IV) is complete in a couple of hours).

Acknowledgment. We are indebted to the Institute for Nuclear Research (IIKW, Brussels, Belgium) for financial support of this work and for granting a research fellowship to one of them (H.V.N.).

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Catalytic Effect of Sulfur Dioxide on the Electrode Kinetics of the Triiodide/Iodide Couple

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Received April 29, 1988

Halides have been shown to undergo a 1:1 complexation with sulfur dioxide in nonaqueous solvents as seen in reaction 1.[1]

$$X^- + SO_2 = XSO_2^- \qquad (1)$$

XSO_2^- adducts are believed to be charge transfer in nature due to the extremely large molar absorptivities in their electronic spectra.[2] Recently, we have been investigating the electrochemistry of these adducts. More specifically, we were interested in the change in SO_2 binding constant when X^- is oxidized to X_3^-. For this study we chose to use iodide since its electrochemistry in the solvent of interest to us has recently been reported.[3] The report showed that in propylene carbonate I^- undergoes a two-step oxidation to I_3^- and then I_2 via reactions 2 and 3.

$$3I^- = I_3^- + 2e^- \qquad (2)$$

$$2I_3^- = 3I_2 + 2e^- \qquad (3)$$

The I_2/I_3^- couple was shown to have relatively fast rates of electron transfer at a platinum electrode while the I_3^-/I^- couple was quite sluggish, more so for the reduction than for the oxidation. Herein, we report the effects of SO_2 on the thermodynamics of these redox couples and also a surprising improvement in electrode kinetics observed for the reduction of I_3^- at high SO_2 concentrations.

Experimental Section

Materials. Tetrabutylammonium iodide, TBAI, and tetrabutylammonium perchlorate, TBAP (Southwestern Analytical Chemicals), were purified by recrystallization from hot absolute ethanol and dried under vacuum for several days. Propylene carbonate, PC (Aldrich), was purified by vacuum distillation and dried with activated alumina. Anhydrous sulfur dioxide (Air Products) was used without further purification.

Instrumentation. Cyclic voltammetry (CV) and electrolysis/potentiometry measurements were made with a PAR Model 371 potentiostat-galvanostat, Model 379 digital coulometer, and Model 175 universal programmer. Working electrodes were polished platinum or gold, and the auxiliary electrode was a platinum wire. The areas of the working electrodes were estimated by measurement with a ruler under a microscope. All potentials are referenced to ferrocene/ferrocenium by internal standard.[4]

Spectral measurements were made on an HP 8452A diode array spectrophotometer interfaced to a IBM-PC-compatible Zenith computer using HP 89530A MS-DOS/UV-VIS operating software.

Solutions of Sulfur Dioxide. Dilute ($\leq 10^{-2}$ M) solutions of SO_2 in PC are relatively stable with respect to SO_2 loss. Concentrations of SO_2 in dilute stock solutions ($\sim 10^{-2}$ to $\sim 10^{-3}$ M) were measured gravimetrically by weighing the solutions before and after addition of gaseous SO_2. Less concentrated solutions were prepared by dilution. The concentration of

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