Short Communication

Oxidation of ruthenium(II) tris(2,2-bipyridine) ions by thallic ions, mediated by ruthenium dioxide hydrate: a classic example of reversible redox catalysis

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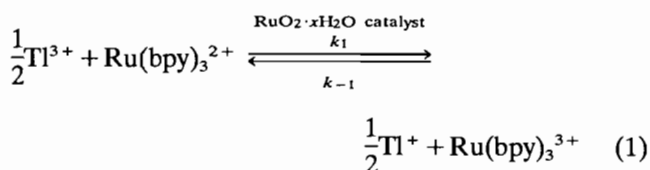(Received February 2, 1993; revised March 6, 1993)

Abstract

The results of an initial kinetic study of the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ by Tl^{3+} ions, catalysed by a dispersion of $RuO_2 \cdot xH_2O$ in 3 mol dm^{-3} HNO_3, as a function of $[Ru(bpy)_3^{2+}]$, $[Tl^{3+}]$, $[Tl^+]$, $[RuO_2 \cdot xH_2O]$ and temperature, are reported. The kinetics of $Ru(bpy)_3^{2+}$ oxidation fit an electrochemical model of redox catalysis involving electron transfer between the two highly reversible redox couples, i.e. $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$ and Tl^{3+}/Tl^+, mediated by the dispersion of microelectrode particles of $RuO_2 \cdot xH_2O$. This work describes a rare example of reversible redox catalysis.

Introduction

Heterogeneous catalysis of redox reactions is at the heart of many industrial processes, including the extraction of minerals from ores, electrodeless plating, chloralkali production, photographic development and the descaling of industrial pipework [1, 2]. In many examples of heterogeneous redox catalysis [1], the catalyst simply provides a medium for electron transfer from one redox couple to another. This electrochemical approach allows the prediction of the kinetics of catalysis, provided the current–voltage curves for the two contributing couples are known and the couples act independently of one another [1] (the Wagner–Traud additivity principle [1]). Despite the importance of redox catalysis, detailed kinetic studies have only emerged during the last decade.

Although it should be possible to mediate electron transfer between two highly reversible couples, using a redox catalyst, in practice the associated homogeneous (non-catalysed) reaction is usually much faster than the heterogeneous (catalysed) one [3]. Interestingly,

the oxidation of $Ru(bpy)_3^{2+}$ by Tl^{3+} ions in strong acid is a slow and irreversible reaction in homogeneous solution, despite the established high degree of electrochemical reversibility of the two participating couples [4–6]. In this work we report the initial results of a kinetic study of the reversible oxidation of $Ru(bpy)_3^{2+}$ by Tl^{3+} ions, mediated by ruthenium dioxide hydrate, $RuO_2 \cdot xH_2O$, in 3 mol dm^{-3} HNO_3, i.e.

$$\frac{1}{2}Tl^{3+} + Ru(bpy)_3^{2+} \underset{k_{-1}}{\overset{\overset{\text{RuO}_2 \cdot x\text{H}_2\text{O catalyst}}{k_1}}{\rightleftharpoons}}$$

$$\frac{1}{2}Tl^+ + Ru(bpy)_3^{3+} \quad (1)$$

Experimental

Materials

The ruthenium(II) tris(2,2-bipyridine) dichloride hexahydrate was purchased from Strem Chemicals UK, the nitrate salts of Tl(I) and Tl(III), i.e., $TlNO_3$ and $Tl(NO_3)_3 \cdot 3H_2O$, were obtained from Aldrich Chemicals UK, $RuO_2 \cdot xH_2O$ (batch no. 061301B) was obtained from Johnson Matthey UK, and concentrated nitric acid used to prepare the 3 mol dm^{-3} HNO_3 was purchased from BDH Chemicals UK. In all cases the chemicals were of the highest purity available and were used as received. The water used to prepare solutions was doubly distilled and deionised.

Methods

The kinetics of reaction (1) were monitored spectrophotometrically, using a Perkin-Elmer Lambda 3 double-beam spectrophotometer, via the observed absorbance changes at 452 nm, due to changes in the concentrations of the $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ ions as the reaction proceeds.

Theory

In our work, the concentrations of Tl^{3+} and Tl^+ ions employed were much greater than those of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$. Assuming an electrochemical model for catalysis [7], and that the two redox couples are electrochemically reversible [5, 6], it follows that the mixture potential, E_{mix}, on the microelectrode

particles of $RuO_2 \cdot xH_2O$, will be fixed and given by the Nernst equation for the Tl^{3+}/Tl^+ couple, i.e.

$$E_{mix} = E_2^\circ + (RT/F) \ln\{[Tl^{3+}]^{1/2}/[Tl^+]^{1/2}\} \qquad (2)$$

and that the mixture current at any time t during the redox reaction, $i_{mix, t}$, will be given by the expression

$$i_{mix, t} = K\{[Ru(bpy)_3^{2+}]_t - [Ru(bpy)_3^{2+}]_{eq}\} \qquad (3)$$

where $K = Fk_dA_{cat}$; k_d is the mass transfer coefficient, A_{cat} is the effective catalyst surface area per unit volume of solution, and $[Ru(bpy)_3^{2+}]_t$ and $[Ru(bpy)_3^{2+}]_{eq}$ are the concentrations of $Ru(bpy)_3^{2+}$ at any time t during the reaction and at equilibrium, respectively.

The mixture current is directly related to the rate of reaction, i.e. $i_{mix, t} = -Fd[Ru(bpy)_3^{2+}]/dt$, and it follows from eqn. (3) of the electrochemical model that the reaction should be diffusion-controlled, first-order with respect to $\{[Ru(bpy)_3^{2+}]_t - [Ru(bpy)_3^{2+}]_{eq}\}$, $[RuO_2 \cdot xH_2O]$ and independent of $[Tl^+]$ and $[Tl^{3+}]$. In contrast, it has been found [4] that the homogeneous (non-catalysed) version of reaction (1) is irreversible, first-order with respect to $[Ru(bpy)_3^{2+}]$ and $[Tl^{3+}]$, independent of $[Tl^+]$ and has an Arrhenius activation energy, 96 kJ mol^{-1}, which is c. 5–6 times greater than that for a diffusion-controlled reaction (15–19 kJ mol^{-1}) [8, 9].

Results and discussion

In one set of experiments, the effect upon the kinetics of reaction (1) of different initial concentrations of Tl^+ ions, $[Tl^+]_0$, varied over the range $(3.6-0.4) \times 10^{-3}$ mol dm^{-3}, with a fixed initial high concentration of Tl^{3+} ions, $[Tl^{3+}]_0$, $= 3.6 \times 10^{-3}$ mol dm^{-3}, was studied. In this work, the other reaction conditions were as follows: $[Ru(bpy)_3^{2+}]_0 = 7.1 \times 10^{-5}$ mol dm^{-3}; $[RuO_2 \cdot xH_2O] = 18$ μg cm^{-3}; $[HNO_3] = 3$ mol dm^{-3} and $T = 30$ °C. The A_t/A_0 (where A_t and A_0 are the absorbances at 452 nm at time t and at the start of the reactions, respectively) versus t profiles, associated with the different kinetic runs, are illustrated in Fig. 1; all gave an excellent fit to first-order kinetics, with respect to $\{[Ru(bpy)_3^{2+}]_t - [Ru(bpy)_3^{2+}]_{eq}\}$, over $2\frac{1}{2}$ half-lives and the measured values for the first-order rate constant, k_1^*, are given in Table 1.

From the results of this work it appears that k_1^* is independent of $[Tl^+]_0$. In a further experiment, the effect upon the kinetics of reaction (1) of different initial concentrations of Tl^{3+} ions, $[Tl^{3+}]_0$, varied over the range $(1.5-0.7) \times 10^{-3}$ mol dm^{-3}, with a fixed initial high concentration of Tl^+ ions, $[Tl^+]_0 = 3.6 \times 10^{-3}$ mol dm^{-3}, was studied. From these initial results, given in Table 1, it appears that k_1^* is independent of $[Tl^{3+}]_0$. Additional experiments established that k_1^* is propor-

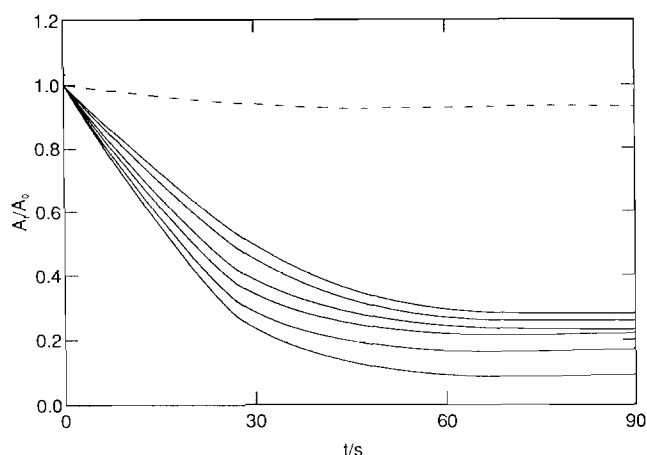

Fig. 1. The A_t/A_0 vs. time profiles showing the effect upon the kinetics of reaction (1) of different initial concentrations of Tl^+ ions, $[Tl^+]_0$, with a fixed initial high concentration of Tl^{3+} ions, i.e. $[Tl^{3+}]_0 = 3.6 \times 10^{-3}$ mol dm^{-3}; A_0 and A_t are the absorbances at 452 nm due to the $Ru(bpy)_3^{2+}$ before, and at time t after, the injection of Tl^{3+} ions, respectively. The reaction conditions were as follows: $[Ru(bpy)_3^{2+}]_0 = 7.1 \times 10^{-5}$ mol dm^{-3}; $[RuO_2 \cdot xH_2O] = 18$ μg cm^{-3} (except in the top, broken line, profile, which is for the homogeneous (non-catalysed) version of reaction (1), where $[RuO_2 \cdot xH_2O] = 0$ μg cm^{-3}); $[HNO_3] = 3$ mol dm^{-3} and $T = 30$ °C. The different solid line profiles correspond, from top-to-bottom, to the following values of $[Tl^{3+}]_0$: 3.6, 2.9, 2.2, 1.5, 0.4 and 0.0×10^{-3} mol dm^{-3}.

TABLE 1. Variation in k_1 and $[Ru(bpy)_3^{3+}]_{eq}/[Ru(bpy)_3^{2+}]_{eq}$ as a function of $[Tl^+]_0$ and $[Tl^{3+}]_0$

$[Tl^{3+}]_0$ $(10^{-3}$ mol dm$^{-3})$	$[Tl^+]_0$ $(10^{-3}$ mol dm$^{-3})$	k_1^* $(10^{-2}$ s$^{-1})$	$\{[Ru(bpy)_3^{3+}]_{eq}$ $/[Ru(bpy)_3^{2+}]_{eq}\}$
No catalyst: fixed $[Tl^{3+}]_0$, fixed $[Tl^+]_0$			
3.6	3.6	0.05	
With catalyst: fixed $[Tl^{3+}]_0$, variable $[Tl^+]_0$			
3.6	3.6	5.94	3.25
3.6	2.9	5.88	3.57
3.6	2.2	5.71	4.27
3.6	1.5	6.20	5.03
3.6	0.4	6.29	11.19
3.6	0.0	6.07	
With catalyst: variable $[Tl^{3+}]_0$, fixed $[Tl^+]_0$			
1.5	3.6	3.25	1.76
0.7	3.6	3.15	1.07

tional to the catalyst concentration, $[RuO_2 \cdot xH_2O]$. From the variation of k_1^* with temperature, over the range 14–39 °C, an Arrhenius plot of the data yielded an activation energy of 26 ± 1 kJ mol^{-1}, which is near to that expected for a diffusion-controlled reaction in aqueous solution, i.e. 15–19 kJ mol^{-1} [8, 9]. All these findings provide good support for the electrochemical model of reversible redox catalysis outlined above.

From the equilibrium absorbances at 452 nm for the different kinetic runs, illustrated in Fig. 1, the different ratios of $[Ru(bpy)_3^{3+}]_{eq}/[Ru(bpy)_3^{2+}]_{eq}$ were derived for the different kinetic runs and the results are collected in Table 1. The electrochemical model predicts that at equilibrium

$$[Ru(bpy)_3^{3+}]_{eq}/[Ru(bpy)_3^{2+}]_{eq} \qquad (4)$$
$$= ([Tl^{3+}]_0/[Tl^+]_0)^{1/2} \exp(\beta F/RT)$$

where β is the difference in the standard redox potentials of the Tl^{3+}/Tl^+ and $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$ couples, respectively, i.e. $\beta = \{E^\circ(Tl^{3+}/Tl^+) - E^\circ(Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+})\}$. The validity of this prediction was confirmed from a plot of $\ln\{[Ru(bpy)_3^{3+}]_{eq}/[Ru(bpy)_3^{2+}]_{eq}\}$ versus $\ln([Tl^{3+}]_0/[Tl^+]_0)$, using the data in Table 1, which yielded a good straight line (correlation coefficient = 0.9990) with a gradient = 0.57 and intercept = 1.16. From the value of this intercept and eqn. (4), a value for $\beta = 30$ mV, for $T = 30$ °C, can be calculated and since the value of $E^\circ(Tl^{3+}/Tl^+)$ is known to be 1.230 V versus NHE [5], it follows that $E^\circ\{Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}\} = 1.200$ V versus NHE. This calculated value for $E^\circ\{Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}\}$ is not that much smaller than that reported previously by others [6] for this couple (1.222 V) in 3 mol dm^{-3} HNO$_3$.

Additional experiments confirm the feature of reversibility associated with the catalysed version of reaction (1). Thus the addition of further amounts of Tl$^+$ to the final equilibrium mixture readily shifts the equilibrium back towards a reactant-rich mixture at a rate, and to an extent, which is fully predicted by the electrochemical model.

Examples of reversible redox catalysis are very rare [7] and the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ by Tl^{3+} ions in 3 mol dm^{-3} HNO$_3$, mediated by $RuO_2 \cdot xH_2O$, appears to be a classic example of such catalysis in which the kinetics also readily fit an appropriate, simple electrochemical model.

Acknowledgement

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