KINETICS AND MECHANISM OF REDUCTION REACTION OF μ-OXO-BIS [AQUATETRACHLORORUTHENATE (IV)] WITH IRON(II) IN ACIDIC MEDIUM

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INTRODUCTION

Dinuclear ruthenium (III,IV) complexes, $[Cl_5RuORuCl_5]^{n-}$ (n = 4, 5), and their aquated derivatives, belong to the group of well – defined ruthenium dimers and oligomers [1- 4] where the link between the metal sites is a μ-oxo bridged ligand. Small structural differences between the oxidized and reduced forms, together with the specific contribution of the oxygen bridges to the electron transfer processes, create favourable conditions to the fast and reversible redox chemistry [5].

In our previous paper [6] we have reported on the kinetics of the reduction of μ-oxo-bis[aquatetrachlororuthenate (IV)] ion with ascorbic acid in acidic solution. Formation of mixed oxidation state complex with a linear Ru(III)-O-Ru(IV) core and dehydroascorbic acid as a reaction products has been observed.

In this paper the kinetics and mechanism of the one-electron reduction of μ-oxo-bis[aquatetrachlororuthenate (IV)] with iron (II) in water-HCl solution are presented:

$$[(H_2O)Cl_4Ru(IV)ORu(IV)Cl_4(H_2O)]^{2-} + Fe^{2+} \rightarrow [(H_2O)Cl_4Ru(III)ORu(IV)Cl_4(H_2O)]^{3-} + Fe^{3+}$$

It is generally accepted that binuclear electron transfer reactions proceed via a sequence of elementary steps: formation of the precursor complex, intramolecular electron transfer within the precursor complex, and dissociation of the successor complex. For outer-sphere reactions, the precursor and successor complexes are ion pairs or outer-sphere complexes. For inner-sphere reactions, the precursor and successor complexes are binuclear complexes in which a bridging ligand connects the two metal centers [7, 8].

EXPERIMENTAL

$K_4[Ru_2OCl_{10}] \cdot H_2O$ was prepared and analysed as described in [9]. $[Ru_2OCl_8(H_2O)_2]^{2-}$ was obtained during four hours lasting aquation process of $[Ru_2OCl_{10}]^{4-}$ in 0.1 mol dm^{-3} HCl solution [2]. After this time more than 99.8% of the complex was in the form of $[(H_2O)Cl_4RuORuCl_4(H_2O)]^{2-}$. Iron (II) perchlorate solution was prepared by dissolving analytical grade iron wire in an excess of previously deaerated perchloric acid. Iron (II) concentration was determined by titrating with permanganate, and excess of acid by potentiometric titration with alcali in absence of oxygen. The ionic strength was adjusted by introducing suitable quantities of 1.0 mol dm^{-3} NaCl solution into the solution to be investigated. HCl and NaCl were an AR grade samples and were used without further purification.

Kinetic measurements were performed under pseudo-first order conditions, with Fe(II) and hydrogen ions concentration in an excess over the ruthenium complex concentration. Electronic absorption spectra, as well as kinetic measurements, were made on Specord UV-Vis spectrophotometer. Reaction was monitored at 470 nm (ε = 5120 [2]) and the observed first order rate constant, k_{exp}, was calculated by linear least-squares fitting of $\log(A_t-A_\infty)$ to time t. A_t and A_∞ are the absorbance of the solution at time t and after 8-10 half-lives. Each kinetic run was repeated 3 to 4 times.

RESULTS AND DISCUSSION

Reaction rate measurements in a broad range of reagents concentration and pH revealed first order kinetics with respect to the ruthenium complex and zero order kinetics with respect to hydrogen ion concentration. The reaction order with respect to [Fe^{2+}] dependens on reductor concentration and changes from 1 to 0 with [Fe^{2+}] increase (Table 1).

Table 1. Kinetic data for the reduction of $[Ru_2OCl_8(H_2O)_2]^{2-}$ by Fe^{2+}

$10^5[Ru_2OCl_8(H_2O)_2{}^{2-}]$ (mol dm^{-3})	$10^3[Fe^{2+}]$ (mol dm^{-3})	[HCl] (mol dm^{-3})	[NaCl] (mol dm^{-3})	10^2k_{exp} (s^{-1})
8.01	0.25	0.10	—	0.563
8.65	0.50	0.10	—	0.691
7.70	1.0	0.10	—	1.23
8.65	2.0	0.10	—	1.57
8.10	3.0	0.10	—	2.07
8.53	6.0	0.10	—	2.27
4.23	6.0	0.10	—	2.31
16.10	6.0	0.10	—	2.23
31.40	6.0	0.10	—	2.26
8.18	1.0	0.10	0.10	1.75
8.07	1.0	0.10	0.20	2.03
8.18	1.0	0.10	0.40	2.83
9.31	1.0	0.10	0.80	2.96
9.81	1.0	0.20	0.70	2.89
11.10	1.0	0.40	0.50	2.95
10.90	1.0	0.90	—	2.41

$k_{et} = 2.20 \times 10^{-2}$ s^{-1}, $K_f = 1.26 \times 10^3$ mol^{-1} dm^3
temp. = 25°C (correlation coefficient r = 0.9674)

At a sufficient excess of the reductor concentration over the ruthenium complex, the reaction display saturation kinetics [4] and a limiting rate is observed. The observed saturation in the reaction rate at higher reductor concentration can be interpreted by the mechanism involving ion pair formation between the highly and oppositely charged reactants, or inner-sphere complex, where two metal ions are bridged by the chloride ion.

The kinetic data together with previous findings for the reduction reaction of µ-oxo-bis[aquatetrachlororuthenate (IV)] ion by ascorbic acid [6] allow to propose the following reaction mechanism (all iron ions are hydrated species) :

$$(H_2O)Cl_4Ru(IV)ORu(IV)Cl_4(H_2O)^{2-} + Fe^{2+} \overset{K_f}{\leftrightarrows} [\text{Intermediate}]$$

$$[\text{Intermediate}] \xrightarrow{k_{et}} (H_2O)Cl_4Ru(III)ORu(IV)Cl_4(H_2O)^{3-} + Fe^{3+}$$

where $[\text{Inermediate}] = [(H_2O)Cl_4RuORuCl_4(H_2O)^{2-} \parallel Fe^{2+}]$

or $[(H_2O)Cl_4RuORuCl_4(H_2O)Fe]$

The rate law of the investigated process is given by the kinetic equation :

$$-\frac{d[Ru_2OCl_8(H_2O)_2^{2-}]}{dt} = \frac{k_{et}\, K_f\, [Ru_2OCl_8(H_2O)_2{}^{2-}][Fe^{2+}]}{1 + K_f\,[Fe^{2+}]} \qquad (1)$$

where: k_{et} - rate constant of electron transfer
K_f - formation constant of intermediate complex

At the pseudo-first order conditions:

$$k_{exp} = \frac{k_{et}\, K_f\,[Fe^{2+}]}{1 + K_f\,[Fe^{2+}]} \qquad (2)$$

The equation (2) in its inverse form:

$$\frac{1}{k_{exp}} = \frac{1}{k_{et}} + \frac{1}{k_{et}\, K_f\,[Fe^{2+}]} \qquad (3)$$

provides useful way of determining of k_{et} and K_f from the intercept and slope of the linear plot of $1/k_{exp}$ against $1/[Fe^{2+}]$ (Fig. 1).

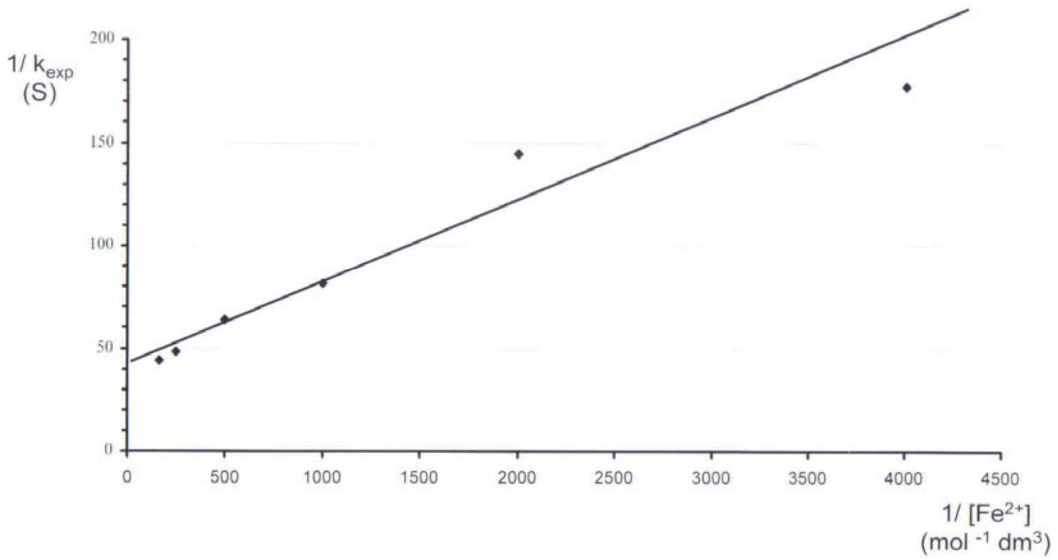

Fig. 1. Plot of $1/k_{exp}$ versus $1/[Fe^{2+}]$ for the reduction reaction of $[Ru_2OCl_8(H_2O)_2]^{2-}$ by Fe^{2+} (test of eq. (3)). Reaction conditions as in Table 1.

Kinetic data for the reduction of $[Ru_2OCl_8(H_2O)_2]^{2-}$ with Fe^{2+} in water-HCl solutions are presented in Table 1.

The positive salt effect is not in agreement with that expected for the reaction between oppositely charged ions. Increase of the rate constant with NaCl concentration increase suggests that electron transfer process proceeds through formation of an chloride bridged intermediate rather than by ion pair formation. Inner sphere electron transfer mechanism has been suggested also for the reduction process of this complex with ascorbic acid [6].

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