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Electron Transfer of $Ru(bpy)_3^{3+}$ in Micellar Solutions[1]

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The catalytic action of micelles has attracted considerable interest recently.[2] However, the effect of micellar systems on reactions involving metal ion complexes and particularly on electron-transfer reactions has received little attention. The complex of ruthenium with phenanthroline- or bipyridine-like ligands have been extensively studied in view of their possible use in solar energy conversion systems.[3] Recently some studies on photolytic and radiolytic behavior of $Ru(bpy)_3^{2+}$ (where bpy = 2,2′-bipyridine) in micellar solutions have been reported.[4]

In this note we wish to report some results on the effect of micellar SDS (SDS = sodium dodecyl sulfate) solutions on electron-transfer reactions of $Ru(bpy)_3^{3+}$ with octacyanomolybdate(IV), hexacyanoferrate(II), and aquoiron(II).

Experimental Section

$Ru(bpy)_3Cl_2$ was a gift from Istituto Chimico "Ciamician" of Bologna. $Ru(bpy)_3^{3+}$ was obtained from $Ru(bpy)_3^{2+}$ both via electrooxidation or by oxidation with PbO_2 in sulfuric acid; no difference was observed in the reaction rate with $Ru(bpy)_3^{3+}$ obtained by the different methods. Sodium dodecyl sulfate (Merck) was recrystallized several times from ethanol and dried in vacuo. When nonrecrystallized SDS was used, immediate reduction of $Ru(bpy)_3^{3+}$ was observed. Potassium hexacyanoferrate(II) was C. Erba reagent grade and potassium octacyanomolybdate(IV) was synthesized according to the literature.[5] A solution of iron(II) perchlorate was prepared by dissolving pure iron wire in perchloric acid and was standardized by oxidimetric titration. The desired quantity of surfactant solutions was added to the two solutions to be mixed.

The kinetic runs were performed by means of a Durrum-Gibson stopped-flow spectrophotometer, with $[Ru(bpy)_3^{3+}] = (4\text{–}5) \times 10^{-6}$ M and $[Mo(CN)_8^{4-}] = (5\text{–}8) \times 10^{-6}$ M or $[Fe(CN)_6^{4-}] = (5\text{–}6) \times 10^{-6}$ M, at $[HClO_4] = 0.015$ M; SDS concentrations ranged from 0.005 to 0.030 M. In some measurements $NaClO_4$ was added; the experiments were carried out at 8.0 °C and some runs also at 25.0 °C. For the reaction between $Ru(bpy)_3^{3+}$ and Fe^{2+}(aq), runs were performed at $[Ru(bpy)_3^{3+}] = (2\text{–}3) \times 10^{-6}$ M and $[Fe^{2+}(aq)] = (2\text{–}3) \times 10^{-6}$ M, at $[HClO_4] = 0.015$ M and SDS ranging from 0.005 to 0.030 M at 6.0 °C.

The rate constants were evaluated according to a second-order rate law by following the reaction progress at 450 nm ($\epsilon_{Ru(bpy)_3^{2+}}$ in SDS 1.35×10^4 M^{-1} cm^{-1}).

Results

Solubilization in Anionic Micelles. When $Ru(bpy)_3^{3+}$ is added to solutions containing SDS, a precipitation occurs. Further additions of SDS cause the solubilization of the precipitate when the region of critical micellar concentration (cmc) of SDS is reached.

Effect of Micelles on Electron Transfer from Iron(II). The electron transfer between $Ru(bpy)_3^{3+}$ and Fe^{2+}(aq) in homogeneous solution has been carefully investigated, and values of 6.4×10^5 M^{-1} s^{-1} (1.0 M $HClO_4$, 25.0 °C)[6] and 7.2×10^5 M^{-1} s^{-1} (0.5 M $HClO_4$, 25.0 °C) have been reported; in addition, very little effect of the temperature has been observed.[6]

In the presence of SDS (in concentrations higher than cmc) the reaction is strongly accelerated, being practically complete during the mixing time of our stopped-flow apparatus. This corresponds to a rate constant $\geq 5 \times 10^7$ M^{-1} s^{-1}, if a second-order mechanism is assumed (in this case in fact the positive Fe^{2+}(aq) could be adsorbed on the surface of the micelle, and the reaction mechanism could be different from a simple second-order treatment).

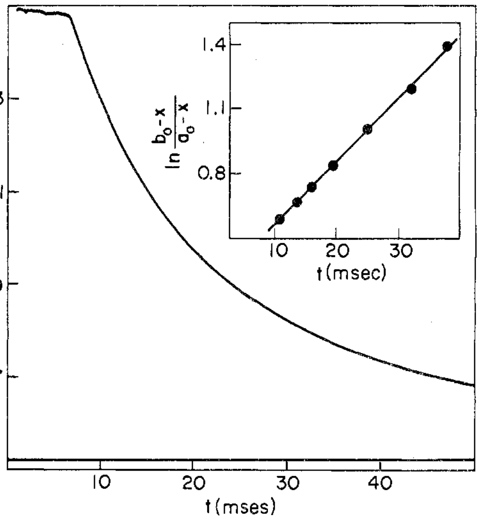

Figure 1. Oscilloscope trace for electron transfer between $Ru(bpy)_3^{3+}$ (4.6×10^{-6} M) and $Mo(CN)_8^{4-}$ (6.0×10^{-6} M) in the presence of 0.015 M SDS ($[HClO_4] = 0.015$ M, 8.0 °C, λ 450 nm). Lower trace represents the final point. Insert: corresponding second-order plot.

Table I. Micellar Effect on Electron-Transfer Rate between $Ru(bpy)_3^{3+}$ and $Mo(CN)_8^{4-}$ [a]

[SDS], M	[$NaClO_4$], M	$10^{-7}k$, M^{-1} s^{-1}
0.005		1.4
0.006		1.5
0.008		1.5
0.010		1.6
0.012		1.8
0.015		1.9
0.020		2.2
0.030		2.2
0.010	0.005	2.4
0.010	0.010	2.8
0.010	0.015	3.8
0.010	0.020	4.5
0.010	0.025	4.6
0.010[b]		3.3

[a] $[HClO_4] = 0.015$ M; 8.0 °C. [b] 25.0 °C.

Effect of Micelles on Electron Transfer from $Mo(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$. The reactions between $Ru(bpy)_3^{3+}$ and $Mo(CN)_8^{4-}$ or $Fe(CN)_6^{4-}$ in the absence of micelles occur at very fast rates, being almost diffusion controlled (observed rate constants of 3.2×10^9 and 2.8×10^9 M^{-1} s^{-1} for the reactions of $Ru(bpy)_3^{3+}$ with $Mo(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$, respectively, in 1 M H_2SO_4, were reported; taking into account the diffusion contribution, the activation-controlled rate constants for electron transfer were estimated as $\geq 2.2 \times 10^{10}$ M^{-1} s^{-1}).[8]

At 8.0 °C, in the presence of SDS concentrations lower than 0.005 M, the oscilloscope traces, recorded at 450 nm, showed a very fast increase in the absorbance leveling off at the expected final level, this being however slightly oscillating.

Above a concentration of 0.005 M SDS (which is probably very near the value of the cmc under the present conditions of temperature, ionic strength, and presence of highly charged ions, nonetheless in low concentration), reproducible traces were observed which refer to the final part of the reaction progress (from ca. 60 to 100%, see Figure 1). The second-order plots were reasonably linear, and averages were made on about 10–20 measurements for each experimental condition. In Table I we summarize the values of the second-order rate constant k at different SDS concentrations; it can be seen that the rate constant exhibits a small increase on increasing the surfactant concentration. A somewhat larger effect can be observed on addition of $NaClO_4$, as reported in the table. In the case of $Fe(CN)_6^{4-}$, the reaction rate was

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faster (by a factor of ca. 2) than that observed for $Mo(CN)_8^{4-}$, and this behavior makes it more difficult to follow the reaction progress; values of 2.4×10^7 M^{-1} s^{-1} at 0.005 M SDS and 3×10^7 M^{-1} s^{-1} at 0.010 M SDS were estimated.

Discussion

The effect of surfactants on the rate of electron-transfer reactions between ions can be represented as follows if we assume that one reactant (A) can interact with micelles while the other is in the bulk (as is the case of $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$).

$$\text{mic} + A_w \overset{K_1}{\rightleftharpoons} A_{\text{mic}'} \tag{1}$$

$$A_w + B_w \xrightarrow{k_w} \text{products} \tag{2}$$

$$A_{\text{mic}} + B_w \xrightarrow{k_m} \text{products} \tag{3}$$

On the assumption that the process (1) always equilibrated, the usual equation is derived where k_{obsd} is the observed second-order rate constant[9]

$$k_{\text{obsd}} = \frac{k_w + k_m K_1[\text{mic}]}{1 + K_1[\text{mic}]} \tag{4}$$

where $[\text{mic}] = (C_{\text{surf}} - \text{cmc})/N$; C_{surf} is the concentration of surfactant and N the aggregation number. Then from the observed decrease in the rate of reaction with $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ it follows that $K_1[\text{mic}] >> 1$, hence

$$k_{\text{obsd}} = k_w K^{-1}[\text{mic}]^{-1} + k_m \tag{5}$$

Since k_{obsd} is more than 2 orders of magnitude smaller than the electron-transfer rate constant in the absence of SDS, we can safely conclude that $K_1[\text{mic}] \geq 2 \times 10^2$, and since $[\text{mic}] \simeq 2 \times 10^{-5}$ to 5×10^{-4} M, we get $K_1 \geq 10^7$ M^{-1}. This latter value is quite reasonable for the present case where both electrostatic interactions (triply charged positive ion and a negative micelle) and hydrophobic interactions (imposed by the hydrophobic bpy ligands) are operative. The data in Table I can now be used to analyze for the location of the electron-transfer reaction, namely, a bulk reaction where k_w plays the dominant role or a micellar reaction where k_m contributes the major part of k_{obsd}. From expression 5 it is clear that the rate of the reaction should be inversely proportional to [mic] when the reaction is a bulk reaction. Although the values of the cmc and N under the present conditions cannot be exactly evaluated, it is safe to assume that by changing the surfactant concentration in the range 0.005–0.030 M, [mic] was changed by at least an order of magnitude. However, the data in the table indicate only a slight increase in k_{obsd}. We therefore conclude that the main pathway for the reaction is at the micelle–water interface. The small increase in k_{obsd} is easily explained by the increased ionic strength with increasing C_{surf} which will facilitate the approach of the negative reactants to the negative micelles.

A similar argument can rationalize the effect of $NaClO_4$. The decrease in the surface potential on increasing the ionic strength is expected to enhance the rate of the reaction at the micellar–water interface. In excess Na^+ ions, the possibility of displacement of $Ru(bpy)_3^{3+}$ by the inert ions should however be considered. In the case of purely electrostatic interaction, the association constant for a triply charged ion can be estimated to be ca. 10^5 times larger than for a singly charged ion.[2,9,10] In the present case where hydrophobic interaction is considerable for the Ru complex this association constant should be even larger. We therefore conclude that even at the highest $[Na^+]$ most of $Ru(bpy)_3^{3+}$ stays attached to the micelle.

Then also the enhancement of the electron-transfer rate observed with Fe^{2+}(aq) can be attributed to the location of $Ru(bpy)_3^{3+}$ in a negative micelle.

In conclusion, the rates of electron transfer to $Ru(bpy)_3^{3+}$, as well as $Ru(bpy)_3^{2+}$ and its excited state,[4] have been shown to be greatly altered by the presence of micelles. In view of the current interest in polyimine complexes of Ru in solar energy conversion, such effects might be useful in these systems. Further investigations are in progress aiming at the elucidation of the mechanisms controlling electron-transfer rates in micellar solutions.

Registry No. $Ru(bpy)_3^{3+}$, 18955-01-6; SDS, 151-21-3; $Mo(CN)_8^{4-}$, 17923-49-8; $Fe(CN)_6^{4-}$, 13408-63-4; Fe^{2+}, 15438-31-0.

References and Notes

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Arene–Transition Metal Chemistry. 2.[1a] Hydrogenation of Metal–Arene and Allylmetal–Arene Complexes

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In our studies of the hydrogenation of arenes catalyzed by discrete coordination or organometallic complexes, we have evidence that an η^4-arene binding of the aromatic hydrocarbon may be a favorable type of intermediate and that an allyl ligand and a $d^8 \rightleftharpoons d^6$ electronic couple may be important to stereoselectivity and chemoselectivity in the catalyst, e.g., as in the η^6-$C_6(CH_3)_6Ru$-η^4-$C_6(CH_3)_6$[2] and the unique[3] η^3-$C_3H_5Co[P(OR)_3]_3$[4] catalyst precursors. We describe here the hydrogen chemistry for a range of metal–arene, allylmetal–arene, and hydridometal–arene complexes.

Two allylmetal–η^6-arene complexes, the d^6 $[\eta^3$-$C_3H_5Mo(\eta^6$-$C_6H_5CH_3)Cl]_2$ dimer and the d^8 η^3-$C_3H_5Ru(\eta^6$-$C_6H_6)Cl$ monomer, reacted with hydrogen at ~85 °C in benzene and toluene solvents, respectively, with exclusive transfer of the hydride hydrogen to the allyl ligand to irreversibly yield propylene.[6] There was no evidence of hydrogenation of either the arene ligand or the arene solvent. This *suggests* a relative resistance to direct hydrogen transfer to an η^6-arene ligand. Consistent with these and earlier observations, a molybdenum complex with both hydride ligands and an η^6-arene ligand, d^4 $H_2Mo(\eta^6$-$C_6H_5CH_3)[P(C_6H_5)_3]_2$, showed no evidence of hydrogen transfer to either the toluene ligand or the benzene solvent up to 85 °C where gross decomposition occurred to