Specific Quenching of the Photoexcited State of Tris(2,2'-bipyridine)ruthenium(II) by Colloidal Prussian Blue

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Static quenching of the photoexcited state of the tris(2,2'-bipyridine)ruthenium(II) complex by colloidal prussian blue (PB) in water has been studied. The quenching behaviour has been analysed in terms of stepwise complex formation between Ru(bpy)$_2^{3+}$ and PB which obeys Poisson statistics. The binding of the Ru complex to the colloidal PB particle is discussed.

The quenching of the photoexcited state of a sensitizer has been studied intensively on so-called microheterogenous systems such as micelles, liposomes and polymer systems. In these systems specific quenching is often observed which is due to interactions between the sensitizer and quencher molecules, or to a distribution of the components in the assemblies. Most effects are explained by both dynamic and static quenching mechanisms. Photochemical processes in these microheterogenous systems are attracting much attention, because they are promising candidates in the chemical conversion of solar energy. The tris(2,2'-bipyridine)ruthenium(II) complex [Ru(bpy)$_2^{3+}$] has become a widely studied photocatalyst, since it can thermodynamically photolysye water under visible-light irradiation. From this point of view, quenching of the excited state of the Ru complex by various quenchers has been studied. We have found that irradiation of an aqueous solution of Ru(bpy)$_2^{3+}$ and colloidal prussian blue (PB) brings about the simultaneous evolution of hydrogen and oxygen by water photolysis. N.m.r. spectroscopy showed that both compounds form a complex in water. Water photolysis is an important subject, and the photochemical process occurring between the Ru complex and PB is unique. Moreover, photochemical and redox processes on colloidal particles are attracting more attention in relation to photochemical-energy conversion. The quenching of Ru(bpy)$_2^{3+}$ by PB colloids is thus analysed from these viewpoints in terms of stepwise binding of the compounds.

Experimental

Ru(bpy)$_2^{3+}$ Cl$_3$ was prepared by the reaction of ruthenium(III) chloride and 2,2'-bipyridine in methyl alcohol. Potassium hexacyanoferrate, K$_3$[Fe(CN)$_6$], and iron(II) chloride, FeCl$_2$, were the purest grade commercially available. PB was usually prepared by mixing aqueous solutions of both the iron salts at an equimolar ratio. The same results were also obtained when PB was prepared from potassium hexacyanoferrate(II) and iron(III) chloride. In order to prevent aggregation of the PB, the colloidal solution was stirred continuously before use and used within one day of preparation. The concentration of PB in the text is represented by that of the starting iron salt.
Results and Discussion

The composition of PB, which was recrystallized or electrodeposited, has been reported as Fe$_3^{3+}$[Fe$_{11}$(CN)$_{18}$]$_{6,8}$. In a colloidal aqueous solution, however, it has a different composition. In order to determine the composition in solution, the visible spectrum of PB in aqueous solution was studied by a continuous variation method. While changing the molar ratio of potassium hexacyanoferrate(II) and anhydrous iron(III) chloride, the absorption of the aqueous mixture at 700 nm was measured, and the results are shown in fig. 1. The plots show a maximum point at a ratio Fe$_{11}$/Fe$^{11+}$ + Fe$^{111}$ = 0.5, indicating that PB is present in water as a Fe$_{11}$/Fe$^{111}$ = 1/1 complex. The composition of PB as a colloidal form in aqueous solution is therefore KFe$_3$[Fe$_{11}$(CN)$_{18}$]. The discrepancy between this composition in solution and that in a precipitated state can be explained by some reconstitution of the coordination structure during the precipitation process.

The Stern–Volmer plots for the quenching of the excited state of Ru(bpy)$_3^{2+}$ by PB are shown in fig. 2. The plots show an upward deviation from linearity. This curve fits the Perrin treatment, i.e., the plots of ln($l_0/l$) against quencher concentration fall on a line. In the Perrin model it is assumed that only the quencher present in a "quenching
sphere' around the excited state is effective for quenching, and that the quenching efficiency within the sphere is unity. However, since this model does not give much information on the present system, the quenching of the excited Ru(bpy)$_2^{2+}$ by PB was analysed as follows.

As was reported,\textsuperscript{20} Stern–Volmer plots based on the lifetime of Ru(bpy)$_2^{2+\ast}$ in the present system fall on a line whose slope is zero, indicating that the lifetime of the excited state is independent of the quencher present. This means that the excited state is quenched only by a static mechanism and that no dynamic quenching occurs. This result strongly suggests complex formation between Ru(bpy)$_2^{2+}$ and PB. The different chemical shifts of the peaks in the n.m.r. spectra of the Ru complex in the absence and the presence of PB gave distinct evidence of complex formation.\textsuperscript{20} Since PB has a negatively charged structure \{Fe$^{3+}$[Fe$^{11}$CN)$_{14}^{-}$\}, the complex formation by PB with cationic Ru(bpy)$_2^{2+}$ must be due to an electrostatic force. Since PB is present as a colloid in solution, the process of complex formation should be the electrostatic adsorption of the Ru complex on the PB particle. The zero slope of the Stern–Volmer plots based on the lifetime of Ru(bpy)$_2^{2+\ast}$ (\textit{vide supra}) indicates further that, when the Ru complex forms a complex with PB, its excited state is entirely quenched.

Complex formation was analysed as follows. The multistep equilibria of reactions (1)–(3)

\[
\begin{align*}
\text{Ru} + \text{PB} \underset{k_a}{\overset{k_{-a}}{\rightleftharpoons}} \text{RuPB}_1, & \quad K_1 = \frac{k_a}{k_{-a}} \\
\text{RuPB}_1 + \text{PB} \underset{2k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{RuPB}_2, & \quad K_2 = \frac{K_1}{2} \\
\text{RuPB}_{i-1} + \text{PB} \underset{ik_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{RuPB}_i, & \quad K_i = \frac{K_1}{i}
\end{align*}
\]

were assumed as the complex formation, where $k_a$ and $k_{-a}$ are the forward and the backward reaction rate constants of the first step of complex formation, respectively, and $K_i$ is the equilibrium constant of the $i$th step. It is assumed that, at each complexation step, the forward rate constant is given by an equal value, $k_a$, while the backward rate constant is proportional to the number of bound PB molecules. $K_i$ is then equal to $K_{i/i}$, where $K_1$ is the equilibrium constant of the first step.

Under these conditions the distribution of the bound PB to the Ru complex obeys Poisson statistics. The probability distribution ($P_i$) that a Ru(bpy)$_2^{2+\ast}$ species is bound with $i$ PB molecules is given by

\[
P_i = \left(\frac{m^i}{i!}\right) \exp\left(-m\right)
\]

where $[\text{Ru}]_t$ is the total concentration of Ru(bpy)$_2^{2+\ast}$ and $[\text{PB}]_b$ is the concentration of PB bound to Ru(bpy)$_2^{2+\ast}$.

When $[\text{PB}]$ and $[\text{Ru}]$ denote the concentration of the respective free species

\[
\begin{align*}
[\text{Ru}]_t &= \sum_{i=0}^{\infty} (\text{RuPB}_i) \\
&= \sum_{i=0}^{\infty} K_1 K_2 \ldots K_i [\text{Ru}][\text{PB}]^i \\
&= [\text{Ru}] \sum_{i=0}^{\infty} \frac{(K_i[\text{PB}])^i}{i!} \\
&= [\text{Ru}] \exp(K_i[\text{PB}])
\end{align*}
\]
Quenching of Ru(bpy)$_3^{2+}$ by Prussian Blue

Therefore

$$1.5$$
$$1.0$$
$$0.5$$
$$0$$
$$1$$
$$2$$

$[\text{PB}]_t/10^{-4} \text{ mol dm}^{-3}$

Fig. 3. Plots of $\ln (I_o/I)$ against [PB] based on eqn (13).

and

$$[\text{PB}]_b = \sum_{i=1}^{\infty} i([\text{RuPB}]_i) = \sum_{i=0}^{\infty} \frac{(K_t[\text{PB}])^i}{i!}$$

$$= [\text{Ru}](K_t[\text{PB}]) \exp (K_t[\text{PB}])$$

$$= K_t[\text{PB}][\text{Ru}]_t.$$  (7)

Therefore

$$m = K_t[\text{PB}].$$  (8)

Since $[\text{PB}] = [\text{PB}]_t - [\text{PB}]_b$

$$[\text{PB}] = [\text{PB}]_t - K_t[\text{PB}][\text{Ru}]_t$$  (9)

and

$$[\text{PB}] = \frac{[\text{PB}]_t}{1 + K_t[\text{Ru}]_t}.$$  (10)

The probability of forming a Ru complex which does not bind with PB, $p_0$, can be written as

$$p_0 = \exp (-m) = \exp (-K_t[\text{PB}]).$$  (11)

Since only the free Ru complex can emit, and no dynamic quenching occurs as described before, the ratio of the relative emission intensity in the absence ($I_o$) and the presence ($I$) of the quencher is expressed by

$$I_o/I = 1/p_0 = \exp (K_t[\text{PB}]).$$  (12)

Consequently

$$\ln (I_o/I) = K_t[\text{PB}] = \frac{K_t}{1 + K_t[\text{Ru}]_t}[\text{PB}]_t.$$  (13)

The plots of $\ln (I_o/I)$ vs. $[\text{PB}]_t$ shown in fig. 3 fall on a straight line, indicating that the stepwise complexations shown in reactions (1)–(3) can explain the experimental results: other binding mechanisms cannot. Stepwise binding reactions similar to eqn (1)–(3) have often been proposed to analyse quenching in micellar systems. The value of $K_t$ is calculated from the slope of fig. 3 as

$$K_t = 8.57 \times 10^3 \text{ (dm}^3 \text{ mol}^{-1}).$$

Under the reaction conditions of $[\text{Ru}]_t = 10 \mu\text{mol dm}^{-3}$ and $[\text{PB}]_t = 1 \text{ mmol dm}^{-3}$ often used for water photolysis, the distribution curve is calculated as shown in fig. 4.
Fig. 4. Probability distribution for the complex (Ru–PB$_j$) when [Ru(bpy)$_2$]$^{3+}$] = 10 µmol dm$^{-3}$ and [PB] = 1 mmol dm$^{-3}$. KCl = 0.5 mol dm$^{-3}$, pH 2, $K_i = 8.57 \times 10^3$ (see text).

Fig. 5. Probability distribution of the ratio [Ru]/[PB] under the same conditions as fig. 4.

Since the actual complexation is the adsorption of the Ru complex onto a PB particle, the probability distribution of the number of Ru complex bound to one PB particle may be calculated from the results described above. The average diameter of the PB colloidal particles measured using an electron microscope was 23 nm, and the size distribution was narrow.$^{20}$ Taking this diameter as the average value, an average PB colloidal particle is calculated to consist of $2.40 \times 10^4$ PB repeating units [KFe[Fe(CN)$_6$]$_2$] from the size of the cubic PB unit cell ($a = 10.2$ Å).$^{27}$ Since a PB particle containing continuous coordination structure can be regarded as one large molecule, the molar concentration of the average PB particle, denoted as [PB]$_{av,p}$, can therefore be expressed by

$$[\text{PB}]_{av,p} = \frac{[\text{PB}]}{2.40 \times 10^4}.$$  

(14)
The number of Ru molecules associated with one PB unit is $1/i$; therefore, the number of Ru complex molecules bound on an average PB particle consisting of $2.40 \times 10^4$ PB units is

$$[\text{Ru}]_{\text{b}}/[\text{PB}]_{\text{av.p}} = 2.40 \times 10^4/i. \quad (15)$$

The probability distribution $P_i$ vs. $[\text{Ru}]_{\text{b}}/[\text{PB}]_{\text{av.p}}$ was shown in fig. 5. The probability has a maximum at ca. 3000 molecules of Ru(bpy)$_2^{2+}$ bound to an average PB particle.

Observing the PB particle in the electron microscope revealed it to have an almost spherical form.\textsuperscript{20} It is calculated that, at the maximum distribution in fig. 5, each Ru(bpy)$_2^{2+}$ molecule bound to a PB particle occupies an area of $0.74 \times 0.74$ nm$^2$ when assuming a perfectly spherical form for PB. The incorporation of Ru(bpy)$_2^{2+}$ into clays,\textsuperscript{31} or a layered zirconium phosphate lattice\textsuperscript{32} has shown that ca. 0.8 nm spacing is required for the complex. This value is close to the size (0.74 nm) of the present system at its maximum distribution. The Ru complex must therefore be bound to PB particles closely packed to each other, almost as a monolayer, at the maximum distribution of fig. 5.

At higher $[\text{Ru}]_{\text{b}}/[\text{PB}]_{\text{av.p}}$ ratios than this maximum point, multilayer adsorption should occur. Such multilayer adsorption could be due to both electrostatic and hydrophobic interactions, the latter of which is based on the bipyridine ligands of neighbouring Ru complexes. The presence of a hydrophobic interaction is supported by the strong interaction between Ru(bpy)$_2^{2+}$ and poly(styrene sulphonate).\textsuperscript{33}

In conclusion, the static quenching of the excited state of Ru(bpy)$_2^{2+}$ by colloidal PB particles has been analysed based on stepwise complex formation which obeys Poisson statistics.

References