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Quenching by unsaturated ferrocene and ferrocenium derivatives of the luminescence of $Ru(phen)_3^{2+}$

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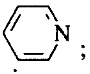
Abstract

A series of unsaturated ferrocene derivatives with the formula FcCH=CH-X (X≡CHO, CN, $COCH_3$, $COOCH_3$,  ; Fc, ferrocene) have been synthesized and oxidized to ferrocenium derivative ions. It has been found that these species can quench the ^{3}MLCT state of $Ru(phen)_3^{2+}$ efficiently. The quenching by the ferrocene and ferrocenium derivatives occur mainly via reductive and oxidative electron transfer on the ferrocenyl group in acetonitrile respectively. The Stern–Volmer plot is linear, from which the bimolecular quenching rate constants of the order of 10^9–10^{10} $dm^3\ mol^{-1}\ s^{-1}$ have been obtained. The rate constants for quenching with ferrocenium derivative ions are at or near the diffusion-controlled limit. Linear relationships have been obtained for a plot of log k_q vs. $-\Delta G$ of both the electron transfer and oxidative process.

Keywords: Quenching; Luminescence

1. Introduction

Quenching of the excited state of tris(2,2′-bipyridine)ruthenium(II) by electron transfer has been demonstrated [1,2]. In order to extend the work on $Ru(bpy)_3^{2+}$, we have investigated the reactions between the MLCT (d-Π*) excited states of the tris(1,10-phenanthroline)ruthenium(II), $Ru(phen)_3^{2+}$ and the ferrocene, the ferrocenium derivatives in acetonitrile.

$Ru(phen)_3^{2+}$ has proved to be an interesting and informative species for the investigation of bimolecular excited-state process. The lowest ^{3}MLCT excited state, $^*Ru(phen)_3^{2+}$, has a long lifetime, 5.0×10^{-7} s in acetonitrile [3], enough to encounter other molecules in fluid solution even when these are present at relatively low concentrations and possesses suitable properties to play the role of energy donor, electron donor, or electron accepter. The energy available to $^*Ru(phen)_3^{2+}$ for energy transfer process is 2.23 eV and its reduction and oxidation potentials are 0.79 V and −0.87 V respectively [4]. We are concerned here with photochemically induced reactions of ferrocene and ferrocenium derivatives with the excited state of $^*Ru(phen)_3^{2+}$.

2. Experimental section

The chemicals were of reagent grade and were used without further purification. All of the unsaturated ferrocene derivatives were prepared by Heck reaction [5] using chloromercuriferrocene [6] as the starting material except for $Fe(Cp)(C_5H_4CHO)$ (Cp, cyclopentadiene) which is commercially available (Aldrich). The unsaturated ferrocene derivatives were purified by column chromatography on acidic alumina using petroleum–chloroform (2:1) as an eluent and were analyzed using elemental analysis, IR, UV, etc. The ferrocene derivatives were oxidized to the respective ferrocenium ions with concentrated sulphuric acid [7], then one equivalent of KI_3 was added to the solution to get the black microcrystals, which are the ferrocenium derivatives of triiodine salt. Acetonitrile (MeCN) was purified as reported previously [8]. Tetraethylammonium perchlorate (TEAP) was recrystallized twice from water and dried in vacuum at 60 °C for several hours. The cyclic voltammograms were measured in a three electrode-cell with two compartments using a potentiostat (Jinan Radio Factory, Model 79-1). Current–voltage curves were recorded on an x–y recorder (Shanghai Co. of Automation Instruments, LZ3-100 Functions recorder). Pt wire electrodes with an area of 0.159 cm^2

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and polished glassy carbon electrodes were used as working electrode. Potentials were recorded vs. a saturated calomel electrode (SCE) for all the electrochemical experiments. All solutions were purged with highly purified nitrogen for 1 h before use, and a nitrogen atmosphere was maintained throughout the experiments.

The luminescence spectra were recorded on an RF-540 spectrophotofluorometer using an Xe lamp as the excitation source. $Ru(phen)_3Cl_2\,6H_2O$ was recrystallized twice before use. Deaerated samples in quartz fluorescence cells (1 cm) were maintained at a constant temperature (±2 °C) of 25 °C. The concentration of $Ru(phen)_3^{2+}$ in acetonitrile was 10^{-4} M. The concentrations of the quenchers, [Q] were around 10^{-5} M. The excitation wavelength was 442 nm and the emission wavelength was scanned between 500–700 nm. The quenching rate constants were measured at the maximum emission intensity (about 608 nm).

3. Results and discussion

3.1. Quenching process by the ferrocenium derivative ions

When two quenchers co-exist, the Stern–Volmer equation must be as follows [7]:

$$I_0/I = 1 + \tau_s(k_{q1}[Q_1] + k_{q2}[Q_2])$$

where I and I_0 are the emission intensity in the presence and absence of the quenchers respectively, k_{q1} and k_{q2} are the quenching rate constants of the two respective quenchers and τ_s is the luminescence lifetime, which is 5.0×10^{-7} s for the $Ru(phen)_3^{2+}$ in MeCN. $[Q_1]$ and $[Q_2]$ are the concentrations of the quenchers, for the $[FcCH{=}CHX]I_3$, $[Q_1] = [Fc^+CH{=}CHX] = [Q]$, $[Q_2] = [I_3^-] = [Q]$.

The quenching of $^*Ru(phen)_3^{2+}$ by various unsaturated ferrocenium derivatives of triiodide salt was monitored by measuring the decrease in the emission intensity at 608 nm as a function of $[Fc\text{–}CH{=}CH\text{–}X]I_3$ concentration. Each individual experiment yielded a value of I_0/I applicable to the particular concentration conditions. The I_0/I values are a linear function of the concentration of the unsaturated ferrocenium derivatives of triiodide salt. This is illustrated in Fig. 1. The quenching rate constants, $k_q = k_{q1} + k_{q2}$, can be obtained by the Stern–Volmer equation; they are listed in Table 1.

Under the same condition, the k_{q2} of the single quencher (KI_3) in acetonitrile is 6.10×10^9 dm^3 mol^{-1} s^{-1}. So the k_{q1} of the ferrocenium derivative ions can be obtained ($k_{q1} = k_q - k_{q2}$) (Table 1).

The results indicate that the k_q of the quenching of $^*Ru(phen)_3^{2+}$ by the ferrocenium derivatives of triiodide salt are of the order of 10^{10} dm^3 mol^{-1} s^{-1}. All the quenching rate constants are at the diffusion-controlled limit or very close to it. If one corrects for the effect of diffusion control with a steady-state formulation, ($k_{cor}^{-1} = k_q^{-1} - k_{dif}^{-1}$, with $k_{dif} = 2.0\times10^{10}$ dm^3 mol^{-1} s^{-1}) the corrected rate constant, k_{cor} are larger than k_q.

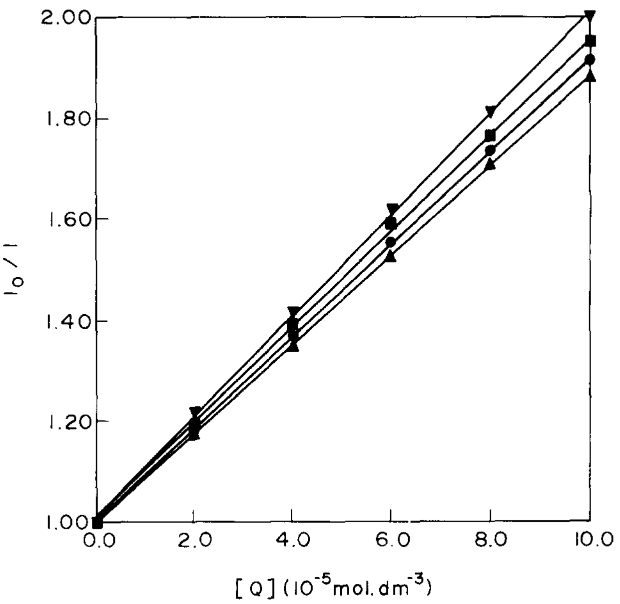

Fig. 1. Quenching of the emission from $^*Ru(phen)_3^{2+}$ by various unsaturated ferrocene derivative triiodine salts following a linear relation of I_0/I vs. $[Fc\text{–}CH{=}CH\text{–}X]I_3$. Kinetic data were obtained in MeCN at 25 °C. In order of increasing rate constant, data are shown for X = 4 – Py (▲), -COOCH3 (●), -CN (■) Fc–CHO (▼).

The k_{q1} is also of the order of 10^{10} dm^3 mol^{-1} s^{-1}. The stronger induced effect of the side chain, the higher the quenching rate constant. The $Fe^+Cp(C_5H_4CHO)$ was used as a quencher and it was found that k_{q1} of the Fc^+–CHO was higher than those of the ferrocenium derivative ions, because the -CHO group in Fc–CHO has the stronger induced effect than those of the ferrocene derivatives. The discussion above allow us to assess that the excited state of $Ru(phen)_3^{2+}$ can be quenched by ferrocenium derivative ions through electron transfer. In fact, the quenching of $^*Ru(bpy)_3^{2+}$ by transition metal ion oxidants and electron-deficient molecules through oxidative electron transfer [1] has been studied thoroughly. Comparative quenching of $^*Ru(phen)_3^{2+}$ by the ferrocenium derivative ion may reasonably consider to take place via oxidative electron transfer which is shown as follows:

$$^*Ru(phen)_3^{2+} + Fc^+CH{=}CHX \longrightarrow Ru(phen)_3^{3+} + FcCH{=}CHX$$

The free-energy change is shown as follows:

$$\Delta G = -nEF = -96\,500 \times [E_{1/2Fe(III)/Fe(II)} - E_{1/2}{}^*{}_{Ru(III)/Ru(II)}]\ J\ mol^{-1}$$

Table 1
The quenching rate constants for both the ferrocene derivatives and ferrocenium triiodine salts and ions

Composition	k_q ($\times 10^9$ M^{-1} s^{-1})[a]	k_q ($\times 10^{10}$ M^{-1} s^{-1})[b]	k_{q1} ($\times 10^{10}$ M^{-1} s^{-1})
X =–CHO	1.52	1.90	1.30
X =–CN	1.52	1.90	1.30
X =–COOCH$_3$	1.84	1.81	1.21
X =–COCH$_3$	2.01	1.78	1.18
X =–4–py	2.31	1.76	1.16

[a] k_q for ferrocene derivatives.

[b] k_q for ferrocenium derivatives triiodine salts.

The $E_{1/2Fe(III)/Fe(II)}$ can be obtained using cyclic voltammograms (Table 2), $E_{1/2}{}^{*}{}_{Ru(III)/Ru(II)} = 0.87$ V (vs. SCE). The ΔG values of the quenching process are shown in Table 2.

The k_{q1} become higher with the increase of the $-\Delta G$, which indicate that the more negative the ΔG are in the reaction, the easier the reaction take place. Actually, linear relationships are shown in the plot of log k_{q1} vs. $-\Delta G$ of the oxidative electron transfer (Fig. 2).

Because $-\Delta G$ are mainly dependent on the $E_{1/2(Q^+/Q)}$ of the ferrocenyl, the k_{q1} are also dependent on the $E_{1/2(Q^+Q)}$. The higher the $E_{1/2(Q^+Q)}$ is, the faster the reactions take place.

.2. Quenching process by ferrocene derivatives

The quenching of the luminescence of $^{*}Ru(bpy)_3^{2+}$ by ferrocene derivatives has been studied thoroughly [9,10]. It has been found that the quenching by α,β-unsaturated ferrocene derivatives can be carried out mainly via the reductive electron transfer on ferrocenyl in acetonitrile and the quenching rate constants are related to the $E_{1/2(Q^+/Q)}$ of the ferrocenyl in those derivatives [9]. The higher the $E_{1/2(Q^+/Q)}$ is, the lower the quenching rate constants. Linear relationships are shown in the plot of log k_q vs. $-\Delta G$ of the reductive electron transfer process. Similarly, the quenching of the excited state of $Ru(phen)_3^{2+}$ by ferrocene derivatives can also take place through reductive electron transfer because the excited state redox properties and energy of $^{*}Ru(phen)_3^{2+}$ are much similar to those of $Ru(bpy)_3^{2+}$. The reaction is shown as follows:

$$^{*}Ru(phen)_3^{2+} + FcCH{=}CHX \longrightarrow Ru(phen)_3^{+} + Fc^{+}CH{=}CHX$$

Table 2
The redox potentials of the ferrocene derivatives and the free-energy changes in the quenching process

Composition	$E_{1/2(Q^+/Q)}$ (vs. SCE)	Reductive process (kJ mol^{-1})	Oxidative process (kJ mol^{-1})
X=CHO	0.634	15.1	145.1
X=CN	0.633	15.1	145.1
X=COOCH$_3$	0.584	19.9	140.3
X=COCH$_3$	0.575	20.7	139.4
X=4–py	0.470	30.9	129.0

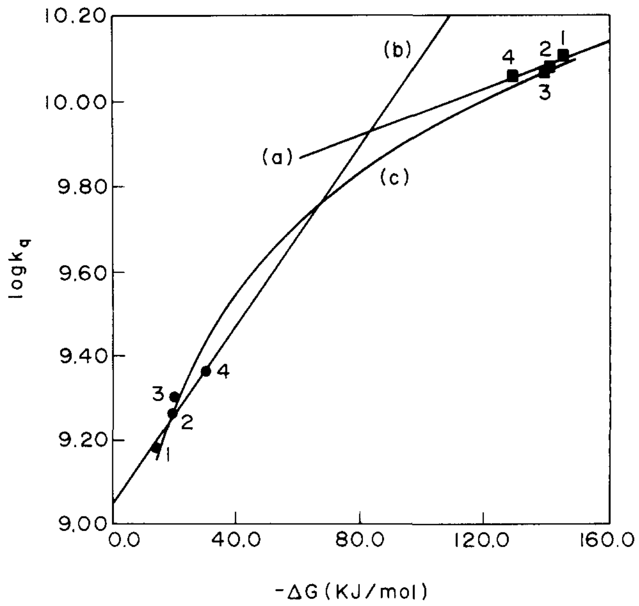

Fig. 2. Plot of log k_q vs. $-\Delta G$ for the quenching process. (a) Quenching process by ferrocenium derivative ions, (b) quenching process by ferrocene derivatives and (c) the whole change curve: 1, X=CN; 2, X=COOCH$_3$; 3, X=COCH$_3$; 4, X=4–*py*.

The k_q and $-\Delta G$ are given in Tables 1 and 2 respectively. The linear relationships are also shown in the plot of log k_q vs. $-\Delta G$ of the reductive electron transfer process (Fig. 2).

It is very interesting that a linear relation is found between log k_q and the free-energy change in both the oxidative and reductive electron transfer processes, respectively (Fig. 2). But in the whole change direction, it is a curve. The plots of log q vs. $-\Delta G$ show a linear region at low $-\Delta G$ values and reaches a plateau at high values of $-\Delta G$. This shows that when $-\Delta G$ is at high values, the rate constants reach a constant value, the rate constant of diffusion process in acetonitrile.

4. Conclusions

The quenching by the title ferrocene derivatives and ferrocenium derivative ions are mainly reductive and oxidative electron transfer process on the ferrocenyl respectively. The quenching rate constants are very fast, at or near the diffusion controlled limit. Linear relationships are shown in the plot of log k_q vs. $-\Delta G$ of both the reductive and oxidative electron transfer process.

Acknowledgements

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