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

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Abstract

A series of unsaturated ferrocene derivatives with the formula Fc–CH=CH–X (X≡CHO, CN, $COCH_3$, $COOCH_3$, 4-py; Fc, ferrocene) were synthesized. They were found to exhibit reversible one-electron oxidation and two one-electron reduction steps. Quenching of the excited state of $Ru(bpy)_3^{2+}$ (bpy, 2,2′-bipyridine) by the ferrocene derivatives was also studied. Quenching occurs mainly via electron transfer on the ferrocenyl group in acetonitrile. The results are confirmed by molecular orbital calculations using the CNDO method. A quenching mechanism is suggested. The bimolecular quenching rate constants were obtained from the Stern–Volmer equation. Linear relationships are obtained for a plot of log K_q vs. $-\Delta G$ of electron transfer.

Keywords: Quenching; Luminescence

1. Introduction

The electronic excited states of molecules have attracted the attention of many research workers over the last two decades [1] due to their intermolecular and intramolecular electron transfer [2] and energy transfer [3] processes and their applications in molecular photodevices [4]. Recently, it has been shown that ruthenium complexes containing 2,2′-bipyridine (bpy) ligands exhibit electron transfer reactions in the excited state [5]. Several theoretical and practical aspects of these reactions, such as the correlation between the rate constant and free energy change [6], have been studied [7]. In this paper, we report the electron transfer quenching of excited $Ru(bpy)_3^{2+}$ by species which can quench the excited state mainly via reductive electron transfer reactions.

Since the discovery of ferrocene in 1951, it has played an important role in the determination of the electronic structures of organometallic compounds and in materials chemistry. A considerable number of ferrocene derivatives have been prepared directly or indirectly from ferrocene, and their properties have been studied extensively both theoretically and experimentally [8], in particular their photochemical and photophysical behaviour [9]. We have synthesized a series of unsaturated ferrocene derivatives via the Heck reaction [10], which can be used as efficient quenchers.

2. Experimental section

The chemicals were of reagent grade and were used without further purification. All of the unsaturated ferrocene derivatives were prepared by the Heck reaction [10] using chloromercuriferrocene [11] as 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 eluent and were analysed by elemental analysis, IR, UV, etc.

Acetonitrile (MeCN) was purified as reported previously [12]. 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 and polished glassy carbon electrodes were used as working electrodes. Potentials were recorded vs. a saturated calomel electrode (SCE)

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for all 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 excitation source. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ 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 $Ru(bpy)_3^{2+}$ in MeCN was 10^{-4} M. The concentrations of the quenchers [Q] were around 10^{-5} M. The excitation wavelength was 450 nm and the emission wavelength was scanned between 500 and 700 nm. The quenching rate constants were measured at the maximum emission intensity (about 613 nm). The quenching rate constants were obtained from the formula [13]

$$I_0/I = 1 + K_q \tau_s[Q]$$

where I and I_0 are the emission intensities in the presence and absence of the quenchers respectively, K_q is the quenching rate constant and τ_s is the luminescence lifetime. For $Ru(bpy)_3^{2+}$ in MeCN, τ_s is 9.0×10^{-7} s [5].

3. Results and discussion

3.1. Electrochemical properties

The cyclic voltammograms obtained using a Pt wire working electrode, for 10^{-3} M solutions of the unsaturated ferrocene derivatives in 0.1 M TEAP–MeCN, show that the Fe(II)/Fe(III) redox couple lies in the range 0.5–0.7 V. The redox potential in the range −1.8 to −2.0 Vis the redox potential of the side-chain. $E_{1/2}(Q^+/Q)$ (redox potential of the ferrocenyl group, Table 1) is obtained from the formula $E_{1/2} = (E_{pa} + E_{pc})/2$. The derivatives show characteristic reversible one-electron oxidation by coupled reaction in the positive potential range. In addition, two cathodic peaks and one anodic peak are obtained for reduction in the negative potential range. This arises from the reduction of groups on the cyclopentadiene ring of the derivatives, because the reduction of ferrocene is not observed in any solvent [14] (Fig. 1).

Table 1
Redox potentials of the derivatives (Fc−CH=CH−X), quenching rate constants and free energy change of the quenching process

Compound	$E_{1/2}(Q^+/Q)$	K_q($\times 10^9$ dm^3 mol^{-1} s^{-1})	$-\Delta G$ (kJ mol^{-1})
X≡−CHO	0.634	1.71	19.9
X≡−CN	0.633	1.71	19.9
$X \equiv -COOCH_3$	0.584	2.10	24.7
$X \equiv -COCH_3$	0.575	2.30	25.6
X≡−4-py	0.470	2.50	35.7

3.2. Quenching by unsaturated ferrocene derivatives

The quenching of $^*Ru(bpy)_3^{2+}$ by various unsaturated ferrocene derivatives was monitored by measuring the decrease in the emission intensity at 610 nm as a function of the Fc−CH=CH−X 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 ferrocene derivatives. This is illustrated in Fig. 2. The quenching rate constants K_q can be obtained by the Stern–Volmer equation; they are listed in Table 1.

The derivatives are effective quenchers of the excited state and all the reactions are rapid. The quenching rate constants are of the order of 10^9 dm^3 mol^{-1} s^{-1}, i.e. slightly lower than that of ferrocene itself (2.5×10^9 dm^3 mol^{-1} s^{-1}). This is not unexpected in view of the large driving force [15].

The electronic and emission spectra of $Ru(bpy)_3^{2+}$ have been studied in detail [16]. The spin-forbidden transition is d–π^* (583 nm), which is related to the metal to ligand charge transfer (^{3}MLCT) transition. When deaerated MeCN solutions containing 10^{-4} M $Ru(bpy)_3^{2+}$ are irradiated with 450 nm light, the ground state of $Ru(bpy)_3^{2+}$ is excited to the higher singlet level (S_1). The electron of the S_1 state can be transferred to the lower triplet level through intersystem crossing.

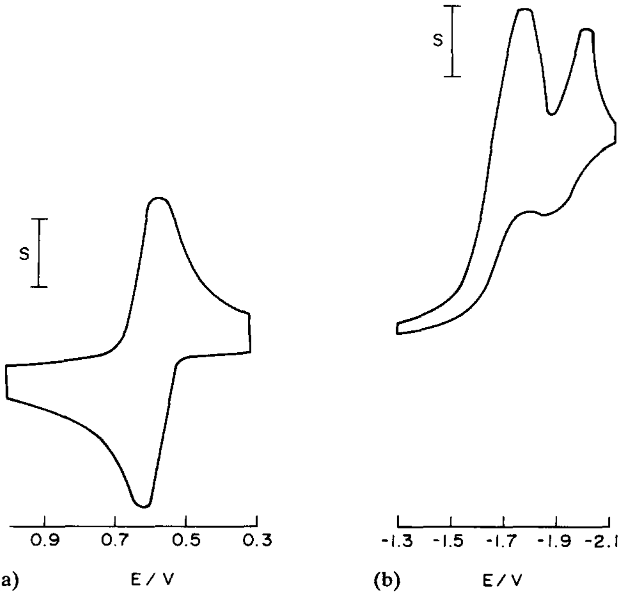

Fig. 1. Cyclic voltammograms at 100 mV s^{-1} in 0.1 M TEAP–MeCN for a Pt wire electrode in a solution containing 1.0×10^{-3} M of Fc–CH=CH−$COCH_3$: (a) anodic region, (b) cathodic region. $S = 1.25$ μA.

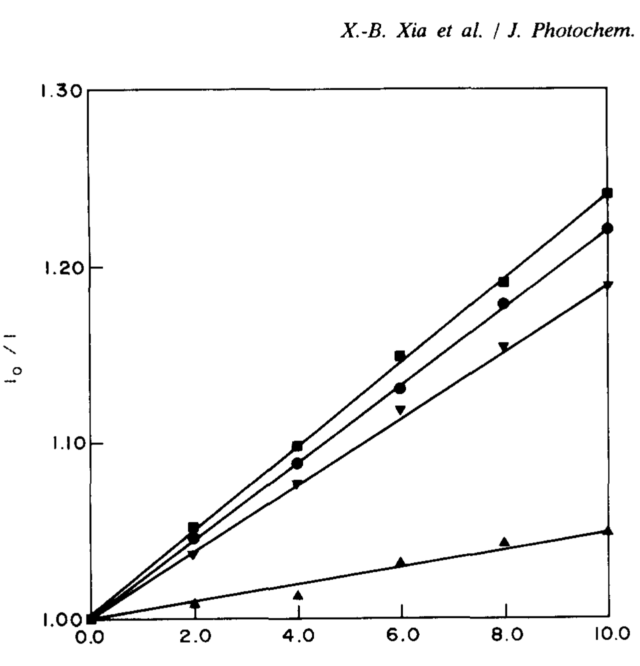

Fig. 2. Quenching of the emission from $^*Ru(bpy)_3^{2+}$ by various unsaturated ferrocene derivatives which shows a linear relation between I_0/I and [Fc–CH=CH–X]. The kinetic data were obtained in MeCN at 25 °C. In order of decreasing rate constant, data are shown for X≡–$COCH_3$ (▲), –$COOCH_3$ (●), –CN (▼) and Fc–CHO (■).

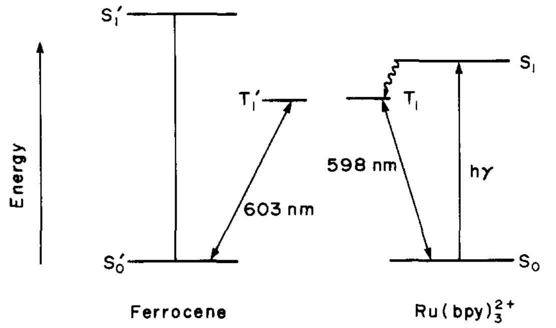

Fig. 3. Energy level diagram for $Ru(bpy)_3^{2+}$–ferrocene.

Finally transfer to the ground state is obtained by the emission of phosphorescence (maximum at 613 nm). Quenchers can quench ^{3}MLCT by either energy transfer [2] or electron transfer [3].

The spin-forbidden transition of ferrocene is $^1A_{1g} \rightarrow {}^3E_{1g}$ (538 nm). In the emission spectrum, the peak at 667 nm is assigned to $T_1 \rightarrow S_0$ ($^3E_{1g} \rightarrow {}^1A_{1g}$) [17]. Under these conditions, the differences between the energies of the ground and triplet states of ferrocene and $Ru(bpy)_3^{2+}$ are 603 nm and 598 nm [18] respectively.

If the triplet of $Ru(bpy)_3^{2+}$ is quenched by ferrocene through energy transfer, the process should be as follows

$$^*Ru(bpy)_3^{2+} + Fe(Cp)_2 \longrightarrow Ru(bpy)_3^{2+} + {}^*Fe(Cp)_2$$

From Fig. 3 (energy level diagram for $Ru(bpy)_3^{2+}$–ferrocene), it can be concluded that the quenching process through energy transfer is unfavourable because $-\Delta G$ is too small. The free energy change of energy transfer from the triplet of $Ru(bpy)_3^{2+}$ (T_1) to that of ferrocene (T_1') is as follows

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= N_0 h\nu_{603\ \mathrm{nm}} - N_0 h\nu_{598\ \mathrm{nm}} - RT \ln 3/3 \\ &= -0.2\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

The redox properties of the triplet level of $^*Ru(bpy)_3^{2+}$ have also been studied. E[Ru(II)/*Ru(I)] = −0.84 V and E[*Ru(II)/Ru(I)] = 0.84 V (vs. SCE). If the quenching process takes place through electron transfer

$$^*Ru(bpy)_3^{2+} + Fe(Cp)_2 \longrightarrow Ru(bpy)_3^{+} + Fe^{+}(Cp)_2$$

the free energy change is as follows

$$\begin{aligned}\Delta G &= -nFE \\ &= -96\,500[E_{1/2}(^*\mathrm{Ru(II)/Ru(I)}) - E_{1/2}(\mathrm{Q^+/Q})] \\ &= -96\,500 \times (0.77 - 0.40) = -36\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Therefore we can conclude that the triplet level of $Ru(bpy)_3^{2+}$ can be quenched by ferrocene mainly through electron transfer.

With regard to the unsaturated ferrocene derivatives, they probably quench the excited state of $Ru(bpy)_3^{2+}$ through electron transfer because their electronic spectra are similar to that of ferrocene. The free energy changes in the electron transfer process are given in Table 1. A linear relationship is obtained for a plot of $\log K_q$ vs. $-\Delta G$ of the reaction (Fig. 4). This indicates that K_q is dependent on the redox properties of the ferrocene derivatives, and suggests that the event involves electron transfer with reduction of the ferrocenyl moiety.

$Fe(Cp)(C_5H_4CHO)$ was also used as quencher. It was found that, because the –CHO group in Fc–CHO has a stronger induction effect than Fc–CH=CH–X,

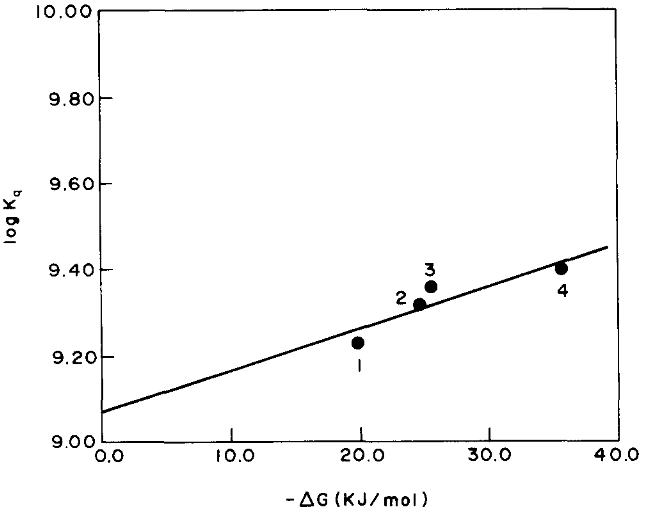

Fig. 4. Plot of $\log K_q$ vs. $-\Delta G$ for the quenching process (1, X≡–CN; 2, X≡–$COOCH_3$; 3, X≡–$COCH_3$; 4, X≡–4-py).

Table 2
Molecular orbital calculations of unsaturated ferrocene derivatives

Compound	HOMO		Net charge on Fe
	Energy (a.u.)	LCAO	
Fc–CH=CH–CHO	−0.3440	$d_{x^2-y^2}$: 0.6324 d_{z^2}: 0.1895	−0.9030
Fc–CH=CH–$COCH_3$	−0.3401	$d_{x^2-y^2}$: 0.6344 d_{z^2}: 0.1868	−0.9014
Fc–CH=CH–$COOCH_3$	−0.3461	$d_{x^2-y^2}$: 0.6301 d_{z^2}: 0.1962	−0.9014
Fc–CH=CH–CN	−0.3423	$d_{x^2-y^2}$: 0.6321 d_{z^2}: 0.1904	−0.9019

LCAO, linear combination of atomic orbitals.

the K_q value (1.08×10^9 dm^3 mol^{-1} s^{-1}) of Fc–CHO is lower than that of the derivatives.

We calculated the molecular orbitals of the derivatives using the CNDO method. It was found that the highest occupied molecular orbital (HOMO) is composed of $d_{x^2-y^2}$ and d_{z^2} orbitals on the central Fe atoms. Typical results of the molecular orbital calculations are given in Table 2. In the quenching process, Fc–CH=CH–X is oxidized to $[Fc-CH=CH-X]^+$ by loss of electrons from the HOMO. The following quenching mechanism is suggested

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3{}^{2+}$$

$$Fc-CH=CH-X + {}^*Ru(bpy)_3{}^{2+} \longrightarrow$$

$$Fc^+-CH=CH-X + Ru(bpy)_3{}^+$$

4. Conclusions

The quenching by unsaturated ferrocene derivatives is mainly due to reductive electron transfer. The stronger the induction effect of the side-chain, the lower the quenching rate constant. A quenching mechanism is suggested

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3{}^{2+}\text{(excitation)}$$

$$Fc-CH=CH-X + {}^*Ru(bpy)_3{}^{2+} \longrightarrow$$

$$Fc^+-CH=CH-X + Ru(bpy)_3{}^+$$

(electron transfer process)

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