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HIGHLY EFFICIENT PHOTOREDUCTION OF METHYLVIOLOGEN BY TRIS(BIS-DIAZADIIMINE)RUTHENIUM(II) COMPLEXES

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Photoreduction of methylviologen (MV^{2+}) by several Ru(II)L_3 (L:bisdiazadiimine) complex was studied in the presence of triethanolamine in aqueous solution. The quantum yield of MV^+ formation (MV^+) was as high as 0.98 or 0.85 in vacuo when L is 2,2'-bipyrazine or 2,2'-bipyrimidine, respectively. These results were interpreted as due to reductive quenchineg of Ru(II)L_3^* by triethanolamine.

Recent advances in transition metal photochemistry provide possible means of solar energy conversion to chemical energy by visible light illumination. Among these complexes, tris(2,2'-bipyridine)ruthenium(II) complex, Ru(bpy)$_3$, has been extensively studied because of its favorable electronic and thermodynamic properties for water splitting. While the study on Ru(II) complex for water splitting has been confined to the bipyridine complex, the preparative, spectroscopic and electrochemical studies have been extended to Ru(II) complexes containing bipyrazine,1) bipyrimidine,2) biimidazole,3) and biquinoline4) as ligands. Surprisingly, these new complexes have been scarcely examined for the ability of photoreducing methylviologen (MV^{2+}) which is an important primary process for water splitting. An exception is the original work by Crutchley and Lever on tris(2,2'-bipyrazine)ruthenium(II) complex which photoreduces MV^{2+} in a 77% yield in the presence of triethanolamine (TEOA).1) In order to test the photeredox ability of Ru(II) complexes, we prepared five poly-diazadiimine ruthenium(II) complexes (RuL_3, Figure 1) and examined the photoreduction of MV^{2+} by RuL_3 in the presence of TEOA.

1 and **2** were prepard according to literature.1,2) **3**, **4**,and **5** were prepared by refluxing $RuCl_3 \cdot 3H_2O$ or $Ru[(CH_3)_2SO]_4 \cdot Cl_2$ with a five-times excess of the ligand in ethanol-water mixture or ethanol for 6 - 70 h. Spectroscopic and electrochemical

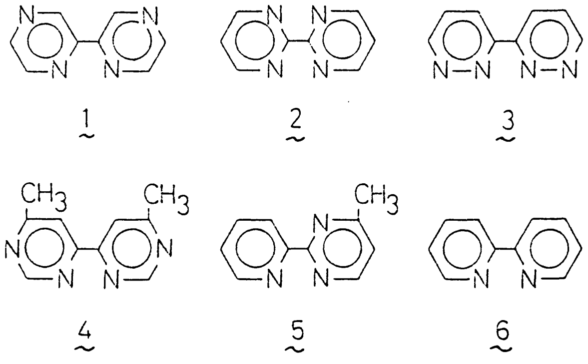

Fig. 1. The structures of ligands (L) and abbreviations of RuL_3.
1 ; Ru(2,2'-bipyrazine)$_3$.Cl_2,
2 ; Ru(2,2'-bipyrimidine)$_3$.Cl_2,
3 ; Ru(3,3'-bipyridazine)$_3$.Cl_2,
4 ; Ru(6,6'-dimethyl-4,4'-bipyrimidine)$_3$.Cl_2,
5 ; Ru(4-methyl-2-(2'-pyridyl) pyrimidine)$_3$.Cl_2,
6 ; Ru(2,2'-bipyridine)$_3$.Cl_2.

properties of **3**, **4**, and **5** will be reported elsewhere.[5)] Photoreactions were carried out in a quartz cell irradiated by monochromatized emission (λ= 435 nm) from a 2-kW xenon lamp. The incident light intensity was determined by a ferrioxalate actinometer. The quantum yields of MV^{2+} photoreduction were determined for the samples deoxygenated by N_2-gas purging for 30 min (ϕ_{N_2}) and by freeze-pump-thaw cycles (ϕ_{vac}).

Table 1 shows the quantum yields of MV^{2+} photoreduction in the system of RuL_3 ($6X10^{-5}$ M) - MV^{2+} (0.02 M) - TEOA (0.6 M) in aqueous solution and the quenching rate constants (k_q) of the excited state of RuL_3 ($*RuL_3$) by MV^{2+} and TEOA in 0.5 M of aqueous KCl solution. For comparison, $Ru(bpy)_3$ was also reexamined under same conditions. The photosensitizer efficiency of $Ru(bpy)_3$ was confirmed to be in good agreement with the reported values (0.19[1)] - 0.24[6)]). The most important results are as follows. i) ϕ_{vac} are 0.98 for **1** and 0.85 for **2**, which are 4 times as large

Table 1. Quantum yields of MV^{2+} photoreduction and rate constants for the quenching of $*RuL_3$ emission by MV^{2+} and TEOA.

			k_q ($M^{-1}s^{-1}$)		$E_{1/2}$(V vs. SCE)$^{a)}$		τ(μs)[5)]
RuL_3	ϕ_{vac}	ϕ_{N_2}	MV^{2+}	TEOA	$Ru^{3+/2+}$	$Ru^{2+/+}$	(in H_2O, 298K)
1	0.98	0.75	$8.6X10^6$	$2.5X10^8$	+1.86$^{d)}$	-0.80$^{d)}$	1.02
2	0.85	0.44	b)	$3.6X10^7$	——	-1.40$^{e)}$	0.06
3	0.27	0.16	$7.6X10^7$	$1.3X10^6$	+1.58$^{f)}$	-1.00$^{f)}$	0.70
4	0.03	—	c)	c)	+1.48$^{f)}$	-0.78$^{f)}$	c)
5	0.02	—	$3.9X10^8$	b)	+1.38$^{f)}$	-1.18$^{f)}$	0.17
6	0.22	0.19	$2.1X10^9$	b)	+1.27$^{f)}$	-1.34$^{f)}$	0.64

a) In CH_3CN. b) No emission quenching was observed in the concentration region of [MV^{2+}] $<$ 0.02 M or [TEOA] $<$ 0.6 M. c) Not determined owing to the low emission quantum yield and the short excited lifetime. See also Ref. 5. d) Ref. 1. e) Ref. 2. f) Ref. 5.

as the value for $\mathrm{Ru(bpy)_3}$. For **1**, ϕ_{vac} is larger than the reported value (0.77) determined under N_2 atmosphere.[1)] We observed strong oxygen effect on MV^{2+} photoreduction yield by **1** and **2**. The ϕ_{N_2} values are 0.75 for **1** and 0.44 for **2**, and the former is in excellent agreement with the result by Crutchley and Lever.[1)] ii) **3** is less effective for MV^{2+} photoreduction than **1** and **2**, but is more efficient than $\mathrm{Ru(bpy)_3}$. iii) The other $\mathrm{RuL_3}$, **4** and **5**, are almost inefficient for MV^{2+} photoreduction. iv) The absorption spectra of $\mathrm{RuL_3}$ before and after photoreaction are identical, indicating good turn-over of $\mathrm{RuL_3}$ as a photocatalyst.[7)]

These results are explainable by the following observations. The quenching rate contants of the excited state of **1** by MV^{2+} and TEOA are $8.6\mathrm{X}10^{6}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $2.5\mathrm{X}10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively. Consequently, the photoexcited **1** is mainly reduced by TEOA to Ru(I) but scarcely oxidized by MV^{2+}. The excited state of **2** is also reduced by TEOA with the rate constant of $3.6\mathrm{X}10^{7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ but not oxidized by MV^{2+} at all. Since the oxidaiton of TEOA is an irreversible process, back electron transfer from Ru(I) to oxidized TEOA ($\mathrm{TEOA}^{\mathrm{ox}}$) is unlikely and consequently, the fate of Ru(I) is to reduce MV^{2+} to MV^{+} to attain the high quantum yield (Scheme I). On the other hand, the excited state of $\mathrm{Ru(bpy)_3}$ is oxidized by MV^{2+} to Ru(III) as shown in Scheme II. Back electron transfer from MV^{2+} to Ru(III) is inevitable so that the overall quantum yield of MV^{2+} photoreduction is lower than that by **1** or **2**.

Scheme I.

$$^{*}\mathrm{RuL}_3^{2+} + \mathrm{TEOA} \longrightarrow \mathrm{RuL}_3^{+} + \mathrm{TEOA}^{\mathrm{ox}} \not\longrightarrow \mathrm{RuL}_3^{2+} + \mathrm{TEOA} \tag{1}$$

$$\mathrm{RuL}_3^{+} + \mathrm{MV}^{2+} \longrightarrow \mathrm{RuL}_3^{2+} + \mathrm{MV}^{+} \tag{2}$$

Scheme II.

$$^{*}\mathrm{RuL}_3^{2+} + \mathrm{MV}^{2+} \longrightarrow \mathrm{RuL}_3^{3+} + \mathrm{MV}^{+} \longrightarrow \mathrm{RuL}_3^{2+} + \mathrm{MV}^{2+} \tag{3}$$

$$\mathrm{RuL}_3^{3+} + \mathrm{TEOA} \longrightarrow \mathrm{RuL}_3^{2+} + \mathrm{TEOA}^{\mathrm{ox}} \tag{4}$$

Strong oxygen effect as manifested by the difference between ϕ_{vac} and ϕ_{N_2} for **1** and **2** (and also **3**) is suggested as due to oxidation of Ru(I) by oxygen. This is supported by the fact that oxidation of Ru(I) is highly exothermic process with a free energy change of -5.3 kcal/mol and -19.1 kcal/mol for **1** and **2**, respectively.[9)] Furthermore, the electron transfer from Ru(I) to oxygen has been directly demonstrated by a laser photolysis study of the $\mathrm{Ru(bpy)_3}$ - N,N-dimethylaniline - O_2 system by Meyer et al.[10)]

The ϕ_{vac} value is larger for **3** than that for $\mathrm{Ru(bpy)_3}$, whereas the quenching rate constant by MV^{2+} for **3** is smaller than that for $Ru(bpy)_3$. The large ϕ_{vac}/ϕ_{N_2} value and the small but finite quenching rate constant by TEOA for **3** suggest that MV^{+} is produced partly by the reductive quenching mechanism (Scheme I). On the other hand, although **4** and **5** have strong reducing and oxidizing powers[5)] and the reductive and oxidative quenching from the excited state of **4** or **5** by TEOA and MV^{2+}, respectively, are both thermodynamically favorable,[11)] these complexes can scarcely photoreduce MV^{2+}. The short excited lifetimes of **4** and **5** may be responsible for such low yields.

In conclusion, **1**, **2**, and **3** are superior photocatalysts to $Ru(bpy)_3$ for MV^{2+} photoreduction whereas **4** and **5** are almost inactive, indicating that the photoredox ability of RuL_3 is highly sensitive to the ligand property.

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11) ΔG(kcal/mol) for electron transfer reactions of $^{*}RuL_3$: ΔG(**4** - MV^{2+}) = +1.3, ΔG(**4** - TEOA) = -6.2, ΔG(**5** - MV^{2+}) = -6.7, ΔG(**5** - TEOA) = -2.5, The value of 0.82 V (vs. SCE) was used as the oxidation potential of TEOA. K. Kalyanasandarum, J. Kiwi, and M. Graetzel, Helv. Chim. Acta, 61, 2720(1978).

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