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Dye-sensitized Photoreduction of Polymolybdates

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Introduction

We have described the water-photoelectrolysis by the photogalvanic cell based on the photoreduction of Mo^{VI} to Mo^V for an aqueous solution of the alkylammonium polymolybdate [1–3]. The system can be extended to polytungstate and polyvanadate [2, 4] and is interesting from a cost standpoint for the chemical storage of solar energy, since it is prepared for readily available chemicals (chemically stable polymolybdate(VI) and alkylamine).

The most obvious difficulty with the proposed system is the lack of absorption of polymolybdate in the wavelength region (>400 nm) of available solar energy [1]. This strongly weak sensitivity to the solar spectrum may be corrected, however, by addition of an appropriate spectral sensitizer. We have found that riboflavin derivatives are important candidates for sensitizing the desired energy storage step [5], since they can strongly absorb light in the 400–500 nm wavelength region. We have undertaken an investigation of the ability of flavin mononucleotide (FMN) to sensitize the photoreduction of polymolybdate(VI). Our initial results, which form part of a program to develop a practical solar energy storage system based on water-photolysis, are reported here.

Experimental

Hexakis(isopropylammonium) heptamolybdate trihydrate $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ was prepared and recrystallized following our procedure [3]. 2-Methyl-2-nitrosopropane (MNP) used for the ESR spin trapping technique, was prepared as described by Emmons [6]. Solutions of $Na_6[Mo_7O_{24}]$ were obtained by adjusting Na_2MoO_4 solution to pH = 5–6 with $HClO_4$. Other chemicals (Tokyo Kasei analytical grade) were used without further purification. The evacuation of solutions was carried out by several freeze-pump-thaw cycles at 10^{-4} Torr.

Irradiation experiments were carried out using a 500-W super-high-pressure mercury lamp in conjunction with Toshiba KL-43 + V-V43 filters for 436 nm wavelength selection. Chemical actinometry was carried out using the potassium ferrioxalate system. The dye-sensitized photoreduction of Mo^{VI} was followed by the measurement of the absorbance appearing at 730 nm due to Mo^V formation [3]. The amount of the photoeliminated FMN was determined from the decrease in the absorbance at 445 nm, corrected for the absorbance due to Mo^V. Absorbance of sample solutions was measured on a Hitachi 624 spectrophotometer. X-band ESR spectra were recorded on a Varian E 12 spectrometer.

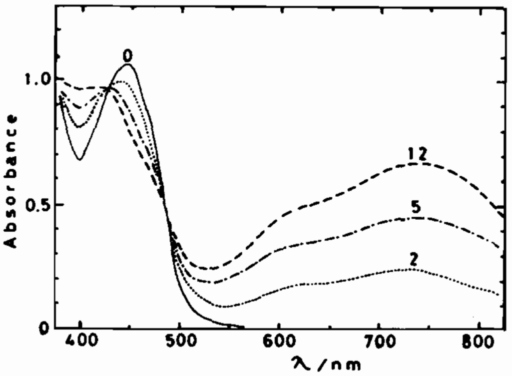

Fig. 1. Absorption spectra of the deaerated solution containing 8.3 × 10^{-5} *M* FMN and 13.6 m*M* $[NH_3Pr^i]_6[Mo_7O_{24}]$. Numbers indicate the irradiation time (min) of 436 nm-light (11.0 × 10^{-4} Einstein dm^{-3} min^{-1}). Absorbance indicates the value for an optical path length of 1 cm.

Results and Discussion

Flavines such as FMN, riboflavin, and flavin adenine dinucleotide, produced detectable sensitization when irradiated at 436 nm in aqueous solutions containing $[Mo_7O_{24}]^{6-}$. Figure 1 shows the absorption spectra of the deaerated solution containing 8.3 × 10^{-5} *M* FMN and 13.6 m*M* $[NH_3Pr^i]_6[Mo_7O_{24}]$ before and after irradiation of 436 nm-light. Photo-excitation of FMN resulted in the sensitized photoreduction of $[Mo_7O_{24}]^{6-}$ as represented by a formation of the blue species (λ_{max} 730, λ_{sh} 620 nm). During the sensitization, in addition, FMN was eventually degraded. For the aerobic solution no significant blue-coloration occurred, probably due to the rapid oxidation process of Mo^V to Mo^{VI}, as described previously for the direct photoreduction of $[NH_3Pr^i]_6[Mo_7O_{24}]$ solutions [7].

Pertinent quantum yields of Mo^V formation are listed in Table I, where only the initial value determined at short irradiation times is reported. The

TABLE I. Quantum Yields (ϕ) for Mo^V Formation and FMN Elimination.[a]

Initial concn. of $[Mo_7O_{24}]^{6-}$[b]/m*M*	Initial concn. of FMN/10^{-5} *M*	Incident 436 nm-light intensity, /10^{-4} E dm^{-3} min^{-1}	NaClO$_4$ concn., /*M*	EDTA concn., /m*M*	$\phi_{Mo}{}^V$	ϕ_{-FMN}
13.6	2.3	11.0			0.09	0.007
	4.6				0.10	0.008
	8.3				0.09	0.006
	24.9				0.07	–
	41.5				0.07	–
6.8	8.3	11.0			0.09	0.007
20.4					0.07	0.006
68.0					0.07	0.008
13.6	7.1	11.0	0.01		0.10	0.006
			0.10		0.10	0.006
			0.50		0.09	0.006
13.6	7.1	5.53			0.09	0.006
		2.76			0.12	0.007
		1.10			0.14	0.008
		0.55			0.16	0.008
14.0 ($[NH_4]^+$ salt)	7.1	11.0			0.09	0.006
14.1 (Na^+ salt)					0.08	0.006
0	9.0	4.5		0		0.013
				2.5		0.061
34.0	9.0	4.5		0	0.09	0.007
	9.5			2.5	0.09	0.007
	94.0			0	0.08	–
	94.0			2.5	0.07	

[a] $\Phi_{Mo}{}^V$ and ϕ_{-FMN} indicate the quantum yields for Mo^V formation and FMN elimination, respectively. All data are given for the deaerated solution at room temperature. [b] Unless otherwise specified, $[NH_3Pr^i]^+$ salt was used as $[Mo_7O_{24}]^{6-}$.

quantum yield decreased as a function of time and the value for Mo^V formation was 10–15 times higher than that for FMN elimination. These indicate that the FMN degradation competes with the sensitization. The quantum yield of Mo^V formation increased with a decrease in 436 nm-light intensity but was almost unchanged with variations of ionic strength and FMN and $[NH_3Pr^i]_6[Mo_7O_{24}]$ concentrations. It should be noted that the sensitized photoreduction of $[Mo_7O_{24}]^{6-}$ occurs irrespective of the variety of cations such as $[NH_3Pr^i]^+$,$[NH_4]^+$, and Na^+, since the continuous irradiation of $[NH_4]_6[Mo_7O_{24}]$ or $Na_6[Mo_7O_{24}]$ solution with UV light brought about no observable photoreduction of $[Mo_7O_{24}]^{6-}$ [7]. The possibility of the transfer of the FMN excited singlet or triplet energy to $[Mo_7O_{24}]^{6-}$ seems unlikely, since in this case $[NH_4]^+$ and Na^+ salts of $[Mo_7O_{24}]^{6-}$ would have to suffer from UV photoreduction as well as the $[NH_3Pr^i]^+$ salt, judging from a very small difference in the structure of $[Mo_7O_{24}]^{6-}$ among the three salts [3, 8]. It is well known that the irradiation of FMN in the presence of ethylenediaminetetraacetate (EDTA) results in a FMN photoreduction to a leuco FMN ($FMNH_2$) and involves an initial one electron reduction of the FMN triplet state to a FMN$^{\cdot-}$ and the subsequent protonation of FMN$^{\cdot-}$ to FMNH• followed by a disproportionation of FMNH• to form $FMNH_2$ and FMN. Table I shows that the addition of EDTA as an electron donor brought about no significant change in the quantum yield of Mo^V formation.

This indicates that the possibility of the electron transfer from FMN$^{\cdot-}$ or FMNH• to $[Mo_7O_{24}]^{6-}$ in the sensitized photoreduction process may be excluded, since the quantum yield of Mo^V formation should be increased by an addition of EDTA if above hypothesis is operative.

436 nm-photolysis of the deaerated sample solution in the presence of MNP gave ESR signal of 3 X

2 lines due to the spin adduct of ·OH (or HO_2·) radicals (a_N = 16.1, a_H = 4.0 G at g = 2.005) which was the same as for UV-photolysis of $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution [3], whereas in the absence of $[Mo_7O_{24}]^{6-}$ there was no observable 3 X 2 lines*. The result of the ESR spin trapping technique implies a similarity in the reduction process of $[Mo_7O_{24}]^{6-}$ between the sensitized and direct photolyses. It has been proposed that the direct photoreduction of $[Mo_7O_{24}]^{6-}$ for $[NH_3Pr^i]_6[Mo_7O_{24}]$ is due to the formation of the charge transfer complex between the aminonitrogen and the terminal oxo-group of the MoO_6 site, preceded by the transfer of a hydrogen bonding proton from an isopropylammonium nitrogen atom to a bridging oxygen atom in the photoreducible MoO_6 site [3]. In connection with the occurrence of the sensitized photoreduction of $[Mo_7O_{24}]^{6-}$ for $[NH_4]^+$ and Na^+ salts, therefore, the sensitization may proceed *via* a charge-transfer complex between the excited FMN and $[Mo_7O_{24}]^{6-}$ (probably isoalloxazine nitrogen atom and the terminal oxo-group of the MoO_6 site which is the same site as for the case of the direct photoreduction of $[NH_3Pr^i]_6[Mo_7O_{24}]$). From the fact that neither initial intensity nor spectrum shape of the FMN fluorescence with a maximum at 524 nm was almost affected by $[Mo_7O_{24}]^{6-}$, the excited triplet FMN seems to be involved in the sensitization. The study of the flash photolysis to understand the sensitization mechanism is in progress.

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*In the absence of $[Mo_7O_{24}]^{6-}$ MNP gives a 1:2:2:1 pattern of four lines (a_N = a_N = 14.4 G) with a very weak signal intensity, which is not yet elucidated.

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