Bull. Chem. Soc. Jpn., 70, 2107—2110 (1997)

Photoreduction of Hydrogencarbonate or Ethylene Catalyzed by Trisodium Trisulfonatophthalocyaninatozincate(II)

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(Received January 28, 1997)

In an aqueous dimethyl sulfoxide (DMSO) solution of triethanolamine (TEOA), the photosensitizer of the title complex (**1**), and 1,1′-dimethyl-4,4′-bipyridinium dichloride ($MVCl_2$), $MV^{\bullet+}$ radicals were formed upon irradiation with visible light; the photoreduction proceeded with light from both the B- (340 nm) and Q- (674 nm) band wavelengths of **1**.

The photoreduction of hydrogencarbonate to methane was performed in an aqueous DMSO solution of an electron donor, **1**, $MVCl_2$, and ruthenium colloid upon irradiation with visible light. Ethylene was also photoreduced to ethane upon the irradiation of an aqueous solution of an electron donor, **1**, $MVCl_2$, and palladium colloid.

Since metallophthalocyanines have intense absorption bands in the wavelength region from 600 to 700 nm, and collect longer wavelengths of visible light in the solar spectrum, they are an attractive sensitizer for the photoreduction of water or carbon dioxide.1) Recently, they were also used for the photodynamic therapy of cancer due to their facile excitation with longer wavelengths of visible light.2)

As a photosensitizer for the reduction of water, complexes such as tris(bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) and sulfonato-substituted porphyrinatozinc(II) have been reported.3,4) Furthermore, the photoreduction of carbon dioxide was performed by nickel(II) tetraazamacrocycle or $[Ru(bpy)_3]^{2+}$.5,6) Willner and his co-workers have also reported on the reduction of ketones,7) the photocleavage of acetylene to methane,8) and the photoinduced hydrogenation of ethylene and acetylene9) using $[Ru(bpy)_3]^{2+}$ as a photosensitizer. They have also reported on the photoreduction of hydrogencarbonate to formate using deazariboflavin as the photosensitizer in the presence of a palladium-β-cyclodextrin colloid.10,11)

We have currently studied the photoreduction of 1,1′-dimethyl-4,4′-bipyridinium (MV^{2+}) catalyzed by such photosensitizers as lanthanoid(III) phthalocyanine,12) amphiphilic phthalocyanine derivative of zinc(II) or silicon(IV),13,14) and trisodium trisulfonatophthalocyaninatozincate(II) (**1**)15) in the presence of triethanolamine {tris(2-hydroxyethyl)amine, TEOA} as an electron donor. In this paper, the photoreduction of hydrogencarbonate or ethylene to methane or ethane using **1**, which does not appreciably form photoinactive dimer species16) as the photosensitizer, is reported.

Experimental

Materials. Trisulfophthalocyaninatozinc(II) was prepared according to a literature method.16) The sodium salt (**1**) was prepared by treating the complex with an aqueous sodium hydroxide solution. Ruthenium,17) palladium,9) and platinum colloids17) were prepared according to literature methods. The other reagents were of analytical grade or of the highest grade available, and were used without further purification.

Irradiation for a Three-Component System. A mixture solution of water and dimethyl sulfoxide (DMSO) (1 : 1, v/v) containing TEOA (1×10^{-1} mol dm^{-3}), **1** (1×10^{-5} mol dm^{-3}), and $MVCl_2$ (5×10^{-3} mol dm^{-3}) was purged by argon, and was irradiated with a Hitachi Fluorescence Photometer 850 at 20 °C for 9 h. The concentration of $MV^{\bullet+}$ radicals was determined by its absorbance at 395 nm (molar absorptivity = 45000 mol^{-1} dm^{-1} cm^{-1}).18)

Photoreduction of Hydrogencarbonate or Ethylene. Steady-state irradiation was performed with a 500-W halogen lamp. Light shorter than 420 nm was filtered through a Toshiba L-42 filter. An aqueous or DMSO mixture solution (10 ml) of an electron donor, **1**, $MVCl_2$, metal colloid, and sodium hydrogencarbonate was purged by argon, being irradiated at 25 °C for 24 h.19) For the photoreduction of ethylene, an aqueous solution (10 ml) of electron donor, **1**, $MVCl_2$, metal colloid, and detergent was purged by argon, and then bubbled by ethylene, being irradiated under an ethylene atmosphere at 25 °C for 48 h. The pH change during the photoreduction was within 0.2 (the final pH is shown in the text). Gas analyses were performed by gas chromatography (Hewlett Packard 5890 Series II) using an active carbon column (30/60 mesh) with helium as the carrier gas and a thermal conductivity detector at 100 °C.

Results and Discussion

A few studies of the photoactivity dependence of phthalocyanine complexes on irradiated wavelengths have been reported.20—22) We investigated the dependence of the yield of $MV^{\bullet+}$ radicals on the irradiated wavelengths in the three-component system of TEOA, **1**, and $MVCl_2$ (Fig. 1). The action spectrum is similar to the absorption spectrum of the dimer species,16,23) which seems to indicate that the dimer species participate in the photoreduction of MV^{2+}. However, a consideration based on the fact that the solution treated by bubbling with air after irradiation to quench $MV^{\bullet+}$ radicals

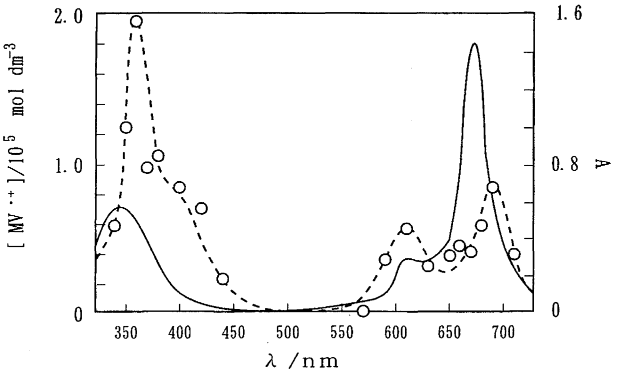

Fig. 1. Action spectrum for the yield of $\mathrm{MV}^{\bullet +}$ radicals in an aqueous DMSO solvent (1 : 1, v/v) at pH 10.7: - - -) action spectrum; —) absorption spectrum of **1**; [complex] = 1×10^{-5} mol dm^{-3}.

showed an absorption spectrum of the monomer species, suggests that the dimer species are not photoactive for the reduction of MV^{2+}.

Although irradiation with light of near B-band wavelengths is more effective for the formation of $\mathrm{MV}^{\bullet +}$ radicals than that with light of the Q-band wavelength, **1** is a useful photosensitizer for the use of longer wavelengths of visible light in the solar spectrum.

Photoreduction of Hydrogencarbonate. Sodium hydrogencarbonate was reduced to methane upon irradiation with visible light of an aqueous DMSO solution containing disodium ethylenediaminetetraacetate ($\mathrm{Na_2edta}$), **1**, MV^{2+}, and ruthenium colloid in the presence of sodium hydrogencarbonate (Fig. 2).

Along with an increase of the DMSO ratio in an aqueous mixture solvent, the yield of methane increased (Fig. 3). It has been reported that the yield of $\mathrm{MV}^{\bullet +}$ radicals in the three-component system increased along with an increase in the DMSO concentration.[14] The yield of methane increased in a similar manner as that of the $\mathrm{MV}^{\bullet +}$ radicals with increasing the DMSO ratio in an aqueous mixture solvent (Fig. 3). That is, the increased concentration of $\mathrm{MV}^{\bullet +}$ radicals enhanced the formation of methane. Since $\mathrm{Na_2edta}$ was slightly soluble in an aqueous mixture solvent of over 50% of DMSO, measurements were not performed over the concentration.

In the absence of **1**, $\mathrm{MV}^{\bullet +}$ radicals were not formed under irradiation, resulting in no evolution of methane. Without sodium hydrogencarbonate, methane was not also formed, indicating that the carbon of methane originated from hydrogencarbonate. While it was previously reported that formate was formed from hydrogencarbonate in the presence of a palladium-β-cyclodextrin colloid,[10,11] the use of a ruthenium colloid gave methane formation in an aqueous DMSO solvent for the present case. The evolution of hydrogen, carbon monoxide, or ethane was not confirmed by gas chromatography.

The optimum pH for methane evolution was 6.6 (Fig. 4). In a high-pH region, the proton concentrations decrease, and reducing the proton also became hard {redox potential for proton = −0.24—0.059pH (V vs. SCE)}.[25] On the other hand, in a low-pH region, the electron donor (edta^{2-}) is protonated, and its ability of electron donation decreases, resulting in a decrease in the formation of $\mathrm{MV}^{\bullet +}$ radicals.[26] The optimum pH values for the photoreduction fell at around 7 as a result of both factors.

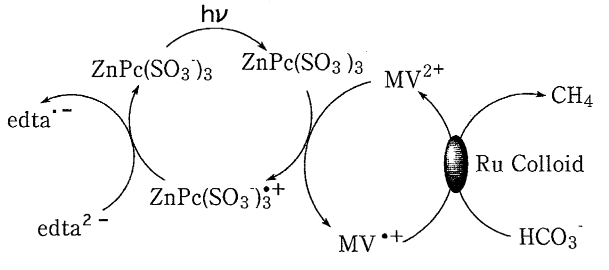

Fig. 2. Four-component system of the photoreduction of hydrogencarbonate.

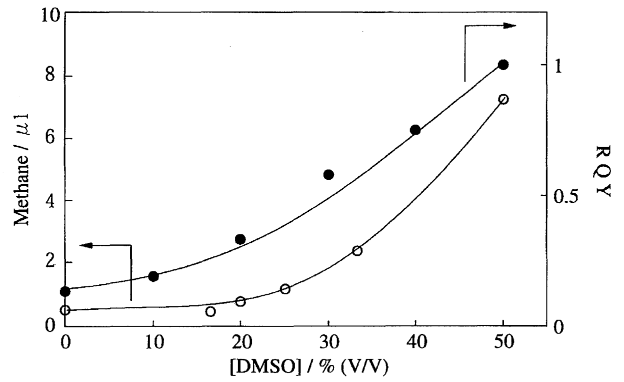

Fig. 3. The dependence of the yields of methane and $\mathrm{MV}^{\bullet +}$ radicals on the DMSO concentration in an aqueous mixture solvent: ●) the relative quantum yield (RQY)[24] of $\mathrm{MV}^{\bullet +}$ radicals.[14] ○) the yield of methane; [$\mathrm{Na_2edta}$] = 1×10^{-2} mol dm^{-3}, [complex] = 6×10^{-5} mol dm^{-3}, [$\mathrm{MVCl_2}$] = 2×10^{-3} mol dm^{-3}, [Ru colloid] = 173 mg dm^{-3}, [$\mathrm{NaHCO_3}$] = 5×10^{-3} mol dm^{-3}; pH = 6.4; reaction time = 24 h.

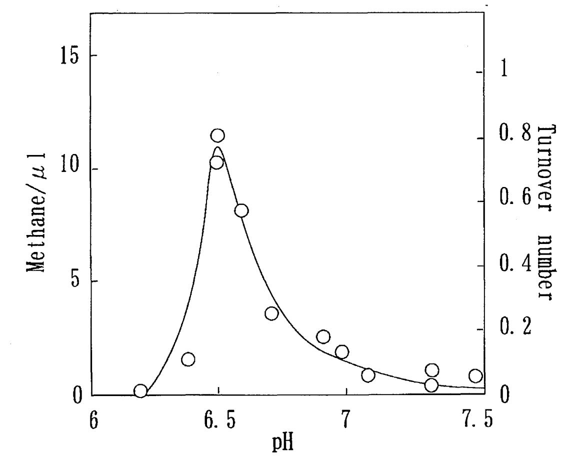

Fig. 4. The pH dependence on the yield of methane in an aqueous DMSO solvent (1 : 1, v/v): [$\mathrm{Na_2edta}$] = 1×10^{-2} mol dm^{-3}, [complex] = 6×10^{-5} mol dm^{-3}, [$\mathrm{MVCl_2}$] = 2×10^{-3} mol dm^{-3}, [Ru colloid] = 173 mg dm^{-3}, [$\mathrm{NaHCO_3}$] = 5×10^{-3} mol dm^{-3}; reaction time = 24 h. Turnover number is based on the complex.

Table 1. Effects of Electron Donors, Inhibitors, and Metal Colloids on the Yield of Methane in an Aqueous DMSO Solvent (1 : 1, v/v)

Run		Methane/μl
1	Na_2edta	1.8
2	TEOA	0.2
3	Cysteine	3.1
4	DTT	1.5
5	TEMPO	0
6	Pd colloid	0.9
7	Pt colloid	0.2

$[MVCl_2] = 2\times10^{-3}$ mol dm^{-3}, $[NaHCO_3] = 5\times10^{-3}$ mol dm^{-3}, [complex] $= 6\times10^{-5}$ mol dm^{-3}; pH = 7.0; reaction time = 24 h. In Runs 1—3, [electron donor] $= 1\times10^{-2}$ mol dm^{-3}, [Ru colloid] = 173 mg dm^{-3}; in Runs 4 and 5, $[Na_2edta] = 1\times10^{-2}$ mol dm^{-3}, [Ru colloid] = 173 mg dm^{-3}, [DTT] or [TEMPO] $= 1\times10^{-3}$ mol dm^{-3}; in Runs 6 and 7, $[Na_2edta] = 1\times10^{-2}$ mol dm^{-3}, [metal colloid] = 173 mg dm^{-3}.

The yield of methane increased in a series of electron donors: TEOA$\ll$Na$_2$edta < cysteine (Runs 1—3 in Table 1). Willner reported that thiol poisoned the ruthenium (palladium) colloid, and depressed the formation of methane or formate from carbon dioxide or hydrogencarbonate under irradiation of an aqueous solution.[6,11] It is noticeable that cysteine was an effective electron donor in the present photoreduction. Furthermore, by the addition of a sulfur-containing poison, such as 1,4-dithiothreitol (DTT), to the solution, the yield of methane was not depressed (Run 4). The different poisonous effects may have resulted from the difference in the solvent employed for the reaction. The yield was extremely depressed upon the addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) for its trap of $MV^{\bullet +}$ radicals (Run 5).[27] Ruthenium colloid was the most active catalyst in the metal colloids used (Runs 1, 6, and 7).

Photoreduction of Ethylene. Ethylene was photoreduced to ethane upon irradiation with visible light of an aqueous solution containing TEOA, **1**, MV^{2+}, and palladium colloid. The optimum pH was estimated to be 7.5 (Fig. 5).

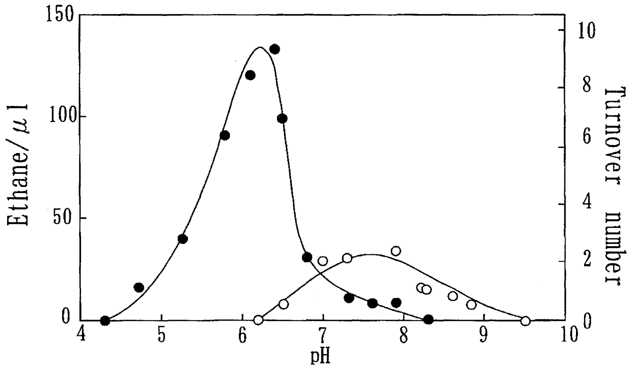

Fig. 5. The pH dependence of the yield of ethane in an aqueous solvent: ○) [CTAB] = 0 mol dm^{-3}, ●) [CTAB] $= 1\times10^{-3}$ mol dm^{-3}; [TEOA] $= 1\times10^{-1}$ mol dm^{-3}, [complex] $= 6\times10^{-5}$ mol dm^{-3}, $[MVCl_2] = 2\times10^{-3}$ mol dm^{-3}, [Pd colloid] = 23 mg dm^{-3}; reaction time = 48 h. Turnover number is based on the complex.

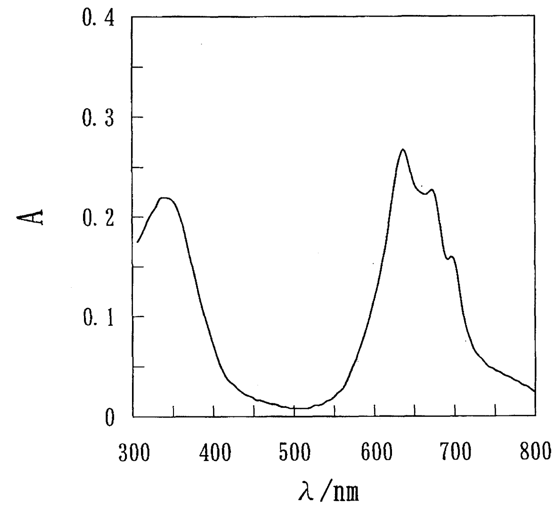

Fig. 6. Absorption spectrum of **1** in the presence of SDS: [complex] $= 6\times10^{-6}$ mol dm^{-3}, [SDS] $= 1\times10^{-2}$ mol dm^{-3}.

The pH effect is explained in a similar manner as that described for the photoreduction of hydrogencarbonate.

Cationic micelles prevented the formation of photoinactive ion-pairs between the complex and MV^{2+}, resulting in an increase in $MV^{\bullet +}$ radicals upon irradiation with visible light.[20] By the addition of cetyltrimethylammonium bromide (CTAB) in the reaction mixture, the optimum pH shifted to 6.4, and the yield of ethane increased to three-times that without a detergent (Fig. 5). On the other hand, an anionic detergent, sodium dodecyl sulfate (SDS), did not increase the yield, probably due to the negative charges of SDS micelles containing **1**; i.e., the negative charges of micelles prefer to combine with $MV^{\bullet +}$ radicals, and back-electron donation is accelerated.[28]

In the absorption spectrum of an aqueous solution of **1** in the presence of SDS, two new bands appeared at 636 and 699 nm around the Q band (674 nm) of the monomer species (Fig. 6). It has been known that cofacial dimerization in phthalocyanines blue-shifts the Q band.[23] Thus, the species with the 636-nm band is ascribed to the cofacial dimer. It

Table 2. Effects of Electron Donors, Inhibitors, and Metal Colloids on the Yield of Ethane in an Aqueous Solvent

Run		Ethane/μl
1	TEOA	67
2	Na_2edta	99
3	Cysteine	0
4	DTT	0
5	TEMPO	0
6	Ru colloid	6
7	Pt colloid	15

[CTAB] $= 1\times10^{-3}$ mol dm^{-3}, [complex] $= 6\times10^{-5}$ mol dm^{-3}, $[MVCl_2] = 2\times10^{-3}$ mol dm^{-3}; pH = 6.2; reaction time = 48 h. In Runs 1—3, [electron donor] $= 1\times10^{-2}$ mol dm^{-3}, [Pd colloid] = 23 mg dm^{-3}; In Runs 4 and 5, [TEOA] $= 1\times10^{-2}$ mol dm^{-3}, [Pd colloid] = 23 mg dm^{-3}, [inhibitor] $= 1\times10^{-3}$ mol dm^{-3}; In Runs 6 and 7, [TEOA] $= 1\times10^{-2}$ mol dm^{-3}, [metal colloid] = 23 mg dm^{-3}.

was further reported that tetrasodium tetrasulfonatophthalocyaninatozincate(II) showed an absorption band at a longer wavelength side of that for the monomer in aqueous acetonitrile; the species was ascribed to a face-to-face slipped dimer.[29)] Then, the species with the 699-nm band might be the face-to-face slipped dimer.

Na_2edta was the most useful electron donor for the photoreduction of ethylene (Run 2 in Table 2). Ethane was not formed by cysteine in an aqueous solvent (Run 3).[9)] The yield of ethane was also depressed by the addition of DTT in the four-component system (Run 4). Ethane was not formed upon the addition of TEMPO due to the same reasons as that for the photoreduction of hydrogencarbonate. In the present photoreduction, palladium colloid was the most effective catalyst (Runs 1, 6, and 7).

This work was supported by a Grant-in-Aid for Scientific Research No. 06453050 from the Ministry of Education, Science, Sports and Culture and by a Grant from the Electric Technology Research Foundation of Chugoku.

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