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PHOTOCHEMICAL HYDROGEN EVOLUTION FROM BENZENETHIOL CATALYZED BY BENZENETHIOLATOBIS(DIMETHYLGLYOXIMATO)COBALT(III)

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Molecular hydrogen was produced catalytically by visible light irradiation of the acetonitrile solution containing benzenethiolatopyridinebis(dimethylglyoximato)cobalt(III) and benzenethiol. Some thioketones were found to photosensitize the reaction effectively.

The disproportionation of benzenethiol to diphenyldisulfide and hydrogen is an endothermic reaction.[1)] We are intending to make the reaction proceed by use of visible light energy.

$$2PhSH \longrightarrow H_2 + PhSSPh \qquad \Delta H^\circ = 5.7\ kcal{\cdot}mol^{-1} \qquad (1)$$

The photochemical cleavage of the cobalt-carbon bond in methylpyridinebis(dimethylglyoximato)cobalt (methylpyridinecobaloxime, $CH_3Co(dmg)_2Py$) has been known to give methyl radical and $Co(dmg)_2Py$.[2)] $Co^{II}(dmg)_2Py$ was found to be formed also by visible light irradiation of benzenethiolatopyridinecobaloxime ($PhSCo^{III}(dmg)_2Py$) as shown in Fig. 1, probably indicating that the homolytic fission of the cobalt-sulfur bond took place. Then, catalytic hydrogen evolution is expected when $PhSCo(dmg)_2Py$ is irradiated in the presence of benzenethiol, because $Co^{II}(dmg)_2Py$ has been known to react with benzenethiol to give molecular hydrogen and $PhSCo^{III}(dmg)_2Py$.[4)]

An acetonitrile solution of benzenethiol was degassed ($\sim 2\times 10^{-5}$ mmHg) and transferred to a cuvette containing $PhSCo(dmg)_2Py$ using a vacuum line. The resulting mixture was irradiated by use of a slide projector equipped with a 650 W halogen lamp and a glass filter ($\lambda > 425$ nm) at ambient temperature of 14 to 18 °C. The absorption maximum of the mixture at 360 nm was shifted to 368 nm by the irradiation for several minutes, but further spectral change was not observed after 3 hr of irradiation. The shift, which was brought about also in the dark in a few hours, may be attributable to the partial exchange of the sixth ligand (i.e., Py) to

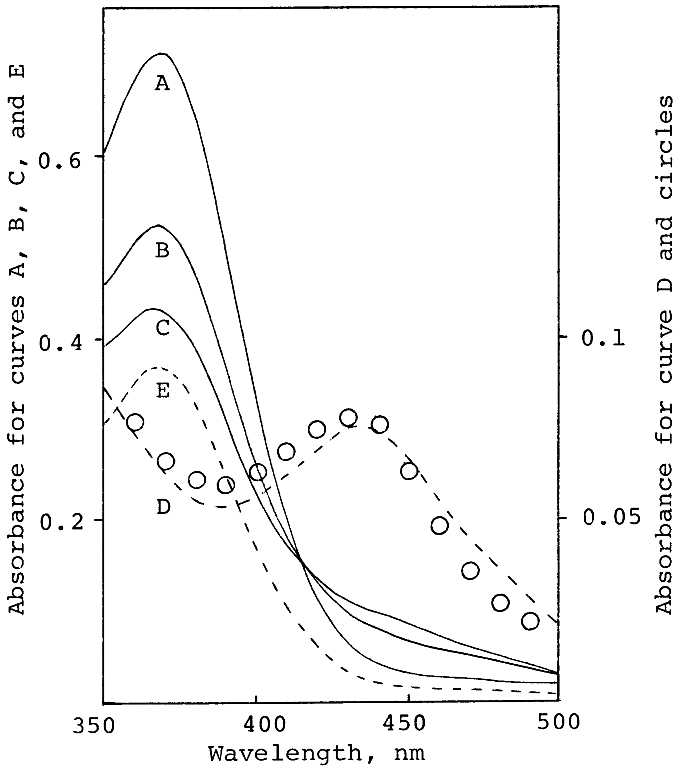

Fig. 1. Photolysis of $PhSCo(dmg)_2Py$ (47.5 μM) in benzene solution containing pyridine (0.1 M) under anaerobic condition. A, 0 min; B, 5 min; C, 10 min. D was derived by subtracting E, corresponding to the spectrum of remaining $PhSCo(dmg)_2Py$ (24.2 μM), from C. Circles indicate the absorbances of $Co(dmg)_2Py$ (23.3 μM) in the same solvent.[3] A slide projector equipped with a 650 W halogen lamp and a glass filter ($\lambda > 425$ nm) was used for the irradiation.

Run	$PhSCo(dmg)_2Py$ μmol	Thioketone μmol	hν nm	Time hr	H_2 μmol
1	0	0	$\lambda>425$	1	0
2	5.03	0	$\lambda>425$	1	2.41
3	5.01	0	$\lambda>425$	3	4.37
4	4.85	0	$\lambda>520$	1	1.06
5[d]	4.85	M[b], 4.89	$\lambda>520$	1	10.0
6	4.78	D[c], 5.30	$\lambda>520$	1	11.7
7	5.05	M, 4.96	$\lambda>520$	3	17.1
8	5.01	M, 0.46	$\lambda>520$	1	4.7
9	0	M, 4.99	$\lambda>520$	1	<0.03

Table 1. Hydrogen production from benzenethiol.[a] a) 5.0 ml of acetonitrile containing benzenethiol (0.54 mmol) was used as a solvent. b) Michler's thioketone. c) 4,4'-Dimethoxythiobenzophenone. d) No hydrogen was produced in experiments corresponding to run 5 in the absence of benzenethiol or in the dark.

Scheme 1.

$PhSCo^{III}(dmg)_2L' + L \longrightarrow PhSCo^{III}(dmg)_2L + L'$ Photo-substitution (2)

$PhSCo^{III}(dmg)_2L \xrightarrow{h\nu} Co^{II}(dmg)_2L + PhS\cdot$ Photo-redox reaction (3)

$Co^{II}(dmg)_2L + PhSH \longrightarrow PhSCo^{III}(dmg)_2L + 1/2H_2$ (4)

$2PhS\cdot \longrightarrow PhSSPh$ (5) benzenethiol. After the irradiation, the cuvette was filled with argon to atmospheric pressure and the resulting gaseous mixture was analyzed for hydrogen by gas chromatography with a molecular sieve 5A column at 25 °C. The results are shown in Table 1.

The yield of hydrogen based on the amount of the cobalt complex used is calculated to be 189 % in run 3, because one mol of hydrogen is liberated from two mols of the cobaloxime. A series of reactions including the regeneration of benzenethiolatocobaloxime is probably taking place (Scheme 1). Side reactions which lead to the destruction of the cobaloxime do not seem to occur frequently, because the spectral intensity of the reaction mixture was not reduced during the irradiation.

The quantum yield of the hydrogen production was found to be 4.8×10^{-4} when the mixture was irradiated for 3 hr with the 546 nm-line of a 500 W super high pressure mercury lamp by use of a monochrometer.

The photoreactions in the presence of some thioketones were tried in order to extend the region of effective light to a longer wavelength. 4,4'-Bis(dimethylamino)thiobenzophenone (Michler's thioketone) and 4,4'-dimethoxythiobenzophenone exibit absorption maxima at 556 and 577 nm in acetonitrile, respectively, which have been assigned to n,π* absorption.[5] The excited thioketone has been known to abstract a hydrogen as follows:[6]

$$\phi_2C{=}S(n,\pi^*) + PhSH \longrightarrow \phi_2\dot{C}{-}SH + PhS\cdot \qquad (6)$$

The mercaptomethyl radical produced, which is none other than the protonated radical anion of a thioketone, is expected to serve as the reductant of $PhSCo^{III}(dmg)_2L$ (reaction 7), because the cathodic peak potential of $PhSCo^{III}(dmg)_2Py$ and the redox potentials of 4,4'-dimethoxythiobenzophenone and Michler's thioketone were found to be -1.25, -1.32, and -1.51 V vs. SCE, respectively, in acetonitrile containing tetra-n-butylammonium perchlorate (0.05 M) as a supporting electrolyte by cyclic voltammetry at a glassy carbon electrode.

$$\phi_2\dot{C}{-}SH + PhSCo^{III}(dmg)_2L \longrightarrow \phi_2C{=}S + PhSH + Co^{II}(dmg)_2L \qquad (7)$$

The oxidation potential of the thioketone radical anion becomes more positive by the protonation, but it does not seem to affect the direction of reaction 7 because of the uptake of a proton in the reductive cleavage of $PhSCo^{III}(dmg)_2L$.

When the acetonitrile solution of benzenethiol, $PhSCo(dmg)_2Py$, and Michler's thioketone was irradiated (λ > 520 nm) for 1 hr, produced hydrogen amounted to 10.0 μmol (run 5) which corresponded to 412 and 409 % yield based on the amounts of the cobalt complex and the thioketone used, respectively, although the photoreaction not sensitized under the same conditions resulted in 1.06 μmol of hydrogen evolution (run 4). The thioketone decreased in concentration during the irradiation as revealed spectrophotometrically because of further reduction of the mercaptomethyl radical to the corresponding thiol.⁶⁾ In the absence of the cobalt complex Michler's thioketone disappeared in ten minutes and only trace amounts of hydrogen were generated (run 9). In an experiment (run 8) in which the ratio of Michler's thioketone to the cobalt complex was 0.09, however, the yield of hydrogen based on the amount of the thioketone used was calculated to be 1570 %, in which the yield from the direct photoreaction of the cobalt complex was not included.

The quantum yield of hydrogen for monochromatic light of 546 nm absorbed by Michler's thioketone for 3 hr was found to be 4.4×10^{-3} in an experiment corresponding to run 8.

The mechanism of the hydrogen production sensitized by thioketone is probably the sequence of reactions 6, 7, 4, and 5 initiated by the light absorption of thioketone. Reaction 4, however, is only an integrated expression of several elementary reactions, and the possibility is not excluded that the energy transfer to $PhSCo^{III}(dmg)_2L$ from the excited thioketone might have brought about the same products as in reaction 3.

In view of the fast exchange of ligands, it is natural that the direct and the sensitized photoreaction presented above were also achieved by use of $BrCo(dmg)_2Py$ instead of $PhSCo(dmg)_2Py$.

Further investigation, including a search for a sensitizer stable and effective for the light of a longer wavelength, is in progress.

References and Notes

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