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Energy-storing Photocatalysis of Transition Metal Complexes with High Quantum Efficiency

Tetsu Yamakawa, Hiroto Miyake, Hiroshi Moriyama, Sumio Shinoda, and Yasukazu Saito*

Institute of Industrial Science, University of Tokyo, 22–1, Roppongi 7 Chome, Minato-ku, Tokyo 106, Japan

A tin(n)-co-ordinated iridium complex catalyst exhibited the highest photoreactivity ever reported for the energystoring reaction of propan-2-ol dehydrogenation, with quantum efficiency and even 'photo-thermal energy conversion efficiency' exceeding unity.

Propan-2-ol dehydrogenation [reaction (1)] yielding acetone and dihydrogen has attracted general attention on account of its energy-storing nature.¹ This reaction

 $Me_2CHOH(l) \rightarrow Me_2CO(l) + H_2(g)$ (1)

 $\Delta H^{\circ} = 69.9 \text{ kJ mol}^{-1}, \Delta G^{\circ} = 25.0 \text{ kJ mol}^{-1}$

proceeds to completion when the product acetone (as well as H_2) is removed from the reaction medium by fractional distillation, and is catalysed by various types of transition

metal complex,^{2—6} including a tin(π)-co-ordinated rhodium complex under photoirradiation.⁷ In the present study, we have extended the photocatalysis to other tin(π)-co-ordinated transition metal complexes, because an unusual rate enhancement with a quantum efficiency exceeding unity, based on the photogeneration of co-ordinatively-active species, was observed.⁷

The catalyst solutions were prepared by dissolving appropriate amounts of the transition metal salt ($IrCl_3 \cdot 3H_2O$, $H_2IrCl_6 \cdot 6H_2O$, K_2PtCl_4 , or $RuCl_3 \cdot 3H_2O$) and $SnCl_2 \cdot 2H_2O$ in propan-2-ol. These catalyst species in solution absorbed

Table	1.	Photocatalysis	using	tin(11)-co-ordinated	transition	metal	complexes	for the	homogeneous	liquid-phase	dehydrogenation	a of propan-
2-ol.			-				-		Ū.			

$T.O.F./h^{-1^{a}}$										
М	Sn ^{II} /M	Unirrad.	Irrad.	$\Delta E_{a}{}^{ m b}$	Quantum ^c efficiency	ηď				
IrIII	6.5	4.5	109	20	12.0	1.41				
Rh ^{III^e}	3.55	4.1	87.5	11	2.2	0.26				
Pt ¹¹	10	0.9	70.4	13	1.4	0.16				
Ru ¹¹	6.5	1.0	47.7	21	2.4	0.28				

^a Turnover frequency: formation rate of acetone or dihydrogen per transition metal species charged. ^b Activation energy in kJ mol⁻¹. ^c Acetone or dihydrogen formed per photon absorbed. ^d Photo-thermal energy conversion efficiency. See text. ^e Ref. 7.



Figure 1. Time dependence of dihydrogen evolution from a propan-2ol solution of a tin(π)-co-ordinated iridium catalyst (H₂IrCl₆·6H₂O, 0.49mM; SnCl₂·2H₂O, 3.20mM; 3 M HCl, 3.0 ml) with the photoirradiation being switched on and off.

>98% of the incident photons, as estimated by the extinction coefficients at 254 nm. Photoirradiation was carried out using a low-pressure mercury lamp (254 nm, 3×24 W) through a quartz vessel inside the reactor, at reflux temperature (82.1 °C), with the evolution of gas being followed volumetrically at atmospheric pressure. It was confirmed by gas chromatography that the evolved gas was solely dihydrogen, with the equivalent amount of acetone being formed in solution. For quantum efficiency determinations, a spectrophotometric reactor (Jasco CRM-FA), equipped with a diffraction grating and a 2 kW Xe lamp, was used; the amount of acetone in the solution was analysed after the reaction (30 °C).

Photoenhancement was observed for catalysis using all the tin(π)-co-ordinated iridium, platinum, and ruthenium complexes, as was observed for the rhodium complex.⁷ Figure 1 shows a typical example; the photoenhanced catalytic activity responded rapidly to the photoirradiation being switched on or off, corresponding to instantaneous changes in the stationary concentration of the catalytically active species. In the iridium example, the photocatalytically active solution contains *trans*-[IrCl₂(SnCl₃)₄]³⁻ and [IrH(SnCl₃)₅]³⁻, according to ¹¹⁹Sn n.m.r. spectroscopy.⁸ This solution retained its photocatalytic activity for more than 500 h, with a turnover number amounting to 3430, in spite of a rate retardation due to accumulation of the product acetone.

As summarized in Table 1, the tin(π)-co-ordinated iridium complex exhibited a marked enhancement of turnover frequency upon photoirradiation, and it is the most active complex under non-irradiated conditions. It is noteworthy that the value of 109 h⁻¹ is the highest ever reported for homogeneous catalysts. Activation energies under photoirradiation were 11 and 21 kJ mol⁻¹, in marked contrast to the 117 and 113 kJ mol⁻¹ obtained in the dark, for the rhodium and ruthenium complexes, respectively.

The quantum efficiencies at 254 nm under refluxing conditions are also listed in Table 1. All the values are higher than unity, even reaching 12.0 in the case of the iridium complex.

If the quantum efficiency in energy-storing photocatalysis is sufficiently high, the 'photo-thermal energy conversion efficiency' η , defined as in equation (2), would exceed unity,

$$\eta = \phi \Delta H / h \nu \tag{2}$$

where ϕ and ΔH are the quantum efficiency and endothermic enthalpy change (55.2 kJ mol⁻¹) stored by reaction (1), respectively, and hv is the energy of incident photons emitted from the low-pressure mercury lamp (254 nm, 471 kJ mol⁻¹).⁹ The magnitude of the 'photo-thermal energy conversion efficiency' was found to exceed unity (η 1.41) for the tin(π)-co-ordinated iridium photocatalysis, the endothermic energy deficit being replenished by the heat taken from the surroundings.

In contrast to the photosynthetic reactions, there is no theoretical limit on the quantum efficiency for photoenhanced exergonic reactions, where the photoexcitation process is included outside the catalytic reaction cycle. As energy amplification of photons is possible in this approach with the aid of abundant and easily-supplied low-quality waste heat, the problem of the diffuseness of solar energy may be surmounted by utilizing both luminous and thermal energies in a hybrid manner.

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