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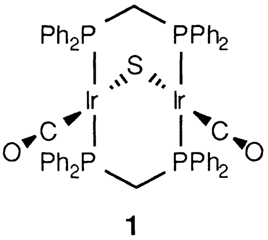
Catalytic Cyclooctane Photodehydrogenation at Unusually Low Photon Energy with a Dinuclear Iridium Complex

Hiroaki ITAGAKI, Hisahiro EINAGA, and Yasukazu SAITO*
Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Photoirradiation on an A-frame dinuclear complex $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ caused catalytic dehydrogenation of cyclooctane, where effectiveness was proved for all the absorption bands in the visible region (λ_{max}: 360, 418, and 520 nm).

Catalytic dehydrogenation of alkane under mild conditions has been one of the most fascinating and challenging targets in reaction chemistry. Recently, thermocatalytic dehydrogenation of cyclooctane was achieved with transition-metal complexes$^{1)}$ and solid metals$^{2)}$ under boiling and refluxing conditions.

Photoirradiation on the Vaska-type rhodium complexes $RhCl(CO)(PR_3)_2$ gave extremely high dehydrogenation activities for alkanes.$^{3)}$ A three-co-ordinated $RhCl(PR_3)_2$ species generated by CO photodissociation$^{4)}$ is deemed as the key active species,$^{3)}$ which was confirmed from the wavelength dependence of photocatalytic alkane dehydrogenation with $RhCl(CS)(PPh_3)_2$.$^{5)}$ Effectiveness of visible light was also reported by use of a mononuclear ethylene complex $RhCl(CH_2{=}CH_2)(PMe_3)_2$ (λ_{max}: 416 nm)$^{6a)}$ or an A-frame dinuclear complex $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$ (λ_{max}: 475 nm).$^{6b)}$ In order to store the solar energy with alkane dehydrogenation effectively, further long-wavelength extension of electronic absorption in addition to photostability should be aimed in designing catalysts. By this reason, a homologous iridium complex $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ (**1**) is adopted here.



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All manipulations were carried out under an argon atmosphere. Photocatalytic dehydrogenation of cyclooctane with **1** prepared by the published method,$^{7)}$ was carried out under boiling and refluxing conditions (151 °C) in a cylindrical quartz cell (diameter 45 mm, cell length 80 mm) by irradiating with an external-type Xenon lamp (2 kW, Ushio) through a cut-off filter UV-34, L-38 or L-48 (Kenko). The product analysis was performed as reported elsewhere.$^{6)}$ The transmitting characteristics of cut-filters together with the electronic absorption spectrum of **1** were shown in Fig. 1. The longest-wavelength absorption maximum appeared in the visible region at

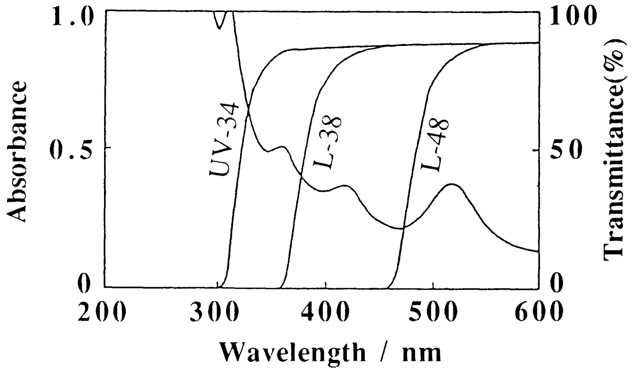

Fig. 1. UV-VIS spectrum of $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$ with reference to transmission characteristics of the cut-off filters; Catalyst concentration 6.9 μmol / 100 ml cyclooctane-toluene (2:1).

520 nm, being longer than λ_{max}(475 nm) for the rhodium dinuclear $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$ and λ_{max}(439 nm) for a mononuclear $IrCl(CO)(PPh_3)_2$. The absorption maxima were assignable to metal-to-ligand charge transfers from the magnitudes of ε_{max} (1090(360 nm), 1190(418 nm) and 3180(520 nm) $dm^3mol^{-1}cm^{-1}$).[8)]

As shown in Fig. 2, all the absorption bands were photoactive for cyclooctane dehydrogenation, including the longest one (turnover number: 4.6 at 46 h). The highest initial rate was obtained with the UV-34 filter, whereas the activity disappeared gradually due to photodecomposition with a total turnover number of 16.2 (2 h). A slight suppression during the initial 3.5 h period with the L-38 filter was in sharp contrast to $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$ using the L-42 filter, the photocatalytic activity of which disappeared completely within 100 minutes.[6b)] The electronic transition in the longest-wavelength band (λ_{max}: 520 nm) attracts our interest, because effectiveness for catalytic alkane dehydrogenation at an unusually low photon energy (2.38 eV) was proved for the first time. Photodissociation of the CO ligand for generating a reaction intermediate would be operative, as has been assumed for the photocatalysis of $RhCl(CO)(PR_3)_2$.[3)]

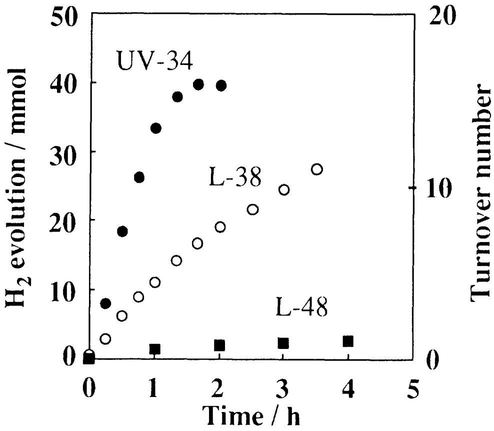

Fig. 2. Time-course plots for photocatalytic dehydrogenation of cyclooctane with $Ir_2(\mu\text{-}S)(CO)_2(dppm)_2$. Catalyst concentration: 2.5 μmol / 100 ml cyclooctane; Reaction temperature: 151°C (reflux); Light source: Xe lamp (2kW).

Persevering bondage of ligand coordination and ascending energy of HOMO through metal-sulfur bond-orbital interactions were recommended for photocatalysis of transition metal complexes.[6b)] This strategy in photostability and wavelength improvements is thus proved to be useful by adopting iridium instead of rhodium in the A-frame dinuclear complex.

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