Nonmetallised CdS-catalysed Photoreduction of Aromatic Ketones to Alcohols and/or Pinacols

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In acetonitrile containing triethylamine as a sacrificial electron donor, non-metallized CdS shows photocatalytic activity for reduction of benzophenone derivatives whose reduction potentials are larger than −1.90 V *vs.* standard calomel electrode (SCE), giving alcohols and/or pinacols under visible light irradiation.

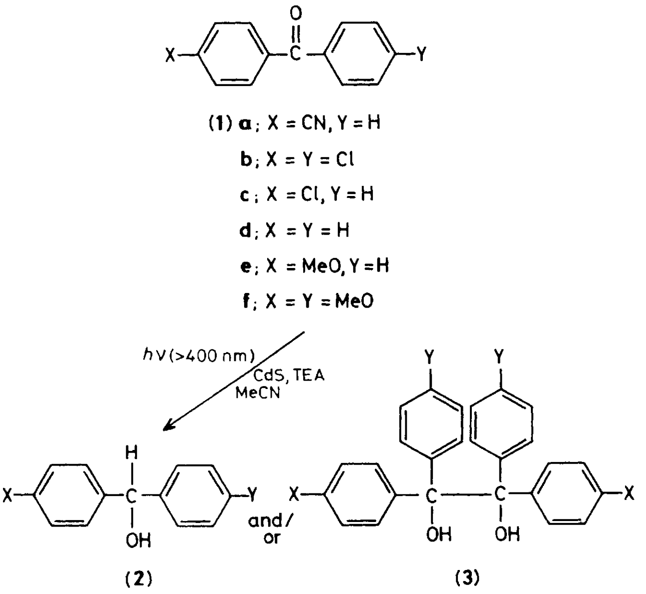
Photoreduction of organic molecules on semiconductor particles is both of substantial interest in synthesis[1] and a means of solar energy conversion and storage.[2] In general, the deposited metal plays an important role as a relay of conduction band electrons to organic substrates, being believed to be a requisite for efficient electron transfer.[3] Recent studies have revealed that some ZnS[4] and colloidal TiO_2[5] can catalyse photoreductions of organic substrates without any metal relays under u.v. light irradiation. Charge separation on an irradiated CdS semiconductor has been widely investigated because of its absorption of visible light. The practical photocatalysis of the semiconductor hitherto has been carried out only after noble metal deposition owing to the photocorrosive property of the reaction.[6,7] Here we report that some commercially available CdS powders catalyse photoreduction of aromatic ketones using triethylamine (TEA) as a sacrificial electron donor under visible light irradiation (>400 nm) in acetonitrile.

Highly pure (99.999%) CdS from Aldrich and Furuuchi and electro-luminescence (EL) grade (99.99%) CdS from Mitsuwa were used. Platinised CdS powder was prepared by illumination of 144.5 mg of CdS (Aldrich) dispersed in a deaerated aqueous solution (10 ml) of 2×10^{-3} M K_2PtCl_4 with a 500 W tungsten-halogen lamp (>400 nm) for 3 h.[6b] A stirred acetonitrile suspension (2 ml) containing CdS powder (10 mg), ketone (2 mM), and TEA (1 M) was flushed with Ar gas while cooling on an ice bath and then irradiated at 25 °C with a 500 W tungsten-halogen lamp through an aqueous sodium nitrite solution filter (>400 nm). The reaction products were analysed by h.p.l.c. using an octadecylsilane (ODS) column.

As shown in Table 1, highly pure Aldrich and Furuuchi CdS powders efficiently catalysed the photoreduction of benzophenone derivatives (**1a**—**e**) to alcohols (**2a**—**e**) and/or pinacols (**3a**—**e**), while no photoreduction occurred with platinised CdS. However, the photoreduction by EL CdS occurred with (**1a**—**c**) only, and low yields were obtained, but failed with (**1d**,**e**). It is of mechanistic significance to note that (**1a**—**e**) having reduction potentials from −1.42 to −1.90 V *vs.* SCE[8] are photoreduced but (**1f**) with a reduction potential of −2.02 V *vs.* SCE is not photoreduced in the CdS-catalysed system.

The flat-band potential of a single crystal of CdS has been generally −0.85 V *vs.* SCE in MeCN.[9] The present observation, however, suggests that the conduction-band potential should be *ca.* 1.0 V more negative than the reported one. Meissner *et al.*[10] reported that the flat-band potential of the clean CdS is −1.8 V *vs.* SCE in water, about 1 V more negative than generally assumed, and clarified that the more positive values so far reported should be due to surface contamination. This fact is consistent with the dependence of the CdS-catalysed photoreduction upon the reduction potentials of (**1a**—**f**).

Diethylamine was detected by g.l.p.c., probably arising from hydrolysis of the imminium intermediate, $Et_2\overset{+}{N}{=}CHMe$, produced by oxidation of TEA. The reflectance absorption spectra were measured by a Photal (Otsuka Electronics) with a spectro multichannel photodiode system (MCPD-100). The active CdS (Aldrich and Furuuchi) powders have comparable absorption spectra with a sharp onset at 500 nm, whereas poorly active EL CdS powder has a gentle-sloping and a red-shifted onset in its absorption spectrum (Figure 1). These results suggest that the distribution of surface states, formed by the lattice defects, or the interstitial impurities, or the band



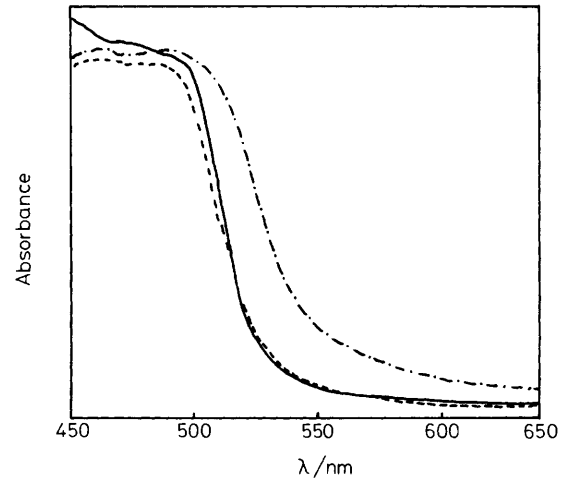


Figure 1. Absorption spectra of CdS powders by reflectance spectrometry using a Photal: ——— = CdS (Aldrich); - - - - - = CdS (Furuuchi); ·—·—·—· = CdS (EL, Mitsuwa).

Table 1. CdS-catalysed photoreduction of aromatic ketones with TEA in MeCN[a].

		CdS (Ald)[c]			CdS (Furu)[c]			CdS (EL)[c]			CdS (Pt)[d]		
		Convn./	Yield/%		Convn./	Yield/%		Convn./	Yield/%		Convn./	Yield/%	
Subst.	$-E^{red}_{1/2}$/V[b]	%	**(2)**	**(3)**	%	**(2)**	**(3)**	%	**(2)**	**(3)**	%	**(2)**	**(3)**
(1a)	1.42	93	47	trace	92	35	trace	15	10	0	0	0	0
(1b)	1.67	69	25	58	63	20	60	17	5	46			
(1c)	1.75	64	28	45	65	20	54	10	2	47	0	0	0
(1d)	1.83	99	22	33	85	15	37	0	0	0	0	0	0
(1e)	1.90	83	8	27	74	6	28	0	0	0			
(1f)	2.02	0	0	0	0	0	0	0	0	0			

[a] Irradiated in MeCN at >400 nm for 6 h. Yields are based on the substrate converted. Unknown products were detected. [b] Polarographic half-wave reduction potentials *vs.* SCE in MeCN. See ref. 8. [c] Ald, Aldrich (99.999%); Furu, Furuuchi (99.999%); EL, Electro-luminescence grade (99.99%) from Mitsuwa. [d] Platinised CdS. [e] Irradiated for 3 h.

gap, differ between these CdS powders. This may be a preferable interpretation of the remarkably differing activity of CdS as a catalyst. The platinisation may generate trapping sites for the active electrons from the conduction band, thus preventing electron transfer to all ketones.

In conclusion, CdS powder leads to photocatalytic reductions of aromatic ketones in acetonitrile through direct electron transfer from the conduction band as was observed in the photocatalysis of freshly prepared ZnS.[4,11]

This work was supported by a Research Grant from the Iwatani Naoji Foundation and by a Grant-in-aid for Special Research Projects from the Ministry of Education, Science and Culture, Japan (No. 62213021).

Received, 16th November 1988; Com. 8/04558E

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