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SEMICONDUCTOR-CATALYZED PHOTOOXYGENATION OF AROMATIC OLEFINS

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Irradiation of semiconductors (TiO_2 and CdS) suspended in organic solvents containing 1,1-diphenylethylene and its derivatives under oxygen afforded the corresponding epoxides and benzophenone. A possible mechanism is discussed.

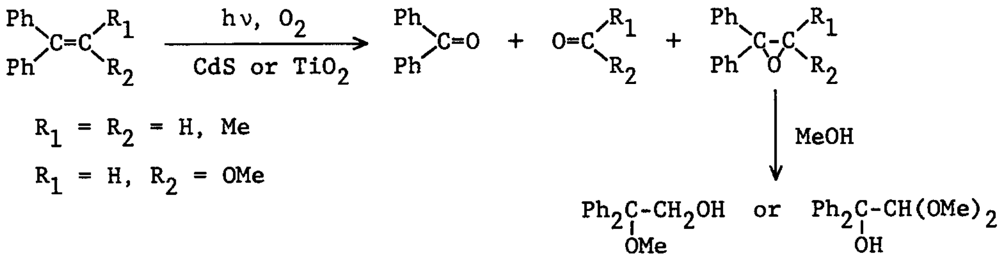
Photoelectrochemical processes at semiconductor electrodes have been extensively investigated and recent attention has been increasingly paid to photocatalytic activity of semiconductors on chemical reactions.[1-5]

We now wish to report on the actions of cadmium sulphide and titanium dioxide (anatase) as photocatalysts on oxygenation[6] of aromatic olefins.

In a typical run, semiconductor powder (ca. 5 mg) was suspended in a solution (ca. 2 ml) containing an olefin (ca. 0.3 mmol) and irradiated under oxygen atmosphere at room temperature at longer wavelengths than 350 nm for titanium dioxide and at longer wavelengths than 430 nm for cadmium sulphide.[7] The products were separated by vpc or tlc for their identification and quantitatively determined by vpc. The representative results are summarized in Table 1.

As Table 1 indicates, irradiation of 1,1-diphenylethylene at longer wavelengths than 350 nm in dimethyl sulphoxide-methanol (1:1 in volume) gave no detectable products, whereas irradiation at longer wavelengths than 430 nm in the presence of cadmium sulphide in the same solvent afforded benzophenone, 2,2-diphenyloxirane, and 2-methoxy-2,2-diphenylethanol. The methoxydiphenylethanol must be derived from the epoxide since in the absence of methanol in dimethyl sulphoxide it was not formed at all.[8] On oxygenation of 2-methoxy-1,1-diphenylethylene under similar conditions benzophenone and 2,2-dimethoxy-1,1-diphenylethanol were produced. The latter is again an addition product of the intermediate epoxide, 3-methoxy-2,2-diphenyloxirane, with methanol.[8]

The reactivity of olefins tends to be reduced with decreasing π-electron donating property of the double bonds; 2-methoxy-1,1-diphenylethylene, 2-methyl-1,1-diphenylpropene, and 1,1-diphenylethylene were easily oxidized



and 4-methoxystyrene was less oxidizable, but ethyl cinnamate, benzylideneacetone, and cinnamonitrile were recovered without suffering oxygenation.

The mechanism of the present reaction is not confirmed so far. However, the oxygenation seems to involve free-radical species but not singlet oxygen. Thus, the cadmium sulphide-catalyzed photooxygenation of 1,1-diphenylethylene,

Table 1. Photooxygenation of Aromatic Olefins Catalyzed with Semiconductors

Olefin	Solvent[a]	Semiconductor	Conversion[b] (%)	Product yield[e] (%)	
				$Ph_2C{=}O$	$Ph_2\underbrace{C-C}_{O}H_2$ + $Ph_2\underset{OMe}{C}\text{-}CH_2OH$
$Ph_2C{=}CH_2$	Me_2SO-MeOH	TiO_2	33	22	26
		CdS	41	15	19
		none	0	-	-
	MeCN-MeOH	CdS	27	15	26
	CH_2Cl_2-MeOH	CdS	30	15	54
	PhH-MeOH	CdS	22	13	29
				$Ph_2C{=}O$	$Ph_2\underbrace{C-C}_{O}Me_2$
$Ph_2C{=}CMe_2$	MeCN	TiO_2	16	11	9
	Me_2SO	CdS	37	1	2
	CH_2Cl_2	CdS	26	7	11
				$Ph_2C{=}O$	$Ph_2\underset{OH}{C}\text{-}CH(OMe)_2$
$Ph_2C{=}CHOMe$	MeCN-MeOH	CdS	100[c]	12	69
	Me_2SO-MeOH	CdS	100[d]	10	31

a) All the mixed solvents were 1:1 in volume. b) Irradiation time was 6 h unless otherwise noted. c) Irradiation time was 7 h. d) Irradiation time was 1.5 h. e) Yields based on the olefin consumed.

2-methyl-1,1-diphenylpropene, and 2-methoxy-1,1-diphenylethylene was inhibited by hydroquinone and 2,6-di-tert-butyl-4-methylphenol.[9] Irradiation of titanium dioxide in acetonitrile containing 2,3-dimethyl-2-butene under oxygen afforded its epoxide (8%) and a trace amount of 2,3-dimethyl-2-buten-2-yl hydroperoxide;[12] the latter would have been efficiently produced if singlet oxygen had been generated.[13,14] In addition, irradiation of titanium dioxide with 2-methylfuran[15,16] in acetonitrile-methanol or dimethyl sulphoxide-methanol under oxygen gave no detectable products. These findings are contrasting with the results reported by Pappas and Fischer that irradiation of titanium dioxide in a methanol solution of furan gave 2-methoxy-5-oxo-2,5-dihydrofuran possibly through oxygenation with singlet oxygen.[17]

Consequently, at present the following reaction pathways could be proposed (Scheme 1). On irradiation of cadmium sulphide at longer wavelengths than 430 nm, an electron is promoted from the valence band (1.60 V vs. SCE)[18,19] to the conduction band (-0.85 V vs. SCE)[18,19] to yield a positive hole in the valence band, the promoted electron being transferred to molecular oxygen (reduction potential: -0.8 V vs. SCE)[20] adsorbed on the semiconductor surface to generate a superoxide anion.[21] Then, 1,1-diphenylethylene,[22] for example, transfers an electron to the positive hole to give a diphenylethylene radical cation, which subsequently interacts with the superoxide anion to afford free-radical species.

Scheme 1

$$\begin{aligned} \mathrm{CdS} + h\nu &\longrightarrow \mathrm{CdS}^{*} \\ \mathrm{CdS}^{*} + \mathrm{O_2} &\longrightarrow \mathrm{CdS}^{+} + \mathrm{O_2}^{\overset{\cdot}{-}} \\ \mathrm{CdS}^{+} + \mathrm{Ph_2C{=}CH_2} &\longrightarrow \mathrm{CdS} + [\mathrm{Ph_2C{=}CH_2}]^{\overset{\cdot}{+}} \\ [\mathrm{Ph_2C{=}CH_2}]^{\overset{\cdot}{+}} + \mathrm{O_2}^{\overset{\cdot}{-}} &\longrightarrow \cdot\mathrm{CPh_2{-}CH_2O_2}\cdot \end{aligned}$$

Investigation extending the scope of the photooxygenation and concerning the mechanism is now in progress.

References and Notes

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7) Irradiation was carried out with a 1 kW super-high pressure mercury lamp equipped with a Toshiba UV35 glass filter for titanium dioxide and with a

1 kW xenon lamp with a Toshiba Y43 glass filter for cadmium sulphide.

8) Irradiation of 2,2-diphenyloxirane and 3-methoxy-2,2-diphenyloxirane under oxygen in the presence of cadmium sulphide in methanol gave 2-methoxy-2,2-diphenylethanol and 2,2-dimethoxy-1,1-diphenylethanol, respectively.

9) In this respect the semiconductor-catalyzed photooxygenation resembles photooxygenation of the olefins by direct irradiation with short wavelength UV-light (313 nm). On direct irradiation the oxygenation presumably proceeds through free-radical chain processes to give the corresponding epoxides and benzophenone (T. Kanno, M. Hisaoka, H. Sakuragi, and K. Tokumaru, to be published). In the semiconductor-catalyzed photooxygenation with the radical inhibitors the possibility that the inhibitors were oxidized more rapidly than the olefins at the semiconductor surface could not be ruled out; however, at least 2-methoxy-1,1-diphenylethylene (oxidation potential: 0.90 V vs. Ag/$AgNO_3$(0.1 M) in acetonitrile containing 0.1 M tetraethylammonium perchlorate)[10] would be more oxidizable than 2,6-di-tert-butyl-4-methylphenol (oxidation potential: 1.21 V vs. SCE).[11]

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