Reduction of C–C Multiple Bonds using an Illuminated Semiconductor Catalyst

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Reduction of C–C multiple bonds using Pt/TiO_2 powders in alcohol when irradiated gives hydrogenated products in good yields; concurrently alcohol solvents are oxidised to the corresponding carbonyl compounds.

Photocatalytic activity of semiconductors has attracted attention in relation to possible applications in organic syntheses as well as in water cleavage reactions. In particularly, oxidation of organic compounds in the presence of illuminated semiconductors has been investigated in detail; for example, carbon–carbon double bonds were found to be oxidised to carbonyl functions in the presence of oxygen,[1,2] and oxidation of benzene and toluene in aqueous solvents was shown to have similar characteristics to the conventional oxidation with Fenton's reagent ($H_2O_2 + Fe^{2+}$).[3] Although the photoexcited semiconductors have both oxidative and reductive potential, the photoreductive ability of the catalysts towards organic substrates in organic media has not been utilised. In this communication we report that reduction of C–C multiple bonds with alcohol takes place readily in good yields in the presence of platinised TiO_2 under illumination conditions.

In a typical run, the semiconductor powder[4] (75 mg) was suspended in ethanol (*ca.* 7.5 ml) in a Pyrex test tube. The magnetically stirred solution was purged with nitrogen, 2-methylpent-2-ene (67 mg) was added, and then the solution was irradiated in a nitrogen atmosphere by a 300 W high pressure mercury lamp at room temperature. Product formation was monitored by g.l.c. After 24 h, the reaction gave 2-methylpentane (63%) as well as recovered 2-methylpent-2-ene (36%), and no other side products were observed. Butyl vinyl ether and mesityl oxide were reduced similarly. Results are summarised in Table 1.

The reaction was found to be accompanied by oxidation of alcohol, forming acetaldehyde from ethanol and acetone from propan-2-ol. If the reaction was carried out in the dark, no products were detected. Thus, the reaction is photocatalysed hydrogenation in the presence of photoexcited catalyst which with alcohol gives carbonyl compounds as well as hydrogen or hydride. Presumably the hydrogen or hydride reacts on the surface of the platinum with the unsaturated substrates to produce the hydrogenated products.

Table 1 shows that a simple monosubstituted olefin (oct-1-ene) is more reactive than sterically crowded olefins, a trend similar to that for conventional catalytic hydrogenation carried out in the dark under hydrogen. Oct-2-yne gave *cis*-oct-2-ene, which was further reduced to n-octane to the extent of 5% (24 h). For oct-1-ene and oct-2-ene isomerised alkenes were observed during the reactions; oct-1-ene isomerised to oct-2-ene (9%) when 51% of n-octane was

Table 1. Yields of semiconductor-catalysed reductions of C–C multiple bonds.[a]

Substrate	Solvent	Product	Yield[b]/% (time/h)
$Me[CH_2]_5CH=CH_2$	EtOH	n-C_8H_{18}	12 (3)
			51 (12)
			85 (24)
			81,[c] 91 (48)
	Pr^{i}OH		66 (24)
	MeOH		63 (24)
$Me[CH_2]_4CH=CHMe$	EtOH	n-C_8H_{18}	53 (24)
$MeCH_2CH=CMe_2$	EtOH	$Me[CH_2]_2CHMe_2$	63 (24)
			94 (48)
	Pr^{i}OH		64 (48)
$Me_2C=CMe_2$	EtOH	$Me_2CHCHMe_2$	53 (24)
$Me[CH_2]_4C\equiv CMe$	EtOH	n-C_8H_{18}	5 (24)
		cis-$Me[CH_2]_4CH=CHMe$	47[d] (24)
Bu^{n}OCH=CH_2	EtOH	Bu^{n}OEt	81 (24)
$Me_2C=CHCOMe$	EtOH	Me_2CHCH_2COMe	69 (24)

[a] Chemical yields were determined by g.l.c. using internal standards. [b] Average of multiple runs. Reproducibility from batch to batch made under identical conditions is better than 8%. [c] 7.5 mg Catalyst was used. [d] No *trans* isomer was detected by ^{13}C n.m.r. spectroscopy.

produced (12 h) and oct-2-ene yielded oct-1-ene (8%) and oct-3-ene† (12%) in addition to n-octane (30%) after 12 h. These isomerised compounds eventually gave the saturated hydrocarbons after a prolonged reaction time. No isomerisation was detected for other substrates. It can also be seen that the hydrogenation rate depends on the solvent used; the reaction is faster in ethanol than in propan-2-ol or in methanol.

Although the reaction conditions have not been fully optimized the reactions gave good yields. The results show that the reductive ability of the photoexcited semiconductor towards organic compounds can be used as effectively as its oxidation ability in a nitrogen atmosphere, and that semiconductor-catalysed reduction can be a practical synthetic method.

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† The structure was not confirmed but estimated from its g.l.c. retention time.