Semiconductor-catalysed [2+2]Photocycloreversion of a Strained Cage Molecule

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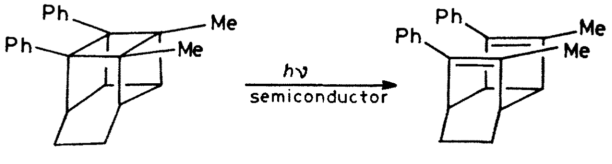
Summary The ZnO- or CdS-catalysed photocycloreversion of the strained cage molecule (**1**) afforded the diene (**2**), which was also produced by a cerium ammonium nitrate-catalysed dark reaction and by photoexcitation of the charge-transfer complex of (**1**) with tetracyanoethylene.

SINCE Honda and Fujishima reported the photoelectrochemical decomposition of water on a semiconductor electrode,[1] the photocatalytic action of semiconductors has received considerable attention.[2] We now report the ZnO- or CdS-catalysed [2 + 2]photocycloreversion of the strained cage molecule (**1**), which has been suggested as a potential molecule for modelling solar energy storage.[3]

When a *ca.* 0·18 M solution of the cage compound (**1**) [λ_{max}(MeCN) 220 nm (sh) and 270 nm (sh)] and a suspension of 15 mg of ZnO or CdS powder in 2 ml of acetonitrile was irradiated (>350 nm) by a 300-W Xenon lamp with a Corning 0-52 glass filter for 3 h under aerated conditions at 25 °C, the diene (**2**) was produced† in 70 or 90% yield, respectively. The reaction was also examined under degassed conditions or in the presence of electron-rich compounds such as 1,4-diazabicyclo[2.2.2]octane (0·45 M), 1,3,5-trimethoxybenzene (0·30 M), and 1,2,4,5-tetramethoxybenzene (0·25 M).



(1) (2)

The following became apparent: (i) in the absence of a semiconductor or light, the diene (**2**) was not produced and the starting cage compound (**1**) was recovered essentially unchanged; (ii) when aerated the reaction was much faster than when degassed, when the yield of the diene (**2**) was decreased to 17% for ZnO and 0% for CdS; (iii) the reaction was efficiently quenched‡ by 1,4-diazabicyclo[2.2.2]octane and 1,2,4,5-tetramethoxybenzene; however 1,3,5-trimethoxybenzene did not quench the reaction and the diene (**2**) was produced in 75 and 95% yield for ZnO and CdS, respectively. Results (i) and (iii) seem to suggest an electron-transfer mechanism, because the oxidation potentials, $E_{\frac{1}{2}}$, are +1·40, +0·68,[4] +1·49,[4] and +0·81[4] V [standard calomel electrode (SCE)] for the cage (**1**), 1,4-diazabicyclo[2.2.2]octane, 1,3,5-trimethoxybenzene, and 1,2,4,5-tetramethoxybenzene, respectively.

To study the cation radical of the cage compound (**1**) we carried out the cerium ammonium nitrate-catalysed dark reaction and the photoexcitation reaction of the charge-transfer (CT) complex of cage (**1**) with tetracyanoethylene (TCNE), both of which would be expected to proceed *via* an electron-transfer mechanism.[5] Treatment of an acetonitrile solution of the cage (**1**) ($3{\cdot}6 \times 10^{-2}$ M) with Ce^{4+} ($2{\cdot}8 \times 10^{-3}$ M) at room temperature in the dark for 5 min afforded the diene (**2**) in 86% yield. Selective excitation of the CT absorption {λ_{max}(CH_2Cl_2) 537 nm, [(**1**)] 0·90 M, [TCNE] 0·78 M} with six 55-W Na-lamps (590 nm) for 1 h in acetonitrile also gave the diene (**2**) in 83% yield.

Thus, it seems reasonable that the semiconductor (S.C.)-catalysed photocycloreversion of (**1**) proceeds *via* an electron-transfer mechanism. Since the aerated reaction is much faster than the degassed reaction, oxygen appears to have an important role. We propose the reaction mechanism shown in the Scheme.

$$\mathrm{S.C.} \xrightarrow{h\nu} (\mathrm{S.C.})_{\mathrm{hole\cdot e}}$$

$$(\mathrm{S.C.})_{\mathrm{hole\cdot e}} + O_2 \rightleftharpoons (\mathrm{S.C.})_{\mathrm{hole}} + O_2^{-\cdot}$$

$$(\mathrm{S.C.})_{\mathrm{hole}} + (\mathbf{1}) \rightarrow \mathrm{S.C.} + (\mathbf{1}^{+\cdot})$$

$$(\mathbf{1}^{+\cdot}) \rightarrow (\mathbf{2}^{+\cdot})$$

$$(\mathbf{1}^{+\cdot}) \text{ or } (\mathbf{2}^{+\cdot}) + O_2^{-\cdot} \rightarrow (\mathbf{2}) \text{ or } (\mathbf{1}) + O_2$$

SCHEME

The electron-transfer process from the conduction band of ZnO or CdS to molecular oxygen (reduction potential, $E_{\frac{1}{2}}$ −0·8 V SCE)[4] or from the cage (**1**) to the valence band of ZnO or CdS seems likely, because the valence and conduction bands of semiconductors are considered to be *ca.* +2·4[6] and −0·8[6] V (SCE) for ZnO and +1·6[6] and −0·9[6] V (SCE) for CdS.

It is not clear whether the chain mechanism, which involves the formation of ($\mathbf{1}^{+\cdot}$) and (**2**) from (**1**) and ($\mathbf{2}^{+\cdot}$), operates or not, although the quinone- or pyrylium salt-sensitized[7] photocycloreversion was found to proceed *via* a chain mechanism which was characterized by a high quantum yield.

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† Prolonged irradiation contaminated the reaction owing to further oxidation of the diene (**2**) which was especially rapid for TiO_2. For this reason TiO_2 is not a good catalyst for the photocycloreversion of cage (**1**).

‡ In all cases, quenching efficiency was complete and the starting cage (**1**) was essentially recovered.

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