Visible Light-induced Splitting of Hydrogen Sulphide and Thiol Formation in CdS Suspensions

Martina Green and Richard M. Elofson*

Alberta Research Council, Edmonton, Alberta, Canada T6G 2C2

The effect of hept-1-ene on the photosplitting of H_2S is described.

Recently, several groups have investigated the visible light-induced generation of H_2 from H_2S over aqueous dispersions of CdS particles loaded with catalysts such as Pt,[1] RuO_2,[2,3] and RuS_2.[4] In all cases, the test solutions were prepared by addition of Na_2S to water under alkaline conditions. The basic experiments involve band-gap excitation ($\lambda < 520$ nm) to produce electrons in the conduction band and holes in the valence band of the semiconductor. H^+ is reduced to H_2 by the electrons, equation (1), while S^{2-} is oxidized to S [2,3] or S_2^{2-},[1] equations (2) and (3).

$$2H^+ + 2e^-_{CB} \rightarrow H_2 \qquad (1)$$

$$S^{2-} + 2h^+ \rightarrow S \qquad (2)$$

or

$$2S^{2-} + 2h^+ \rightarrow S_2^{2-} \qquad (3)$$

In general, the initial H_2 production is high but decreases with time owing to accumulation of oxidation products (elemental sulphur and/or polysulphides). Addition of SO_3^{2-} enhances the H_2 production, presumably because of its reaction with the oxidized species to form $S_2O_3^{2-}$ ions. However, $S_2O_3^{2-}$ in high concentration inhibits H_2 production and its removal is difficult. Consequently, a search for other molecular species which will intercept the oxidation products is warranted.

Since atomic S is known to be extremely reactive towards alkenes in the gas phase, yielding episulphides,[5] it was felt that it would be of interest to examine the potential of alkenes as interceptors. Hept-1-ene was chosen as the trial alkene. The solvent was acetonitrile previously saturated with H_2S. This solvent promotes solubility of the alkene and consequently reaction of hept-1-ene with the products described in reactions (1), (2), or (3).

CdS powder (Fluka, Puriss) was loaded with 1% RuO_2 by either air oxidation of $RuCl_3 \cdot 3H_2O$ (Alfa) in the presence of CdS at 360 °C[3] or spontaneous decomposition of RuO_4 (Polyscience) in an aqeuous suspension of CdS.[2] Catalysts prepared by either method showed similar activity in aqueous Na_2S solutions. Saturated solutions of H_2S in MeCN were obtained by passing H_2S through the solvent to obtain 0.11 M solutions.

Stirred reaction mixtures (40 ml containing 20 mg CdS/RuO_2) in a Pyrex cell maintained at 21 °C were purged with argon prior to irradiation. The light source was a 450 W Xe arc lamp (Osram). A 10 cm water filter fitted with a Schott 113 glass filter and a 408 nm cut-off filter were used to remove i.r. and u.v. radiation respectively. Quantum yield measurements were obtained using ferrioxalate dosimetry[6] at 447 nm. H_2 production was measured either by a gas volumeter or by g.c. Sulphur products were analysed by g.c.–mass spectrometry and n.m.r. The CdS/RuO_2 catalyst used in the aqueous Na_2S solution was found to regain its activity when heated under flowing air at 400 °C. Presumably, this removed the deposited sulphur species.

When a suspension of CdS/RuO_2 in acetonitrile saturated with H_2S was irradiated at $\lambda > 408$ nm, the initial H_2 production rate was much lower than that observed in the aqueous Na_2S system: $\Phi(\frac{1}{2}H_2)$ in MeCN *ca.* 0.04 *vs.* $\Phi(\frac{1}{2}H_2)$ in H_2O *ca.* 0.39.[3] Furthermore, the rate dropped off very rapidly with time. This is not surprising since the SH^- concentration in basic aqueous solution would be much higher than in acetonitrile. It has been claimed that in aqueous solution the adsorbed SH^- ions on CdS/RuO_2 lower its flat-band potential, thus facilitating H_2 production.[3]

When the H_2S–MeCN solution was irradiated in the presence of 0.05 M hept-1-ene, the H_2 production behaved in a drastically different manner as shown in Figure 1. The initial rate was very low, but remained constant, suggesting that accumulation of sulphur on the catalyst did not occur. Indeed, mass spectral analyses of CCl_4 washings of the solutions containing hept-1-ene showed that only trace quantities of S_8 were present. Analyses of washings from the catalyst used in the absence of heptene indicated significant amounts of S_8.

G.c.–mass spectroscopic analyses of the solutions after irradiation indicated that in the presence of hept-1-ene, sulphur addition products were formed in large quantities. The major product was heptane-1-thiol, comprising about 95% of the total sulphur containing products. The remaining products were heptane-2-thiol (about 4—5%) and diheptyl sulphide, diheptyl disulphide, and diheptyl trisulphide (total < 1%).

The formation of heptane thiols and the depletion of hept-1-ene as a function of irradiation time are shown in Figure 2. The rate of thiol formation is initially slow, possibly because of adsorption on the catalyst surface, but eventually rises to a steady value. The concentration of hept-1-ene drops steadily and appears to level off when roughly 70% has been consumed. The fact that the rate of H_2 production did not drop suggests that the apparent levelling off in heptene disappearance is not real. The quantum yields for total thiol and hept-1-ene depletion were measured and found to be 0.15 and 0.50, respectively. The lower quantum yield for thiol formation could be due to adsorption of the thiols on the catalyst surface and/or existence of heptene-consuming reactions that were not observed because they did not yield volatile products that could be detected by g.c.

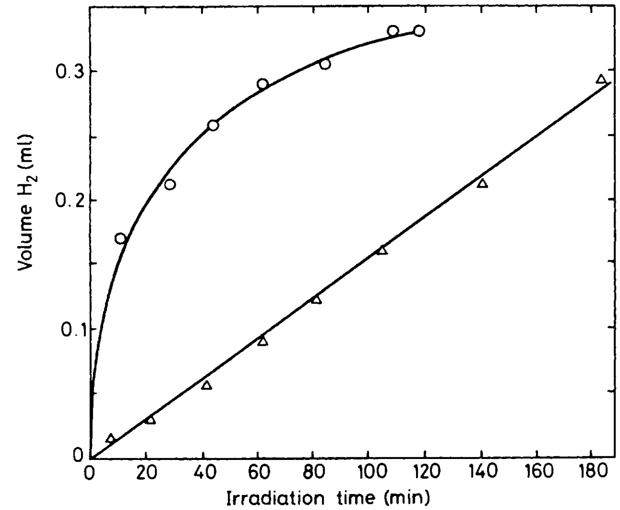


Figure 1. H_2 production as a function of irradiation time in the H_2S saturated MeCN systems: ○ no hept-1-ene present, △ 0.05 M hept-1-ene present.

The production of significant quantities of heptane thiols and the suppression of sulphur formation in the presence of hept-1-ene unambiguously demonstrates that alkenes intercept the oxidation product or products of CdS/RuO_2 catalysed H_2S splitting. However, the alkene apparently also intercepts most of the hydrogen ions, resulting in a low yield of H_2, $\Phi < 0.01$. Based on the mechanism proposed for the electrolysis of H_2S in H_2SO_4,[7] we suggest the steps (4)—(6) for the CdS/RuO_2 mediated splitting of H_2S in MeCN. H_2 is produced by reaction of the band-gap electrons with H^+ formed in reactions (4) and (5).

The alkene could react with either the $\dot{S}H$ moiety to form a radical or with S to form an episulphide. Radical formation would lead to thiol production as shown in steps (7) and (8).

$$H_2S(ads.) + h^+ \rightarrow \dot{S}H(ads.) + H^+(ads.) \quad (4)$$

$$\dot{S}H(ads.) + h^+ \rightarrow S(ads.) + H^+(ads.) \quad (5)$$

$$2S(ads.) \rightarrow S_2(ads.) \xrightarrow{S(ads.)} S_3(ads.) \ldots S_8 \quad (6)$$

$$\dot{S}H + C_5H_{11}CH{=}CH_2 \rightarrow C_5H_{11}\dot{C}HCH_2SH(ads) \quad (7)$$

$$C_5H_{11}\dot{C}HCH_2SH + \dot{H}(ads) \rightarrow C_7H_{15}SH \quad (8)$$

A chain reaction involving abstraction of $\dot{H}$ from H_2S, as in

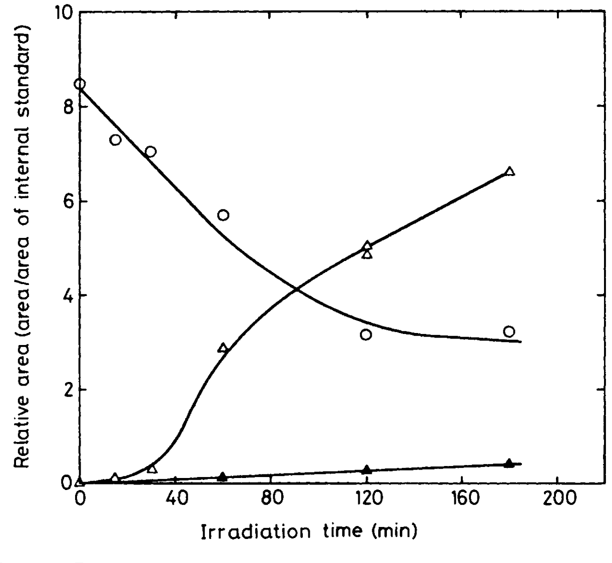
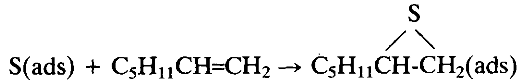


Figure 2. Formation of heptane thiols and depletion of hept-1-ene as a function of irradiation time in the H_2S saturated MeCN system, [hept-1-ene] = 0.05 M: ○ hept-1-ene, △ heptane-1-thiol, ▲ heptane-2-thiol.

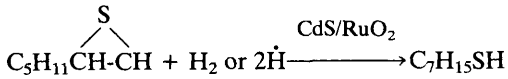
the case of the u.v.-initiated addition of H_2S to alkene,[8] seems unlikely, since reaction (9) implies no effect on H_2 production.

$$C_5H_{11}\dot{C}HCH_2SH + H_2S(ads) \rightarrow C_7H_{15}SH + \dot{S}H \quad (9)$$

Episulphide formation followed by addition of H_2 or 2H would lead to thiol formation, equations (10) and (11). The relative importance of $\dot{S}H$ and S addition is of interest, since it might be possible to prevent addition of H_2 to the episulphide and so preserve the more interesting product. However, at present there is no evidence to differentiate the two possibilities.



$$S(ads) + C_5H_{11}CH{=}CH_2 \rightarrow C_5H_{11}\overset{S}{\overbrace{CH\text{-}CH_2}}(ads) \quad (10)$$



$$C_5H_{11}\overset{S}{\overbrace{CH\text{-}CH}} + H_2 \text{ or } 2\dot{H} \xrightarrow{CdS/RuO_2} C_7H_{15}SH \quad (11)$$

The overall reaction reported here concerns the light-induced addition of H_2S to a double bond under unusual circumstances: only visible light ($\lambda > 400$ nm) was employed, and the process is apparently not a chain reaction. This is one of very few CdS catalysed reactions involving organic molecules to be reported.[9,10]

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