

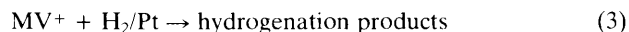
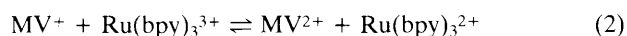
## Use of Inclusion Complexes of Hydrophobic Viologens with Cyclodextrin to Protect the Pyridinium Moiety from Hydrogenation in Photochemical Hydrogen Formation

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Cyclodextrin inclusion complexes of viologens with hydrophobic tails increased the stability of the pyridinium moiety of the viologen to hydrogenation, which resulted in up to five times higher efficiency in terms of hydrogen produced per viologen consumed.

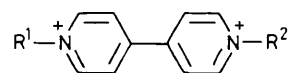
Reduction of methyl viologen,  $MV^{2+}$ , (1), by the charge-transfer excited state of  $Ru(bpy)_3^{2+}$  ( $bpy = 2,2'$ -bipyridine) appears to be one of the most promising model systems reported for splitting water using visible light, a relay compound [such as  $MV^{2+}$ ]<sup>1-4</sup> or a ferredoxin model  $Fe_4S_4(SCH_2Ph)_4^{2-}$ ,<sup>5</sup> and an electron donor (such as ethylenediaminetetra-acetic acid (EDTA) and triethanolamine). The reduction process is very efficient and hydrogen can be formed in the presence of an appropriate redox catalyst (*e.g.*, colloidal Pt<sup>1</sup>) according to equation (1).



To improve the quantum efficiency of this method, it is important to be able to retard the back reaction between  $MV^+$  and  $Ru(bpy)_3^{3+}$ , which occurs near or at diffusion rate

[equation (2)].<sup>2,6</sup> This could be accomplished by means of micelles,<sup>7</sup> semiconductors, and membranes as in photosynthesis.<sup>8</sup> Another problem is the loss of the relay compound by hydrogenation using the hydrogen produced, catalysed by the platinum redox catalyst that is also necessary for efficient water reduction [equation (3)].<sup>6,9</sup>

We have prepared viologens possessing a short tail (ethyl group) on one end and a hydrophobic tail on the other, and examined the effect of their inclusion complexes with cyclodextrins (CD) on the hydrogen production. Such viologens with two different chain lengths in one molecule are



(1);  $MV^{2+}$ ,  $R^1 = R^2 = Me$

(2);  $R^1 = R^2 = n-C_7H_{15}$

(3);  $R^1 = n-C_{12}H_{25}$ ,  $R^2 = Et$

(4);  $R^1 = CH_2Ph$ ,  $R^2 = Et$

useful for controlling the hydrophobicity.<sup>†</sup> Cyclic voltammetry in 10% aqueous acetonitrile revealed that the redox potentials are similar to that of methyl viologen;  $-0.32$ ,  $-0.31$ ,  $-0.31$ , and  $-0.28$  V (vs. normal hydrogen electrode), for, respectively, MV<sup>2+</sup>, (2), (3), and (4). They should therefore be suitable for water reduction. N.m.r. spectra in D<sub>2</sub>O showed shifts for the inner protons at 3-H and 5-H of  $\beta$ -cyclodextrin from  $\delta$  3.97 and 3.82, to  $\delta$  3.88 and 3.72 respectively, in the presence of (4), indicating the formation of inclusion compounds.<sup>10</sup> No such behaviour was observed with (1). Fluorescence quenching of excited Ru(bpy)<sub>3</sub><sup>2+</sup> by (1)–(4) showed that Stern–Volmer constants ( $k_q\tau$ ) decreased in the presence of  $\beta$ -cyclodextrin, and that the extent depended on the hydrophobicity of the viologen used [e.g.,  $k_q\tau$  for (1) was 180 in the absence of CD and 162 with  $\beta$ -CD; similarly, (2): 203 and 136; (3): 239 and 112; and (4): 202 and 164].

Absorption spectra of the reduced viologens in the absence of CD exhibited a band at ca. 550 nm, suggesting dimer and/or multimer formation which is disadvantageous for hydrogen formation.<sup>11</sup> However, the addition of  $\beta$ -CD to this solution (> 1 mol equiv.) gave a normal absorption maximum at 603 nm.<sup>12</sup> A typical example is shown in Figure 1. Photochemical hydrogenation of the viologens in the presence of colloidal Pt was examined. After 3 h, the amount of viologen present had been reduced by 42.4, 40.4, 29.3, and 22.5%, for, respectively, (1) alone, (1)- $\beta$ -CD, (3)- $\beta$ -CD, and (4)- $\gamma$ -CD. This suggests that inclusion formation retards the hydrogenation of the pyridinium moiety, which in turn should improve the net hydrogen generation in the system.

Irradiation of a solution containing Ru(bpy)<sub>3</sub><sup>2+</sup> ( $5 \times 10^{-5}$  M), EDTA ( $2.5 \times 10^{-2}$  M), viologen V<sup>2+</sup> ( $5 \times 10^{-3}$  M), and colloidal Pt<sup>1</sup> using a projector lamp ( $\lambda > 390$  nm) caused continuous evolution of hydrogen as determined by g.l.c., as described previously.<sup>1,5</sup> Loss of V<sup>2+</sup> by the hydrogenation reaction was concomitantly followed by the absorbance change at 260 nm.<sup>‡</sup> No significant differences in both net hydrogen formation and viologen consumption were observed using MV<sup>2+</sup> regardless of the presence of cyclodextrins, whereas disappearance of the modified viologens in the presence of cyclodextrins ( $5.5 \times 10^{-3}$  M) was decreased to a significant extent. After 4 h illumination, for example, the turnover numbers, which were defined as  $2 \times \text{H}_2$  produced ( $\mu\text{mol}$ ) per viologen consumed ( $\mu\text{mol}$ ), reached 290 and 200, respectively, by the use of (3)- $\beta$ -CD and (4)- $\gamma$ -CD. For the former this represents a five-fold increase in efficiency; in the case of (1) alone the turnover number was only 58. A similar effect is found with other combinations of the viologens and cyclodextrins, and typical examples are summarized in Table 1. Although inclusion of the side chains has been suggested, the results show that the complex formation of hydrophobic viologens with cyclodextrins is effective in stabilizing the pyridinium moiety with respect to the hydrogenation reaction, accounting for the enhanced hydrogen yield per viologen consumed.

In preliminary experiments using a sunlight lamp,<sup>5</sup> which may be closer to operative conditions, consumption of the viologens after 18 h was 34.1, 35.2, 23.0, and 17.8%, with

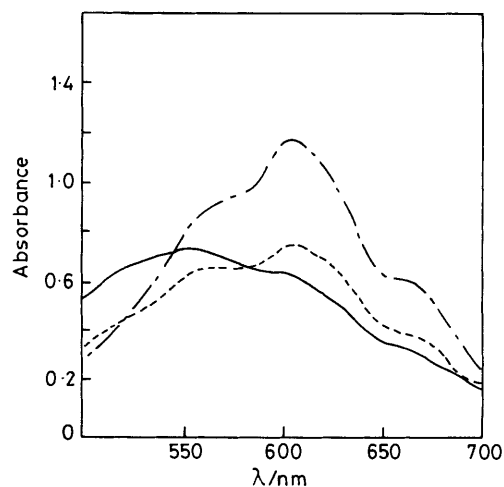


Figure 1. Effect of  $\beta$ -CD on absorption spectra of reduced (3). — no CD. ---- (3): $\beta$ -CD 1:0.5. - · - · (3): $\beta$ -CD 1:2.8.

Table 1. Effect of inclusion by CD on viologen consumption and hydrogen formation.<sup>a</sup>

Viologen	CD	Rate $\mu\text{mol/h}$	Viologen consumed/ $\mu\text{mol}$	Relative turnover
(1)	—	129	11.4	100 <sup>b</sup>
	$\beta$	119	12.4	96
(3)	$\beta$	60	1.7	499
	$\gamma$	53	2.8	231
(4)	$\alpha$	124	4.1	301
	$\gamma$	106	3.0	344

<sup>a</sup> After 4 h illumination. <sup>b</sup> 331  $\mu\text{mol}$  of hydrogen produced.

accompanying hydrogen evolution of 430, 435, 358, and 402  $\mu\text{mol}$ , respectively, by means of (1) alone, (1)- $\beta$ -CD, (3)- $\beta$ -CD, and (4)- $\gamma$ -CD.

In summary utilization of cyclodextrin–viologen complexation has been shown to prevent consumption of viologen when used as a relay compound in photochemical hydrogen formation. We are indebted to Dr Masao Tokuda for provision of facilities and help in measuring the redox potentials.

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<sup>†</sup> Satisfactory microanalyses and n.m.r. spectra were obtained. E.g. (3)  $\delta_{\text{H}}([\text{C}_6\text{H}_6]\text{Me}_2\text{SO}$ , 100 MHz) 0.87 (t, 3H,  $J$  8 Hz, dodecyl-CH<sub>3</sub>), 1.27 (s, 18H, dodecyl-CH<sub>2</sub>), 1.63 (t, 3H,  $J$  8 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 2.0 (m, 2H, -NCH<sub>2</sub>CH<sub>2</sub>), 4.73 (t, 2H,  $J$  8 Hz, NCH<sub>2</sub>), 4.80 (t, 2H,  $J$  8 Hz, NCH<sub>2</sub>), 8.82 (d, 4H,  $J$  7 Hz, Ar-H), 9.45 (d, 4H,  $J$  7 Hz, Ar-H). Throughout this work concentrations below the critical micelle concentration were employed.

<sup>‡</sup> Absorbance at 260 nm by species other than viologen is less than 1.8% under these conditions.