

## Formation of Two-Carbon Acids from Carbon Dioxide by Photoreduction on Cadmium Sulphide

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Aqueous solutions of CO<sub>2</sub> containing tetramethylammonium chloride were photolysed with visible light in the presence of colloidal CdS to yield glyoxylic acid as well as formic and acetic acids and CH<sub>2</sub>O.

Model systems emulating the photosynthetic process have been reported, mainly concentrating on the splitting of water.<sup>1</sup> McAuliffe<sup>2</sup> studied O<sub>2</sub> evolution/quinone reduction using manganese(II) complexes, and more recently<sup>3</sup> reduction of unsaturated organic substrates including CO but excluding CO<sub>2</sub> with a ruthenium bipyridyl/methyl viologen/platinum-metal colloid system.

Simpler systems involving semiconductor electrodes, suspensions, and colloids have been used both to split water photolytically<sup>1,4,5</sup> and also by Honda<sup>5</sup>, Halmann,<sup>6</sup> and Henglein<sup>7</sup> and their co-workers to reduce CO<sub>2</sub> mostly with the production of formic acid and/or CH<sub>2</sub>O and sometimes CH<sub>3</sub>OH. Malati<sup>8</sup> has reported the formation of carbon as well as CH<sub>2</sub>O from Na<sub>2</sub>CO<sub>3</sub>.

**Table 1.** Yields of glyoxylic acid and other products generated by the photoreduction of CO<sub>2</sub> on CdS.

Solution	pH	Irradiation time/h	Yield/ $\mu\text{mol dm}^{-3}$					
			Glyoxylate	Acetate	Formate	CH <sub>2</sub> O	MeOH	$\phi'_e$
H <sub>2</sub> O	4	94	A	3.5	75	11	87	$3.5 \times 10^{-4}$
TMACl (0.1 M)	4	42	53	40	27	7.0	A	$3.3 \times 10^{-4}$
TAMCl (0.1 M)	6	42	66	A	136	6.1	N	$5.3 \times 10^{-4}$
TAMCl (0.1 M) (susp)	6.6	64	10.7	N	37	5.5	N	$8.7 \times 10^{-5}$
TAMCl (0.1 M)/SO <sub>3</sub> <sup>2-</sup>	6	36	116	A	220	7.0	N	$1.03 \times 10^{-3}$
TAMCl (0.1 M)/SO <sub>3</sub> <sup>2-</sup>	4	36	11	A	79	5.8	N	$2.5 \times 10^{-4}$
TAMCl (0.1 M)/QH <sub>2</sub>	6	80	28	T	770	69	N	$1.25 \times 10^{-3}$

All solutions contained colloidal CdS ( $5 \times 10^{-2}$  M) except (susp.) which contained 0.3 g CdS suspension in 100 cm<sup>3</sup> solution; TMACl = tetramethylammonium chloride; SO<sub>3</sub><sup>2-</sup> = sodium sulphite ( $5 \times 10^{-3}$  M); QH<sub>2</sub> = hydroquinone (0.01 M);  $\phi'_e$  = photon/electron quantum efficiency; N = not analysed; A = not detectable; T = trace (ca.  $10^{-6}$   $\mu\text{mol dm}^{-3}$ ).

In our studies, using mainly cadmium sulphide suspensions or colloids, we have observed similar products.<sup>9</sup> In addition we sometimes found glyoxylic acid, and also acetic acid and acetaldehyde. Further work has now confirmed the formation of glyoxylic acid and we now report the formation of two-carbon products from carbon dioxide by photoelectrochemical reduction on cadmium sulphide. We recently reported the electrochemical reduction of carbon dioxide to glyoxylic acid.<sup>10</sup>

Colloidal cadmium sulphide was prepared by the addition of sodium sulphide (5 cm<sup>3</sup>,  $10^{-2}$  M) to cadmium chloride (5 cm<sup>3</sup>,  $10^{-2}$  M) in water (90 cm<sup>3</sup>) with stirring. The solution was then diluted to give  $5 \times 10^{-4}$  mol dm<sup>-3</sup> colloidal cadmium sulphide and the appropriate electrolyte and other additive was incorporated. Carbon dioxide was bubbled continuously through the solution which was then irradiated with light ( $\lambda$  320–580 nm) from a Phillips medium pressure arc lamp, of intensity  $2.5 \times 10^{-3}$  einsteins per hour (determined by actinometry) for periods up to 120 hours.

Samples of the solution were passed through an ion-exchange column to remove tetra-alkylammonium salts and then analysed for formic acetic and glyoxylic acids by h.p.l.c. with an Aminex HPX-87H ion exclusion column eluted with 0.016 M sulphuric acid and detected at 210 nm. Glyoxylic acid was further identified and estimated by a violet colour reaction with phenylhydrazine/ferricyanide which was monitored at 540 nm. Formaldehyde was estimated using Hantzsch reagent (acetylacetone in ammonium acetate/acetic acid) monitored at 412 nm. Further samples were analysed for formaldehyde, methanol, and acetaldehyde by head-space g.l.c. on a 20 m Carbowax column.

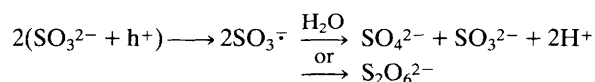
Blank runs in which nitrogen was used instead of carbon dioxide, or the cadmium sulphide omitted, gave no detectable amounts of the above products.

A summary of results is given in Table 1.

The best conditions for the formation of glyoxylic acid are low radiation intensities, colloidal cadmium sulphide solutions containing tetramethylammonium chloride (0.1 M) and sodium sulphite ( $5 \times 10^{-3}$  M) or hydroquinone (0.01 M) at pH 6. No glyoxylic acid was found at higher pH (in contrast to the electrochemical reduction in which best results were obtained at pH 9–10). Sometimes acetic acid was formed as well as glyoxylic acid and occasionally acetaldehyde was also present. Presumably these products came from further reduction of glyoxylic acid.

Several factors could be responsible for the relatively low photon–electron quantum efficiencies ( $\phi'_e$ ). One could be the reoxidation of products by the holes.<sup>9,11</sup> Otherwise corrosion of the cadmium sulphide may occur. Henglein<sup>7</sup> suggests that low efficiencies are expected if the overall redox process involves both two electrons and two holes as with CO<sub>2</sub>/

formate and H<sub>2</sub>O/O<sub>2</sub> or CdS/CdO. However with a one-electron/two-hole or a two-electron/one-hole process high quantum efficiencies may be obtained. CO<sub>2</sub>/CO<sub>2</sub><sup>-</sup> is a one-electron process (though subsequent reduction of oxalate to glyoxylate is *via* two electrons). Henglein<sup>7</sup> used added sulphite as a hole acceptor with ZnS to give yields of formate from CO<sub>2</sub> with  $\phi'_e = 0.8$ . He suggests that sulphite is oxidised by a one-hole disproportionation mechanism or a dimerisation.



We found that hydroquinone as a hole acceptor gave some improvement in  $\phi'_e$ .

Surprisingly, we have found no more than occasional traces of oxalate (readily detectable by h.p.l.c.) of ca.  $10^{-6}$  mol dm<sup>-3</sup>. Perhaps it is more readily reduced under these conditions than CO<sub>2</sub> itself. Oxalate is a likely intermediate in the reduction scheme, as shown by its photolysis with CdS to give glyoxylate, some tartarate, much formate, and carbon dioxide.

The quantum yields reach a maximum at around 40 hours, after which they decline, presumably due to back reactions such as the photolysis of formate<sup>11</sup> and of oxalate<sup>9</sup> back to carbon dioxide.

Received, 26th April 1988; Com. 8/01651H

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