Photoreduction of Carbon Dioxide on Zinc Sulfide to give Four-carbon and Two-carbon Acids

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Aqueous solutions of CO_2 containing tetramethylammonium chloride were photolysed with visible light in the presence of colloidal ZnS to yield tartaric acid, glyoxylic acid, oxalic acid, formic acid and formaldehyde.

Since 1979 when Inoue and coworkers announced the splitting of water by photolysis in the presence of TiO_2,[1] there has been considerable interest in photolytic oxidations and reductions using semiconductors as catalysts.[2] Some investigators have looked for oxygen evolution from water,[3] others have looked for CO_2 reduction, simulating photosynthesis,[4,5] and yet others have studied a wide range of reductions of unsaturated organic substances.[6,7] Interesting developments involve the use of enzymes as well as semiconductors to fix CO_2 in oxoglutaric and pyruvic acids with various photosensitisers including CdS.[8,9]

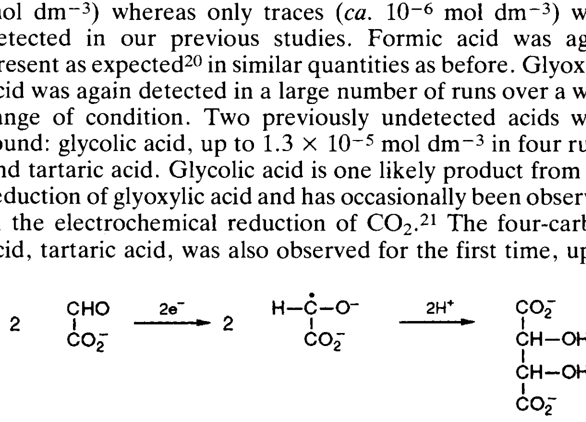
The use of simple semiconductor particulates to reduce CO_2 was first reported by Halmann and coworkers.[4,10] Their products were mainly formate ion and occasionally formaldehyde and methanol. Henglein[11] developed these studies further using mainly CdS or ZnS. He reported quantum yields of formate up to $\Phi = 0.8$ with sulfite or propan-2-ol as electron donors (hole acceptors). Previously[12,13] we described the formation of glyoxylate and acetate as well as formate, formaldehyde and methanol using mainly CdS but also ZnO and SiC. The solutions used contained tetramethylammonium chloride.

Interest has continued with the recent publication of further work with a Pt–CdS–RuO_2 system[14] and with ZnS[15] to reduce CO_2 to formate with $\Phi = 0.001$ and more significantly by Yanagida *et al.*[16] who obtained formate and carbon monoxide with $\Phi = 0.24$ using ZnS. The latter group also studied the photoreduction of CO_2 catalysed by oligo-(*p*-phenylenes).[17] Wilner *et al.* have reduced CO_2 on Pd-doped TiO_2.[18] None of these workers obtained dimerised products such as oxalate or glyoxylate and none used tetraalkylammonium salts in their solutions.

We are now able to confirm our previous results[12,13] with ZnS and also report the formation of the four-carbon molecule, tartaric acid, and glycolic acid as well as oxalic, glyoxylic and formic acids and formaldehyde. Experimental methods were similar to those previously reported.[12] Colloidal zinc sulfide was prepared by the addition of sodium sulfide (5 cm^3) to zinc sulfate (5 cm^3) in water (90 cm^3) with stirring. The solution was then diluted to give 0.01 to 0.05 mol dm^{-3} zinc sulfide and the appropriate electrolyte and other additive was incorporated. These were much higher colloidal concentrations than those used previously (5×10^{-4} mol dm^{-3}). Carbon dioxide was bubbled continuously through the solution which was then irradiated with light (λ 320–580 nm) from a Phillips medium-pressure arc lamp of intensity 2.5×10^{-3} einsteins per hour for periods of 24–72 h.

Samples of the solution were passed through an ion-exchange column to remove tetraalkylammonium salts and then analysed by HPLC for organic acids using an Aminex HPX-87H ion exclusion column eluted with 0.016 mol dm^{-3} sulfuric acid and detected at 210 nm. Product concentrations were calculated from peak areas. Glyoxylic acid was further identified and estimated by the violet colour reaction with phenylhydrazine–hexacyanoferrate(III) which was monitored at 540 nm.[19] Formaldehyde was estimated using the Hanzsch reagent (pentane-2,4-dione in ammonium acetate–acetic acid) monitored at 412 nm. Tartaric acid could be detected using Fenton's reagent (fresh $FeSO_4$–H_2O_2–NaOH) but this test was not very sensitive below 10^{-3} mol dm^{-3}. The results are summarised in Table 1.

No acetic acid was detected, but a substantial amount of oxalate was found which was expected[20] (up to 6×10^{-3} mol dm^{-3}) whereas only traces (*ca.* 10^{-6} mol dm^{-3}) were detected in our previous studies. Formic acid was again present as expected[20] in similar quantities as before. Glyoxylic acid was again detected in a large number of runs over a wide range of condition. Two previously undetected acids were found: glycolic acid, up to 1.3×10^{-5} mol dm^{-3} in four runs, and tartaric acid. Glycolic acid is one likely product from the reduction of glyoxylic acid and has occasionally been observed in the electrochemical reduction of CO_2.[21] The four-carbon acid, tartaric acid, was also observed for the first time, up to



Scheme 1

Table 1 Yields of products generated by photoreduction of CO_2 on ZnS[a]

pH	Irradiation time/h	Sulfite	Yield/μmol dm^{-3} Oxalate	Glyoxylate	Formate	Glycolate	Tartrate
2	36	+	900	1.9	—	—	—
2	36	−	78	—	—	—	—
4	24	+	220	7.6	—	—	—
4	24	−	1400	2.1	2.3	13	16
6	36	+	4	0.63	320	—	—
6	36	−	0.26	0.98	—	—	—
7	48	+	400	3.5	180	3.8	6.7
7	48	−	200	22	—	—	9.6
10	60	+	—	2.7	—	0.59	4.1
10	60	−	—	1.2	3.2	0.2	—
14	48	+	2300	—	—	—	—
14	48	−	360	—	—	—	—

[a] Solutions contained colloidal ZnS (5×10^{-2} mol dm^{-3}) and Me_4NCl (0.1 mol dm^{-3}), with (+) or without (−) sodium sulfite. Analysis by HPLC.

9×10^{-5} mol dm^{-3} in five different runs. Tartaric acid is the other likely reduction product from glyoxylic acid which could be formed by pinacol-type dimerisation (Scheme 1).

We have observed the electrochemical reduction of glyoxylate to glycolate and tartrate,[22] and the electrochemical reduction of CO_2 to glyoxylate, glycolate and tartrate.[23] The formation of the dihydroxy tartrate ion from CO_2 under these conditions is particularly interesting as it parallels the photosynthetic conversion of CO_2 to the polyhydroxy five- and six-carbon sugars.

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