Photochemical Formation of Glycine and Methylamine from Glycolic Acid and Ammonia in the Presence of Particulate Cadmium Sulphide

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Photochemical formation of glycine and methylamine from glycolic acid and ammonia occurs in the presence of platinized CdS particles under irradiation.

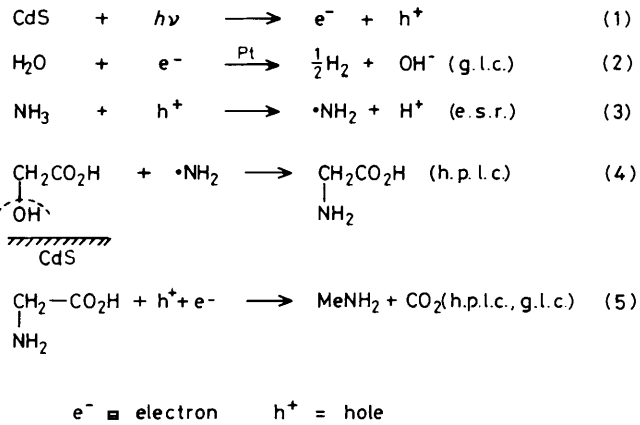
Taking advantage of the strong redox power of a particulate semiconductor, Bard and his co-workers have reported that traces of amino acids, such as glycine, can be formed from methane and ammonia in aqueous solution in the presence of TiO_2 with a Pt deposit.[1] We have examined the photochemical reaction of glycolic acid with ammonia in the presence of particulate CdS, with and without a Pt deposit, and have found that the platinized CdS particles are active in promoting the formation of glycine and methylamine. We have also shown that the $\cdot NH_2$ radical plays an important role in glycine formation, and that electrons and 'holes' are necessary for methylamine formation.

An aqueous solution containing glycolic acid (10 mmol) and ammonia (100 mmol) with CdS (300 mg; Katayama Chemical; mixture of cubic and hexagonal) was irradiated with a 500 W Xe lamp for 24 h in the absence of air. Platinized CdS was prepared by mixing the particulate semiconductor with Pt black (10 wt %) in an agate mortar.[2] Reaction products in solution were separated by using a cation exchange resin (BIO RAD, AG 50W-X2), and analysed by h.p.l.c. (Shimadzu LC-5A, ZORBAX ODS column); gaseous products were analysed by g.l.c. (Ohkura 1–802, MS-5A column).

Glycine and methylamine were formed from irradiated glycolic acid and ammonia in the presence of platinized CdS (Table 1). Hydrogen gas was produced simultaneously. In order to show that these products were formed through photochemical reaction with the semiconductor, three blank experiments were carried out as follows: (1) a photochemical reaction in the absence of CdS/Pt particles, (2) a thermal reaction at 97 °C in the presence of CdS/Pt, and (3) a reaction in the presence of the photoinactive catalyst SiO_2/Pt, under irradiation. As shown in Table 1, neither glycine nor methylamine was obtained. In order to elucidate the roles of photogenerated electrons and holes in the CdS/Pt particles on

Table 1. Amounts of glycine and methylamine formed from glycolic acid and ammonia over platinized CdS under irradiation for 24 h. The effects of electron and hole scavengers on the yields are also given.

	Scavenger	Gly (μmol)	$MeNH_2$ (mmol)
		13	3
CdS/Pt	O_2	30	0.3
	EtOH	9	0.2
Blank (light only)		None	None
Blank (heated at 97 °C)		None	None
SiO_2/Pt		None	None



Scheme 1

the formation of glycine and methylamine, we examined the effects of electron and hole scavengers on product yields. Oxygen (160 Torr) was used as an electron scavenger, and EtOH (20 mmol) as a hole scavenger (see Table 1). The amount of glycine increased about 3-fold in oxygen atmosphere, and decreased by 25% in the presence of EtOH. Thus photogenerated holes play an important role in glycine formation whereas electrons do not. The amount of methylamine decreased to 10% in the presence of either scavenger. Therefore, both electrons and holes are necessary for methylamine formation. The yields of glycine and methylamine under the best conditions were 0.1% and 30%, respectively.

Although TiO_2 is known to have a high activity in various photocatalytic reactions, such as the production of hydrogen from water[3] (similar to that of CdS), even platinized TiO_2 had no activity for glycine formation. Since TiO_2 has a deeper valence band position [+3.0 V *vs.* normal hydrogen electrode (n.h.e.)] than that of CdS (+1.8 V *vs.* n.h.e.), photogenerated holes in TiO_2 particles may induce decomposition of glycolic acid rather than glycine formation. The remarkable effect of platinization of CdS is considered to be due not only to the efficient separation of electrons and holes in the particles, but also to the catalytic effect of Pt.[4]

The large effect of the electron scavenger indicates that photogenerated holes play an important role in glycine formation. Indeed, $\cdot NH_2$ radicals generated by holes in CdS during irradiation were detected by e.s.r. by adding a spin trapping agent, 5,5-dimethyldihydropyrrole *N*-oxide. Since $\cdot NH_2$ radical species and glycine were formed only under irradiation, the $\cdot NH_2$ radical formed by holes is considered to be involved in glycine formation. For methylamine formation, both photogenerated electrons and holes are necessary and the amount of methylamine is decreased by scavengers of electrons or holes.

From the foregoing results, the mechanism of photochemical formation of glycine and methylamine from glycolic acid and ammonia in the presence of CdS/Pt particles is suggested to be as shown in Scheme 1. Irradiation of the CdS powder produces electrons in the conduction band and holes in the valence band [reaction (1)]. Photogenerated electrons reduce H_2O to form hydrogen and OH^- [reaction (2)].[5] Photogenerated holes attack ammonia to form $\cdot NH_2$ radicals [reaction (3)], which reacts with glycolic acid adsorbed on the CdS surface to produce glycine [reaction (4)]. The glycine formed is decomposed by photogenerated electrons and holes to form methylamine and CO_2 [reaction (5)].[6] The effect of platinization enhances the rate of reaction (2), so that holes are effectively consumed by $\cdot NH_2$ radical formation.

Although formation of glycine could conceivably occur through the addition of ammonia to the C=O double bond of glyoxylic acid ($CHOCO_2H$), which could be produced from glycolic acid by holes, glycine was not formed on irradiation of glyoxylic acid in the presence of CdS/Pt.

In conclusion, (1) glycine and methylamine are formed from glycolic acid and ammonia in the presence of CdS/Pt under irradiation; (2) $\cdot NH_2$ radicals generated by holes play an important role in glycine formation; (3) both photogenerated electrons and holes are necessary for methylamine formation. The suggested mechanism agrees with these observations.

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