

Photochemical Nucleic Acid Base Formation with Particulate Semiconductors under Irradiation

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Using particulate semiconductors, such as TiO_2 and CdS , hypoxanthine, one of the nucleic acid bases, is formed under irradiation.

From their studies of chemical evolution, Bard and co-workers¹ have reported photochemical amino acid formation from CH_4 , NH_3 , and H_2O , taking advantage of the strong redox power of TiO_2 . We have also reported photochemical amino acid and peptide formation using TiO_2 and CdS

particles.^{2,3} However, to date there have been no reports of photochemical nucleic acid base formation using semiconductor particles. We have examined nucleic acid base formation from KCN , NH_3 , and H_2O using various kinds of particulate semiconductors, and found hypoxanthine, one of the nucleic

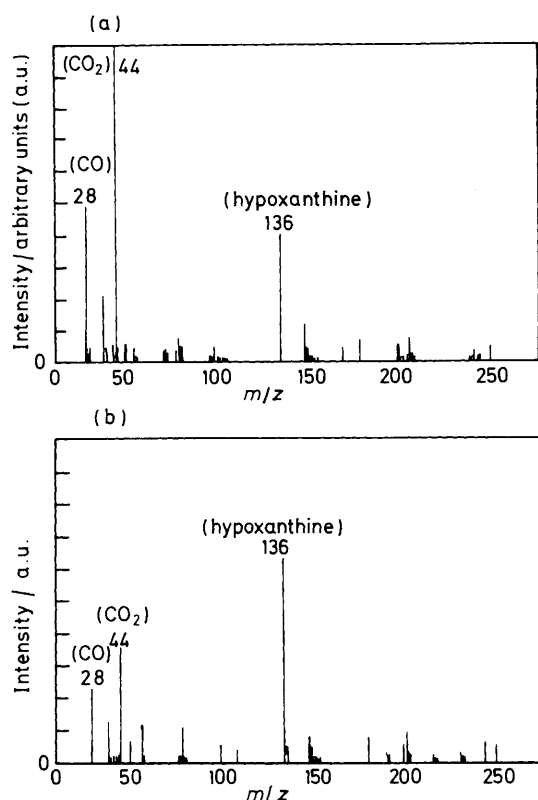


Figure 1. G.c.-mass spectra of (a) the t.l.c. spot of the solution after the irradiation in the presence of CdS/Pt and (b) an authentic sample of hypoxanthine.

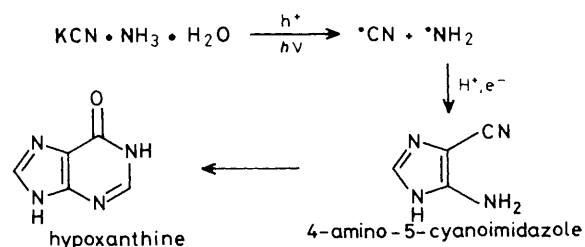
acid bases which forms part of the anticodon of t-RNA, can be formed with these particulate semiconductors under irradiation.

On irradiation of semiconductor particles, electrons are excited to the conduction band, leaving positive holes in the valence band. Photogenerated electrons and holes diffuse to the surface, and are used for reductive and oxidative reactions, such as $H_2 + O_2$ production from water, respectively.⁴ We have utilized this redox power for the nucleic acid base formation.

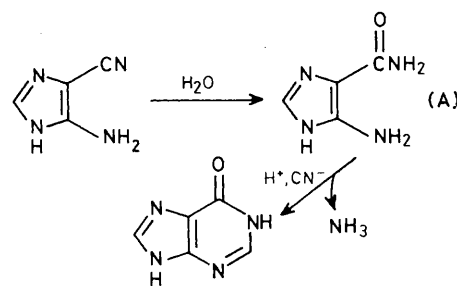
An aqueous solution (10 ml) containing KCN (1 mmol) and NH_3 (1 mmol) in the presence of semiconductor particles (300 mg) was irradiated with a 500 W Xe lamp under deaerated conditions. A platinized semiconductor, such as TiO_2/Pt and CdS/Pt, was prepared by mixing the semiconductor particles with 10 wt% Pt black in an agate mortar.⁵ Reaction products in the solution were analysed and identified using t.l.c., h.p.l.c., and g.c.-mass and u.v. spectrometry.

After irradiation for 24 hours, hypoxanthine was found (t.l.c.) in the solution, as judged by comparing the retention time of the products with that of an authentic sample. The t.l.c. spot was further analysed by g.c.-mass spec. which confirmed it to be hypoxanthine (Figure 1). Analyses after irradiation by h.p.l.c. and u.v. spectroscopy also indicated the formation of hypoxanthine. The other nucleic acid bases, such as adenine or guanine, were not observed.

Table 1 summarizes the yields of hypoxanthine with various kinds of particulate semiconductors. Without Pt deposit, only TiO_2 was active for hypoxanthine formation. Hypoxanthine was formed with all the platinized semiconductors with TiO_2/Pt and CdS/Pt having higher activities than the other semiconductors. The differences in the activities of the



Scheme 1. h^+ = hole and e^- = electron in the TiO_2/Pt semiconductor particles.



Scheme 2

semiconductors are similar to the differences in photocatalytic activity of the particles as established for hydrogen production.⁶ The enhancing effect of platinization is considered to be caused not only by efficient separation of electrons and holes in the semiconductor particles,⁷ but also by the catalytic effect of the Pt itself. The quantum yield of hypoxanthine for TiO_2/Pt is 0.1% (at λ 380 nm).

Three blank experiments were carried out as follows: (1), irradiation with no semiconductor, (2) heating in the presence of the semiconductors in the dark, and (3) irradiation using a photoinactive catalyst, SiO_2 . As shown in Table 1, no hypoxanthine was produced in these experiments. Hypoxanthine was only formed from KCN, NH_3 , and H_2O , *via* photochemical processes in the presence of the semiconductor particles.

A radical reaction may be involved in the mechanism of the hypoxanthine formation. Actually, $\cdot CN$ and $\cdot NH_2$ radical species were detected under irradiation with e.s.r. using a spin trapping agent, 5,5-dimethylpyrroline-*N*-oxide (DMPO). Both hypoxanthine and the $\cdot CN$ and $\cdot NH_2$ radicals were only produced under irradiation, so these radical species generated by the irradiation of the semiconductor seem to be necessary for hypoxanthine formation. If we assume that hypoxanthine formation occurs *via* intermediates similar to those in the thermal nucleic acid base formation from HCN and ammonia,⁸ the intermediate, 4-amino-5-cyanoimidazole, should be present in the solution during irradiation, and 4-amino-5-cyanoimidazole was indeed identified in the solution by the tosylation method⁹ using u.v., n.m.r., i.r., and g.c.-mass spectra. The formation of 4-amino-5-cyanoimidazole under irradiation was observed, but could not be observed when the solution was heated at 97 °C with no irradiation, indicating that this intermediate is photochemically formed in the presence of semiconductor.

To elucidate the role of the photogenerated electrons and holes in the semiconductor particles, in the hypoxanthine formation, oxygen (as an electron scavenger) or ethanol (as a hole scavenger) was added to the solution and the mixture was

Table 1. The amount (nmol) of hypoxanthine formed from KCN, NH₃, and H₂O with various particulate semiconductors after irradiation for 24 h.

Semiconductor	Pt ^a	Hypoxanthine/nmol
TiO ₂	—	3
CdS	—	none
CdSe	—	none
MoS ₂	—	none
In ₂ O ₃	—	none
GaP	—	none
TiO ₂	+	10
CdS	+	15
CdSe	+	4
MoS ₂	+	7
In ₂ O ₃	+	2
GaP	+	<1
blank 1 ^b	—	none
blank 2 ^c	+	none
SiO ₂ (blank 3)	+	none

^a —: Non-platinized semiconductor; +: platinized semiconductor.

^b Irradiation with no semiconductor present. ^c Heated (97 °C) in the presence of semiconductors.

irradiated. Hypoxanthine was not formed in the presence of these strong electron or hole scavengers, indicating, that photogenerated electrons and holes are both closely involved in the hypoxanthine formation.

Considering the above results, we propose Scheme 1 to represent the formation of hypoxanthine under irradiation with semiconductor particles.

Although the formation of adenine from HCN and NH₃ in a thermal reaction has been reported,⁸ it was not detected in the present system. This cannot be clearly understood at this stage, but presumably is due to the presence of water in the present system, as shown in Scheme 2. Water added to the CN group of 4-amino-5-cyanoimidazole to form a compound (A). The NH₂ group of (A) is then protonized to eliminate ammonia, and a CN⁻ anion and a proton are added to form hypoxanthine.

We also examined the effects of temperature and pH on the hypoxanthine formation. The optimum conditions were found to be *T* 30 °C and pH 9.5.

In conclusion, one of the nucleic acid bases, hypoxanthine, can be formed from KCN, NH₃, and H₂O with particulate semiconductors under irradiation around room temperature; platinization caused a marked increase in the yield of hypoxanthine for all the semiconductors tested; conditions for the optimum yield of hypoxanthine are *T* 30 °C and pH 9.5; 4-amino-5-cyanoimidazole has been identified as one of the intermediates in this reaction; CN and NH₂ radicals produced by photocatalysis may play an important role in the hypoxanthine formation.

Finally, it should be noted that amino acid, peptide, and nucleic acid base have been formed with particulate semiconductors under irradiation, from simple molecules which are considered to have been present in the primitive earth. The results presented here may indicate that particulate semiconductors existing in nature might have been involved in chemical evolution on the primitive earth.

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