Nitrite Ion Reduction to Ammonia in Illuminated Aqueous Suspensions of Powdered Semiconductors in Alkaline Sulphide Solutions

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The photoassisted reduction of the nitrite anion to ammonia in alkaline aqueous sulphide solutions was achieved by illumination with visible light in the presence of suspended $SrTiO_3$, TiO_2, CdS, or CdS–ZnS.

Alkaline aqueous sulphide in the presence of suspended semiconductor powders under illumination with bandgap light has previously been applied extensively for the photoproduction of hydrogen.[1] Nitrogen and sulphur oxides, NO_x and SO_x, are important pollutants released from fossil fuel power stations, internal combustion engines, and many industrial operations. There exists thus a need for the conversion of these pollutants into harmless, or even useful, products. The illumination of aqueous mixtures of sulphide and sulphite in the presence of dispersed semiconductors was shown to lead to the efficient generation of hydrogen, while simultaneously causing the conversion of the sulphite ion into innocuous sulphur compounds, such as thiosulphate, sulphate, or dithionate.[1a] On the other hand, there seems to have been no previous report on the conversion of nitrogen oxyanions into ammonia with visible light. In the present work we explored the photoassisted reduction of nitrogen oxyanions to ammonia in aqueous alkaline media in the presence of suspended semiconductors.

The first objective was to find out if dinitrogen does undergo photocatalysed reduction to ammonia in the presence of various semiconductor materials in an alkaline sulphide medium. Results presented in Figure 1 show that ammonia is indeed released from illuminated suspensions of CdS–ZnS in 1 M KOH–0.1 M Na_2S. As shown in Table 1, this rather small release of ammonia was faster in the presence of TiO_2 (runs g,h), $SrTiO_3$ (run j), or CdS–ZnS (runs e,f) than of CdS (run d). There was no reaction in the dark. However, the rate of release of ammonia was unchanged whether the gas bubbling through the medium was argon or nitrogen (Figure 1). This experiment suggested that the medium contained a nitrogenous component, which underwent photoassisted conversion into ammonia. An analogous conclusion had been reached previously in an electrochemical study on the reduction of nitrogen oxyanions in aqueous alkali.[2] In an effort to identify this component, 0.20 M KNO_3 in 1 M KOH–0.1 M Na_2S was illuminated in the presence of CdS (run c). The rate of release of ammonia was similar to that without added nitrate. Thus, the unknown component was probably not the nitrate ion. In further experiments, KNO_2 was added to the above KOH–Na_2S solutions with various catalysts. This time there was a

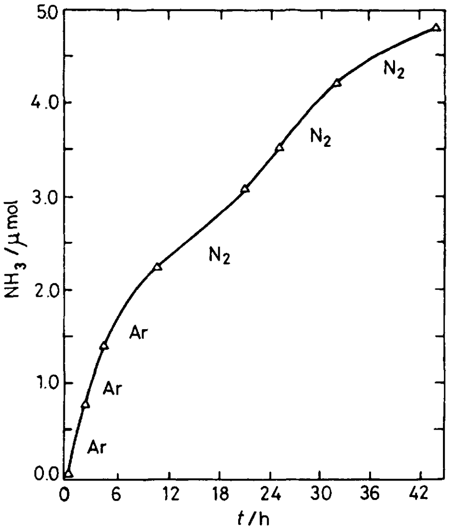

Figure 1. NH_3 produced (μmol) as a function of illumination time (hours) in the photocatalytic reduction of nitrogenous impurities in suspensions of powdered CdS–ZnS (as in Table 1, run e) in aqueous 1 M KOH–0.1 M Na_2S at 61 °C, while bubbling Ar or N_2 through the reaction flask at 65 ml min^{-1}. Light source: 150 W xenon lamp.

Table 1. Photocatalysed reduction of nitrite ion to ammonia in 1 M KOH in aqueous suspensions of semiconductors.[a]

Run	Catalyst	Medium	Added nitrite	Flux	Temp. /°C	Gas	Rate
a	—	0.1 M Na_2S	—	250	62	N_2	0.01
b	—	0.1 M Na_2S	0.21 M	250	62	N_2	0.09
c	CdS	0.1 M Na_2S 0.2 M KNO_3	—	42	29	N_2	0.03
d	CdS	0.1 M Na_2S	—	42	46	Ar	0.001
e	CdS/ZnS	0.1 M Na_2S	—	42	61	Ar	0.018
f	CdS/ZnS	0.1 M Na_2S	—	42	61	N_2	0.017
g	TiO_2	0.1 M Na_2S	—	42	45	N_2	0.02
h	TiO_2	0.1 M Na_2S	—	100	61	Ar	0.02
i	TiO_2	0.1 M Na_2SO_3	—	42	61	N_2	0.01
j	$SrTiO_3$	0.1 M Na_2S	—	100	61	Ar	0.02
k	TiO_2	—	0.12 M	34	62	Ar	0.02
l	TiO_2	0.1 M Na_2SO_3	0.12 M	42	61	N_2	0.006
m	TiO_2	0.1 M Na_2S	0.13 M	34	62	N_2	0.8—1.0
n	TiO_2	0.1 M Na_2S	0.20 M	100	61	Ar	0.3
o	CdS	0.1 M Na_2S	0.12 M	34	62	Ar	0.2—0.5
p	CdS–ZnS	0.1 M Na_2S	0.12 M	42	61	N_2	0.2—0.3
q	CdS–ZnS	0.1 M Na_2S	0.12 M	42	61	Ar	0.4—0.5
r	$SrTiO_3$	0.1 M Na_2S	0.12 M	100	61	Ar	0.7—1.1
s	CdS–ZnS	0.1 M Na_2S 0.1 M Na_2SO_3	0.12 M	42	61	Ar	0.3

[a] Rate = production rate of NH_3 in µmol/h^{-1} cm^{-2} (illuminated area). Reactions performed in double-walled thermostatted borosilicate flask, illuminated from outside with 150 W Xe lamp. Flux = incident light flux in mW cm^{-2}. Gas bubbled through at 100 ml min^{-1}. NH_3 in reaction effluent trapped in 0.1 M HCl and analysed by colour reaction.[9] Catalyst concentrations, 1 mg ml^{-1}. Sources: runs c,d, CdS prepared as described;[1b] runs e,f, mixture of CdS (Fisher), ZnS (BDH); run h, TiO_2 (Fisher) vacuum heated for 6 h at 600 °C; runs g, i, k, l, m, TiO_2 (Degussa P25); runs j, r, $SrTiO_3$ (Ventron) vacuum heated for 9 h at 1300 °C; runs p, q, s, CdS–ZnS coprecipitated on SiO_2 as described.[1c]

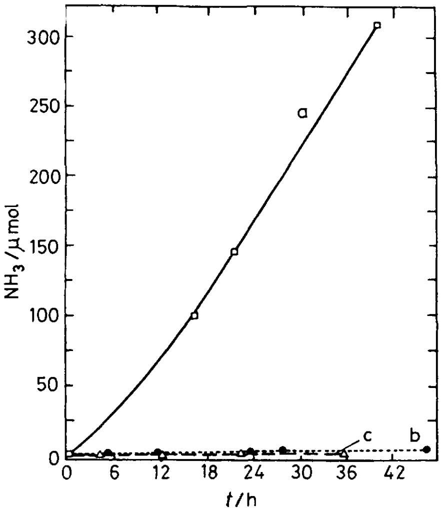

Figure 2. Medium effect on NH_3 produced (µmol) as a function of illumination time (hours) in the photocatalytic reduction of potassium nitrite (0.12 M) on TiO_2 (1.1 mg ml^{-1}) in 1 M KOH at 61 °C. Run a, also 0.1 M Na_2S. Runs b, c, no Na_2S. In c, 0.1 M Na_2SO_3.

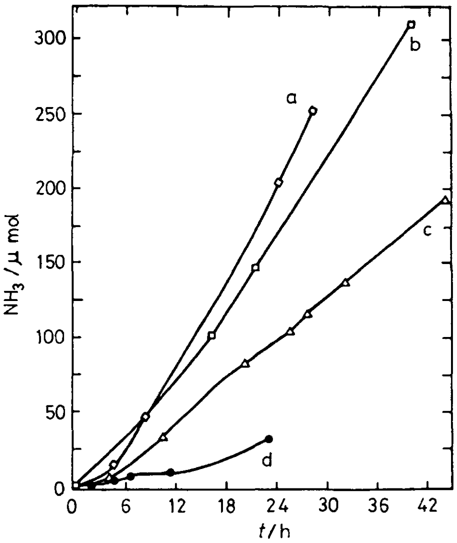

Figure 3. Effect of added semiconductors on NH_3 produced (µmoles) as a function of illumination time (hours) in the photocatalytic reduction of potassium nitrite (concentration, runs a, d: 0.21 M; b, c: 0.12 M) in 1 M KOH–0.1 M Na_2S. Catalysts: a, $SrTiO_3$; b, TiO_2; c, CdS–ZnS (as in Table 1, run p); d, none.

dramatic increase in the rate of production of ammonia. In a reaction mixture containing TiO_2 and 0.12 M NO_2 (run m), the release of ammonia was more than an order of magnitude larger than in the absence of added nitrite (runs g,h). Hence, in the above experiments (in the absence of added nitrite) traces of nitrite ion impurities could presumably be the source of the photoinduced production of ammonia. As shown in Figure 2a, this production of ammonia in the presence of TiO_2 is approximately linear with time during a period of up to about 40 h. This production of ammonia was much slower in a medium of only 1 M KOH and 0.12 M KNO_2 with TiO_2 (see Figure 2b and Table 1, run k). Thus the presence of the Na_2S component is essential for the reaction. If 0.1 M sodium sulphite was substituted for the sulphide, the rate of ammonia release was also very small (Figure 2c and Table 1, run l). In the presence of both 0.1 M Na_2S and 0.1 M Na_2SO_3, the rate of NH_3 release (run s) was similar to that with only 0.1 M Na_2S (runs p,q). Thus, the reduction process of nitrite to ammonia differs from the visible light induced formation of hydrogen from aqueous sulphide solutions, in which the addition of sulphite had a synergistic effect.[1a] Hydroxylamine was not produced in detectable amounts[3] during the photocatalytic reduction of nitrite ions in aqueous KOH–Na_2S in the presence of either TiO_2 or CdS. A comparison of the time course of evolution of ammonia with different catalysts in 1 M KOH–0.1 M Na_2S is given in Figure 3. As shown in curve d, there is a slow release of ammonia from nitrite under illumination even in the absence of added semiconductor, which could be due to a homogeneous photochemical reaction. This ammonia release was observed in both the absence and presence of added nitrite (Table 1, runs a and b).

According to current concepts on photocatalytic processes induced by illumination of suspensions of semiconductors, the mechanism involves electron–hole pair separation. Thus, the particles act as microscopic electrolysis cells, with different sites on the surface serving as the anode and the cathode.[4] While there have been many studies on the electrochemical reduction of the nitrite and nitrate ions in acid media,[5—7] there have been no reports on the photocatalytic reduction in alkaline solutions. The electrocatalytic reduction of NO_2^- ions at a platinized platinum electrode in alkaline media was recently shown to involve two maxima on the polarization curves,[8] thus indicating the occurrence of at least two stages of reduction. Electrocatalytic reduction of nitrite to ammonia on carbon electrodes in the pH range 6.5—7.4 was demonstrated using a water-soluble iron porphyrin as catalyst.[10] Photocatalytic oxidation of NO_2^- to NO_3^- with aqueous suspensions of several semiconductor powders was recently reported.[11] With TiO_2, in the presence of oxygen, this oxidation caused very rapid and almost complete conversion of nitrite into nitrate. The photocatalytic reduction of the nitrite ion to ammonia observed in the present work in suspensions of semiconductors differs from the electrochemical reduction in acid media in the failure to detect hydroxylamine, which is an important product and probable intermediate in acid solutions. Presumably, any hydroxylamine, if formed, is rapidly converted into either ammonia or nitrogen. An interesting result of the present work in alkaline media is the preferential reduction of nitrite, apparently without affecting the nitrate ion.

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