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Photocatalyzed Transformation of Cyanide to Thiocyanate by Rhodium-Loaded Cadmium Sulfide in Alkaline Aqueous Sulfide Media

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Cyanide dispersed in the aquatic and atmospheric ecosystems represents one of the more hazardous environmental contaminants. A process is described that totally disposes of CN^- by photocatalytic transformation to SCN^- , a 100-fold less toxic derivative of cyanide. The method employs a Rh-loaded (0.2% by weight) CdS suspension, visible irradiation (≥ 405 nm or simulated AM1 solar radiation), and an alkaline aqueous sulfide medium. The quantum efficiency of the conversion process is ≥ 0.25 .

Introduction

Cyanide is ubiquitous in nature. Long known as a respiratory depressant, it is among the most hazardous of water pollutants. It is a common metabolite, formed from a variety of precursors widely distributed in nature.² With increasing use of cyanide in various industrial processes, the amount of cyanide dispersed in the environment is greatly accelerating.³ Future potential sources of cyanide contamination of the water supplies include the coal gasification processes in syngas production from coal. The present detoxification methods are directed toward the transformation of CN^- to less toxic forms (e.g., OCN^- or SCN^-). The most often used methods involve oxidation of CN^- by alkaline chlorination, ozonation, and permanganate, as well as electrolytic decomposition.⁴

Cyanide contamination of water supplies is not insignificant.⁵ Fairly polluted natural waters have cyanide contents between 0.7 and 2.1 $\mu\text{g/L}$ with peak concentrations reaching 5 $\mu\text{g/L}$. Rivers that are polluted by peak discharges from galvanic industries show cyanide concentrations of up to 200 $\mu\text{g/L}$. In mine tailing ponds, levels as high as 10–30 mg/L have been uncovered.⁶ By comparison, the water quality objective is ≤ 10 $\mu\text{g/L}$ of total cyanide.⁷

Both OCN^- and SCN^- are formed in vivo in the course of detoxification of cyanide. The level of SCN^- in blood is ≤ 2 mg/100 mL;⁸ it is 100 times less toxic than CN^- .⁹

A promising aspect of photocatalysis with semiconductors is the conversion and/or destruction of environmental contaminants in waste streams and in the atmospheric environment.¹⁰ Semiconductor dispersions offer the advantages of being excellent light harvesting units, good photocatalysts, and relatively inexpensive and easily prepared materials.^{10a} For example, CN^- is oxidized

photocatalytically to OCN^- and SO_3^{2-} to SO_4^{2-} over TiO_2 , CdS, ZnO, and Fe_2O_3 .¹¹ Equally important, the photocleavage of hydrogen sulfide over redox catalysts (RuO_2 , Rh) loaded onto CdS has been implicated as a possible efficient alternative (to the Claus process) in the sulfur detoxification of natural gas and coal.¹² Another application of semiconductor photocatalysts is in the photodegradation of surfactants and aliphatic and aromatic chlorinated hydrocarbons.^{10b,10c,13}

Herein, we report an efficient process that uses visible-light irradiation (≥ 405 nm) for the disposal and total conversion of CN^- to SCN^- in the presence of Rh-loaded CdS dispersed in an alkaline aqueous sulfide medium. Bard^{11a} has demonstrated the transformation of CN^- to OCN^- over TiO_2 dispersions (quantum efficiency 0.06) and has hinted at the use of CdS dispersions in alkaline solutions in the presence of oxygen. The advantages of the system described here is the relatively high quantum efficiency (≥ 0.25), the use of a waste byproduct (H_2S) as the oxidizing agent, irradiation with visible light (thus the obvious utilization of natural sunlight), and the relative long-term stability of the CdS/Rh catalyst to cyanide attack and to photocorrosion. For comparison, we also report data for CdS/ RuO_2 and for the combination of two efficient photocatalysts, CdS + TiO_2 / RuO_2 , earlier used in the photocleavage of hydrogen sulfide.^{12a}

Experimental Section

CdS (Fluka, purissimum 99.999%) was used as supplied. Other chemicals were at least reagent grade and used as received. Rhodium (0.2% by weight) loading on CdS was carried out photochemically by addition of the appropriate quantity of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ to a CdS suspension in a solution of 0.1 M $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and 1 M NaOH followed by irradiation with ≥ 405 -nm light. Argon purging or the presence of air in the preparation of the catalyst did not affect the catalytic activity of the CdS/Rh.¹⁴ At the completion of the photoreduction of Rh(III) on CdS, the suspension was centrifuged (~ 20 min at 1000 rpm) and the powder was subsequently washed with monodistilled water to remove the S^{2-} , SO_3^{2-} , and $\text{S}_2\text{O}_3^{2-}$ ions from the surface of the catalyst. Thiosulfate is formed from the oxidation of S^{2-} by the valence band holes ($h\nu^+$) of CdS.^{12,14} The complete removal of the above sulfur species was verified by pulse polarography using a Metrohm 626 Polarecord coupled to an E-505 polarograph stand and a BM-505 inverse polarograph. Rhodi-

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- For further details regarding the preparation and characterization of the catalyst, see: Borgarello, E.; Serpone, N.; Pelizzetti, E.; Barbenni, M. *J. Photochem.* **1986**, *33*, 35.

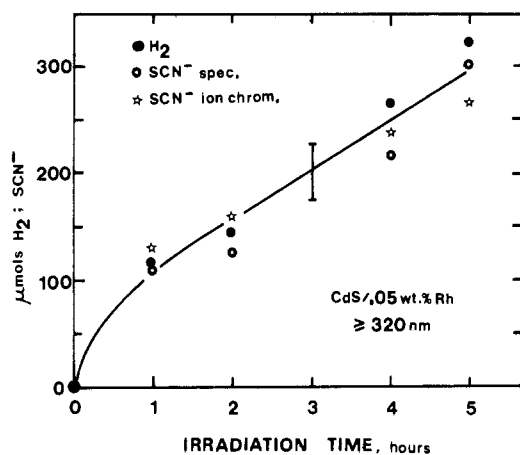


Figure 1. Micromoles of H_2 and SCN^- produced as a function of irradiation time (h). See text for further experimental details.

um(III) reduction on the CdS particles was monitored by atomic absorption techniques employing a Perkin-Elmer 503 atomic absorption spectrometer; the monitoring light source was a Rh hollow-cathode lamp (Spectrex Ltd.), and the measurements were done at 343.5 nm. The preparation of RuO_2 -loaded CdS or TiO_2 was performed as reported earlier.^{14,15}

Typically, experiments were carried out by irradiating (≥ 405 nm) 5-mL samples containing 10 mg of CdS/0.2 wt % Rh, 0.1 M Na_2S , and 0.1 M NaCN in a 1 M NaOH solution. When argon purging was required, the sample was deoxygenated for ~ 15 min just prior to irradiation. The illumination source was a 1000-W Hg/Xe lamp (global irradiance 243 mW/cm², Scientech 362 energy power meter), equipped with a 10-cm water jacket and a 405-nm cutoff filter to remove IR and UV light, respectively. Alternatively, a Solarbox (CO.FO.MEGRA.) reactor was used as the irradiation source to simulate AM1 sunlight conditions. Hydrogen was detected by gas chromatographic methods (Gow-Mac 69-550 gas chromatograph; Carbosieve 5A column; argon was the carrier gas), and SCN^- was monitored spectrophotometrically at 480 nm on a Perkin-Elmer 552 UV-visible spectrophotometer following the formation of the $\text{Fe}^{3+}/\text{SCN}^-$ complex,¹⁶ as well as by ion chromatography (IC) with a Waters liquid chromatograph coupled to a Waters 130 conductivity detector. A Hamilton PRP-X100 column was used, and potassium hydrogen phthalate was the eluent (4×10^{-3} M; pH 4.2; flux 2.0 mL/min).

Results

Figure 1 depicts the temporal evolution of the two products (SCN^- and H_2) of the reaction between S^{2-} and CN^- mediated by the irradiated CdS/0.2 wt % Rh catalyst, and performed under air-equilibrated conditions and simulated AM1 sunlight radiation. The data points are the GC, IC, and spectrophotometric measurements of the results (see above). It is noteworthy that the quantities of SCN^- and H_2 formed are identical within the experimental error of the measurements (molar ratio is 1:1). In another experiment, 3.5-h irradiation gave 345 μmol of SCN^- and 380 μmol of H_2 . Neither cadmium nor rhodium species were ever detected in solution after irradiation, under our conditions. This demonstrates the photochemical stability and integrity of the catalyst even in the presence of 0.1 M CN^- (see below). The stoichiometry of the transformation reaction (1) was ascertained under four different experimental conditions with the catalyst always present.

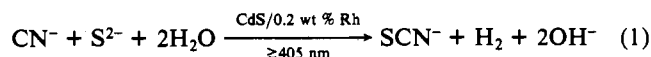


Table I summarizes the results and shows that 100% conversion of CN^- to SCN^- is achieved for about 5×10^{-4} mol of CN^- and S^{2-} . Two different syntheses of catalyst were investigated in which the Rh(III) was photoreduced on CdS: one in the presence of air and the other in the presence of argon. The various catalytic

Table I. Total Conversion of CN^- to SCN^- by Visible Irradiation of CdS/0.2 wt % Rh Dispersions in 0.1 M CN^- and 0.1 M S^{2-} Solutions (1 M NaOH)

catalyst prepd under	irradn under	amt of H_2 , μmol	amt of SCN^- , μmol
air	air	500	553
air	argon	740	650
argon	air	510	600
argon	argon	640	635

Table II. Effect of Cyanide on the Hydrogen Evolution Rates (STP) in Catalytic Systems^a

catal syst	$r(\text{H}_2)$, mL/h	CN^- present
CdS	0.25 ± 0.03	no
CdS	0.026 ± 0.003	yes
CdS/1 wt % RuO_2	0.46 ± 0.05	no
CdS/1 wt % RuO_2	0.47 ± 0.05	yes
CdS + $\text{TiO}_2/0.5$ wt % RuO_2^b	0.99 ± 0.10	no
CdS + $\text{TiO}_2/0.5$ wt % RuO_2^b	0.042 ± 0.005	yes
CdS/0.2 wt % Rh	4.8 ± 0.5	no (SO_3^{2-})
CdS/0.2 wt % Rh	4.3 ± 0.5	yes

^a 10 mg of CdS or redox catalyst loaded CdS; 0.1 M S^{2-} , 0.1 M SO_3^{2-} or CN^- , 1 M NaOH; illumination ($\lambda \geq 405$ nm) with a 1000-W Hg/Xe lamp (243 mW/cm²); 5 mL argon-purged solution. ^b 10 mg of RuO_2 -loaded TiO_2 .

dispersions behaved the same, irrespective of the fact that in air (O_2) the molar ratio of H_2 to $\text{S}_2\text{O}_3^{2-}$ (when SO_3^{2-} is present) is different from that in argon-purged solutions.¹⁴ In the reaction with CN^- , the molar ratio of H_2 to SCN^- is constantly unity, regardless of the treatment of the solution before irradiation (Table I). We noted earlier, in the synthesis of $\text{S}_2\text{O}_3^{2-}$ from S^{2-} and SO_3^{2-} with the same CdS/0.2 wt % Rh catalyst,¹⁴ that the presence of O_2 has no effect on the evolution rate of the products. This implies there is no competition between O_2 and H_2O in the cathodic reaction on the catalyst particles.

Table II summarizes the effect of CN^- on the hydrogen evolution rate, $r(\text{H}_2)$, in various catalytic systems. The purpose of the experiments was to determine and compare the efficiency of the systems. Naked CdS particles are not attacked by CN^- ions (in 0.1 M S^{2-} and 1 M NaOH) in the dark, and this confirms the observations of Frank and Bard.^{11a,17} However, when naked CdS particles are illuminated with visible light in the presence of cyanide (0.1 M) and under the same experimental conditions as in the dark, $\text{Cd}^{2+}(\text{aq})$ ions are detected in solution and the $r(\text{H}_2)$ value decreases by 1 order of magnitude (0.25 mL/h to 0.026 mL/h). The former result is consistent with that reported previously for the CdS/ CN^-/O_2 system under illumination.^{11a} We also investigated the CdS + $\text{TiO}_2/0.5$ wt % RuO_2 combination since this catalytic aqueous slurry earlier showed maximum efficiency in H_2 evolution in the photocleavage of H_2S in alkaline aqueous media. The process is thought to involve an interparticle electron-transfer pathway.¹⁵ The presence of CN^- leads to a 24-fold decrease in $r(\text{H}_2)$: 0.99 mL/h vs. 0.042 mL/h. Here also, $\text{Cd}^{2+}(\text{aq})$ was found in solution. No doubt, loading a redox catalyst such as RuO_2 or Rh protects the CdS from photochemical attack by the CN^- , inasmuch as no $\text{Cd}^{2+}(\text{aq})$ is observed. Rhodium loading onto CdS at 0.2 wt % showed the highest efficiency in the conversion of CN^- to SCN^- and in the formation of H_2 from H_2O . $r(\text{H}_2)$ increases by 1 order of magnitude relative to that from CdS/ RuO_2 dispersions. By comparison, a 165-fold increase in $r(\text{H}_2)$ obtains with respect to that in naked CdS slurries. It is also remarkable to note (Table II) that $r(\text{H}_2)$ values are, within experimental error, identical for the same catalyst in $\text{OH}^-/\text{S}^{2-}$ media whether SO_3^{2-} or CN^- is added to the suspension. This leads us to believe that the mechanism(s) of the conversion of

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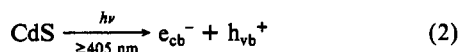
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(17) The sensitivity of the atomic absorption technique to detect cadmium in solution under our experimental conditions was 0.2 ppm. Thus, in an experiment in which 2 g/L of CdS was equilibrated in the dark for about 2 h with a solution 0.1 M in S^{2-} and CN^- and 1 M in NaOH, the free $\text{Cd}^{2+}(\text{aq})$ concentration was ≤ 0.2 mg/L.

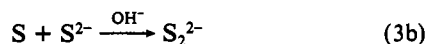
SO_3^{2-} to $\text{S}_2\text{O}_3^{2-}$ and CN^- to SCN^- are very similar, if not identical.

Discussion

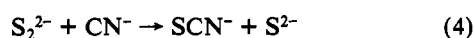
The presently available results suggest the following pathway for the complete photocatalyzed transformation of cyanide to the less toxic form thiocyanate. The CdS particles absorb visible light to produce electron/hole pairs according to reaction 2. The



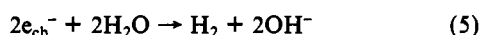
valence band holes react with S^{2-} to give sulfur, which dissolves in alkaline solution as polysulfides S_n^{2-} (eq 3) containing sulfane



sulfur. Polysulfide ions are known to react with CN^- , a powerful thiophile,¹⁸ to form SCN^- (eq 4)¹⁹ in a manner parallel to the one



observed in the transformation of SO_3^{2-} to $\text{S}_2\text{O}_3^{2-}$.²⁰ No conversion occurs between S^{2-} and CN^- in the absence of CdS/0.2 wt % Rh and/or light, confirming that h_{vb}^+ is necessary to oxidize S^{2-} and thereby mediate the CN^- to SCN^- transformation. The conduction band electrons, e_{cb}^- , reduce water to hydrogen (eq 5)



and are involved in the electron/hole pair recombination. The presence of a redox catalyst (RuO₂ or Rh) on CdS is necessary to ensure SCN^- formation and prevent photocorrosion, a result that might be due to photocomplexation of Cd²⁺(lattice) by CN^- ions; the mechanism is not yet clear.²¹

Insofar as the reactivity of the CdS/0.2 wt % Rh catalyst in the presence and absence of O₂ is concerned, the results confirm

some of our earlier findings in the $\text{S}_2\text{O}_3^{2-}$ synthesis.¹⁴ However, in the present instance, oxygen does not alter the 1:1 distribution of the products ($\text{H}_2:\text{SCN}^-$). Experiments to elucidate the difference(s) between the behavior of SO_3^{2-} and CN^- are under investigation.²²

The quantum efficiency for the CN^-/SCN^- conversion is $\geq 0.25 \pm 0.05$ at 436 nm (see ref 14 for details). It is important to note that this value is a lower limit and is based on the total number of incident photons that reach the sample. No doubt, a more efficient CdS powder^{14,23} and optimization of the photoreactor^{10a} may lead to improvements in the quantum efficiency of the process.

Conclusions

Disposal of CN^- ions by photochemical methods with the participation of the Rh-loaded CdS catalyst (or an equivalent one) opens up a potential practical alternative to the present methods in the transformation of CN^- to SCN^- that employs inexpensive materials and abundant sunlight.^{10a} The conversion is efficient even in the presence of air and, more important, even at very high cyanide concentrations. As an added advantage, hydrogen is a useful byproduct. Moreover, where both sulfide and cyanide are available, the conversion process(es) can dispose of two toxic materials.^{2,9,24}

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Registry No. CN^- , 57-12-5; SCN^- , 302-04-5; CdS, 1306-23-6; Rh, 7440-16-6; Na₂S, 1313-82-2; NaCN, 143-33-9.

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- (22) The reaction between S^{2-} and O₂ to give S and O₂²⁻ is under investigation (D. Meisel, personal communication) and ought to be compared to $\text{S}^{2-} + \text{SO}_2^{2-} \rightarrow$ (intermediates) and $\text{O}_2^{2-} + \text{CN}^- \rightarrow$ (intermediates) in order to confirm or deny the validity of our hypothesis.
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Electrochemistry and Spectroscopy of $\text{Fe}(\text{phen})_2(\text{CN})_2$, $\text{Cp}_4\text{Fe}_4(\text{CO})_4$, and $\text{CpFe}(\text{CO})_2\text{CN}$ in an Acidic Molten Salt

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Three basic organometallic compounds, $\text{Fe}(\text{phen})_2(\text{CN})_2$ (1), $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ (2), and $\text{CpFe}(\text{CO})_2\text{CN}$ (3), have been studied in the AlCl_3/n -butylpyridinium chloride (BPC) molten salt system. IR and UV-vis spectroscopies show that the ligands of all three complexes interact with Lewis acids contained in the melts, i.e. FeCN-Al and $\text{Fe}_3\text{CO-Al}$. Melts with molar ratios of AlCl_3 to BPC less than 1, previously referred to as "basic", behave as weak Lewis acids relative to compound 1, and melts with ratios greater than 1 behave as strong Lewis acids toward all three compounds. A comparison of spectral shifts for these compounds in the various melts with shifts previously reported for isolated Lewis acid adducts of the same compounds provides insight into the relative electron pair acceptor ability of the various melts. Cyclic voltammetry of 1 in the molten salts demonstrates a very large shift in the oxidation potential whereas the oxidation potential of 2 is unchanged. We infer that the HOMO of 1 is strongly perturbed by interaction with the Lewis acids in the molten salt whereas for 2 the HOMO is unaffected. This interpretation is consonant with simple molecular orbital calculations.

Introduction

Lewis acids can dramatically influence the electronic structure of metal complexes having basic CN and CO ligands. For example, Lewis acid adducts of these complexes often exhibit altered

electronic spectra,^{1,2} electrochemistry,¹ and reactivity.³⁻⁵ In all of these cases, the Lewis acid appears to perturb the metal complex

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