PHOTOCHEMICAL REDUCTION OF GOLD(III) ON SEMICONDUCTOR DISPERSIONS OF TiO₂ IN THE PRESENCE OF CN⁻ IONS: DISPOSAL OF CN⁻ BY TREATMENT WITH HYDROGEN PEROXIDE

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Summary

The reduction and recovery of gold from samples containing CN⁻ ions have been investigated employing TiO₂ semiconductor dispersions irradiated with either UV light ($\lambda \geqslant 210$ nm) or AM1 simulated sunlight ($\lambda \geqslant 310$ nm). The photoreduction is very efficient at low pH; disposal of cyanide, which acts as a buffer to a pH of about 9.3, was imperative. The degradation of CN⁻ was investigated employing two peroxides, H_2O_2 and $S_2O_8^{2-}$, in the presence and absence of light. Treatment of cyanide solutions with H_2O_2 and UV light irradiation leads to efficient conversion of CN⁻ to NH_3 and CO_2 (the main products detected). The H_2O_2 decomposition of CN⁻ also occurs in the dark, but to a lesser extent. The kinetics of the conversion process(es) have been studied; under irradiation, k_{obs} is about ten times the rate of the dark process. A mechanism involving OH· radicals is proposed for the cyanide decomposition by UV light. Cyanate ion, OCN⁻, is the intermediate in both the dark and the illuminated pathways. Recovery of gold on TiO₂ powder, following cyanide oxidation and removal of unreacted H_2O_2, is favored in acidic aqueous media. The implications of our findings towards practical disposal of cyanide and recovery of gold from actual industrial waste samples are discussed.

1. Introduction

Gold is a metal widely used in the manufacture of jewelry and in several important processes (*e.g.* plating) [1]; its recovery from industrial wastes is

of economic importance. In an earlier paper [2], we demonstrated the photochemical deposition and recovery of gold(III) from aqueous chloride media in the presence of TiO_2; gold was present as the chloride complex. We remarked that gold(III) proved difficult to photoreduce on TiO_2 in the presence of excess CN^- ions [2]. We interpreted our findings on the basis that $Au(CN)_4^-$ was formed under the experimental conditions used. The driving force for the reduction is small; the reduction potential of $Au(CN)_4^-$ is -0.4 V(NHE) (NHE, normal hydrogen electrode) [3] compared with $+1$ V(NHE) for $AuCl_3$ [4] and with the value of the flat-band potential V_{fb} of TiO_2 at some appropriate pH:

$$V_{fb}(NHE) = -0.05 - 0.059 \text{ pH} \tag{1}$$

This equation was given for anatase in ref. 5.

The impetus for investigating the photochemical reduction of gold(III) in cyanide solutions stemmed from the industrial utilization of cyanide baths in the separation and recovery of gold from other minerals, and its potential recovery from industrial wastes. Normally, gold is extracted from gold-containing ores by the cyanadation process [6]. After flotation and other concentration processes, gold is dissolved by cyanide leaching

$$4Au + 8KCN + O_2 + 2H_2O \longrightarrow 4KAu(CN)_2 + 4KOH \tag{2}$$
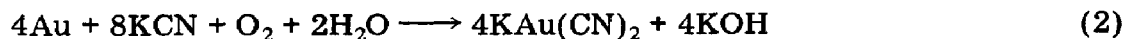
followed by zinc precipitation [7, 8]

$$2KAu(CN)_2 + Zn \longrightarrow K_2Zn(CN)_4 + 2Au \tag{3}$$

$Au(CN)_2^-$ is slowly oxidized to $Au(CN)_4^-$ in the presence of excess CN^- (aging process) [6, 9] and air.

Two major problems were encountered in the photochemical reduction of gold(III) on TiO_2 in the presence of CN^- ions: the high toxicity of cyanide [10] and the great volatility of HCN [11]. In order to carry out the photoreduction process at a pH below 10 ($pK_a(HCN) = 9.21$ at 25 °C) [11], we also investigated the possible disposal of free CN^- by oxidation with peroxides prior to irradiation in the presence of TiO_2 dispersions.

The detoxification of CN^- is well documented in the literature [12 - 28]. Recently, we proposed a photocatalytic method of converting CN^- ions to SCN^- over a CdS–Rh catalyst [29]. In the present work, practical considerations dictated the use of the peroxide treatment with H_2O_2 (or oxidation with $S_2O_8^{2-}$). This method provides a rapid means of obtaining cyanide-free gold(III) solutions, which are ready for treatment with TiO_2 and irradiation by UV light or by AM1 simulated sunlight for recovery of the precious metal.

Herein we report our results on the elucidation of the oxidation reactions of CN^- and of Au^{III}–CN^- solutions in the presence of H_2O_2 or $S_2O_8^{2-}$. We also compare the dark and the UV-catalyzed processes. A similar comparison was reported by Masson in 1907 [12]; however, the earlier study focused attention on the decomposition of H_2O_2 by various anions, including CN^-, to evolve O_2, and *not* on the degradation of CN^-. In this regard, our

present findings represent an extension of Masson's work. Moreover, advantages are pointed out for removing cyanide before the photoreduction of gold(III) over irradiated TiO_2 is undertaken.

2. Experimental details

All the chemicals were at least reagent grade and were used as received from the vendor. $AuCl_3 \cdot H_2O$ (Johnson Matthey) was dissolved in an NaCN solution to form an $Au^{III}-CN^-$ complex. (The reaction product between $AuCl_3 \cdot nH_2O$ and CN^- is not well characterized in the literature [3]. We have assumed that $AuCl_4^-$ is formed together with other gold complexes containing OH^-, CN^-, H_2O and other ligands formed during the reaction. We have made no attempt to characterize these complexes. It is worth noting that the color of the $AuCl_3$ solution is pale yellow; the solution turns colorless upon addition of CN^-, consistent with formation of a gold–cyanide complex.) TiO_2 Degussa P-25 was a generous gift from Degussa Canada Ltd. In general, experiments were carried out under various conditions and with various set-ups depending on whether the reactions proceeded in the dark or under illumination by UV light (or simulated sunlight).

Unless otherwise noted, a reactor of capacity 1 l containing (typically) 250 ml solution was employed for reactions carried out in the dark. The temperature was either 25 or 35 °C. The same reactor was used to investigate the effects of simulated AM1 sunlight on the rate of oxidation of CN^- by H_2O_2; the light source was a CO.FO.MEGRA (Milan, Italy) Solarbox ($\lambda \geqslant$ 310 nm; global irradiance, about 100 mW cm^{-2}). When UV light was used, the reactor was a 5 ml quartz cell. UV illumination ($\lambda \geqslant 210$ nm; global irradiance, about 290 mW cm^{-2}) was provided by a 1000 W Hg–Xe lamp. Exposure to light was allowed only for short times so as not to raise the temperature inside the cell to above 25 °C. The optimum concentration of TiO_2 was always 2 g l^{-1}. The concentrations noted throughout the text refer to initial concentrations before mixing, unless stated otherwise. All the reactions were carried out in air-equilibrated solutions.

Analyses of the reactants and products of the reactions were carried out by employing the following techniques. Variations in the CN^- concentration were monitored (a) with an ion-specific electrode (Orion model 94-06) and (b) by pulse polarographic techniques using a Methrom 626 Polarecord coupled to an E-505 polarograph; $E_{1/2}$ for CN^- in KOH–borate buffer at pH 9.7 (dropping mercury electrode) was −0.3 V(NHE). Changes in [CN^-] were also followed by ion chromatographic methods with a Waters liquid chromatograph, equipped with a Waters 430 conductivity detector and a Hamilton PRP X-100 column; a solution of KOH (of pH about 11.4) was used as the eluent. The combination of the above three techniques allowed us to monitor changes in CN^- concentration down to 10 ng ml^{-1}. Neither H_2O_2 nor $S_2O_8^{2-}$ had any influence on the determination of CN^- ions in solution; TiO_2 did not interfere with our measurements either. The concentration of

uncomplexed CN^- in Au^{III}–CN^- solutions was easily determined. No attempts were made to determine the concentration of complexed cyanide in the Au^{III}–CN^- complex or complexes (see above).

Gold was analyzed by employing a Perkin–Elmer 503 atomic absorption spectrometer. The light source was a hollow cathode single-element lamp (detection limit, about 0.05 μg ml^{-1}). Special attention was devoted to the analysis of the reaction products. According to the literature [12 - 28], OCN^- is the major product of the oxidation of CN^- by H_2O_2. A generally accepted method for the analysis of OCN^- in solution is the determination of the spectrophotometric absorbance of the Cu^{II}–pyridine–OCN^- complex extracted in chloroform [30]. Unfortunately, under our experimental conditions both H_2O_2 and gold(III) interfered with this method. An additional observation based on a change in pH (range 10 - 8) during the course of the reaction, which depended on the $[H_2O_2]$ and on whether the reaction was catalyzed by UV light, also led us to consider the possible hydrolysis of OCN^- to NH_4HCO_3 [11]. Free $HOCN$ (pK_a = 3.89) decomposes in solution to NH_3, H_2O, and CO_2 [11]. A different set-up was therefore employed to monitor the reaction products. The reactor consisted of a 100 ml container (50 ml solution) connected to three traps for liberated gases; the first two traps contained 0.1 M H_2SO_4 and the third contained 0.1 M NaOH. H_2SO_4 acid was used to trap any basic gas such as NH_3, and the NaOH was used to trap both HCN escaping from the reaction container and CO_2 evolved in the course of the reaction. On completion of the reaction, nitrogen gas was flushed through the reactor and the traps to ensure complete removal of any gaseous products from the reaction mixture. Subsequently, the solutions in the reactor and in the traps were analyzed for NH_3, CN^- and CO_2.

NH_3 was analyzed by back-titrating the H_2SO_4 solution(s) with 0.1 M NaOH using methyl red as the indicator. CO_2 was analyzed by gas chromatographic methods (Gow–Mac gas chromatograph; Poropack N 80/60 column; carrier gas, argon; thermoconductivity detector) after acidification of the NaOH trap with concentrated H_2SO_4. Blank experiments were run to ascertain the appropriateness of the method; the error was about $\pm(10\%$ - $15\%)$. The remaining reaction mixture was also treated with concentrated H_2SO_4 and any CO_2 evolved from CO_3^{2-}, HCO_3^- and/or OCN^- present in solution [31, 32]

$$NaOCN + H_2SO_4 \longrightarrow HOCN + NaHSO_4 \qquad (4)$$

$$HOCN + H_2O + H_2SO_4 \longrightarrow CO_2 + NH_4HSO_4 \qquad (5)$$

was analyzed by gas chromatography. After addition of NaOH and warming the resulting solution, the NH_3 evolved was trapped in an H_2SO_4 solution and analyzed as before by back-titration. The possible formation of CO was verified by connecting the reactor to a CO-sensitive tube (Gastec Co.).

The kinetics of the disappearance of gold(III) from solution in the presence of TiO_2 were investigated by taking aliquots of 5 ml from the suspension. These were centrifuged and at times also filtered through a

0.22 μm membrane filter to remove traces of colloidal material prior to atomic absorption analysis.

3. Results

3.1. Effect of light on the oxidation of CN$^-$ by peroxide

Figure 1 illustrates the results of a typical experiment in which 184 μg ml^{-1} (7.08 × 10^{-3} M) CN$^-$ in aqueous solution was oxidized by H$_2$O$_2$ (0.2 M; 0.6%) in the dark and under UV light at 25 °C. Clearly, oxidation is more rapid when the solution is irradiated. For instance, no CN$^-$ was detected after 30 min of UV illumination, while only 24% of the CN$^-$ is degraded in the dark. Exposure of the reaction mixture to simulated AM1 solar radiation did not improve the reaction rate of the dark process. Apparently, under simulated sunlight, the extent of absorption of photons by 0.2 M H$_2$O$_2$ precludes a reaction that involves OH$^\bullet$ radicals [33]. We also found that no HCN escapes from the reactor and that no CO is formed in the degradation process. During the course of the reaction, the pH changed from 10 to about 9 for the UV-light-induced oxidation; no pH change was observed in the dark. Analysis of the ln[CN$^-$] vs. time plots of Fig. 1 suggests a single mechanism for the UV-light-induced degradation of CN$^-$ ions; the break in the plot of the dark process may implicate two different pathways.

3.2. Oxidation of CN$^-$ ions by persulfate ions

Persulfate, S$_2$O$_8^{2-}$, is a very good oxidant under strongly alkaline conditions for high concentrations of cyanide [19]. Under UV light, the rate of oxidation of cyanide is considerably enhanced. In 0.1 M KOH solu-
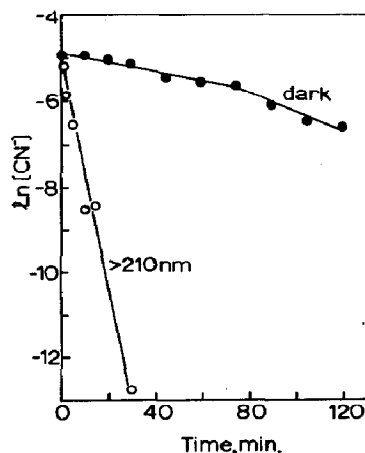

Fig. 1. Semilogarithmic plot of ln[CN$^-$] vs. time for the degradation of cyanide via oxidation by H$_2$O$_2$ in the dark and under UV light illumination ($\lambda \geqslant 210$ nm): [H$_2$O$_2$] = 0.2 M; 25 °C; initial [CN$^-$], 7.08 × 10^{-3} M (dark process) or 7.94 × 10^{-3} M (UV light). For other details, see Section 2.

tions at 25 °C, 64% of the initial CN^- degrades after treating a solution 8.9×10^{-3} M in NaCN with a 0.02 M solution of $K_2S_2O_8$ for 1 h in the dark. Exposure to UV light for the same time period resulted in 75% degradation.

3.3. Effect of $[H_2O_2]$ on the rate of degradation of CN^-

Table 1 summarizes the values of k_{obs} for the reaction

$$CN^- + H_2O_2 \xrightarrow{\ k_{obs}\ } \text{products} \tag{6}$$

for both the dark and the UV-light-induced processes in which 8.9×10^{-3} M CN^- solution was treated with 0.02 M, 0.2 M, 1 M or 2 M H_2O_2. For the dark process, increasing $[H_2O_2]$ from 0.025 to 1 M increases k_{obs} 12-fold (0.37×10^{-4} s^{-1} to 4.5×10^{-4} s^{-1}), indicating a clear dependence of the rate on $[H_2O_2]$. By contrast, k_{obs} is an order of magnitude larger and remains nearly constant (3.9×10^{-3} s^{-1} to 4.8×10^{-3} s^{-1}) under UV illumination irrespective of the 100-fold increase in $[H_2O_2]$ from 0.02 to 2.0 M; conditions were such that $[H_2O_2] > [CN^-]$.

Figure 2 illustrates semilogarithmic plots of $\ln[CN^-]$ vs. time for the reaction carried out in 1 M H_2O_2 (i) in the dark, (ii) under UV illumination and (iii) under AM1 simulated sunlight conditions. (No quantitative comparison is implied between (ii) and (iii) since irradiation conditions were different in wavelength and intensity.) At this concentration, H_2O_2 absorbs enough photons at $\lambda \geqslant 310$ nm to undergo a reaction via a radical-type mechanism. Where $[H_2O_2] < [CN^-]_i$ ($[CN^-]_i$, initial cyanide concentration), the extent of cyanide oxidation is dependent on the conditions chosen. For

TABLE 1

Kinetics of the oxidation of CN^- by H_2O_2 under various conditions[a]

$10^3\,[CN^-]$ (M)	$[H_2O_2]$ (M)	k_{obs} (s^{-1})	Remarks
Effect of H_2O_2 concentration			
8.90	0.025	0.37×10^{-4}	Dark
7.94	0.2	2.5×10^{-4}	Dark
8.90	1.0	4.5×10^{-4}	Dark
8.90	0.02	3.9×10^{-3}	Irradiated[b]
7.08	0.2	4.2×10^{-3}	Irradiated[b]
8.90	2.0	4.8×10^{-3}	Irradiated[b]
Effect of CN^- concentration			
7.94	0.2	2.5×10^{-4}	Dark
1.38	0.2	0.95×10^{-4}	Dark
0.089	0.2	1.6×10^{-4}	Dark
7.08	0.2	4.2×10^{-3}	Irradiated[b]
1.32	0.2	9.5×10^{-3}	Irradiated[b]
0.27	0.2	(6×10^{-3})	Irradiated[b]

[a]Temperature, 25 °C; concentrations shown refer to initial concentrations before mixing.
[b]Irradiation was carried out with an Hg–Xe lamp at wavelengths of 210 nm or longer.
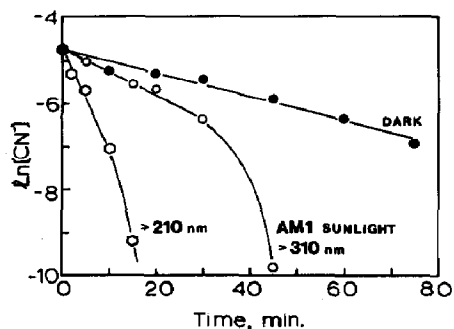
Fig. 2. Plots of $\ln[CN^-]$ vs. time showing the degradation of cyanide in the presence of H_2O_2 in the dark, under UV light illumination and under AM1 simulated sunlight conditions: $[H_2O_2] = 1$ M; initial $[CN^-]$, 8.9×10^{-3} M; 25 °C. See Section 2 for additional details. Note that no quantitative comparison is implied between UV irradiation and AM1 simulated sunlight.

TABLE 2

Degradation of aqueous solutions of NaCN by H_2O_2 at 25 °C or 35 °C in the dark[a]

Time of reaction (h)	25 °C	35 °C	$[H_2O_2]$	$[CN^-]$[b] (M)
0	—	—	—	8.9×10^{-3}
15	—	yes	—	8.5×10^{-3}
15	yes	—	—	8.9×10^{-3}
15	—	yes	yes	6.3×10^{-3}
15	yes	—	yes	6.6×10^{-3}
24	—	yes	—	7.1×10^{-3}
24	—	yes	yes	5.0×10^{-3}

[a]Initial concentrations before mixing are $[NaCN] = 8.9 \times 10^{-3}$ M and $[H_2O_2] = 2 \times 10^{-3}$ M.
[b]Concentration of unreacted CN^-.

instance, the data of Table 2 show that for the dark process the ratio of CN^- to H_2O_2 consumed is unity after reaction times of 15 and 24 h. That is, 2×10^{-3} M H_2O_2 oxidizes 2.2×10^{-3} M CN^-. However, after 85 min of UV illumination (8.9×10^{-3} M of CN^- treated with 2×10^{-3} M H_2O_2), the concentration of CN^- was 4.2×10^{-3} M, while after 180 min $[CN^-] = 2.5 \times 10^{-3}$ M. This suggests that the ratio of CN^- to H_2O_2 consumed is greater than unity, and a radical mechanism is not improbable [33].

At low $[H_2O_2]$, some CN^- might escape as HCN since the pH of the reaction is quite similar to the pK_a of HCN [11]; however, where $[H_2O_2] > [CN^-]$, the rate of oxidation of CN^- is faster than the loss of cyanide (as HCN) during the reaction. Under UV illumination and where $[H_2O_2] < [CN^-]$, no escape of HCN occurred from the reaction mixture in the time frame of the experiment at 25 °C.

3.4. Effect of $[CN^-]$ on the rate of degradation of CN^-

The data depicting the effect of CN^- concentration $((8.9 \times 10^{-5})$ - (7.9×10^{-3}) M) on the rate of oxidation of cyanide are summarized in Table 1 for both dark and UV illumination conditions $([H_2O_2] = 0.2$ M). The measurements at very low $[CN^-]$ required very careful analysis in order to discriminate between the extent of the degradation process from the possible escape of small amounts of cyanide (as HCN), which become critical at $[CN^-] \approx 2$ - 3 μg ml^{-1} (about 10^{-4} M) [34]. No dramatic dependence of k_{obs} on $[CN^-]$ was noted (cf. Table 1).

3.5. Photocatalytic reduction of gold(III) in the presence of CN^- ions and TiO_2

When a TiO_2 suspension containing gold(III) and CN^- ions is irradiated, CN^- is oxidized to OCN^- as described by Frank and Bard [21] for pure solutions of cyanide; gold(III) is not reduced however. Figure 3 illustrates the results when a solution of 1.83×10^{-2} M CN^- and 9.31×10^{-3} M gold(III) is irradiated in the presence of 2 g l^{-1} TiO_2 under simulated AM1 solar radiation for 15 h. For comparison, the results from the H_2O_2 (0.2 M) oxidation of cyanide (1.96×10^{-2} M; $[Au] = 9.31 \times 10^{-4}$ M), under the same experimental conditions (solar reactor; 35 °C) in the absence of TiO_2, are included. It is clear that H_2O_2 oxidation of cyanide occurs much faster than oxidation by irradiated TiO_2. After the complete removal of unreacted H_2O_2 (flushing nitrogen gas through the reaction mixture), addition of TiO_2 followed by irradiation with UV light led to the photoreduction of gold(III) on the surface of the semiconductor [2]. It is important to remove H_2O_2 to avoid peroxotitanium species forming from the interaction of TiO_2 with
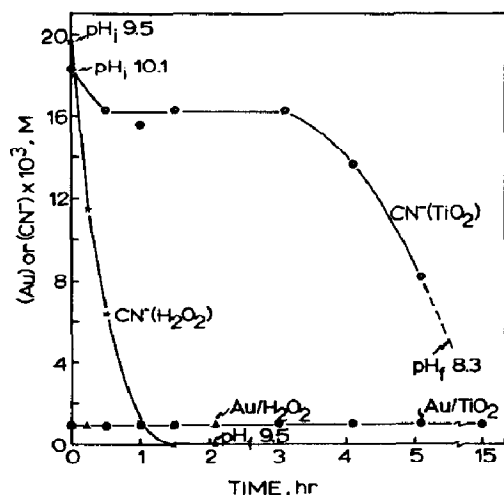

Fig. 3. Plots illustrating the changes in $[Au]$ and $[CN^-]$ as a function of time that compare treatments of $Au–CN^-$ solutions by H_2O_2 and TiO_2 under AM1 simulated sunlight ($\lambda > 310$ nm): initial $[CN^-]$, 1.83×10^{-2} M; $[Au] = 0.931 \times 10^{-3}$ M; $TiO_2 = 2$ g l^{-1}; $[H_2O_2] = 0.2$ M; 35 °C. See Section 2 for additional details.
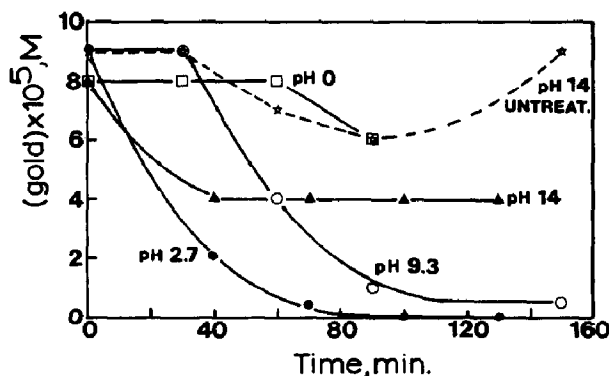
Fig. 4. Plots showing the reduction of Au(III) in the presence of TiO_2 with initial pH 0, 2.7, 9.3 and 14 after treatment of the cyanide solution with H_2O_2; for the untreated solution the initial pH was 14; 25 ml solution; $[Au^{III}] = (8 - 9) \times 10^{-5}$ M; $[TiO_2] = 2$ g l^{-1}; $[CH_3OH] = 10$ vol.%; 35 °C. For other details, see Section 2.

H_2O_2 [31]. Such species have a detrimental effect on the photocatalytic activity of TiO_2.

Figure 4 depicts the photoreduction of gold(III) at different initial pHs for the H_2O_2-treated gold solution. Irradiation of a 25 ml solution, consisting of 8×10^{-5} M gold(III), 2 g l^{-1} TiO_2 and 10 vol.% CH_3OH to enhance the rate of the process [2], was carried out in the solar reactor (AM1 simulated sunlight). Under these conditions, CH_3OH is oxidized to formaldehyde by the valence band holes of TiO_2 [35]. Also evident in Fig. 4 is the faster rate of reduction at pH 2.7; this confirms our earlier findings regarding the pH dependence of this process [2]. At pH 9.3, the reduction of gold(III) is slower, and we have already remarked (Fig. 3) that no reduction occurs if CN^- is present. At pH 14, an adsorption–reduction process takes place when the solution is previously treated with H_2O_2, while no reduction of gold(III) occurs when an untreated solution is illuminated in the presence of TiO_2. This suggests that gold exists in various (but not determined) complexed forms involving such ligands as CN^-, OH^-, H_2O and possibly NH_3 in the treatment with peroxide. It is worth noting that reduction of the Au^{III}–CN^- complex at pH 2.7 is slower than the reduction of the Au^{III}–Cl^- complex reported earlier under similar experimental conditions [2]. Moreover, no HCN was ever detected during the reduction process at pH 2.7.

3.6. Analysis of the reaction products

The reaction between CN^- and H_2O_2 clearly produces OCN^- as demonstrated in the literature [12 - 28]. However, we encountered some difficulties in detecting OCN^- ions [30]. In a typical experiment, 50 ml of a solution containing 975 μmol NaCN (1.95×10^{-2} M; natural pH, 10.6) was treated with 0.2 M H_2O_2 at 35 °C *in the dark*. At the completion of the reaction, no CO was detected and no HCN escaped during the reaction period (within the limits of detection). However, 80 μmol NH_3 were produced, and after treatment of the resulting mixture with concentrated H_2SO_4 to hydrolyze the OCN^- formed, the total NH_3 collected was 655

μmol. This value represents 67% of the initial concentration of cyanide and is in good agreement with previous findings [17]. According to Broucek [17], the remaining 33% of CN^- forms N_2 and nitrogen oxides. No CO_2 evolved during the reaction (not unexpected at pH 9.6); after the treatment with concentrated H_2SO_4, the total CO_2 was 750 μmol. This accounts for 77% of the initial [NaCN] and confirms previous work [12]. The remaining 23% of CN^- is present as NaOOCH. When the reaction was carried out *under UV light*, only 67% of the initial amount of CN^- was detected as CO_2; 975 μmol NaCN gave 655 μmol CO_2. Irradiation of a CN^- solution (also containing gold(III)) with UV light in the presence of 2 g l^{-1} TiO_2 yielded OCN^- [21]; 915 μmol CN^- produced 710 μmol CO_2. Treatment of the cyanide solution with H_2O_2 in the dark (no TiO_2) produced 725 μmol CO_2.

With regard to the reduction of gold(III) on TiO_2, the clear demonstration of formation of gold(0) was evident from the color change of the TiO_2 powder from white (initially) to purple (the purple of Cassius); this indicates deposition of colloidal particles of gold(0) onto TiO_2 [1]. Recovery of the deposited metal was achieved by dissolution of the Au^0–TiO_2 powder in concentrated HCl–HNO_3, in which TiO_2 is chemically stable [2].

3.7. Treatment and analysis of an industrial waste sample

Gold plating is widely used as a decorative finish in jewelry, and the physical properties of gold make it the material of choice for many applications in the electronics industry. A commonly used plating bath for this application is the gold–cyanide bath [1, 9].
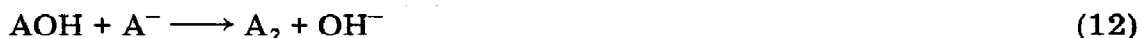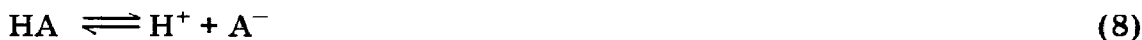
Two different samples originating from the wastes of an industrial plating bath solution were analyzed and treated for gold recovery and cyanide disposal. Sample A contained 463 μg ml^{-1} CN^- (pH 10.2); it also contained gold, copper, silver and zinc in various amounts. Sample B contained 2600 μg ml^{-1} CN^- (pH 11.6) and gold, copper, silver and zinc in various amounts. The amount of gold in both samples was about 100 μg ml^{-1}, as determined by atomic absorption techniques.

Sample A (25 ml) was treated with 1 ml 30 vol.% H_2O_2 until the CN^- completely disappeared (reaction temperature, 35 °C). A similar procedure was employed for sample B except that 5 ml of the peroxide solution were used. (Caution should be exercised when carrying out these reactions in small-volume containers. Pressure build-up of oxygen can be drastic! Large-volume reactors which have a lot of free head-space are recommended to avoid potential hazards.) Completion of the cyanide degradation gave a precipitate and a solution in both of which we found Au^{3+}, Cu^{2+}, Ag^+ and Zn^{2+}. The precipitates from both samples A and B were dissolved in aqua regia ([HCl]:[HNO_3] = 3:1) and subsequently added to their respective solutions from the reaction. For sample A, the composition of the solution (after removal of AgCl) was 97 μg ml^{-1} Au, 95 μg ml^{-1} Cu, 3.4 μg ml^{-1} Ag and more than 120 μg ml^{-1} Zn (pH 0.8). Addition of 50 mg TiO_2 to 25 ml of this solution A, together with 5 ml CH_3OH (17 vol.%) and followed by irradiation resulted in the deposition of gold(0) on the TiO_2 powder (purple

color; see above) [1]. Centrifugation and analysis of the solution gave the following result: 0 μg ml^{-1} Au, 56 μg ml^{-1} Cu, 1.4 μg ml^{-1} Ag and more than 120 μg ml^{-1} Zn. The purple powder was subsequently treated with an HCl–HNO$_3$ mixture to dissolve the deposited metal(s); analysis gave 78 μg ml^{-1} Au, 26 μg ml^{-1} Cu, 0.7 μg ml^{-1} Ag and 0 μg ml^{-1} Zn. The discrepancy in the concentrations of gold, copper and silver may result from the several manipulations required in the treatment procedures and from small changes in pH [2]. No titanium was ever detected in solution after treatment of TiO$_2$ with aqua regia [2]. The amount of copper photoreduced together with gold can be controlled by limiting the amount of CH$_3$OH used to about 4 vol.% and terminating the irradiation at the end of the photoreduction of gold [2].

4. Discussion

The reduction of H$_2$O$_2$ by various oxidizable anions [12], and the oxidation of a variety of reductants by H$_2$O$_2$ [36 - 44] is well documented in the literature. The general mechanism for the base-catalyzed nucleophilic attack of reductant HA on H$_2$O$_2$ has recently been proposed by Leung and Hoffman [44]:

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad (pK_a = 11.8; 20\ °C) \tag{7}$$

$$HA \rightleftharpoons H^+ + A^- \tag{8}$$

$$A^- + H_2O_2 \longrightarrow AO^- + H_2O \tag{9}$$

$$A^- + HO_2^- \longrightarrow AO^- + OH^- \tag{10}$$

$$AO^- + H^+ \longrightarrow AOH \tag{11}$$

$$AOH + A^- \longrightarrow A_2 + OH^- \tag{12}$$

HA denotes the nucleophile. We tentatively consider this same pathway for the photodegradation of pure CN$^-$ solutions and of Au^{III}–CN$^-$ solutions that contain free cyanide and complexed cyanide. To our knowledge, no reports have appeared in the literature regarding reactions between H$_2$O$_2$ and Au^{III}–CN$^-$ solutions. One report [12] has dealt with the UV-light-catalyzed oxidation of CN$^-$; however, the focus was on the kinetics of oxygen evolution from the decomposition of H$_2$O$_2$ by CN$^-$ ions. These do not appear to be easily oxidized by air [34]; at pH < 10, HCN is slowly evolved in the presence of air [6] and, at pH > 10, CN$^-$ ions are partially adsorbed onto glass walls [34]. The pK_a of HCN [11] is such that difficulty may be encountered and *caution* must be exercised in working with CN$^-$ solutions at pHs below 10; at pH > 10, oxidation of CN$^-$ is rather slow, in agreement with earlier work [12]. Considering the mechanism of Leung and Hoffmann [44], the results reported here for the degradation reaction *in the dark* can be understood on the basis of the following steps:

$$CN^- + H_2O_2 \longrightarrow OCN^- + H_2O \qquad (13)$$

$$OCN^- + H_2O \longrightarrow H_2NCOO^- \qquad (14)$$

$$H_2NCOO^- + H_2O \longrightarrow NH_3 + HCO_3^- \qquad (15)$$

Cyanate ions are the major product; at pH 9 - 10, OCN^- hydrolyzes [11] to yield the carbamate anion (eqn. (14)), an unstable species in aqueous media that decomposes to NH_3 and HCO_3^- (eqn. (15)). NH_3 is evolved in the oxidation of cyanide (see Section 3). The excess H_2O_2 can lead to further oxidation (of NH_3) to N_2 and NO_x [17]. No pH change was expected and none was observed for the dark reaction at pH 9 - 10; steps (10) - (12) are negligible under the experimental conditions used [31]. The important reaction is that given by step (9) or by its equivalent reaction (13). (Dissolution of NaCN in water leads to rapid hydrolysis: $CN^- + H_2O \rightarrow HCN + OH^-$; addition of H_2O_2 to such a solution will result in the formation of HO_2^- via the reaction $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$. This should lead to a lowering of the pH from 10.6 (the natural pH of the hydrolyzate, see text) to about 10, as observed. An astute reviewer has suggested that the rate-determining step in the *dark reaction* is the equivalent reaction (10), $CN^- + HO_2^- \rightarrow OCN^- + OH^-$, and not reaction (13). It was also suggested that this would explain the observed decrease in the rate of oxidation of CN^- at pHs above 10. We wish to point out the following. Firstly, under our conditions, $[HO_2^-] \approx 6 \times 10^{-7}$ M at pH 10 - 10.6, too small to effect significantly the oxidation of CN^-, particularly since the ratio of CN^- to H_2O_2 consumed is unity. Secondly, it should also follow that if reaction (10) were rate determining, then to the extent that $[HO_2^-]$ increases at pHs above 10, the rate of oxidation should increase, contrary to our observations.) Where $[H_2O_2] < [CN^-]$, the molar ratio of CN^- consumed to H_2O_2 consumed is about 1 (Table 2) as expected from reaction (13). It is intriguing to note that while our results demonstrate 100% degradation of CN^-, the mechanism proposed can only account for about 80% of the total initial CN^-. No agreement seems to exist in the literature for this discrepancy [12 - 28]. The remaining 20% or so may be attributed to the occurrence of the reaction [12]

$$CN^- + 2H_2O \longrightarrow NH_3 + HCOO^- \qquad (16)$$

and/or the reactions [44]

$$OH^\cdot + CN^- \longrightarrow HO\dot{C}=N^- \qquad (17)$$

$$H_2O + HO\dot{C}=N^- \rightleftharpoons HO\dot{C}=NH + OH^- \qquad (18)$$

$$HO\dot{C}=NH \longrightarrow O=\dot{C}NH_2 \qquad (19)$$

and

$$2O=\dot{C}-NH_2 \longrightarrow \begin{matrix} O=C-NH_2 \\ | \\ O=C-NH_2 \end{matrix} \qquad (20)$$
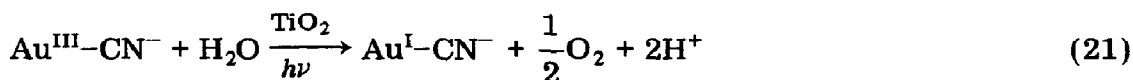
The oxidation of cyanide by irradiated TiO_2 semiconductor powder as well as the mechanism have already been reported by Frank and Bard [21]; cyanate ions were also the major product, as is confirmed in the present work. As illustrated in Fig. 3, a rapid photo-oxidation process is preceded by a slow adsorption process in TiO_2–CN^- suspensions; the pH changed from 10.1 to 8.3 during the course of the experiment and this may arise from the competitive or parallel reaction (21), during the reduction of gold(III) to gold(0), to give the stable Au^I–CN^- complex [3].

$$Au^{III}\text{–}CN^- + H_2O \xrightarrow[h\nu]{TiO_2} Au^I\text{–}CN^- + \frac{1}{2}O_2 + 2H^+ \tag{21}$$

The presently available results from the degradation of cyanide by H_2O_2 on irradiation with UV light ($\lambda \geqslant 210$ nm) suggest a pathway which implicates radical species and is based on knowledge of oxidation processes mediated by the $OH^{\bullet}$ radical [33, 46]:

$$H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet} \tag{22}$$

$$OH^{\bullet} + CN^- \longrightarrow OH^- + CN^{\bullet} \tag{23}$$

$$CN^{\bullet} + OH^{\bullet} \longrightarrow HOCN \tag{24}$$

$$HOCN \rightleftharpoons H^+ + OCN^- \tag{25}$$

$$CN^{\bullet} + CN^{\bullet} \longrightarrow (CN)_2 \tag{26}$$

$$(CN)_2 + OH^- \longrightarrow HCN + OCN^- \tag{27}$$

$$HCN \rightleftharpoons H^+ + CN^- \tag{28}$$

$$CN^{\bullet} + H_2O_2 \longrightarrow HCN + HO_2^{\bullet} \tag{29}$$

$$OH^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \tag{30}$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \tag{31}$$

In addition, the molar ratio of cyanide consumed to the amount of peroxide consumed, $[CN^-]/[H_2O_2]$, under illumination is greater than unity for $[H_2O_2] < [CN^-]$, and this also implicates a radical mechanism. The near constancy in the k_{obs} values on varying $[H_2O_2]$ and $[CN^-]$ in the light-driven reaction (see Table 1) identifies k_{obs} with the formation of $OH^{\bullet}$ species and eqn. (22) as rate determining [33]. A decrease in pH during the course of the reaction may result from the occurrence of steps (25), (27) and (28), or their equivalents. We have confirmed previous observations [33] that UV irradiation of aqueous H_2O_2 solutions increases the alkalinity of the solution. Therefore, the pH change must depend on the $[H_2O_2]/[CN^-]$ ratio. The dismutation of $(CN)_2$ in alkaline solutions is a well-known process [11].

The results of the degradation of cyanide in 1 M peroxide solution under AM1 simulated sunlight conditions are illustrated in Fig. 2. The rate

of degradation is smaller than that of the dark reaction. The pathway for the reaction may be a combination of the steps described above, inasmuch as the concentration of H_2O_2 under illumination with $\lambda \geqslant 310$ nm is such that photons are absorbed by the peroxide. (No pH change occurred in the case of the dark reaction under these conditions; under UV-light illumination, the pH decreases by about 1 pH unit. When the reaction was carried out under AM1 simulated sunlight, the pH drop was about 0.3 - 0.5 pH units. The initial pH was 9.) This does not appear to be the case for 0.2 M H_2O_2 (see Fig. 3), where the extent of absorption is not significant.

When irradiated TiO_2 is employed as the oxidizing agent, band-gap illumination generates conduction band electrons, e_{cb}^-, and valence band holes, h_{vb}^+, the actual species that oxidize CN^- [21]. In the presence of gold(III), the e_{cb}^- reduce gold(III) to gold(0), while the h_{vb}^+ oxidize water to oxygen [2]:

$$4Au^{III} + 6H_2O \xrightarrow[TiO_2]{h\nu} 4Au^0 + 12H^+ + 3O_2 \qquad (32)$$
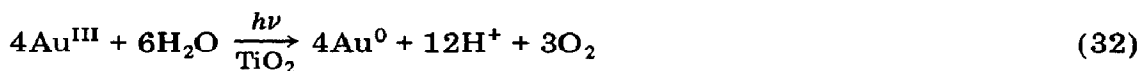
The rate of the reaction is pH dependent and the present observations parallel those found previously in the photoreduction of the $Au^{III}-Cl^-$ complex [2]. The photoreduction of the $Au^{III}-CN^-$ complex (we assume $Au(CN)_4^-$ forms to some extent) becomes thermodynamically less favorable with respect to the chloride complex: $E^0\{Au(CN)_4^- \rightarrow Au(0) + 4CN^-\} = -0.4$ V [3] and the V_{fb} of TiO_2 at pH 10 is -0.64 V(NHE) [5]. The limiting factor is the pH of the solution; at pH > 10 reduction is slow (see Fig. 4). As noted in Fig. 3, gold(III) is not reduced on irradiated TiO_2 under these conditions. No reduction occurs at an initial pH of 14 (Fig. 4), even in the presence of a hole scavenger such as CH_3OH. By contrast, when the initial pH is 2.7, the photoreduction of gold(III) is relatively facile and parallels the results for $AuCl_3$ [2]; however, prior disposal of CN^- is necessitated at such low pHs. In acidic aqueous media (pH < 5), the $Au^{III}-CN^-$ complex interacts with the positive surface of the illuminated TiO_2 [47] (isoelectric point, 5.5) [2]. At pH 14, the Au^{III}-cyanide complex is not adsorbed onto TiO_2, unless the solution is treated with H_2O_2 prior to photoreduction.

5. Conclusions

In the present paper we have described a route to the photochemical recovery of gold from industrial wastes containing cyanide ions. The practical samples taken from industrial sources illustrate the potential application of the procedure described here, and offer an alternative to the method presently in use [7, 8]. The disposal of CN^- ions by peroxide and the subsequent photochemical reduction of gold(III) on TiO_2 powder represents a good example of the application of photochemistry and photocatalysis to resolving environmental and industrial issues. An important part of the

present investigation is the observation that simulated AM1 sunlight can enhance the rate of the photochemical H_2O_2 oxidation of CN^- provided $[H_2O_2] \geqslant 3$ vol.%, a concentration of hydrogen peroxide commercially available. The oxidation of cyanide by means of the persulfate species is also promising, and under certain conditions this might be the preferred oxidizing agent [19]. Additionally, the procedures developed here could also be used in the recovery of rhodium from cyanide plating baths. Photochemistry and photocatalysis provide a pool of resources with which to tackle such issues as the environment, energy and the recovery of precious metals [48].

Acknowledgments

References

1 J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 3, Longmans, New York, 1923, p. 491.
2 E. Borgarello, R. Harris and N. Serpone, *Nouv. J. Chim.*, 9 (1985) 743.
3 A. J. Bard (ed.), *Encyclopedia of Electrochemistry of the Elements*, Vol. 4, Dekker, New York, 1973, p. 87.
4 *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, OH, 1971 - 1972, 51st edn, pp. D-111 - D-116.
5 M. D. Ward, J. M. White and A. J. Bard, *J. Am. Chem. Soc.*, 105 (1983) 27.
6 N. Hedley and H. Tabachnick, *Chemistry of Cyanadation, Mineral Dressing Notes, No. 23*, American Cyanamid Co., December, 1968.
7 M. I. Brittan, *Am. Sci.*, 62 (1974) 402.
8 E. M. Wise, *Gold Recovery, Properties, and Applications*, Van Nostrand, Princeton, NJ, 1964.
9 Y. Kinata and C. Wolowodiuk, *Plating Surf. Finish*, 66 (1979) 50.
10 H. E. Christiansen and E. J. Fairchild (eds.), *Registry of Toxic Effects of Chemical Substances*, U.S. Department of Health, Education and Welfare, Rockville, MD 20852, 1976 (HEW Publ. No. (NIOSH)76-191).
11 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1980, 4th edn, p. 369.
12 O. Masson, *Proc. Chem. Soc.*, 23 (1907) 117; *J. Chem. Soc.*, 91 (1908) 1449.
13 W. Henry and R. Wurinser, *C. R. Acad. Sci.*, 284 (1913) 157.
14 J. H. Matthews and H. A. Curtis, *J. Phys. Chem.*, 18 (1914) 166, 521.
15 S. G. Siderova, *Farmakol. Toksikol.*, 7 (1944) 39; *Chem. Abstr.*, 39 (1945) 3843[4].
16 J. T. Byrne, W. S. Turnley and A. K. Williams, *J. Electrochem. Soc.*, 105 (1958) 607.

17 J. Broucek, *Koroze Ochr. Mater.*, (1962) 95.
18 R. C. Sheridan and E. H. Brown, *J. Org. Chem.*, *30* (1965) 668.
19 H. Claude and J. C. Boeglin, *Trib. CEBEDEAU 331* (1971) 282.
20 A. Nergarazian and M. C. Merkahan, *J. Phys. Chem.*, *67* (1963) 2679.
21 S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, *99* (1977) 4667; *99* (1977) 303; *J. Phys. Chem.*, *81* (1977) 1484.
22 T. L. Rose and C. Nanjundiah, *J. Phys. Chem.*, *89* (1985) 3766.
23 K. Katsuyuki, Y. Hiroshi and T. Ideo, *J. Phys. Chem.*, *84* (1980) 1705.
24 A. T. Kuhn, *J. Appl. Chem. Biotechnol.*, *29* (1971) 21.
25 A. T. Kuhn, in J. O'Bockris and B. E. Conway (eds.), *Modern Aspects of Electrochemistry*, Vol. 8, Plenum, New York, 1972, p. 273.
26 W. E. Beckenn, *Electroplat. Met. Finishing, 25* (1972) 20.
27 R. H. Cherry, *Finishers Managements,* (July, 1971) 39.
28 B. Drabeik and V. Komendova, *Fortsch. Wasserchem., 3* (1965) 103.
29 E. Borgarello, R. Terzian, N. Serpone, E. Pelizzetti and M. Barbeni, *Inorg. Chem., 25* (1986) 2135.
30 E. L. Martin and G. McLelland, *Anal. Chem., 23* (1951) 1519.
31 A. I. Vogel, *Macro and Semimicro Qualitative Inorganic Analysis,* Longmans, London, 1954, 4th edn.
32 J. G. Dick, *Analytical Chemistry,* McGraw-Hill, New York, 1973.
33 J. H. Baxendale and J. A. Wilson, *Trans. Faraday Soc., 53* (1957) 344.
34 B. A. Perekalin, *Vodosnabzh, Sanit. Tekh., 14* (1939) 76; *Chem. Zentr. I.,* (1940) 1934; *Chem. Abstr., 35* (1941) 6860[5].
35 E. Borgarello and E. Pelizzetti, *Chem. & Ind. (Milano), 65* (1983) 474.
36 M. R. Hoffmann, *Environ. Sci. Technol., 11* (1977) 61.
37 J. V. McArdle and M. R. Hoffmann, *J. Phys. Chem., 87* (1983) 5425.
38 M. R. Hoffmann and J. O. Edwards, *Inorg. Chem., 16* (1977) 3333.
39 M. Daukleff, R. Curci, J. O. Edwards and H. Y. Pyun, *J. Am. Chem. Soc., 90* (1968) 3209.
40 I. R. Wilson and G. M. Harris, *J. Am. Chem. Soc., 82* (1960) 4515.
41 I. R. Wilson and G. M. Harris, *J. Am. Chem. Soc., 83* (1961) 286.
42 H. A. Liebhafsky and A. Mohammed, *J. Am. Chem. Soc., 55* (1933) 3977.
43 H. A. Liebhafsky, *J. Am. Chem. Soc., 56* (1934) 1680.
44 P. S. K. Leung and M. R. Hoffmann, *J. Phys. Chem., 89* (1985) 5267.
45 H. Buechler, R. E. Buehler and R. Cooper, *J. Phys. Chem., 80* (1976) 1549.
46 T. Ogita, H. Hatta, S.-I. Nashimoto and T. Kagiya, *Bull. Chem. Soc. Jpn., 5* (1985) 970.
47 N. Jaffrezic-Renault, P. Pichat, A. Foisy and R. Mercier, *J. Phys. Chem., 90* (1986) 2733.
48 E. Pelizzetti and N. Serpone (eds.), *Homogeneous and Heterogeneous Photocatalysis,* Reidel, Dordrecht, 1986.