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PHOTOCATALYTIC DESTRUCTION OF SOME TRANSITION METAL CYANIDE COMPLEXES

by

Barbara A. Mullins

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
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ABSTRACT

Photocatalytic Destruction of some Transition Metal Cyanide Complexes

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The oxidation of several transition metal cyanides by illuminated colloidal titanium dioxide has been studied with attention to end products and rate of reaction. Tetracyanozinc, a weak complex, and ferricyanide, a stable complex were the primary focus. The rate of complex dissociation of ferricyanide was found to depend on pH. The rate of oxidation of cyanide was found to be the same both complexed and as alkali cyanide. Although the precipitation of metal oxide onto the catalyst occurred, there was no evidence that it interfered in the oxidation of cyanide.
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Introduction

The photochemical, or at least photoelectrical behavior of semiconducting materials has been known since the early nineteenth century, though its explanation remained a mystery.\(^1\) The development of interest in the unique chemistry, especially the photo effects, that can occur at single crystal semiconductor electrodes came in the 1960's.\(^2\) That metal oxide surfaces catalysed many reactions - with or without photon assistance - was also known well before it was understood, as the earliest volumes of *Chemical Abstracts* attest. It has been known since 1927 that ZnO, a wide bandgap semiconductor, produced H\(_2\)O\(_2\) when exposed to ultraviolet light in the presence of water.\(^3\)

Increased understanding of the behavior of semiconductors has developed with the disciplines to which they relate, but the exponential increase in interest in semiconductor sensitized photocatalysis is traceable to the energy crisis of the 1970's when many investigators pursued photogenerated hydrogen as an effective use of solar energy. The idea of using photochemical catalysts to solve another prominent technical problem, pollution, seemed to come as an afterthought. Indeed, the current massive activity in the field cannot be attributed to any one paper or researcher, but the time of inception can be closely isolated. A review published in 1980\(^4\) cites only ten published studies: three fuel generation reactions, four chemical waste disposal reactions and three that could be classified as organic syntheses. The number of studies in any of these fields today could fill volumes.
Although one of the earliest pollutants to be reported photochemically decomposed was the cyanide ion,\textsuperscript{5} only recently has attention been given to the more practically important metal cyanide complexes.\textsuperscript{6,7,8} Metal cyanide electroplating and the use of large quantities of cyanide in extracting precious metals from ores are the major source of cyanide as a water pollutant. Prussian Blue pigment is still prepared commercially as well. To varying extents, the method of cyanide disposal in current use, generally treatment with NaOCl,\textsuperscript{9} is ineffective or inadequate for disposing of metal cyanide complexes. Therefore there are cases in which the question is not whether photocatalysis is faster than chlorine treatment but whether it works at all.

This thesis is a sequel to the work of Deepak Bhakta, et al.\textsuperscript{80} at HARC in 1991, which was able to demonstrate that ferricyanide, one of the most stable cyanide complexes did in fact disappear when exposed to ultraviolet light in the presence of colloidal TiO\textsubscript{2}. It has been the object of this work to identify products of that reaction as well as to verify the expectation that other stable and technologically important complexes could be decomposed as well.
Semiconductor Chemistry

Semiconductors are a category of inorganic solid crystalline materials whose bonding ranges from covalent to ionic-covalent. A description of their electronic structure can, in principle, be reached by starting with a molecular orbital approach and extending these orbitals to an infinite three dimensional structure, i.e., a perfect crystal. Such an approach is simpler conceptually than calculationally. For this reason the methods of solid state physics are generally used, qualitatively as well as quantitatively, to describe semiconductors. Core electrons are neglected. All bonding orbitals are assumed to be delocalized over the extent of the crystal. Thus, electron energies are described not by individual orbitals but by bands constructed from an infinite number of equivalent orbitals. Since the delocalized orbitals cannot all have the same energy, they are spread out over a band in a manner analogous to the pi orbitals of a benzene ring. Both the energy density and local density of electron states are on the order of Avogadro's number. As in molecular chemistry the highest occupied states, those associated with bonding, are of the most interest. There are virtual states which can be thought of as constructed from the higher unoccupied atomic orbitals of the atoms in the solid, and these also form bands. In metals these higher bands are of little interest; however, the distinction between metals, semiconductors, and insulators is defined by the size and existence of a gap between these occupied and unoccupied states. Again there is an analogy between the bandgap and the HOMO-LUMO gap. The distinction between insulators and semiconductors is somewhat arbitrary. Both (intrinsic) semiconductors and insulators have completely filled valence bands. When the
energy gap to the next available state, i.e. the conduction band, is from a few tenths of an electron volt to as much as 3.2 eV, the material may be considered a semiconductor. A further distinction is made between semiconductors of direct and indirect bandgap. An indirect bandgap is one in which the minimum energy transition does not occur without phonon interaction. This is somewhat analogous to the Franck-Condon principle.

There are no perfect crystals, of course, and the presence of either vacancies or impurities in the lattice can contribute either extra electrons to be accommodated by the conduction band, or empty states that allow for electron movement in the valence band. They also create localized points which differ in energy from the rest of the crystal. If the defect is the presence of a more positive atom than the constituent atoms, or absence of a negative constituent ion, an electron may lose energy at this localized state and be trapped. Conversely, if the defect involves a higher potential, it is more likely to become vacant and not be refilled. In some cases, a defect may exist whose energy is so near the middle of the bandgap that both electrons and holes may be drawn to it, resulting in recombination.

The existence of a surface in an ideally infinite lattice is obviously such a defect. It results in large numbers of under-coordinated atoms, and generally has a different potential from the bulk of the material. The potential of the surface of a semiconductor immersed in an electrolyte is equal to the potential of the solution, by the definition of chemical equilibrium. For single crystals in electrochemical systems the magnitude, extent and direction of band bending at the edges of the crystal can predicted. In colloidal particles and fine powders, the assumptions of band bending lead to the prediction of a space charge layer -
the layer over which the effects of band bending are felt - that is larger than the
diameter of the particle. Obviously the potential of the whole particle must be
affected.

Photochemistry of Semiconductors

As indicated above, the photochemical behavior of semiconductors can
be quite well predicted from their electrical properties. As in molecular
chemistry, light with an equal or greater energy than the HOMO - LUMO gap/
band gap can be absorbed by electrons in the valence band, exciting them to the
conduction band. As a result a current may flow through the semiconductor if
there is a well defined directional potential. In the absence of such, electrons
and holes - the vacancies they left behind- will move randomly until they
encounter traps, recombine, or (hypothetically) manage to tunnel to oxidizable or
reducible species in solution.

Recombination may be either a radiative or non-radiative transition.
Some authors have carelessly asserted that all energy given up on recom-
bination is dissipated as heat, but there is enough literature on luminescence of
semiconductors,\textsuperscript{10} even indirect semiconductors such as TiO\textsubscript{2}, to refute this.
Besides, the amount of energy transferred by UV photons, if it were all converted
to heat, as in a very inefficient reaction, would result in a very noticeable rise in
the temperature.

The probability of either holes or electrons encountering reactive species
without first being trapped at the surface, is acknowledged because it has not
been definitively disproven. Gerischer and Heller\textsuperscript{11} have calculated that the
chances of diffusion bringing a reactive electron or hole within tunneling
distance of a reactant beyond the semiconductor surface, are too small to account for observed phenomena, especially if the availability of the reactant is also diffusion controlled. It is therefore generally expected that reactions other than recombination occur because of trapping of both electrons and holes at different sites on the surface of the semiconductor. The redox potential of these sites is by definition lower than that of a free carrier, but not greatly lower. The potentials of the bulk semiconductor where they are known, can be used to estimate the probability of a particular oxidation or reduction.\textsuperscript{12}

Since both electrons and holes are produced simultaneously by the absorption of photons, particulate semiconductors have been likened to micro-electrochemical cells.\textsuperscript{13} The analogy is limited, but one valid point derived from it is this: electrochemistry ceases if only one half cell is reacting. Rates of reaction are dependent on the rate at which both holes and electrons are consumed.

Another analogy that has been used to describe particulate photocatalysts is that of photochemical sensitizers.\textsuperscript{12} This is more nearly an accurate statement, but with some reservations. Unlike classical photochemical sensitizers, semiconductors have never been reported to transmit simply the excitation energy of the electron. They simply promote one electron redox reactions. They also may stabilize radicals created by these processes by chemisorption.
Colloidal Particles

A colloid can be defined as a mixture which resembles a true solution in its apparent stability, appearance, and the interactions of the solvent phase with the solvated phase, while the "solvated" phase is not molecularly or ionically dissolved and has characteristics of its own bulk phase. The scope of colloid chemistry has changed since its heyday when solutions of polymers and large biological molecules were presumed to be included. That there are pronounced similarities between true solutions of large molecules and colloidal suspensions is indicative of their somewhat ambiguous nature. Many inorganic colloids have smaller dimensions than polymers in solution. The interactions between their surfaces and the solvent are also comparable to interactions between solvents and molecules.

Sols are generally prepared in situ from reagents that are soluble in the solvent with at least one component at low concentration. Thus relatively few atoms will be brought together by diffusion into more or less the solid structure of the material. The unfinished edges of the particles will tend to be completed by either coordination with the component present in excess, or in aqueous sols with H⁺ or OH⁻. A AgI sol might have either Ag⁺ or I⁻ as its outermost layer. In either case the particle has a charge proportional to its surface area. Surrounding the particle in solution would be a high concentration of ions of the opposite charge. These two layers of charge are known as the inner and outer Helmholtz layers. The electrostatic repulsion between these particles stabilizes them as long as the magnitude of the repulsion is greater than the van der Waals attraction between them. Since electrostatic repulsion is proportional to \(1/r^2\), while van der Waals forces are proportional to \(1/r^6\), where \(r\) is the distance
between particles, the repulsion dominates provided the dielectric constant of the solution is not too high, provided the particles are not too concentrated, and provided the kinetic energy of the particles is not so high as to overcome the repulsion. Thus increasing ionic strength, especially using multivalent ions of charge opposite the sol, and heat are two ways to destabilize a sol.

It is obvious that particles formed under these circumstances are likely to be far from the ideal crystal structure. The degree of disorder depends on the nature of the solid. The breadth of the size distribution of particles will also. It has been observed that the dispersity decreases with the age of the sol. That is, assuming some degree of solubility, atoms tend to migrate from small particles to larger ones until the smaller ones are gone. The component of Gibbs free energy associated with surface tension insures that migration will be in that direction. Whatever degree of annealing is possible within the particles at room temperature may also be presumed to occur. Still x-ray diffraction patterns that show a high degree of amorphicity are not surprising.

Since the conditions under which colloids are stable are somewhat more limited than conditions of their potential use, methods of stabilizing them are of interest. Various surfactants have been applied. The use of a polymer with some affinity for the solid and good solubility in the solvent is the most common method.

The theory used to predict the effectiveness of polymeric stabilization and polymer solubility in general is the Flory-Huggins theory. (More sophisticated modifications are necessary to deal with high temperature effects.) It furnishes expressions for the entropy and enthalpy of solution of both polymer and solvent, and demonstrates that only the entropy of the solvent favors solution. It
does not take into account hydrogen bonding or ionic interactions between solute and solvent, but no theory of that level of complexity has yet been proposed. It can give qualitative predictions only. Theory, confirmed by most experiments, predicts that particles with polymers bound to their surface will remain suspended under any circumstance in which the polymer is soluble. The polymers are presumed (with some experimental confirmation\textsuperscript{14}) to attach to the particles end on. Any event that brings two particles close together compresses the polymer molecules in a way that excludes solvent. Since this would lower the entropy, it does not proceed very far.

Three properties of colloids make them of interest in photocatalysis. First, the virtually invisible particles do not interfere with \textit{in situ} spectrophotometry of a reaction.\textsuperscript{17} Second, the activity of a heterogeneous catalyst is presumed to be proportional to the number of active sites on its surface, hence to its surface area. The small size of colloidal particles maximizes their surface area, and if active sites can be presumed to be associated with surface irregularities, their activity should be enhanced even more. Third, colloidal particles can be prepared that are so small that they do not have the full electronic character of the bulk solid, that is, they manifest quantum size effects.\textsuperscript{18,19} Since the bandgap of these is blueshifted, greater energy is required to excite them, but is also available for reactions. There are reports in the literature that 'quantum size' particles have catalysed reactions that should not be feasible according to the bulk potential of the substance.\textsuperscript{19,20}
Properties and Use of Titanium Dioxide as a Photocatalyst

Several factors have singled out TiO$_2$ as the substance of choice for photooxidation. (1) It is stable and insoluble in aqueous solution. Although it has been proven by isotopic exchange experiments$^{21}$ that the oxygen on the surface of TiO$_2$ may be lost during photoreaction, it will generally be replaced by more oxygen. CdS, by comparison, loses sulfide by oxidizing it to SO$_4$$^{-}$, but can be stabilized by sulfide$^{22}$ in the solution, or by attaching RuO$_2$ to its surface.$^{23}$ Neither is likely to be convenient. ZnO, on the other hand, is prone to lose zinc to the solution.

(2) TiO$_2$ has a wide bandgap, too wide from the perspective of harvesting solar energy. However, the width of the bandgap allows both the oxidizing and reducing potentials (the top of the valence band and the bottom of the conduction band, respectively) to be great enough to facilitate many reactions. Table 1 lists some semiconductors commonly used in both solar energy and photocatalytic applications and their bandgaps and band positions. Several could not be expected to reduce O$_2$, and some, though more effective as reducing agents, have little oxidizing potential.

(3) It is non-toxic and relatively cheap, both important considerations for its use in air and water clean-up. By contrast, CdS or CdSe are themselves considered more toxic than many of the substances they could be used to decompose.

(4) Empirically, when several photocatalysts are compared, TiO$_2$ usually gives higher rates of reaction.$^{5b,24,25}$
Potentials of Some Semiconductors

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band gap(^a)</th>
<th>Valence band edge(^b)</th>
<th>Conduction band edge(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>1.1</td>
<td>0.6</td>
<td>-0.5</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.4</td>
<td>1.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>GaP</td>
<td>3.2</td>
<td>2.2</td>
<td>-1.0</td>
</tr>
<tr>
<td>CdS</td>
<td>2.5</td>
<td>2.1</td>
<td>-0.4</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.7</td>
<td>1.6</td>
<td>+0.1</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
<td>2.3</td>
<td>-1.3</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>3.0</td>
<td>-0.2</td>
</tr>
<tr>
<td>WO(_3)</td>
<td>2.8</td>
<td>3.0</td>
<td>+0.2</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>2.0</td>
<td>2.2</td>
<td>+0.2</td>
</tr>
<tr>
<td>TiO(_2) anatase</td>
<td>3.2</td>
<td>3.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>TiO(_2) rutile</td>
<td>3.0</td>
<td>2.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>SiC</td>
<td>3.0</td>
<td>1.6</td>
<td>-1.4</td>
</tr>
</tbody>
</table>

\(^a\) in eV
\(^b\) in volts versus NHE
TiO$_2$ is known in three solid phases: anatase, rutile, and brookite. Brookite is quite uncommon. Rutile is the form most often found in nature, while anatase is the more easily prepared in the lab, being the expected product when TiO$_2$ is prepared at low temperature.$^{27}$ Cotton and Wilkinson$^*$ notwithstanding, since anatase can be converted to rutile by heat and the reverse is not true, rutile must be presumed to be the more stable.$^{26,27}$ All three forms have Ti(IV) octahedrally surrounded by oxide, while the oxide is coordinated with a plane triangle of Ti(IV). The octahedra are distorted in anatase and brookite, with one dimension being flattened. Rutile and anatase both have tetragonal symmetry (D$_{4h}$) with rutile being near cubic.$^{28}$

Rutile was an early favorite as a solid state electrode. It has a slightly smaller bandgap, 3.0 eV, as opposed to 3.2 eV for anatase. However, in studies of particulates, anatase has nearly always been reported to show greater reactivity. The activity of both forms has been shown to vary greatly with history as well as particle size.$^{29,30}$

Possibly, a major reason for the acceptance of anatase as the most promising candidate among photocatalysts is the existence of DeGussa P-25. It is certainly the most widely used TiO$_2$ powder. It is reported to have highly consistent properties. Its surface area varies only from 35 to 65 m$^2$/g. It is prepared by "high temperature (>1200°C) flame hydrolysis of TiCl$_4$ in the presence of O$_2$ and H$_2$. From the burner a coagulation of primary particles takes place during cooling which results in the final particle size and distribution... The product is then subjected to steam to remove HCl ".$^{31}$ The primary particles

$^*$ Advanced Inorganic Chemistry on p.655 states that "Anatase is 8–12 kJ/mol more stable than rutile." No reference is cited for this statement.
produced are 21 nm in diameter and non-porous. By electron micrographs they are known to aggregate into stringlike particles which still leave much of the primary particles' surface area exposed. Different studies have estimated the composition to be 70% to 80% anatase with the rest rutile. The discrepancy is attributed to the overlap of the two phases. The juxtaposition of the two phases has been suggested as the reason for the preparation's reactivity. It is speculated to promote electron-hole separation.\textsuperscript{31}

Although colloidal TiO\textsubscript{2} can be prepared from either the tetrachloride or any tetraalkoxide, the alkoxide must be added to an acid solution. The point of zero charge (commonly abbreviated pzc) of TiO\textsubscript{2} (the pH at which there is no excess of either positive or negative surface ions) has been reported between 3 and 6.0,\textsuperscript{27} an indication that TiO\textsubscript{2} is an acid. There are no reports of TiO\textsubscript{2} sols being prepared directly in alkaline solution, nor of their being resuspended by alkali once precipitated from solution. They can be stabilized in alkaline solution by changing the pH of the acid sol quickly enough that coagulation cannot occur\textsuperscript{18} (provided this does not raise the electrolyte concentration excessively).

The sizes of particles in TiO\textsubscript{2} sols have been reported between 50 angstroms and 150 nm, with the smaller particles showing surprisingly little polydispersity as determined by photon correlation spectroscopy.\textsuperscript{32} None of these showed quantum size effects. Anpo, et al.\textsuperscript{19} and Kormann et al.\textsuperscript{18} have reported particle sizes of 3.8 nm and <3 nm respectively, both of which did show quantum size effects. Either very cold aqueous (TiCl\textsubscript{4} at -20\degree C, H\textsubscript{2}O at 1\degree C) or almost dry organic solvents (on the order of 0.1\% H\textsubscript{2}O) were required to synthesize particles this small. The onset of absorption was 330 nm. This
compares with the tetra(n-propyl) and tetra(iso-propyl) titanium molecules which absorb slightly below 330 nm. 33

Every class of photochemical application that has been attempted using any semiconductor has been tried using TiO₂. Most recently even a solar cell using a paste of TiO₂ in an organic solvent between two conducting layers has been patented. Energy harvesting by the photolysis of water and the hydrogenation of small molecules, and the precipitation and collection of noble metals, and the environmentally interesting reduction of chromate to Cr(III), employ conduction band electrons. Fujishima and Honda 34 reported the photolysis of water on a solid state electrode in 1971 and are sometimes credited with starting the interest in photocatalysis.35a Schrauzer and Guth 36 found that N₂ was reduced to NH₃ and N₂H₄ in the gas phase on damp, illuminated TiO₂. This reaction is more probable in the gas phase, since N₂ solubility is very low; however, some objections were raised to the description of the reaction as catalytic, as it is stoichiometric in the amount of water preadsorbed on the TiO₂.37,4 TiO₂ has been compared to other semiconductors for the reduction of carbon dioxide, and for this purpose was found less satisfactory than those with more negative flatband potentials.38 It produced less methanol than formic acid and formaldehyde. The photo-Kolbe reaction,39 which at high light intensities builds larger hydrocarbons from smaller carboxylic acids was originally studied on TiO₂. The rates of most reactions involving hydrogen are greatly improved by depositing platinum on the TiO₂.39

Every class of organic compound recognized as a concern in the environment has been oxidized to CO₂ and 'mineral' anions. Many of these reactions have been described with details of intermediates and kinetics.
Aliphatic chlorocarbons were the first to be treated thoroughly. Pruden and Ollis ⁴⁰ and Hsiao et al.⁴¹ described the destruction of first chloroform, then chlorinated ethylenes, then \( \text{CH}_n\text{Cl}_{(4-n)} \), \((n=1-4)\). These were careful studies that accounted for surface area of the catalyst, actinometry, and mass balance of products. In addition, stable intermediates were followed. The decomposition of chloroform was found to proceed through methanol. The design of the reactor used by this group allowed for only limited available oxygen, which probably accounts for the apparent hydrogenation of chloroform as well as the stability of dichloroacetaldehyde as an intermediate in the decomposition of trichloroethylene. The importance of \( \text{O}_2 \) in driving total oxidations was not generally appreciated at this time, although Ollis was apparently aware of it. ⁴² Some difficulty was reported in oxidizing \( \text{CCl}_4 \). The proposed explanation was the lack of adsorption on the \( \text{TiO}_2 \). Although the resistance of carbon tetrachloride to oxidation is well known, it is more perplexing that trichloroacetic acid was even more stable (and there is evidence that carboxyl groups have an affinity for \( \text{TiO}_2 \) ⁴³ at least negative of the point of zero charge).

Chlorinated phenols and biphenyls were another early focus, as well as simple aromatics. In 1981, Izumi et al. ⁴⁴ reported the partial decomposition of benzoic acid. In addition to \( \text{CO}_2 \), they found salicylic acid and a resinous material with an IR spectrum similar to phenolic resin. Fujihira et al. ⁴⁵ studied reactions with toluene both neat and in aqueous solution. They found cresols, benzaldehyde, bibenzyl and \( \text{CO}_2 \) under different circumstances. Chlorinated aromatics being a major environmental concern, they were studied by several groups,⁴²,⁴⁶ the most thorough of which was Barbeni et al. ⁴⁷ They examined nearly a dozen substances including DDT, 2, 7-dichlorodibenzo-p-dioxin,
chlorobenzene, a dichlorobiphenyl, and several chlorophenols. In many cases conversion to CO₂ and Cl⁻ occurred so rapidly that no intermediates were detected. The intermediates were presumed to remain adsorbed on the catalyst until the reaction was complete. The ratio of Cl⁻ appearance to reactant disappearance tended to confirm this: it remained constant throughout the reaction. By contrast reactions in which an intermediate desorbed showed a change in Cl⁻ concentration that depended on the rate of decomposition of the intermediate. Intermediates that were observed were phenol, catechol, and quinone. Minero et al. compared these results with decomposition of fluorophenols. They found that reaction was much slower, probably because fluoride binds to titanium and blocks reaction sites.

Surfactants have been thoroughly studied by an international consortium of researchers. First dodecyl benzyl sulfonate, an anionic surfactant, was observed. The sulfone moiety was believed to be the first cleaved from the molecule, because the rate of increase in surface tension indicated the loss of surfactant character. Then the ring decomposed - detected by loss of an absorbance peak - and the long chain remained virtually untouched but then slowly decomposed. Later, the same group studied the decomposition of a cationic and a non-ionic surfactant.

Pesticide residues have also been addressed. Maillard et al. chose benzamide as a small molecule suitable for representing the behavior of several classes of pesticides. They compared the reaction on TiO₂ with H₂O₂ photochemistry and Fenton's reagent. The photocatalyst and hydrogen peroxide were found to be comparable, and to result in complete oxidation with relatively few objectionable intermediates. Fenton's reagent was not effective,
but was found to be competitive for molecules with hydroxylated rings. Atrazine, an herbicide, (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has received much attention recently. Pelizzetti et al.\textsuperscript{52} reported that the path of its degradation differed significantly on ZnO as opposed to TiO\textsubscript{2}, but that decomposition stopped at cyanuric acid on both. (Their reactor restricted available oxygen.) Low et al.\textsuperscript{53} have reported mineralization of atrazine.

The latter paper systematically studied the fate of heteroatoms on TiO\textsubscript{2} using ion chromatography to follow the course of reaction. Sulfur and phosphorus were invariably oxidized. Nitrogen was detected as both ammonium ion and nitrate. By the fact that the nitrate:ammonium ratio usually rose after all carbon had been oxidized, it appears that oxidation of carbon is much more favorable. There was some evidence that even nitrogen from nitro groups could be reduced to ammonia. Bravo et al.\textsuperscript{54} have confirmed that NH\textsubscript{4}\textsuperscript{+} can be oxidized to nitrate and reported that the intermediate nitrite could be detected in solution, if the surface of the catalyst was nearly saturated with nitrate. Neither group was equipped to detect N\textsubscript{2}, but this has been reported by Hidaka et al.\textsuperscript{8}

Several investigators have studied the interaction of halides on TiO\textsubscript{2}. Herrman and Pichat\textsuperscript{55} reported that I\textsuperscript{-} was efficiently oxidized to I\textsubscript{2}, Br\textsuperscript{-} was more slowly oxidized to Br\textsubscript{2}, and Cl\textsubscript{2} was not detectable. Moser and Gratzel\textsuperscript{56} were able to detect Cl\textsubscript{2}. They reported that as the pH was raised hydroxide ion competed with chloride. Both Henglein\textsuperscript{57} and Moser and Gratzel agree that the photon efficiency for Cl\textsuperscript{-} oxidation is about 0.01.

The photocatalyses of several categories of organic reactions have been studied, some with potential synthetic uses, some that seem mostly to elucidate the mechanism of reactions on TiO\textsubscript{2}. Rudham and co-workers\textsuperscript{58} made several
studies of the oxidation of alcohols to ketones or aldehydes. Fox 59 has published several reviews of potentially useful organic reactions. Al-Ekabi 60 and co-workers have examined a series of cis-trans isomerizations, and cyclo-dimerizations that proceed through a radical cation intermediate. One interesting, though not particularly practical reaction was the rearrangement of hexamethyl(Dewar)benzene to hexamethylbenzene. The photon efficiency was only slightly greater than 1.0. The homogeneous photoreaction proceeds by a chain mechanism with efficiency much greater than unity. The conclusion proposed was that radicals formed on TiO₂ tend to remain bound to the surface because they are stabilized by it. A mechanism was proposed that is partly Langmuir-Hinshelwood and partly Eley-Rideal, that is reaction with substrate in solution occurs at high concentrations after the surface is saturated.61

Dye molecules have often been the subject of redox reactions, most often because of their convenience in following the reaction by spectrophotometry, but they have also been proposed as electron relays or as electron scavengers to promote an oxidation reaction. Brown and Darwent 16,62 reported that methyl orange was reduced when polyvinyl alcohol was used to stabilize TiO₂, but was oxidized when unreactive stabilizers were used instead. Kolle et al. 63 described the advantages of cobalticenium dicarboxylate as an electron relay. It and dimeric and polymeric methyl viologen were proposed for use in artificial photosynthesis.64 Muzyka and Fox 65 used a series of dyes, of which methyl viologen was the most successful, as electron traps in order to promote a cation-radical dimerization in the absence of O₂ which tended to oxidize their substrate.

Obviously, many of these reports have shed light on the nature of the mechanism of TiO₂ reactions. Several controversies are only now being
resolved. The easiest aspect of the mechanism to resolve was the rate of charge carrier trapping and the rate of recombination. These studies were done by laser photolysis and time resolved spectroscopy and necessarily used colloidal TiO₂. Henglein reasoned that recombination occurred faster than the reactions he was able to observe with 30 ns resolution, but calculations by Gratzel and Frank used by Rothenberger et al. estimated a lifetime of 30 ns for charge carriers on a 120 A particle. This was dependent on the rate of carrier generation as well as particle size. Picosecond resolution was required to detect the rate of electron trapping. The blue peak associated with it was already formed after 20 ps. The trapped hole was said to form more slowly. This might be debated since the hole trap they identified was the peroxo complex, -Ti-O-O-Ti-, which is very stable in acid solution and clearly not the oxidizing species associated with surface bound hydroxyl groups. It is only reasonable that a state characterized by the absence of an electron would not absorb light, therefore its existence could only be detected indirectly. Nosaka and Fox determined quantum yield dependence on pulse width for conditions in which both methyl viologen and PVA were adsorbed and by use of a competitive reaction model were able to conclude that rates for both electron and hole transfer were greater than 10¹⁰ s⁻¹ while the rate for recombination was less than 10⁻⁶ cm³/sec. Rates obtained under these conditions are now known to be optimum possible rates.

* Peroxo complexes formed on the surface of TiO₂ powder were not desorbed until dried and heated to 420° to 670° C. Peroxide does, however, desorb in alkaline solution.
Before the rate of electron trapping could be followed, the identity of the electron trap had to be demonstrated. The blue color associated with excess electrons has been reported by several observers. Kolle et al.\textsuperscript{49} argued that this was due to Ti(III) ions at the surface of the particle and that the absorption of free electrons in the conduction band was in the infrared. Somorjai \textsuperscript{35b} found by Auger spectroscopy that the same absorbance on a TiO\textsubscript{2} single crystal was indeed Ti(III). The confirmation that this was the electron trap was reported by Howe and Gratzel \textsuperscript{70} using low temperature esr. They also concluded that the hole trap was not the adsorbed hydroxyl radical, but an electron deficient oxygen one layer removed from the surface. Lawless et al.\textsuperscript{71} used pulse radiolysis to generate hydroxyl radicals in the presence of TiO\textsubscript{2} and were able to demonstrate that the radicals were virtually all adsorbed on the particle surface and behaved in the same way as illuminated TiO\textsubscript{2}. They proposed that there was a resonance stabilization between the surface adsorbed radical and the O\textsuperscript{-} identified by esr. This conclusion has been generally accepted, but despite evidence from this and other sources \textsuperscript{60} that radicals are stabilized by adsorption on TiO\textsubscript{2} and are therefore unlikely to desorb, some still entertain the possibility. Peterson et al.\textsuperscript{72} detected a current in an electrochemical slurry cell that they believe to be due to desorbed OH\textsuperscript{-}.

Besides this question, several points of contention still exist: 1) Must the charge carriers be trapped? 2) Must the reactant be adsorbed? 3) Must the hydroxyl radical always be involved in oxidation? Gerischer and Heller \textsuperscript{60} have published calculations that affirm both one and two. They calculated the fraction of time that a freely diffusing electron would be within two to three angstroms tunneling distance of a freely diffusing O\textsubscript{2} molecule and concluded that the rate
would be impossibly low and that both needed to be localized at the surface. However, Trillas et al. \textsuperscript{73} found in studying the rate of decomposition of phenoxyacetic acid, that there were two maxima in a graph of rate versus pH. One corresponded to a point of maximum adsorbance of the reactant on the catalyst, the other to the maximum adsorbance of hydroxide. The two were of comparable magnitude. There is generally more agreement that the charge carriers should be trapped, but Moser et al. \textsuperscript{43} have claimed that a series of oxygen bearing aromatics complex with the surface Ti and raise its potential so that electrons are not trapped. They concluded that higher rates of reduction of methyl viologen that were observed in the presence of these "surface complexes" were due to the higher potential of the untrapped electron. The third question is still the subject of debate. \textsuperscript{66,74} A very good case can be made that under some circumstances oxidation occurs by direct electron transfer from an adsorbed substrate to TiO\textsubscript{2}.

**Use of Titanium Dioxide to Treat Metals, Cyanide and Metal Cyanides**

It is obvious that if TiO\textsubscript{2} will reduce hydrogen, it should also reduce any metal with a more positive potential that H\textsubscript{2}. Little use was made of the knowledge at first except for Kraeutler and Bard's \textsuperscript{39} method of precipitating platinum on TiO\textsubscript{2} particles. Serpone et al. \textsuperscript{75} used TiO\textsubscript{2} to recover gold from a spent plating solution. More recent studies \textsuperscript{76,48} have confirmed that mercury can be gathered on TiO\textsubscript{2}. These demonstrated the decomposition of organomercurials, but for the precipitation of mercury from the tetraiodide complex see
the next chapter. TiO$_2$ will also reduce Cr(VI) to Cr(III) at a pH as high as 5, at which the Cr(III) can be removed as a hydrous oxide.\textsuperscript{76,25} The reduction causes a rise in pH which must be controlled, because the reaction proceeds in the opposite direction at greater than neutral pH. (Again see chapter 3) Copper has received attention recently with conflicting results being reported by different groups. Prairie et al.\textsuperscript{76} found no reaction in a simple copper salt, pH 6, with salicylic acid present to balance the reaction. Foster et al.\textsuperscript{77} treating a spent electroless plating bath found copper precipitated on the TiO$_2$ as a mixture of Cu(I) and metal. Peral and Domenech\textsuperscript{6} found that copper disappeared from solution more quickly than cyanide and accelerated the oxidation of cyanide on TiO$_2$, but not on ZnO.

After Frank and Bard's initial report of decomposition of cyanide, Rose and Nanjundiah sought to optimize the reaction by varying particle size, TiO$_2$ concentration, and pH as well as examining the effect of platinization. The effect of particle size was predictable, but the quantity of TiO$_2$ of the same particle size was by no means linear. A tenfold increase in catalyst gave only a 20\% increase in rate. The rate decreased with increasing pH starting from a pH of 11. Platinization had the effect of accelerating the reaction many times. This could only mean that platinum provides a much faster means of disposing of electrons than O$_2$.

In the past five years, three more kinetic studies of decomposition of cyanide have been published. These have pursued the question of end products more thoroughly than the earlier works. Peral et al.\textsuperscript{78} reported that at long times relative to disappearance of cyanide, the cyanate concentration decreased and they were able to confirm the presence of carbonate. The rate
for the second reaction was approximately 500 times slower. Pollema et al. followed the reaction by the formation of nitrate. They also oxidized cyanate as separate reaction and found only about half the rate of oxidation as cyanide. Hidaka et al. expected to find N₂, and since the nature of such an experiment required sealing the reactor, limiting O₂, they succeeded. Although Pollema et al. reported near stoichiometric production of nitrate with air bubbling through their solution, the difference in conditions resulted in nearly stoichiometric quantities of CO₂ and N₂ being found. The rate of reaction was much slower and mostly did not proceed past cyanate.

Two of these groups reported an experiment with a metal cyanide complex or actual plating waste. The effects of the metal on the reaction was not investigated in any detail. Peral and Domenech later reported the work mentioned above. They prepared their Cu(CN)₂⁻ in solution losing both copper oxide and (CN)₂ in the process and resulting in a fairly low concentration, which contained more copper than cyanide. They were able to analyse both components however, and to distinguish between complexed and free cyanide, an important matter, since complexed cyanide is not detected by most analytical methods for cyanide. The reaction was compared at pH 11 and 13, on TiO₂ and ZnO. Copper accelerated the rate on TiO₂, on which it precipitated, but slowed the reaction on ZnO. Besides Bhakta et al., only three other groups have published studies of photocatalysis of iron cyanide complexes. Yamasaki et al. primarily studied homogenous degradation under a low pressure lamp. The 187 nm line is capable of oxidizing OH⁻ to OH⁺, so that complete decomposition occurs. When various semiconductor powders were added to the reactor, most accelerated the rate, but the details of these reactions were not
followed. Rader et al. 7 note that Zaida and Carey (their reference 10) found no evidence of either direct or photocatalysed reaction in iron cyanide mining wastes. Rader et al. have done a most thorough study of both homogenous and photocatalysed decomposition of both ferrocyanide and ferricyanide. Being located in Nevada, they found it convenient to use sunlight as their radiation source. The TiO₂ catalysed complexes were destroyed in 17 days; the homogeneous reaction stopped short of completion with a significant concentration of free cyanide present. Another 13 days with fresh TiO₂ removed about half the remaining cyanate from the catalysed ferricyanide sample. Nitrate was the major product detected.

Stable Cyano Complexes of First Transition Metals

All the transition metals from vanadium to zinc form at least one cyano complex that is stable in water. The basis of the extraordinary stability of some of the complexes is the back bonding from electrons in the metal 3d orbitals to the π antibonding orbitals of the cyanide ligand. Therefore, the stability of the complexes tends to increase with the number of electrons present, at least until there are enough electrons to occupy the 3d(z²) and 3d(x²-y²) orbitals, excluding cyanide from them. The most stable complexes are, therefore, the Fe(II), Fe(III) and Co(III) complexes. All the stable complexes from chromium through Co(III) are octahedral. Co(II) forms a binuclear complex in solution with a bond forming between the unpaired electrons of the two cobalt atoms and the ligands otherwise distributed as they would be in an octahedral complex. The nickel complex, still outstandingly stable, excludes ligands from the 3d(z²)
positions, resulting in a square planar complex. Cu(I) forms all the stable copper cyano complexes. KCu(CN)₂, KCu₂(CN)₃·H₂O and K₃Cu(CN)₄ are known. Zinc forms a tetrahedral four cyanide complex, but with the ligands completely excluded from the 3d orbitals, the bonding is not especially strong and mixed complexes of CN⁻ and NH₃ or OH⁻ are possible.

All the cyano complexes except copper and zinc have some known homogeneous photochemistry. Since neither Cu(I) nor Zn(II) have any open 3d orbitals, they absorb only at wavelengths below 250 nm, presumably due to charge transfer from ligand to metal. The photochemistry of the iron cyanides has been studied in detail since the 1920's. The peak at 270 nm in ferrocyanide is associated with charge transfer to solvent, and in the presence of electron scavengers, the oxidation is permanent.

The longer wavelength peaks in all the octahedral complexes are associated with d-d transitions. When an electron is shifted to an orbital associated with the cyano ligands, it temporarily displaces a ligand from the complex. The cyanide can be completely displaced from the chromium complex, one ligand at a time being replaced with H₂O. The entire series of octahedral complexes, Cr(CN)ₓ(H₂O)₆-x has been tentatively identified. In the more stable complexes the cyanide quickly returns to its place. Stability constants for iron or cobalt complexes smaller than five members are not known. They have not been observed in solution.

The shorter wavelength peaks are associated with charge transfer from the ligand to metal or vice versa. It is evident that even this high energy photochemical reaction does not tend to decompose the cyanide (with the possible exception of zinc; see chapter 3).
Experimental Procedures and Methods

Reagents

All water used in reactions, reagent preparation, and analysis was distilled using a Dow-Corning Megapure continuous flow still.

TiO₂, P-25 was a gift of the DeGussa Corporation. TiO₂ sols were prepared from TiCl₄ or in two cases from titanium tetra-isopropionate.

Two methods were used in the preparation of sols from TiCl₄. About 100 ml water were chilled in a beaker and placed in a glove bag with a stirring plate under it. 0.44 ml of TiCl₄ were measured as accurately as possible and added to the water with vigorous stirring. This formed a transparent sol with a concentration of 0.04 moles TiO₂ per liter and 0.08 M HCl. Without polyvinyl alcohol (PVA) it was not stable at a pH higher than 4, and more concentrated sols were not stable even in acid. A four percent solution of PVA (average molecular weight 18,000) was prepared and mixed 1:1 with the sol. This concentrated stock solution could be diluted by 50% on adding the metal cyanide solution and raising the pH to give a 0.01 M concentration of TiO₂.

Titanium tetra-isopropionate was dissolved 1:4 in isopropyl alcohol. TiO₂ never forms stable sols without the presence of free acid, so it was added to a 2% H₂SO₄ solution, i.e. 1 ml conc. H₂SO₄ was added to 49 ml 2% PVA solution followed by one ml dilute titanium isopropionate. This produces a cloudier sol. The choice of an acid with a divalent anion has obvious disadvantages, but it was hoped that it might shed some light on whether oxidized Cl⁻ played any part in the reaction. In later work, the dilute isopropionate (12.5 ml) was added to 400 ml of water +13 ml 1:1 HCl. The resulting mixture had to be stirred for 10
min to become reasonably clear. No PVA was added, but the liquid was dialysed. Even after two changes of water in the bath, the resulting sol had an odor of isopropanol.

The later TiCl₄ sols were prepared from a solution of TiCl₄ in 6 M HCl. Twenty ml of 1-1 HCl were placed in a glovebag with approximately 5 ml TiCl₄ which were measured into a 10 ml graduated cylinder and poured into the acid. This method produces a clear slightly yellow solution which can be handled in air and even outside of a fume hood. Three to 4.5 ml of this solution were measured with a graduated pipet and dropped slowly into a well-stirred beaker of 450 ml water. At this point, the liquid in the beaker was water clear. The resulting sol was poured into a dialysis sack (Spectrapor #2) and left in a 10 L bath of distilled water overnight. As many as four sacks were prepared at one time. The water was changed the next morning and the pH was usually around 3.5 after a few hours. To reverse the pH of the sol, 200 ml of water and 0.5 ml 10 M NaOH were vigorously stirred in a 3 L beaker and the sol was poured slowly down the side of the beaker to maximize the rate of mixing. When the pH of the mixture began to go down, another 0.5 ml NaOH was added, until all the sol had been added. Usually the total amount of NaOH used was about 3 ml. At this point the sols were hazy but basically transparent, and remained stable in storage for several months.

A sample of one of these sols was sent to Polyhedron Laboratories, Inc. to determine the particle size by light scattering. Because the particles were smaller than the 633 nm wavelength of the HeNe laser, it was necessary to use a Zimm plot, a method of taking light scattering data at several dilutions and extrapolating to infinite dilution. It gives more data than can be obtained from a
single Rayleigh scattering experiment. Both a weight average molecular weight and a radius of gyration were reported by the lab. The weight average "molecular" weight was $2.37 \times 10^7$, and the radius of gyration was 125.8 nm. Either of these figures can be used to estimate the surface area of the particles. The simplest estimate assumes a spherical particle with a radius related to the radius of gyration by: $R_g^2 = \frac{3}{5} R^2$ where $R_g$ is the radius of gyration and $R$ is the radius of the particle. The other necessary assumption is that the bulk density of anatase is applicable to the spherical particle. Neither of these assumptions is strictly probable for particles composed of agglomerations of smaller particles, but it would give an outside estimate of the surface area. The volume and surface area of one particle were calculated. The volume was multiplied by the density to obtain the weight of one particle. The weight of one particle was divided into the weight concentration of TiO$_2$ to determine the number of particles. This number was multiplied by the surface area of one particle to obtain total surface area. The number obtained was distressingly low, 4.7 m$^2$/g, much smaller than that of DeGussa P25 (50 m$^2$/g). When the number of particles is estimated by dividing the weight average molecular weight into the weight concentration of TiO$_2$, the number is larger by three orders magnitude. Obviously, the simplifying assumptions lead to very serious errors.

The primary particles from which these particles were formed have been characterized in the literature using TEM and photon correlation spectroscopy as spherical, 3.3 to 10 nm in radius, and having a small disperesity.$^{16,63,68}$ The way to reconcile the particle weight with the radius of gyration is to assume a particle composed of these primary particles having dimensions on the order of $R_g$ and a density on the order of 1/1000 of the bulk density of anatase. That is,
a few particles spread over a considerable volume, having minimal contact with each other. This assumes the primary particles have the bulk density, again only a limiting assumption. Contact between the liquid phase and most of the surface area of the primary particles should be possible. When the weight of a 10 nm primary particle is calculated at the bulk density, only 2.4 particles have a total weight of 2.37 X 10^7. When the same calculation is made using 5 nm particles, the number is 19 particles. At 3.3 nm, 67 primary particles could be involved in the composition of one agglomerated particle. It is evident that the smaller diameter particles are more probable, since they could (allowing for lower than bulk density) be stretched out to the dimensions of the radius of gyration, while the small number of larger particles could not. The total surface area for 5 nm radius spheres at the bulk density is 154 m^2/g; for 3.3 nm particles, it is 233 m^2/g. Contact between ideal spheres is visualized as one point; the area of contact between real particles cannot be calculated from such a model. If an octahedral shape is used as an approximation for estimating the amount of surface area lost to contact between primary particles with the further assumption that most particles contact only two other particles, the surface area is reduced by 25%, giving a total surface area of 115 m^2/g to 175 m^2/g. The smallest particles would have a higher probability of having more than two octahedral faces in contact with other particles; thus the higher figure is almost certainly too high.

$\text{K}_3\text{Fe(CN)}_6$ and $\text{K}_4\text{Fe(CN)}_6$ were available from the shelves of the lab and were reagent grade. $\text{K}_3\text{Co(CN)}_6$, $\text{K}_2\text{Ni(CN)}_4$, $\text{K}_3\text{Cr(CN)}_6$, $\text{K}_2\text{Zn(CN)}_4$, and $\text{KCu(CN)}_2$ were prepared and recrystallized twice before use. All except the chromium complex were prepared by adding KCN to chloride salt of the metal.
(nitrate for copper) until an insoluble self salt of the cyano complex was precipitated (e.g. Ni[Ni(CN)₄]). The precipitate was filtered off and dissolved while warming in a small volume of KCN. The solutions were concentrated if necessary and the crystals were collected either by decantation or filtration. K₃Cr(CN)₆ was prepared by precipitating Cr(OH)₃ and dissolving in acetic acid. This solution was then mixed with a strong KCN solution while warming.

K₂Fe(C₂O₄)₃ was prepared according to instructions in Photochemistry by Calvert and Pitts, and recrystallized twice, using a photographer's red light as the only light in the lab.

All other chemicals were analysed reagent grade except for vinegar (5% acetic acid in water), which was presumably food grade, at least, having been purchased from a grocery store.

Equipment

In the earliest experiments, three milliliter quartz cuvets were used as reaction vessels. They were exposed to a 100 watt high pressure mercury lamp, sunlight, or to one of two 4 watt mineralogist’s blacklights.

The 100 watt lamp was an HBO 125/2 Osram high pressure lamp with a Hanovia power supply, installed in a Ealing housing with a quartz lens adjusted to focus the beam to about a 2.5 cm area.

The light intensity experiment involved the 100 watt lamp and the cuvettes, but required a much more precise structure. It is illustrated in Figure 1. The apparatus was set up in a darkroom. The lens, installed in a copper tube
Figure 2. Configuration of Apparatus
for Light Intensity Experiments
was adjusted to focus the beam to less than a centimeter. Even after focussing, there was a considerable amount of stray light, so an aperture was added to the system. It was prepared by using a cork borer to cut a hole in a piece of corrugated cardboard. Neutral density filters were taped over the hole without the tape being in the light path. The structure that held the cuvettes consisted of two blocks of wood taped together and to the countertop. Two strips of corrugated cardboard were taped to the top of the blocks leaving a slot precisely the width of the cuvettes. An aluminum flange approximately 13 cm in diameter and 1.3 cm in thickness, with a hole near its edge approximately the same size as the cardboard aperture, could be rolled into a position that allowed the two holes to coincide to illuminate the cuvettes. Stirring was accomplished by two 1/32" diameter Teflon tubes which introduced helium into the ferrioxalate and oxygen into the ferricyanide - TiO₂ mixture.

Two other containers were used in connection with the 100 watt lamp. The first consisted of a modified 100 ml beaker with a smooth lip over which a quartz cover was placed. A side tube had been added to the beaker for sampling, but it turned out to be useless, because of lack of mixing with the rest of the contents of the beaker. A framework was built to hold the 100 watt high pressure lamp in a horizontal position so that the light shone down through the quartz cover. The light had to be started in a vertical position and then placed in the frame. An extra fan was also required.

The second container was adapted from use as an IR water filter. It had the advantage that the light did not have to be put into a horizontal position to be used effectively with it; however, it was not efficient in exposing the maximum
amount of volume to the light. It held about 90 ml, a convenient volume. When full, it had very little interface with the air.

A 3.5 L photochemical reactor was purchased from Ace Glass which credits the design to Dr. Dennis Kreil of Dow Chemical Company. It uses a 12 cm long cylindrical medium pressure 550 watt mercury vapor lamp housed in an immersion well in the middle of a conical reaction vessel. The quartz immersion well has a double wall allowing for about a centimeter thickness of cooling water between the reacting solution and the light. The temperature of exiting cooling water could be kept at 35° C, by maintaining a fairly high flow rate. The fact that the temperature of the reaction mixture usually exceeded 35° after 1.5 to 2 hours indicated that this thickness was not sufficient to eliminate all of the near infrared radiation produced by the lamp. The reactor was placed in a bucket filled with approximately 10 L water to slow the heating effect.

The reactor used a mechanical stirrer consisting of a glass rod connected to a 0.05 horsepower electric motor and brought into the reactor by a glass bearing surface which required lubrication.

Aeration was provided by an aquarium pump connected to a U-tube with a plug of glass wool at the bottom so that one arm of the U could be filled with drierite and the other with ascarite. The flow rate was evaluated using a floating ball type flow gage.
Figure 2. Three Liter Reactor
Analytical Methods

Equipment

A Perkin-Elmer Coleman 295 visible spectrophotometer was used for most quantitative colorimetric work. One centimeter diameter test tubes were used as sample containers. All were permanently numbered and a record kept of the blank value obtained at various wavelengths when filled with distilled water. Most blanks were negligible, but some at shorter wavelengths required corrections. Blanks did not change when checked after a year. On one occasion, all tubes were filled with the same colored solution and compared to verify that all were precisely the same diameter. Any that gave high readings were removed from use.

A PE/ Hitachi UV-visible spectrophotometer was used where a scanned spectrum was needed. Quartz cuvettes transparent to 190nm> were used for all work.

Cyanide analysis was done using comparison standards and an Orion ion sensing electrode with a double junction reference electrode connected to a Fisher Accumet 815MP pH meter. The optimum range of concentration for the electrode is $10^{-3}$ M to $10^{-5}$ M.

No functional pH electrode was available; therefore all pH detection was done using pHdrion wide spectrum pH paper. Any pH higher than 11 was estimated from the amount of base present.

Measurement of volumes smaller than one milliliter was done using a graduated pipet, either 10 ml or one ml with tenth ml gradations. Generally measurement of reagent volumes less than 10 ml was done using a 10 ml
graduated pipet. Measurement of samples and standards was done with volumetric pipets.

Standards

All the methods used for routine analysis required comparison standards. Primary standards were not generally available, but solutions used as comparison standards were analysed by gravimetry or titrimetry to determine their exact concentration.

Cyanide standards were prepared from KCN. Since the reagent had been on the shelf for a long time, and the reaction KCN + H₂O → KOH + HCN is likely to occur with exposure to humidity, it was washed with hot methanol, since KOH is much more soluble in methanol than KCN, and dried in a desiccator. Then 0.1628 g were weighed and dissolved in a 250 ml volumetric flask with 2.5 ml 10 M NaOH added. This gave a nominal 0.01 M solution. When checked by titration with silver nitrate the actual concentration was found to be 0.0087 M. For simplicity the 0.01 M value was used in preparation of standards and corrections were made in the calculations later. Dilutions of 0.001 M, 1X10⁻⁴ M, and 1X10⁻⁵ M were prepared with 1 ml of 10 M NaOH added per 100 ml.

For an ammonia standard, NH₄Cl was dried at 120⁰ C. A weighed amount (0.0861g/50 ml) was dissolved in distilled water. The concentration was checked by titration of the Cl⁻ ion with standardized silver nitrate. A concentration of 0.0030 M was determined. After determining that one and two ml aliquots of this solution, when reacted with the reagent gave about the same reading, a further 1:10 dilution was made to use as a standard.
Barium nitrate was used a standard for nitrate. The known solubility of barium nitrate at room temperature is 90 g/L. First a supersaturated solution was prepared. After crystals appeared at the bottom of the solution, two ml were taken from the supernatant, diluted first to ten ml, then 2:100, then further as needed to reach the most nearly linear range of the reagent.

A 0.02 M FeCl₃ solution was prepared. It was analysed gravimetrically using 8-hydroxyquinoline. The true concentration was found to be 0.0299 M. A nominal dilution to was 0.001 M was made from this stock solution.

A 0.0625 M NiCl₂ solution was prepared. It was analysed gravimetrically by precipitation and drying as the di-methyl glyoximate.

Methods
I. Analysis of Free Cyanide

The manufacturer of the electrode recommends that all analyses be made with a uniform background ion concentration of 0.1 M NaOH. This was customarily acheived by putting a 1.0 ml aliquot of the solution to be analysed into a 50 ml volumetric flask with 0.5 ml 10 M NaOH and diluting to mark. When the solution to be analysed was expected to contain less than 10⁻⁵ M CN⁻, 1 ml of the 10⁻³ M standard was also added and the 2X10⁻⁵ M concentration of added cyanide was subtracted from the amount calculated from the reading.

The readings were taken by pouring the sample into a Teflon beaker and mechanically stirring the solution while the electrode reached equilibrium. The usual time required to be sure the reading was stable was about four minutes.
The meter was read in millivolts and conversion to concentration was done using the formula:

$$\log(\text{conc.}) = (m\text{v}_1 - m\text{v}_{\text{reading}})/d\text{mv}$$

where $d\text{mv}$ is the difference in readings in millivolts for a concentration difference of one order of magnitude, typically 59 mV, and $m\text{v}_1$ is the hypothetical reading to be expected for a 1M cyanide solution. These values were calculated from the standards.

Since the ion sensing electrode detects only the CN$^-$ ions that are available in solution, it could not be used to estimate total cyanide concentration. It was originally expected to be useful for the zinc and chromium complexes, which release cyanide easily. Neither moderate concentrations of acid nor strong alkali will displace cyanide from iron, cobalt or nickel. EDTA is also reported to be ineffective.

Calculations were made using the equilibrium formation constants for both the complexes Zn(OH)$_4$$^{2-}$ and Zn(CN)$_4$$^{2-}$ and assuming both equations were simultaneously applicable. Solving numerically and assuming a pH of 13 and a low concentration of Zn with a stoichiometric amount of cyanide, it was found that 98% of the Zn would be expected to be complexed by hydroxide. No attempt was made to predict the quantity of mixed complexes of cyanide and hydroxide, although they are expected to exist. Zn containing solutions analysed by the method of additions occasionally gave slightly negative results because of competition. Metals that form insoluble hydroxides or hydrous oxides at this pH, e.g. iron, are less likely to interfere.
II. Cyanate and Ammonia

Cyanate hydrolyzes spontaneously to CO$_2$ and NH$_4^+$ when the pH is lowered to 4 or below. Apparently the same occurs at higher pH, only more slowly. Finding a standard for direct analysis of cyanate would be difficult for this reason, even if a satisfactory method had been found. A blue complex of copper, pyridine and cyanate was examined and found unsatisfactory because chloride formed a similar complex under the same conditions. Therefore cyanate was analysed by reacting with acid and evaluating the resulting NH$_3$.

Approximately 5 ml of sample were poured into a test tube (about 15 ml capacity), and one drop conc. HCl was added. Usually the samples were heated, primarily to encourage the settling of solids, but also to insure the completeness of the reaction. Sweating occurred on the inner sides of the test tubes, but generally the volume did not change significantly.

Iron tends to form Prussian Blue under these conditions. When heated, it tended to coat the TiO$_2$ as it coalesced and settled, thus removing both the complex and the uncomplexed iron from possible interference. It was never demonstrated that zinc interfered in the reaction, but generally a drop of NaOH was added after heating zinc containing solutions to precipitate zinc hydroxide while leaving the pH near neutral. Because of the reaction

$$\text{NH}_4^+ \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_3 + \text{H}_2\text{O},$$

ammonia is potentially volatile in alkaline solution.

Ammonia was then analysed using the Nessler Reaction. The reagent was prepared by dissolving 3.5 g of KI in a small amount of water and adding a saturated solution of HgCl$_2$ until no more would dissolve. Then the solution was filtered and 12 g of NaOH were added. The solution was then diluted to 100 ml.
and allowed to stand overnight. The clear solution was poured into a brown bottle.

The alkaline complex $K_2HgI_4$ forms an amide, $Hg_2I_3NH_2$ that becomes a colloidal solid under conditions of sufficient dilution, suitable for spectrophotometric analysis. It broadens the absorbance of the $HgI_4^{2-}$ complex from the near UV into the visible. It is most sensitive at 400 nm. Unfortunately, colloidal color reactions are very sensitive to conditions which do not affect molecular chromophores. The extent of reaction was dependent on the concentration at the time of the reaction. The fact that what is observed is a shoulder rather than a peak is also a complication. With careful attention to the linear range and allowance for the value of a blank, acceptable results can be obtained.

For cyanate analysis, one ml of solution prepared as described above, was put in a 50 ml volumetric flask, diluted to 35 or 40 ml and 0.4 ml Nessler's Reagent added.

For ammonia analysis, two ml of the original solution were put in a 25 ml flask and 0.2 ml Nessler's Reagent were added. No provision was made for possible interferents. Most of these analyses were done on zinc solutions. The zinc apparently deposited on the $TiO_2$ after some extent of photolysis and precipitated both, removing them from solution. Free cyanide apparently interfered by removing mercury from its iodide complex, yielding results lower than the blank. Adding $HgCl_2$ to take up the free cyanide was tried, but it was found to have the effect of raising the absorbance even of standards which contained no cyanide. Since a high cyanide concentration is not compatible with the expectation of much ammonia, the problem was generally dealt with by analysing only late samples for ammonia.
III. Nitrate

A 0.006 M solution of sodium diphenylamine sulfonate in water was prepared. One ml of sample was placed in a 10 ml volumetric flask, and 1 ml of a 100 g/L solution of KCl was added. (This generally caused TiO₂ to settle out.) The flask was filled to the mark with distilled water. Two ml of this solution were mixed with two ml concentrated H₂SO₄ in a test tube and cooled in ice water. When cooled to 2⁰C or less, the tube was removed, one drop diphenylamine solution was added, and the mixture was poured into a spectrophotometer tube. The absorbance was read at 565 nm usually after about 20 minutes.

This is only a marginally acceptable method. In theory the extent of the color reaction is dependent on the nitrate to the third order. The set of standards run with each batch was different. Given an indefinite amount of time the color apparently would continue to intensify almost indefinitely, possibly because of slow air oxidation. The reaction is not specific to nitrate, and Fe(III) could interfere. It was necessary to run an entire set of standards with each analysis and to keep the concentration of nitrate in the samples within that range. In calculating the results, a line could be fit between any two adjacent standards or a line could be fit using the logarithms of the standards versus the logarithms of the concentrations. In the resulting equation:

\[ \text{conc} = \text{intercept} \times \text{absorbance}^{\text{slope}} \]

the exponent of the absorbance was usually about 0.75.
IV. Fe(CN)$_6^{3-}$ by Prussian Blue

When both free and complexed iron are available in acid solution, the intensely blue pigment, Prussian Blue is formed. Older literature describes both Prussian and Turnbull's Blue, the former supposedly consisting of Fe$^{+3}$ and Fe(II)(CN)$_6$, and the latter from Fe$^{+2}$ and Fe(III)(CN)$_6$. It has been known for many years that the two are one and the same, consisting of Fe$^{+3}$ ions octahedrally coordinating the nitrogen ends of the cyanides bound to Fe(II). Although a demonstration and explanation of this fact, based on simple kinetic arguments, was published in the Journal of Chemical Education in 1937, researchers are still verifying the conclusion by such means as Mossbauer and photoelectron spectroscopies. The reason for doubt is simply that the equilibrium

$$Fe^{+3} + Fe(II)(CN)_6 \rightleftharpoons Fe^{+2} + Fe(III)(CN)_6$$

proceeds far to the right. The constant for the reaction is $K = 10^6$. Therefore only a small fraction of the ions present will be in the correct valence to react. However, as these are removed from solution (to a colloidal solid phase) the equilibrium results in more being formed. Eventually all the cyano complex will be consumed. The size of the primary particles will be limited by the fact that their structure dictates a 1:1 ratio, while their valences are mismatched. The outermost layer of the particles is coordinated with alkali ions in solution. The stability of the sol is not dependent on the pH in the straightforward way of oxide sols. It also seems to bond to glass surfaces as well as to TiO$_2$ particles. It is rarely stable overnight.

The procedure for using the reaction quantitatively had to be developed slowly. The amount of acid has to be controlled because it affects both the
intensity of the observed absorbance and the duration of stability. PVA has no
direct effect on the stability of the Blue particles themselves, but was added to
prevent the precipitation of TiO₂, which would bring down the Blue with it. Fe⁺³
and Fe(III)(CN)₆ react very slowly without a trace of reducing agent, but a
strongly reducing environment can form Fe(II)Fe(II)(CN)₆, a white pigment. The
lack of any reduced iron species was most likely to be a problem in unirradiated
samples. These were also the samples in which a need for added soluble iron
was obvious. Originally, it was assumed that a sample that had reacted long
enough to contain uncomplexed iron would not need any added; however,
FeO(OH) redissolves only slowly in weak acid solutions.

This procedure had to be adapted several times. In early work, PVA was
already present so that all that was necessary was to put a one ml sample in a
25 ml flask and dilute slightly and add 1.0 ml distilled 5% vinegar. In later work,
0.5 ml PVA was added to the sample first and allowed to stand at least half an
hour before proceeding further.

One ml 0.001 M FeCl₃ or Fe(NH₄)₂(SO₄)₂ was added to the unirradiated
sample, which was used as a standard. The Fe(NH₄)₂(SO₄)₂ was discarded
because of its tendency to oxidize. When FeCl₃ began to be used instead (with
a trace of ascorbic acid added) it was observed that absorbances were always
lower. Both iron salts had been dissolved with added acid to stabilize the
solution. Apparently, the acid concentration in the ferrous ammonium sulfate
was much higher, so that even the concentration in one milliter enhanced the
intensity of color. After this a small quantity of strong acid (conc. HCl) was
added with the vinegar.
Reacting mixtures of one ml each 0.001 M FeCl₃ and K₃Fe(CN)₆ at three
different dilutions resulted in three different intensities of color. Therefore it was
desirable to control the quantity of water added. Since samples from later in a
reaction had less complexed iron present, it was appropriate to add less water to
them than to the earlier samples. Less FeCl₃ was also preferrable, since an
excess would tend to accelerate precipitation.

In its final form, the procedure consisted of putting one ml of each sample
into a 25 ml (early in reaction) or 10 ml (late in reaction) flask, adding 0.5 ml PVA
and allowing to stand about a half an hour. A reagent was prepared from 5 ml
vinegar, 45 ml water, one to two drops conc. HCl, and either 1 ml 10% ascorbic
acid solution or a few grains of the dry acid. Five ml of this reagent were added
to the 25 ml flasks and one ml to the 10 ml flasks. Then 0.001 M FeCl₃ was
added in descending quantities from one ml to 0.2 ml. If the color seemed to be
developing too fast more water would be added quickly. The more slowly
developing samples were allowed to stand for up to 20 minutes before diluting.
All were allowed to stand at least one hour before taking readings at 675 nm.
Later samples were also read again after several hours to see if the reading
increased significantly. It was assumed that the highest reading obtained was
likely to be accurate, since both underdevelopment and overdevelopment
produced lower readings.

V. Fe(III) by KSCN

This procedure was used in following only one reaction. It has several
complications, including the possible oxidation of SCN⁻ to (SCN)₂, and the fact
that two different complexes with maxima at different wavelengths can be formed.

Two ml 10% KSCN were placed in a 10 ml volumetric flask, followed by six drops concentrated HCl and a little water. A one ml sample was drawn directly from the reactor and added to the volumetric. The mixture was diluted up and read within 10 minutes at 480 nm.

VI. Fe(II) and Total Available Iron by o-Phenanthroline

1,10-phenanthroline is a bidentate ligand which forms complexes with both Fe(II) and Fe(III). The Fe(II) complex is strongly colored, while the Fe(III) complex has a much weaker absorbance and is blue. The oxidizing potential of the Fe(III) (o-phen)_3 complex is greater than that of aqueous Fe^{3+} so that it tends to be reduced to the Fe(II) complex on long standing, even without a reducing agent.

0.125 g o-phenanthroline was dissolved in 5 ml methanol and diluted to 50 ml with water. The solution was kept in a brown bottle.

Fe(II) was followed in only one reaction. One ml was taken from the reactor and placed in a 10 ml flask with a little water, 4 drops o-phenanthroline and 1 ml vinegar. This was diluted and allowed to stand one hour and then readings were taken at 510 nm.

Total available iron was determined by placing one ml of sample in a 50 ml volumetric. A little water and 0.5 ml o-phen were added followed by one drop conc HCl. A 10% solution of ascorbic acid was prepared as needed. One ml was added to each flask. More water was added followed by one drop 10 M
NaOH. These were diluted to volume and allowed to stand, preferably overnight. Readings were again made at 510 nm.

The results of ferrioxalate actinometry were followed by using the procedure of Halchard and Parker except that the o-phenanthroline used was that already on hand, 0.25g/100ml instead of 0.1 g/100ml. One half ml sodium acetate buffer and one ml o-phenanthroline solution were added to a 100 ml volumetric flask, followed by 1 ml of exposed ferrioxalate, diluted to volume. These samples were kept in the dark until brought to the spectrophotometer. When there was cause for doubt, more o-phenanthroline was added after taking a reading, to verify that the amount present was sufficient to react with all the Fe(II). When a greater amount produced a greater absorbance, the reaction was repeated using shorter exposure times.

VII. Available Nickel by Dimethyl Glyoxime

   When Br₂ is added to a solution of Ni²⁺, and DMG is added, a soluble oxidized complex is produced. Unfortunately for its use in following this reaction, Br₂ also destroys the Ni(CN)₄⁻² complex. In order to separate the liberated nickel from that which was still complexed, an extraction was made into chloroform. In the absence of the oxidizing agent DMG forms a water insoluble complex with Ni²⁺, which is soluble in chloroform. This complex does not displace cyanide completely, but does compete for the complexed nickel in a way that can be fairly well described using the equilibrium constants for the formation of both complexes and solving simultaneously. This was first determined by extracting samples that contained only Ni(CN)₄⁻² at several
concentrations. When the concentration was halved twice, the resulting absorbance decreased by linear amounts.

A reagent mixture was prepared using 11.7 g tartaric acid, 50 ml concentrated NH₄OH, and 10 ml of a 30 g/L solution of DMG in methanol. One ml of sample was placed in a beaker with 5 ml 1% H₂SO₄. Five ml of the mixed reagent were then added. The contents of the beaker were poured into an extraction funnel and extracted with two portions of 5 ml of chloroform. The chloroform was backwashed with dilute ammonia, then the nickel was back extracted into 10 ml of 5% conc HCl in water. After filtering through Na₂SO₄, the HCl containing the nickel was poured into a 50 ml volumetric flask and treated with one ml of a saturated aqueous solution of Br₂ and 5 ml of the mixed reagent. On dilution, it was read at 465 nm.

VIII. Cobalt by Nitroso-R

Nitroso-R is the common name for sodium 1-nitroso-2-naphthol sulfonate when used as a complexing agent for cobalt. Two ml of solution to be analysed were put in a 50 ml volumetric flask. Five ml of a prepared buffer, consisting of 0.1 M sodium acetate with the pH adjusted to 4 using H₂SO₄, and 0.7 ml of a solution of Nitroso-R (0.10 g in 50 ml water) were added. The mixture was heated for 20 minutes below boiling. A reagent blank had to be used to zero the spectrophotometer because the strong yellow color of the unreacted reagent interfered with the red color of the complex at every wavelength.
Procedure

I. Early Work

In early work 100 ml quantities of mixtures of TiO₂, PVA, and hexacyano iron complex (0.001 M), with pH adjusted to 10, were prepared and stored. They were dispensed approximately three ml at a time to quartz cuvets and placed in front of an appropriate light source. Either the loss of absorbance at 420 nm in ferricyanide or the gain in absorbance at the FeO(OH) band edge by both complexes could be followed without loss of the sample, which could then be returned to the light source. The development of analytical techniques that consume reaction mixture was begun using samples illuminated by this method, but obviously not much data could be accumulated, except that the techniques did detect qualitative changes on exposure to light.

In reactions using larger reaction vessels, the reaction mixture was prepared as a batch for each reaction. For the early reactions a generous excess of the mixture was held in reserve for use as a blank or starting basis of measurement as the case might be. In many cases a blank was run along side each later sample. It was possible to confirm that the unexposed mixture remained stable, because it was analysed over an extended period.

No arrangements were made for either stirring or aeration except in the 3.5 L reactor and the light intensity experiments. The lack of aeration contributed to the very low rates observed in the beaker and water filter reactors. Both these reactors were subjected to illumination for four to eight hour periods, as much as possible of a working day, and then the light was turned out and a
sample was removed. Analysis of the sample was performed as quickly as possible after it was obtained and usually none was saved for future comparison.

The time at which the light was turned on, or the sample was exposed to it was recorded to the nearest minute, as well as the time it was turned off, or the sample removed. Because the warm up time of the lamp was short compared to the total time, it was included in the total, if the sample was exposed to it during that time.

II. Reactions in the Large Reactor

The time to complete a reaction in the large reactor, once aeration was installed, was as short as four hours in some cases. Samples were taken without interrupting illumination by withdrawing them from another small inlet using a 10 or 25 ml pipet. Since the same pipet was used throughout a run, it was rinsed with liquid drawn from and returned to the reactor before each sample was taken. The samples were placed in 25 ml vials, labeled with the time to the nearest minute, and accumulated to be analysed in batches. The one exception was cyanide analysis, which in some cases was the only way to determine the end of the reaction. Generally the temperature at the time of sampling was taken and written on the label of each vial. The rate of flow from the exit tube of the cooling water and the flow rate of air were checked at sampling times and adjusted if needed.

The variation of temperature in the reactor never seemed to have a demonstrable effect of the rate, even when a reaction was interrupted and started again later. Peral et al. 78 have reported a value of 5.5 kJ/mol for the activation energy of the oxidation of cyanide on TiO₂. Using this value, the expected difference in rate between the lowest temperature, 24° C, and the
maximum temperature of 46\(^{\circ}\) C, is about 17\%. However, the first ten degrees of temperature increase occurred within the first hour, while the remaining increase occurred gradually over several hours. A 7.6\% change in rate, between 34\(^{\circ}\) and 46\(^{\circ}\), could easily be obscured by the level of uncertainty of the analytical methods.

Once the general pattern of decomposition was delineated, an effort was made to follow reactions just long enough to determine the effect of the varied parameter on rate, and then to dispose of the rest of the cyanide by adding H\(_2\)O\(_2\). This had surprisingly little effect. It worked considerably better if the TiO\(_2\) were precipitated and filtered off first, but that was also time consuming.

III. Light Intensity Studies

Four different strength ferricyanide - TiO\(_2\) mixtures were prepared by adding 5 ml 0.05 M K\(_3\)Fe(CN)\(_6\) to 25 ml volumetric flasks and 5, 10, 15, and 20 ml of a 0.012 M TiO\(_2\) sol. A 0.006 M solution of K\(_3\)Fe(C\(_2\)O\(_4\))\(_3\) in 0.1 N H\(_2\)SO\(_4\) was also prepared.

Three different neutral density filters were used, yielding absorbances of 1.0, 0.60, and 0.40. The same series of experiments was performed for each. First, 3 ml of ferrioxalate, measured with a volumetric pipet, were put in a cuvet which was placed at the front of the slot next to the filter. The capillary tube bubbling helium at a reasonable rate (set at the beginning of the experiments and not adjusted) was added to the cuvet. After taking note of the time to the nearest second, the aluminum flange was rolled into the open position. (The lamp was allowed to warm up for at least 15 minutes before starting). Two or three minutes were allowed, depending on the strength of the filter. The flange was rolled back to the off position. The cuvet was removed from its position to
an area behind the lamp housing lighted by a photographer's red light, and a
one ml aliquot was developed using o-phenanthroline and stored in a cabinet
until several samples accumulated. No reading was taken on any sample that
had not stood at least a half an hour.

Next, a cuvet of distilled water was placed in front of the filter and another
cuvet of ferrioxalate was placed directly behind it. The oxygen capillary was
placed in the distilled water and the helium capillary in the ferrioxalate. They
were exposed to light for the same amount of time as the previous sample. Then
the ferrioxalate was analysed and stored. Then a ferricyanide - TiO₂ sample,
also measured with a 3 ml pipet, was put in front with another ferrioxalate
sample in back. Illumination times given to these were 20, 15, and 10 minutes
each for the three different filters. The ferricyanide samples were stored in 5 ml
vials and developed later as a group. The ferrioxalate samples were all
developed as described.

There was quite a bit of scattered light from the sides of the lamp housing
and from unfocussed light even in the area where the samples were prepared.
For one 30 minute run a cuvet was placed behind the wooden blocks on which
the sample cuvets stood, so that it received reflected light from the walls and
during any time that the door of the darkroom was open. It was brought through
the development process along with the sample that had been exposed to direct
light (that is the direct light that was transmitted by the ferricyanide - sol sample).
The absorbance of the developed sample was 0.031. A correction to all
readings based on 0.001 per minute of exposure was made in the calculations.
Observations

I. Preliminary Work

Several useful qualitative observations were made before systematic quantitative work began.

A dark reaction of $\text{K}_4\text{Fe(CN)}_6$ and an unexpected photoreaction were stumbled upon while investigating a reported homogeneous reaction. A 0.001 M solution of ferrocyanide was prepared and put in a cuvette in front of the 100 watt mercury vapor lamp. After several hours, the light was turned off and the yellowing of the previously pale liquid was noted. The report that ferrocyanide was converted to ferricyanide was confirmed. The following day an orange precipitate was found at the bottom of the cuvette, obviously Fe$\text{O}$(OH).

This was unexplainable at the time, and surprising considering the reputation for stability of both cyano complexes. Then since it was both more accurate and more convenient to make a concentrated stock solution for further work, a 0.01M ferrocyanide solution was prepared. At the time, it was noted in the lab notebook that an error must have been made in weighing in preparing the first solution since it was more intensely yellow than the ten times stronger solution. After 48 hours, however, the colors of the two were in the expected proportion. It was concluded that contact with oxygen in solution had oxidized the ferrocyanide.

On very long standing – on the order of six months - Fe$\text{O}$(OH) can be found at the bottom of a solution of ferricyanide. Thus, while the complexes are stable enough to be a challenge to dispose of, they are far from inert.

A mixture containing only TiO$_2$ and PVA was irradiated to determine if PVA was degraded to carbonate. A spot test (two drops of CaCl$_2$) proved
negative, but during the time of exposure a dark blue color appeared in the liquid. This was the Ti(III) surface state, which occurs only when all dissolved oxygen has been exhausted. When working with PVA it was a fairly common occurrence. That it was observed under these conditions was fortunate, since it excluded the possibility that the color was due to a byproduct of iron-cyanide decomposition.

The anaerobic condition slows reaction drastically, but it was ideal for pursuing the first expected intermediate in the decomposition of ferrocyanide, Fe(CN)$_5$H$_2$O$^{-3}$. Under oxygen free conditions $N_3^-$ can displace the water producing a purple complex. The reaction has been observed in the homogeneous photochemistry of ferrocyanide, but was never seen when TiO$_2$ was present. After reproducing the literature for the homogeneous reaction, and still finding nothing under the same conditions for the sensitized reaction, it was concluded that the pentacyano complex is never present in significant quantity in the presence of TiO$_2$.

When the mercury lamp burst, other sources of light had to be employed and therefore two of Bhakta's experiments were replicated. (Several complexes other than ferricyanide had been mixed with TiO$_2$-PVA and spectra taken. TiO$_2$ obscured the spectral features of all of them. Therefore ferricyanide was the only choice for this experiment.) Cuvettes were filled and placed outdoors in the sun. It was eventually possible to confirm a reaction spectro-photometrically. It was slower than artificial light, probably because the shape of the cuvette was less efficient for overhead illumination.

Indoors, four watt lamps were used. Every hour to two hours, the cuvette would be removed from its stand in front of the lamp and a scanning spectrum
taken. The changes in absorbance were measured and an attempt was made to calculate the rate. A first order rate looked almost plausible when plotted, but a zero order rate of $3.75 \times 10^{-6}$ M/min fits the data. At the time, it was assumed that this was the rate of decomposition of the complex.

A mixture of TiO$_2$ - PVA with 0.001 M FeCl$_3$ with the pH adjusted to 10 was prepared to simulate the expected end product of the reaction. It showed substantial absorbance as high as 500 nm and went off scale at 400 nm, approximately 40 nm sooner than the TiO$_2$ alone. It was immediately obvious that this product was not present in the reaction just observed. Several attempts were made to simulate a hypothetical Fe(II) end product, but these either produced FeO(OH) or a green half oxidized product.

When the 100 watt lamp was replaced, one reaction was done in the "beaker reactor". 75 ml of the isopropoxide sol and ferricyanide to make a 0.001 M solution were diluted to 100 ml. Most of this was put in the reactor, with 10 ml reserved for comparison. This reactor was illuminated during working days for several weeks. At the end of the day a sample was taken from the reactor to fill a cuvette. The decline in absorbance was followed as before, but the contents of the cuvette were then analysed in various ways. Prussian blue prepared with Fe(NH$_4$)$_2$(SO$_4$)$_2$ declined in absorbance steadily, as the absorbance due to ferricyanide declined, but when prepared with FeCl$_3$, it increased almost proportionally. It was possible to detect both Fe(II) and Fe(III) as uncomplexed species by the end of thirty hours, although not in high proportions. The pH declined throughout the experiment as well. This was commonly observed while working with TiO$_2$ sols; the cause was never resolved. Additional NaOH was added at 18 hours; the pH rose to 11, but then gradually declined to 9 by 29
hours. After 29 hours the lamp had become too unstable to operate in a horizontal position and the experiment was discontinued.

The objective at that time was to confirm that the reaction between TiO$_2$ and ferricyanide did proceed beyond simple change of valence to decomposition of the complex. Although it was not possible to follow the reaction to completion, (The sol was precipitating by the time the experiment was abandoned.) the reactions with o-phenanthroline and thiocyanate confirmed that there were methods that discriminated between complexed and uncomplexed iron. It was hoped that methods could be found to follow the decomposition of all the transition metal complexes.

The fact that reaction in the beaker had to be followed more nearly by days than hours is an indication of the inefficiency of its geometry. It is unlikely that light of any wavelength absorbed by TiO$_2$ reached more than half the solution. In fact, the beaker had the benefit of a greater interface with the atmosphere than the cuvettes, and was making more efficient use of the light that reached it. The IR water filter that replaced it shared its inefficient shape, and when full excluded almost all air. It was only used for two reactions, one with Ni(CN)$_4$$^{-2}$ and one with ferrocyanide. The reaction of the nickel complex is described later. The other was the first reaction to be demonstrated to have reached completion.

The 0.001 M ferrocyanide-TiO$_2$-PVA mixture was originally prepared for use with the cuvettes and had stood on the shelf for several months. Tests for uncomplexed iron of either valence gave an insignificant response although the pH was down to 9. It was illuminated for several days without correcting the pH. Very little reaction was observed during that time except the further deterioration
of the pH to 8. In theory, HCN can form at a pH of 8, if CN⁻ is present, making possible the loss of cyanide by evolution. The pH was corrected and thereafter followed systematically. Approximately three ml of liquid were removed for analysis daily. After several days the interface of the liquid with air had increased dramatically, and so did the rate of reaction. The fact that any reaction was observed at all, was probably due to the fact that more hours were spent overnight passively dissolving and diffusing oxygen than under illumination. For the first several days, the blue color of Ti(III) was observed; then significant reaction began. The graph on the following page shows the rates of appearance and disappearance of various iron species. Each point on the graph represents one milliliter removed from a 90 ml container. By the time the reaction was over another kind of inefficiency was obvious: Much of the light was shining through the empty portion of the reactor. No attempt is made to quantify the rate or fit the data to a curve. It should be zero order in ferrocyanide and this is plausible from the time that aeration existed in the reactor. However, it is evident that conditions changed considerably over the course of the reaction, making the value of a rate constant doubtful.
Figure 3. Photochemical Decomposition of Ferrocyanide in the presence of TiO$_2$ and PVA
Reactions with $K_2Zn(CN)_4$

I. Zinc cyanide in the presence of PVA

Zinc does not form a particularly tenacious complex with cyanide. If there were any difficulty disposing of cyanide while in the complex, it could be easily displaced by raising the pH to 13. The logarithms of the overall formation constants for the tetracyano and tetrahydroxo complexes from $Zn^{+2}$ and anions are $\beta_4=19.6$ and 17.6, respectively. 89,90 By solving the two equilibrium equations simultaneously, it can be shown that at least 97% of the cyanide will be displaced at high pH. There is, however, an economic interest in disposal of zinc plating wastes, which motivated the inclusion of zinc cyanide in the compounds to be studied. It was the first reaction to be studied in the large reactor.

This first effort is illustrated in Figure 4. This was the last reaction to be done using PVA. The sol coagulated in spite of its presence soon after exposure to light. Stirring kept the bulk of it in suspension. The first three hours of reaction without aeration produced a deep blue color, especially at the bottom of the reactor, but very little loss of cyanide. When an air pump was obtained, it could not be used continuously because of the foam generated in the presence of PVA. A valve was obtained to restrict the flow and the reaction was finished at a much faster rate. In the course of this reaction, much was also learned about the difficulty of keeping the vessel cool. At one point the flow of cooling water diminished to practically nil and the temperature in the reactor reached $74^\circ$ C. The average temperature, even with the cooling water running was probably $52^\circ$ C. The procedure was changed to include checking the flow of cooling water periodically, and for later reactions, the reactor was placed in a
Figure 4. Disappearance of Cyanide from Millimolar Zinc Cyanide Using TiO₂ in the Presence of PVA
four gallon bucket and immersed in water.

Even with extraordinary temperatures, the reaction from the beginning of aeration took seven hours. By this time it was known that PVA competed with cyanide for oxidation. As the cyanide decreased, the quantity of PVA was negligibly diminished resulting in the decreasing rate at the end of the run. The yellow color that was present at the end of the reaction after all TiO₂ had separated (and the zinc apparently with it) could only be caused by oxidation of the PVA. A short reaction with only PVA and TiO₂ in the reactor confirmed this.

The end product of this reaction and the Zn(CN)₄⁻² reaction were analysed for carbonate, and significant amounts were found in both, but since aeration would add CO₂ this was inconclusive. (A tube of ascarite was added to the line that brought the air into the reactor at that time.) The dried remains of the PVA were ground with KBr and pressed to take an IR spectrum. The spectrum revealed the presence of double bonds, whether carbonyl or olefinic was difficult to resolve. This suggested that the oxidation of alcohol to ketone was occurring. Whether any further oxidation occurred could not be proved by this technique.

II. Effect of Concentration of TiO₂ on the Rate of Decomposition of Zinc Cyanide

The factors either known or expected to have an effect on the rate of reaction are light intensity, temperature, pH, surface area of catalyst, and availability of an electron acceptor, i.e. O₂. Since light intensity could not be varied in this reactor, and temperature could only barely be controlled, only the last three could be examined. A series of reactions were run with decreasing amounts of TiO₂, expecting to find decreasing rates. All reaction mixtures
contained 0.001 M K₂Zn(CN)₄ and 1 ml/L of 10 M NaOH to give a supposed pH of twelve, though it was usually less because of the buffering effect of the sol. The valve controlling the air flow was not adjusted during this series of runs. The temperature, though it increased as much as 17° C in the course of a run, always did so at approximately the same rate. The surface area of the catalyst was not known at that time, but since all were prepared in the same way, they could be assumed not to vary greatly from batch to batch. Expressed as a not quite appropriate molar concentration, the three reaction mixtures contained 0.010 M (0.8 g/L), 0.006 M (0.48 g/L), and 0.004 M (0.32 g/L) TiO₂. They yielded rates for disappearance of cyanide of 1.79x10⁻⁵, 1.76x10⁻⁵ and 1.67x10⁻⁵ M/min respectively. The difference in the rates is so slight as to give the appearance that the reaction is zero order in catalyst as well as substrate. The three are compared in the graph in Figure 5.

A fourth batch was prepared. The reactor was deliberately filled to only two thirds of its capacity. The same quantity of K₂Zn(CN)₄ was used as had been used in the higher volume reactions, but 1 ml / L of NaOH was added only for the volume actually present. No TiO₂ at all was put in the mixture. It was assumed that no significant reaction would occur and that it would be necessary to add TiO₂ as soon as the point had been proven. Instead the reaction proceeded more rapidly than the previous ones. A linear fit to the data for the first two thirds of the reaction gave 2.24x10⁻⁵. Toward the end, the rate decreased and some TiO₂ was added to speed it up. In reality, this reaction was first order in the zinc cyanide complex, as the graph in Figure 6 shows. The first order rate constant is 0.0087/min.
Figure 5. Compared Rates of Decomposition for Tetracyanozincate with Three Different Concentrations of TiO₂
Figure 6. Homogeneous Decomposition of $K_2Zn(CN)_4$
with first order fit, from which data points diverged after addition of $TiO_2$
A UV spectrum of $\text{K}_2\text{Zn(CN)}_4$ reveals that it only absorbs in the far UV and very weakly compared to TiO$_2$. Since the solution used for the spectrum was alkaline, of course, both zinc cyanide and zinc hydroxide were present in the spectrum. Zinc hydroxide can be seen as a precursor molecule of ZnO, which is also a semiconductor. Charge transfer from hydroxide to zinc would be the nearest equivalent to excitation to the conduction band. It may also be that coordination to zinc stabilizes a charge transfer from the cyanide and that this begins the oxidation process directly, provided O$_2$ intercepts the electron before it returns to the cyanide. In either case, there is a homogeneous decomposition of the zinc cyanide complex. Because the TiO$_2$ has a much higher extinction coefficient, it must block most of the homogeneous reaction when it is present, but the efficiency of the homogeneous reaction is much greater. The reaction observed in the varied concentrations of TiO$_2$ must be the sum of the two reactions.

Methods of analysing for further products of reaction were developed at this time. Cyanate, ammonia and nitrate were followed for most zinc cyanide reactions. It was observed that concentrations of nitrate remain virtually nil until nearly all the cyanide is gone; in fact cyanate is only slightly attacked until after cyanide is no longer present to compete. Ammonia may be formed catalytically to the extent that cyanate is attacked; however, it is as likely, as Hidaka$^8$ et al. have suggested, that it occurs as a product of hydrolysis. The graph in Figure 7 is typical of the results observed.

* Reduction of nitrogen to ammonia is energetically possible and judging by the results of Low et al.,$^{53}$ more likely as long as carbon is present to be oxidized.
Figure 7. Formation of Decomposition Products in $K_2Zn(CN)_4$
III. Effect of Flow Rate of Air on Decomposition of Cyanide

When a flowmeter was added to the air train, it made it necessary as well as possible to optimize air flow. Considering the similarity of all the observed rates, it was reasonable to suspect that availability of O$_2$ was the limiting factor. Neither the solubility of oxygen in water nor its adsorption on TiO$_2$ are very great. The range of the air pump was somewhat limited as well, but it could be varied enough to determine if higher rates were within easy reach. First a reaction using only 0.16 g/L TiO$_2$ was run at what was believed to be the flow rate of the previous reactions, 0.1 L/min. It gave a rate of $2.11 \times 10^{-5}$ M/min, a little faster than the earlier rates. Then another batch was run using the same amount of sol and a flow rate of 0.25 L/min. The rate was $1.26 \times 10^{-5}$ M/min. The sol used in the second run was from a different batch. It seemed possible that the reversal of the expected increase in rate was caused by larger particle size, resulting in lower surface area. Another reaction 0.007 M in the same sol was run at the same air flow rate. If more surface area was needed, this should have provided it. This time, the rate was only $1.20 \times 10^{-5}$ M/min. By now the possibility of contamination of the sol was the only alternative to the idea that an excess of oxygen, or some other component of air, adversely affected the rate. A small bottle of O$_2$ replaced the air pump in one more reaction. This time the concentration of TiO$_2$ was 0.003 M, from a new batch of sol. If oxygen could adversely affect the rate, the use of pure O$_2$ should enhance the effect; if contamination were the cause, it should be eliminated and the effect of the higher concentration of available oxygen should be apparent. In fact, the rate determined for this run was $1.55 \times 10^{-5}$ M/min, almost back to normal, but
nothing exceptional. It leads to the conclusion that the amount of oxygen that can react with the sol has been provided, that an excess has no effect, and that a flow rate of 0.1 L/min is apparently adequate.

Reaction with KCN

One reaction with 0.004 M KCN and 0.8 g/L TiO₂ sol was run to compare with literature values and with reactions of zinc cyanide complexes. The rate found was 1.20 × 10⁻⁵ M/min, about 30% lower than the best rates for the zinc cyanide complex. This suggests that even at the highest concentration of TiO₂, which was the same concentration used for KCN, the homogeneous reaction makes a significant contribution. A graph of the reaction of KCN is shown in Figure 8.

An attempt was made to correlate this rate with those already available in the literature. A difficulty arose because the available published rate constants are expressed as pseudo-first-order rate constants. A 'rate constant' can be extracted from the KCN data by imposing a least squares fit on the logarithms of the data points. It can also be demonstrated that it is a much poorer fit than the simple linear fit.

The table on page 69 compares some published first order rate constants for this reaction. It can be seen that despite variations in pH, light intensity, and quantity and surface area of catalyst, the closest correlation is between rate constant and initial concentration. Rose and Nanjundiah ²⁹ acknowledge that at high concentrations and high light intensities a linear rate with no dependence
Figure 8. Photocatalysed Decomposition of Potassium Cyanide
on [CN⁻] is observed. Pollema et al. 79 suggest that their apparent first order rate constant is a special case of Langmuir - Hinshelwood kinetics:

\[
d[CN^-] / dt = kK[CN^-] / (1+K[CN^-])
\]

(in which K is an equilibrium constant for the adsorption of CN⁻, and k is a pseudo first order rate constant for oxidation of CN⁻). If \( K[CN^-] >> 1 \), k will be the dominant factor, and [CN⁻] is effectively cancelled.

It is generally agreed that reactions on TiO₂ give a pattern that is at least close to the L-H expression; it is also agreed that negatively charged ions do not adsorb on negatively charged surfaces. The ingredient that is adsorbed on the surface and whose concentration is necessarily proportional to it is OH. As Serpone et al. 66 point out, L-H kinetics are merely a special case of saturation kinetics. Turchi and Ollis 91 have generated equations to describe all possible cases of adsorbed and desorbed reactions and found that experiment would not be able to determine whether the reactant were adsorbed or only the hydroxyl radical. In fact, the Langmuir - Hinshelwood equation can apply although the assumptions behind it do not. K must be reinterpreted as an expression for the equilibrium concentration of hydroxyl radicals on the surface.
First Order Rate Constants for Cyanide Oxidation on TiO\textsubscript{2}

<table>
<thead>
<tr>
<th>Source</th>
<th>[TiO\textsubscript{2}]</th>
<th>pH</th>
<th>[CN\textsuperscript{-}]</th>
<th>light</th>
<th>k</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>g/L</td>
<td>mol\textsuperscript{a}</td>
<td>E/min</td>
<td>min\textsuperscript{-1}</td>
<td></td>
</tr>
<tr>
<td>Rose and Nanjundiah\textsuperscript{29}</td>
<td>10</td>
<td>11</td>
<td>0.001</td>
<td>7.1x10\textsuperscript{-5}</td>
<td>2x10\textsuperscript{-2}</td>
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<tr>
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<td>5</td>
<td>11</td>
<td>0.001</td>
<td>7.1x10\textsuperscript{-5}</td>
<td>1.2x10\textsuperscript{-2}</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>11</td>
<td>0.001</td>
<td>7.1x10\textsuperscript{-5}</td>
<td>1.0x10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Peral et al.\textsuperscript{78}</td>
<td>5</td>
<td>13</td>
<td>2x10\textsuperscript{-4}</td>
<td>9.2x10\textsuperscript{-4}</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10.5</td>
<td>2x10\textsuperscript{-4}</td>
<td>9.2x10\textsuperscript{-4}</td>
<td>0.61</td>
</tr>
<tr>
<td>Hidaka et al.\textsuperscript{8}</td>
<td>2</td>
<td>12</td>
<td>0.02</td>
<td></td>
<td>1.3x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Pollema et al.\textsuperscript{79}</td>
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<td>10</td>
<td>4x10\textsuperscript{-4}</td>
<td></td>
<td>0.36</td>
</tr>
<tr>
<td>This work</td>
<td>0.8</td>
<td>10</td>
<td>0.001</td>
<td>0.0146 \textsuperscript{*}</td>
<td>0.011</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Estimated from data supplied by Ace Glass, using power estimates only for wavelengths shorter than 400 nm.
Reactions with Ferricyanide

I. Effect of Varying the Concentration of TiO$_2$ at pH 10

The reaction with ferricyanide was more sensitive to the concentration of TiO$_2$. Reactions with three different concentrations of sol were compared: 0.004 M, and 0.006 M, 0.008 M. The reaction at 0.006 M is shown on the following page. A comparison of the three concentrations (see Figure 11) shows, as would be expected, that the rate increases with increasing concentration of TiO$_2$. It is tempting to assign a first order rate constant for the decrease in ferricyanide, which can be made to fit an exponential curve with some plausibility. In fact, rate constants derived from such a fit, 0.0018 min$^{-1}$, and 0.0041 min$^{-1}$, 0.0074 min$^{-1}$, respectively, are proportional to the squares of the concentrations of TiO$_2$. It should be noted that this fit is seriously flawed in the initial stages of reaction.

A plot of the concentration of uncomplexed iron on a logarithmic scale clearly shows two different straight lines: the early one steep, and the late one almost flat, simply a more exaggerated version of the original curves. No attempt has been made to extract a first order rate constant from these data. The ferricyanide concentration should be the mirror image of uncomplexed iron. The fact that it is not is, possibly, due to free cyanide ions which may recombine with iron under the conditions of the Prussian blue reaction, but which are excluded by the reaction with o-phenanthroline. In any case, the difference underscores the fact that the initial rates of both are much faster than the later reaction.
Figure 9. Decomposition of Ferricyanide with Illuminated 0.48 g/L TiO$_2$
Figure 10. Decrease in Ferricyanide and Increase in Available Iron at pH=10.5, showing dependence on the concentration of TiO$_2$ and apparent first order dependence on the concentration of ferricyanide at low concentrations; red, 0.64 g/L TiO$_2$; green, 0.48 g/L TiO$_2$; blue, 0.32 g/L TiO$_2$
The pH in this set of reactions was set to ten by adding 0.3 mls of 10 M NaOH to the reactor. However, it was observed that once the light was turned on the pH subsided to 9.5 or 9. This pH borders on permitting formation of HCN. With air bubbling through the mixture during the reaction, the chance of losing cyanide by vaporization rather than photodecomposition would be a concern. Cyanate was analysed for two of these reactions and, in fact, concentrations as high or higher were found than in later reactions at higher pH. During these first three reactions, cyanide content was being followed by the Prussian Blue reaction, which detects only the iron-complexed cyanide, because it was assumed that free cyanide would be negligible. Later, the run with 0.48g/L TiO₂ was repeated with a cyanide analysis. It confirmed that at this relatively low pH, cyanide tended to remain bound to iron; however, enough was released into solution to be detected easily by the cyanide electrode. The results of this reaction are shown in Figure 12.

The direct photolysis of K₃Fe(CN)₆ was also observed at this pH. It is illustrated in Figure 13. Relatively few samples were taken during this reaction because it was not expected to proceed very quickly or very far. Obviously, this was a bad assumption. The results are comparable with those of Rader et. al. except that less cyanate is formed. Their reaction proceeded to complete dissociation of the complex, and it seems obvious that this reaction would have also. There is also, to some extent, oxidation of the cyanide ion. Unlike the reactor of Kisaki et. al., 24 which reported total decomposition of cyanide, there is no radiation as short as 187 nm available (at least, it is not mentioned in the literature furnished by the manufacturer.) so neither OH⁻ nor CN⁻ can be oxidized directly by the available light. All the cyanate that formed in the Nevada
Figure 11. Decomposition of Ferricyanide with Illuminated 0.48 g/L TiO$_2$ Showing Liberation of Cyanide Ions
Figure 12. Comparison of Rate of Homogeneous Reaction with Photocatalysed Reaction at pH 10; Increase in Available Iron, Above; Decrease in Ferricyanide, Below
red, 0.64 g/L TiO₂; green, 0.48 g/L TiO₂; blue, 0.32 g/L TiO₂; black, 0.0 g/L TiO₂
group's reaction formed while the ferricyanide complex was still in existence. Oxidation of free cyanide to cyanate by reducing ferricyanide to ferrocyanide is a known reaction. The ferrocyanide is capable of being re-oxidized by O₂ in solution. These are dark reactions and the first, at least, must be fairly slow. The time scale of the sunlight reaction (days as opposed to hours) allows it to occur to a significant extent. The more likely oxidant in the reactor is FeO(OH), which has some photocatalytic capacity, although much less than TiO₂. This can explain why the rate of cyanate formation seems approximately constant while the concentration of ferricyanide drops to 20% of its initial value as FeO(OH) takes its place.

A comparison of the direct reaction with the sensitized one, as illustrated on the following page, shows that the rate at which the complex disappears and the uncomplexed iron appears is between that of the maximum and minimum concentrations of TiO₂ and close to that of the 0.006 M reaction. The rate of release of free cyanide is much higher, and the rate of its oxidation much lower, as discussed above. The mechanism for the direct photolysis is not certainly known. It is obvious, however, that if the catalysed reaction is slower than the direct reaction, as is the 0.004 M reaction, the catalyst must be interfering with the direct reaction, probably by absorbing light of the wavelength involved in the direct reaction. The fact that a higher concentration of catalyst then gives a higher rate suggests that the catalysed reaction is not dependent on the direct reaction. That is, the TiO₂ is not simply oxidizing the free cyanide ions released by the direct reaction.
Fraction of starting material

Time in Minutes

- Free Cyanide
- Uncomplexed Iron
- Ferricyanide
- Cyanate
- Total Cyanide

Figure 13. Homogeneous Reaction of Ferricyanide in UV Light
II. Effect of Varying pH

Two reactions were run with 3 mls rather than 0.3 mls of 10 M NaOH added, at 0.48 g/L and 0.72 g/L TiO₂, and one with 30 mls NaOH and 0.72 g/L TiO₂. The pH paper could only confirm that the pH was at least 11, but it can be estimated that 3 mls should produce a pH of around 11.5 and the 30 mls should be approximately 13. The 30 ml mixture definitely did exceed the buffering capacity of the TiO₂. In fact, it raised the electrolyte concentration to the point of coagulating the sol even before the light was turned on. The reaction was allowed to proceed. With stirring and air, the particles remained in suspension. The loss of surface area could not be estimated, but the general pattern of reaction at high pH could be observed.

The results of these reactions, as indicated in the graphs in Figures 15 and 16, present a different picture from the reaction at pH 10. There are two different reactions occurring: dissociation of the complex and oxidation of cyanide. The dissociation of the complex occurs at virtually the same rate in all three, and faster than it does at pH 10. Free cyanide rises to a higher concentration at the higher pH. There is no apparent dependence on the concentration of TiO₂. Obviously, the pH is having some effect, but it is not proportional to [OH⁻].

The rate of oxidation of cyanide can be seen by adding the results of free cyanide to 0.006 x the Prussian blue result. As shown in Figure 15, the rates at all pH's are best described as linear. They are all comparable to the rate for oxidation of KCN, varying between 0.0112 and 0.0121 mmols/min, except for the reaction at pH 13, with a rate of 0.009 mmols/min. The rates are not directly
Figure 14. Rates of Disappearance of Cyanide from 0.001 M Ferricyanide at Various pH and TiO₂ Concentrations
Figure 15. Comparison of Rate of Homogeneous Reaction with Photocatalysed Reaction at Higher pH; Increase in Available Iron, Above; Decrease in Ferricyanide, Below
red, 0.48 g/L TiO₂, pH=11.5; green, 0.72 g/L TiO₂, pH=11.5;
blue, 0.72 g/L TiO₂, pH=13; black, 0.0 g/L TiO₂, pH=10.5
proportional to the concentration of TiO$_2$, if at all, and no dramatic difference is observed with the change in pH. The lower rate at pH 13 may be due to lower surface area after agglomeration, but is more likely associated with a decrease in surface hydroxide. (At very high pH, some surface hydroxide may be deprotonated.) A third possibility is that increasing negative charge on the TiO$_2$ increasingly repels the anionic reactants.

The likeliest explanation for the virtual equality of the rates of complex dissociation at pH>11 is that the rate determining step is not photocatalysed.

The reaction:

$$H_2O + [Fe(CN)_{6}]^{3-} \rightleftharpoons [Fe(CN)_5OH_2]^{2-} + CN^- \quad (1)$$

is reported to occur as both a (direct) photoreaction and a thermal reaction. The back reaction is ordinarily very fast, unless a more stable substituent than water is available. Several stable pentacyano complexes with nitro, nitroso, ammine, azido, phosphine, and sulfite ligands have been prepared and described in the literature. No stable pentacyano complex with hydroxide has been reported.

Since the ferricyanide complex is thermodynamically unstable relative to FeO(OH), it is reasonable to speculate that the hydroxopentacyano complex is inherently unstable, resulting in the reaction:

$$2OH^- + [Fe(CN)_5 OH]^3- \rightarrow FeO(OH) + 5 CN^- + H_2O \quad (2)$$

$pK_a$ for the reaction:

$$[Fe(CN)_5 OH_2]^2 \rightleftharpoons [Fe(CN)_5 OH]^3- + H^+ \quad (3)$$

is not known, but estimating a value near 10 allows an explanation of the observed rates of complex dissociation. As a photoreaction, reaction (1) should not be directly affected by the pH. Equilibrium (3) determines whether the aquopentacyano complex survives long enough for the reverse reaction to
occur. (It is necessary to assume that equilibrium is reached in the amount of
time that it takes for the cyanide ligand to return to its original position.
Considering that a proton is a smaller, more mobile particle, and that at pH>11
there are more hydroxide ions than cyanide ions in solution, this does not seem
too unreasonable). Once the pH is higher than 11, the hydroxopentacyano
complex would be formed almost every time reaction (1) occurs. Reaction (2)
is expected to be irreversible.

As stated above, the fact that at pH ~10 the photocatalyst, at low
concentration, slows and, at higher concentration, accelerates the dissociation
reaction, suggests that TiO₂ must be reacting directly with the complex, rather
than simply consuming displaced cyanide ions. The same thing must still be
occurring at the higher pH's. The fact that at higher pH's neither this reaction
nor the oxidation of cyanide show any dependence on the concentration of TiO₂
is harder to explain. Both Peral et al. and Pollema et al. report finding a
maximum useful amount of TiO₂ beyond which no detectible improvement in rate
was observed. In both their experiments the reason appears to be the limit of
the available light. In this reactor, however, the available light is greater and the
quantity of TiO₂ absorbing it is smaller, although the surface area may be as
great or greater. Something still appears to be limiting the reaction. Since
oxygen is presumed to be the adsorbed reactant, which by consuming electrons
determines the quantity of holes which cannot recombine, it must be suspected.

Either the rate at which O₂ can diffuse into solution or the rate at which it
adsorbs could limit the rate of oxidation of cyanide. The quantity of O₂ which is
adsorbed when TiO₂ is exposed to UV light has been measured in the gas
phase.²¹ The quantity found is 0.366 molecules/ nm². Whether this number is
applicable to aqueous solution is uncertain, but it is reasonable to assume it is
not higher in solution. It should be somewhat dependent on the concentration of
oxygen in solution. The saturation concentration of oxygen in aqueous solution
can be calculated from:

\[ C = 0.02925 \text{ M} \times 0 \text{ C}^{-1} \times (31.6 \text{ C} + T (\text{ C})) \]

for temperatures less than 50°C and pressures less than 4 atmospheres.\(^9\)
Assuming the pH has no effect on solubility of O\(_2\), the concentration present at
the start of a reaction should be 5.3 \times 10^{-4} \text{ M}. The solubility at 46°C, the apparent
equilibrium temperature of the reactor at long times, would be 3.8 \times 10^{-4} \text{ M}. At
the most optimistic estimate of the surface area of the TiO\(_2\), this quantity would
have to 'turn over' three times to be consumed. Unfortunately a turnover rate for
O\(_2\) is not available.

Since both the cyanide ion and the complex are negatively charged,
neither adsorbed on the TiO\(_2\) nor attracted to it, the reaction with holes provided
by the consumption of electrons by O\(_2\) is not likely to be 100% efficient.
However, the next likeliest reaction for these holes is the oxidation of water to
produce O\(_2\). Hence, this inefficiency is not greatly depletion the dissolved
oxygen. If consumption of oxygen is estimated from the rate of cyanide oxidation
alone, it takes over half an hour to consume the oxygen initially present. In this
amount of time, it is hard to imagine that stirring and air bubbling could not
replace the oxygen consumed. Given a stable concentration of oxygen in
solution, adsorption is dependent on surface area; rate of adsorption is not a
reasonable explanation for the lack of dependence on surface area.

At this point the only limitation left is available light. A scanning spectrum
was obtained using a 1:50 dilution of a 0.012 M sol. It was used to estimate
coefficients of extinction at various wavelengths. By using this dilution and a scale of 0 to 4.0 absorbance units, it was possible to keep the entire spectrum on scale and verify that it was within the limit of detection. No correction was made for scattered light. At near visible wavelengths none appears to be needed. Considering that the radius of gyration is more than half of 200 nm, scattering should be expected to make some contribution at that end of the spectrum. Unless it increases quite dramatically between 350 nm and 220 nm, it can probably be neglected, compared to the magnitude of the absorption. From these values it is easy to determine that even the 366 nm line will be greatly diminished by the time it traverses 3 to 5 cm from the immersion well to the edge of the reactor. A 50% increase in concentration means only that the volume of solution that effectively participates in the reaction is smaller. Therefore, even in this reactor, the rate is limited by the available light.

III. Reactions of Ferricyanide with P25

Two reactions were followed with DeGussa P25, one at 3 g/L and one at 0.5 g/L. The pH of the former was >11 and the latter was 10.5. The 3 g/L concentration was expected (at best) to have similar or slightly greater surface area to 0.72 g/L sol. The mass of TiO2 present was four times as much and the absorbance per volume was correspondingly greater. It is, therefore, not surprising that the rate was substantially slower. The second concentration was run to see what effect concentration would have on the rate. It was slower, although not proportionally. This quantity is actually lower than the weight concentration of the sols, but light scattering was much greater. Even the lower concentration produced a milky opaque appearance in the reactor. If Raman
scattering is significant for TiO$_2$, the useful light could be attenuated by scattering; otherwise, visual impressions notwithstanding, available UV light should not be decreased, only redirected.

The result of these reactions are shown in Figures 17 and 18. No available iron was analysed, since it is precipitated on the particles. The powder had to be removed by filtration before any photometric procedure could be used. The rate calculated for destruction of cyanide for the 3 g/L run is $k = 0.0092$ mmol/min. If only the first seven hours results are considered, the rate becomes $k = 0.0116$ mmol/min, comparable with the results for the sols. The reason for the decrease, which is much more pronounced in looking at the free cyanide analysis, was discovered when the reactor was shut down and the immersion well was removed. The well was coated with a dark orange mixture of TiO$_2$ and FeO(OH). When this was removed and the reactor was restarted the remaining cyanide decomposed in a reasonable amount of time.

The tendency of P25 to coat the immersion well was observed in other reactions as well. It is reasonable considering that more of the light is absorbed in a volume close to the well. It may also have to do with aging of the immersion well. Because of concern that TiO$_2$ could become permanently bonded to the quartz, the immersion well was always stored in 1:3 HCl when not in use.

The rate of the 0.5 g/L reaction was 0.0044 mmol/min. This was calculated from the inverse of the increase of cyanate; the apparent horizontal line for total cyanide is due free cyanide recombining with iron in the Prussian blue reaction and thus being counted twice.

This reaction was not discontinued at the point, but data beyond this point were distorted by an attempt to increase the rate. The precipitation of easily
Figure 16. Decomposition of Ferricyanide in the Presence of 3 g/L of P-25, blue, ferricyanide; red, free cyanide; green, total cyanide; cyan, cyanate
Figure 17. Decomposition of Ferricyanide in the Presence of 0.5 g/L of P-25. Blue, ferricyanide; red, free cyanide; cyan, total cyanide; green, cyanate.
reduced metals on TiO₂ has been reported to increase the rate of oxidation both because the metals consume electrons in being reduced and because they tend to trap electrons once precipitated. Platinum is the metal most favored in the literature, but mercury is also precipitable. A saturated solution of HgCl₂ was added to give a concentration of 0.001 M. Aeration was discontinued at that time. Mercury has a very high affinity for cyanide and promptly formed Hg(CN)₂⁻ and Hg(CN)₃⁻ in solution. The detectable free cyanide decreased in a manner consistent with the presence of these two complexes. It was expected that the neutral complex would have more affinity for adsorption on TiO₂. It may have, but the potential for the reduction of Hg(CN)₂⁻ is considerably greater than that for Hg(II) in solution and no metallic mercury was precipitated as long as free cyanide was available in solution.

It required eleven more hours of illumination before free cyanide decreased from the plateau to which it settled when the mercuric chloride was added. This would indicate that the rate of cyanide decomposition remained about the same after the addition of mercuric chloride. There was no method developed for quantitative detection of mercury. A visible darkening of the powder was expected as qualitative evidence of the reaction. No conclusive change in appearance was observed on the powder, but the immersion well, again, was coated with metallic mercury mixed with TiO₂ powder. Some mercury was probably still present in solution at the point that the reaction was stopped. When the last sample was analysed for cyanide by the method of additions, the amount of cyanide detected was less than the known amount added. The conclusions that can be drawn from this experiment are: 1) that the combination of mercury and cyanide with TiO₂ is not particularly synergistic, 2) that mercuric
cyanide complexes, which are the most stable cyanide complex of all, can be decomposed by this method.

Reactions with Other Complexes and Other Oxidants

I. Hexacyanochromate

A 0.001 M solution of $K_3Cr(CN)_6$ was prepared and mixed with 0.5 g/L of P25. The pH was adjusted to 10.5. The results of the reaction are shown on the following page. No colorimetric reaction was developed for chromium. Dissociation of the complex occurs by a direct photoreaction, very quickly, as the graph demonstrates. The zero order rate of oxidation of cyanide from that point is $k = 0.0041$ mmol/min. This rate is comparable to that of the ferricyanide reaction with the same quantity of catalyst. This is surprising because a great deal more oxidation was occurring in this reaction than in the previous ones.

The expected fate of chromium in this reaction was that it would be adsorbed as an oxide coating on the TiO$_2$. A light green coating was observed after the first half hour of reaction. The coating never darkened with increasing accumulation and the solution appeared colored, whether yellow or green was difficult to determine without filtering. A UV-visible spectrum of the filtered solution did not resemble the known spectra of any of the mixed complexes of Cr(III) with hydroxide and cyanide. It did match the spectrum of a dilute alkaline solution of $K_2CrO_4$ that was prepared for comparison.
Figure 18. Photocatalysed Decomposition of Hexacyanochromate
Several studies have appeared in the literature describing the reduction of chromate in weakly acid solution using TiO₂. There is a shift in the potential of the chromate ion at higher pH which favors its formation. No one has studied this reaction since it is not in the generally desired direction. It was easily enough reversed by acidifying after the decomposition of the cyanide. Since an adsorbed ion is in the best position to be oxidized, it is safe to say that the reason Cr(III) did not accumulate on the TiO₂ is that it was continually being oxidized and dissolving away. As cyanide was consumed and the solubility decreased, more Cr(III) was deposited.

As chromate increased the solution pH decreased; the last sample taken had a pH of 8. It is not clear if a point was, or could be, reached at which oxidation and reduction of chromium occurred in equilibrium. Readings of filtered portions of various samples were taken at 400 nm and 420 nm. The longer wavelength was chosen so that all readings would be in linear range without requiring dilutions. They revealed that chromate continued to increase until late in the reaction, reached a plateau and finally increased again. The late increase could be accounted for by the lack of competition as nearly all cyanide was oxidized.

II. Hexacyanocobaltate

The cobalt(III) complex of cyanide is reputed to be even more stable than the iron cyanide complexes. The pentacyanocobalt(II) complex, which forms dimers in solution, is known to be an oxidation-reduction catalyst, itself. Since the cobalt(II) complex is at least a likely intermediate in the destruction of the hexacyano complex, there were two reasons for taking an interest in this complex.
The reaction was studied using a millimolar solution of $K_3Co(CN)_6$ with 0.56 g/L TiO$_2$ sol at a pH of at least 11. The results are shown on the following page. The amount of cyanide ions released into solution is much less than is observed in ferricyanide solutions. Cobalt(III) is much more prone to form soluble complexes than oxides, and therefore is still present to take up ions that are released by the decomposition of other complex molecules. In ferricyanide solution, the absence of cyanide ions in solution is adequate evidence that the reaction is complete. Here the reaction was continued for several hours after essentially zero readings were obtained because of the possibility that cyanide could still be present in complexed form.

Although the uncomplexed cobalt is less than 100%, it was confirmed by a UV-visible spectrum that the complexed cobalt species in solution was not the hexacyano complex, although it was not possible to identify what it was. A broad, but very weak peak at 240 nm with a tail that extends into the visible does not resemble any cyano-transition metal complex, which generally have a sharp peak around 220 nm assigned to charge transfer from ligand to metal. Cobalt is capable of forming complexes with both carbonate and ammonia, the hexammine complex being almost as stable as the cyanide complex. Carbonate and ammonia are the only other potential ligands available as cyanate is a very weak complexing agent. It is not certain whether ammonia bound in the cobalt complex would react with Nessler's reagent. This might explain the low cyanate readings, although a better explanation is that at this pH any ammonia formed in solution is susceptible to being carried out with the air stream.
Figure 19. Photocatalysed Decomposition of Hexacyanocobaltate
III. Tetracyano-nickelate

Three attempts were made to decompose the tetracyano-nickelate complex. None was entirely successful. The most presentable data come from an early reaction on PVA stabilized TiO$_2$. The concentration of nickel in this reaction was 0.0017 M; the concentration of TiO$_2$ was 0.01 M. It was illuminated in the water filter reactor. The reaction continued until the PVA deteriorated to the point that it would not remain in solution. Only the concentration of uncomplexed nickel was followed. As evidence that TiO$_2$ does, in principle, decompose this complex, the results are illustrated in Figure 21.

Two reactions have been attempted in the large reactor. One used the sol that had been prepared from iso-propanol and apparently inadequately dialysed. Because of the odor of isopropanol the sol was illuminated for about an hour before the solution containing the nickel complex was added. A much longer time would have been preferable. The various odors of ethanol, acetone and methyl ethyl ketone persisted above the reactor after 10 hours of illumination. After fifteen hours, less than 50% of the complex was decomposed. An attempt to analyse cyanate was defeated by interference from the organic material, which caused clouding. Negligible free cyanide was detected.

A third attempt at this reaction was made using 1 g/L of P25 as the catalyst. It was followed by uncomplexed nickel. After eight hours, the reactor was turned off and TiO$_2$ was wiped off of the immersion well. After two more hours, the results were still negligible.
Figure 20. Liberation of Nickel from Tetracyanonickelate
IV. Copper cyanide

A salt of potassium, copper and cyanide was prepared and originally presumed to be KCu(CN)$_2$. UV spectroscopic data$^{95}$ indicates that it was actually K$_3$Cu(CN)$_4$. Peral and Domenech$^6$ decomposed a mixture of copper and cyanide and reported that copper metal precipitated onto TiO$_2$ and accelerated the decomposition of cyanide. This is another metal capable of enhancing oxidation rates by trapping electrons. As a means of getting more work per photon, this reaction was of special interest.

A one millimolar solution was prepared based on the assumption that the starting material was the dicyano complex. The pH was raised to $>$11 and 1 g/L of P25 was added. Since the number of cyanide ligands per molecule was presumed to be unusually low, and the reaction rate was expected to be enhanced, only 5.5 hours of illumination were given. Then the collected samples were analysed for free cyanide, copper, and cyanate. Nothing was detected.

Since complexes containing two, three, or four cyanide ligands are stable, no cyanide ions were detected in solution. This was not surprising. When cyanide was analysed by the method of addition, the results were only slightly lower than for the added cyanide alone, which should have been a hint that the predominant complex was the tetracyano complex.

Copper was to be detected by a complex formed with oxalyl bis(cyclohexadienyl hydrazide). When compared to a 0.001 M standard prepared from copper metal, only the faintest trace of copper was detected either in filtered solution that had been boiled with nitric acid to destroy the cyanide and oxidize the copper, or in the filtered TiO$_2$ which was rinsed with nitric acid to dissolve
any copper metal present. A very old report in *Chemical Abstracts* explained the problem: Titanium is the only ion that interferes significantly in the formation of this complex.

When cyanate was analysed every sample gave about the same reading as a reagent blank. This was harder to explain, and led to the speculation that the starting material was not a copper cyanide complex at all, but since very little else was present in the solution in which it was prepared, the possibility had to be rejected. The remaining possibilities were: 1) Little or no reaction had occurred; or 2) The presence of metallic copper catalysed some reaction that decomposed cyanate, perhaps forming N₂. The second speculation is more intriguing, but it lacks any solid support.

The first evidence that a reaction had occurred, at least, to some extent, was found on opening the reactor. The immersion well was coated with red-brown material that resembled powdered copper. It rinsed away easily in concentrated nitric acid leaving a coating of white powder under it. Since metals are expected to have high coefficients of extinction, it is possible that from whatever time this layer formed all reaction was limited to the surface of the immersion well.

After filtering several of the samples were examined by UV scan. It was necessary to conclude that some copper cyanide is left in the solution. An attempt was made to correlate concentration with the absorption at 270 nm, a low shoulder before a very steep absorbance around 235 nm. When this was done using the complete line of samples, it was obvious that some factor was involved other than the concentration of the copper cyanide complex. The wavelengths associated with the shoulder shift by 10 to 20 nm in the three
different complexes. The general trend of the absorbance was downward, but there were substantial fluctuations. It appears that the tricyano complex may be the predominant complex in the later samples.

V. Reactions with Hydrogen Peroxide

Two reactions, one each with ferricyanide and tetracyanozincate, were run with hydrogen peroxide as the oxidant. \( \text{H}_2\text{O}_2 \) reacts only with very short wavelengths, but produces hydroxyl radicals in solution, rather than stabilized by adsorption. Their oxidation potential is higher than those on TiO\(_2\), and being uncharged, they are not affected by electrostatic repulsions. Hydrogen peroxide is also in industrial use as a novel waste treatment method. 51

In both cases millimolar solutions were prepared with enough KOH added to make the pH at least 10. A sample was taken before \( \text{H}_2\text{O}_2 \) was added, and another after it was added, before the light was turned on. (This was done to observe dark reactions. None was observed in the zinc solution. The ferricyanide was reduced to ferrocyanide, but nothing else was observed.) Seven ml of 30\% \( \text{H}_2\text{O}_2 \) were added to the zinc cyanide solution with two more added late in the reaction. Thirty ml were added to the ferricyanide initially and two five ml additions later. The zinc reaction, was followed by cyanide analysis; the ferricyanide, by Prussian blue. The results of these two reactions are exhibited on the following page.

First, it is obvious that both reactions are much faster than the corresponding reactions on TiO\(_2\). The major reasons for preferring TiO\(_2\) seem to be that it is more stable in storage and can react with the wavelengths available in sunlight. There is one more problem with \( \text{H}_2\text{O}_2 \) when treating metal
Figure 21. Destruction of Cyanide by H$_2$O$_2$
bearing wastes, however. As can be seen, the initial rate of reaction with ferricyanide was very fast, but then slowed drastically. More peroxide was added to the reactor twice to see if it had all been consumed. It had no effect on the rate. Most of the iron in solution had gone to FeO(OH) by the end of 15 minutes of illumination. The absorbance from suspended hydrous iron oxide is about as great as TiO₂. Once it forms, it blocks the light that drives the H₂O₂ reaction. About five days after the reaction shown the mixture was illuminated for another hour with aeration, but no additional peroxide. The remaining cyanide was gone at the end of the hour.

**Photon Efficiency of Ferricyanide Oxidation on TiO₂**

Because the recombination of holes and electrons competes with any external reactions, and has a second order dependence on the intensity of light, the efficiency of photocatalysis is predicted to be dependent on the square root of intensity of illumination. Where this relationship has been explored, it has been confirmed, but generally without determining whether any of the decrease in efficiency was due to illumination in excess of what the amount of TiO₂ present could absorb. Augugliaro et al. have proposed an ideal reactor configuration for such a study, and also a way to estimate the losses from scattered light. Their glass reactor was surrounded on the sides by an annulus filled with a potassium ferrioxalate solution, with another container of ferrioxalate under the reaction vessel. (It was illuminated from the top.) They were able to evaluate scattering as well as photon efficiency. Side scattering was found to be negligible. The quantity of light transmitted was found to vary with the quantity
and qualitative characteristics of the TiO$_2$ in suspension. They found significant transmitted light even at relatively high TiO$_2$ concentrations.

The set-up illustrated in Figure 1 (page 31) is similarly able to detect light not absorbed in reaction. Some light of longer wavelengths than are absorbed by either TiO$_2$ or ferricyanide will react with ferrioxalate. This amount will not depend on the concentration of TiO$_2$. The varied concentrations of TiO$_2$ allow an estimate of the amount transmitted in the range that could have been absorbed. As seen in the following table, it is small, but real. The amount that would be transmitted in any case is an even more worthwhile correction.

The photon efficiency of ferrioxalate varies over the range of wavelengths absorbed by TiO$_2$ from about 1.5 to 1.2. It decreases to less than 0.5 at longer wavelengths present in the lamp. The amount of ferrioxalate decomposed by the longer wavelengths per unit time should not vary. This amount was therefore subtracted from the calculated total flux per minute before correcting for efficiency of more than 1.0. There is no manufacturer’s estimate of the power distribution by wavelength for this lamp, but a spectrum shows reasonably even distribution. Wavelengths below 254 nm, where efficiency also decreases, are negligible. As a rough approximation, the factor of 1.4 has been used.

The large differences between the photons counted in the front cuvet as opposed to the back, with only distilled water in the light path were surprising. This seems to indicate that the interface between the two cuvets causes considerable reflection. Since reflected light would be returned to the reaction, no correction has been made for it.
Photon Absorption Measurements

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<th>Absorbance of Filter:</th>
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<th>0.60</th>
<th>1.0</th>
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<tr>
<td>Photons/Min Absorbed by Ferrioxalate Alone (in Einsteins):</td>
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<tr>
<td>Front Cuvet</td>
<td>4.65x10^{-6}</td>
<td>2.94x10^{-6}</td>
<td>1.56x10^{-6}</td>
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<td>Back Cuvet</td>
<td>4.36x10^{-6}</td>
<td>2.18x10^{-6}</td>
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<td>3 min</td>
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<tr>
<td>Photons/Min Absorbed Behind TiO$_2$ - Ferricyanide Mixtures:</td>
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<tr>
<td>0.19 g/L TiO$_2$</td>
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<td>0.48x10^{-6}</td>
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<td>0.58 g/L TiO$_2$</td>
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<tr>
<td>Time of exposure:</td>
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<td>20 min</td>
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<td>Estimate of Photons Absorbed by TiO$_2$ - Ferricyanide:</td>
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**Photon Efficiencies**

<table>
<thead>
<tr>
<th>Total Uncomplexed Iron: (in moles x 10^8)</th>
<th>62</th>
<th>78</th>
<th>83</th>
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<tbody>
<tr>
<td>0.19 g/L TiO₂</td>
<td>62</td>
<td>78</td>
<td>83</td>
</tr>
<tr>
<td>0.38 g/L TiO₂</td>
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<td>43</td>
<td>45</td>
</tr>
<tr>
<td>0.58 g/L TiO₂</td>
<td>64</td>
<td>56</td>
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<tr>
<td>0.77 g/L TiO₂</td>
<td>49</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

**Photon Efficiency as Total Uncomplexed Iron / Total Absorbed Photons**

<table>
<thead>
<tr>
<th>Total Uncomplexed Iron: (in moles x 10^8)</th>
<th>Photon Efficiency</th>
<th>Photon Absorbed</th>
<th>Total Absorbed</th>
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<tr>
<td>0.19 g/L TiO₂</td>
<td>0.0157</td>
<td>0.0211</td>
<td>0.0303</td>
</tr>
<tr>
<td>0.38 g/L TiO₂</td>
<td>0.0131</td>
<td>0.0116</td>
<td>0.0162</td>
</tr>
<tr>
<td>0.58 g/L TiO₂</td>
<td>0.0156</td>
<td>0.0143</td>
<td>0.0188</td>
</tr>
<tr>
<td>0.77 g/L TiO₂</td>
<td>0.0129</td>
<td>0.0254</td>
<td></td>
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</tbody>
</table>
These efficiencies are, of course, mixed efficiencies for two photoreactions. The fact that uncomplexed iron is greater at 0.19 g/L TiO₂ than at twice that concentration clearly indicates that the direct photoreaction of ferricyanide dominates at that concentration. In reality some amount of absorbance and reaction will be due to this reaction at all concentrations; however, at the higher concentrations the proportion should be small enough to be neglected.

Although the lowest intensity light is clearly the most efficient, the data are two imprecise to draw conclusions as to whether the dependence of the rate is proportional to the square root of light intensity. It is possible to conclude from the quantity of iron liberated in the amount of time given, that the intensity in the illuminated cuvet is similar to that in the large reactor. They should have similar photon efficiencies.

As expected, no free cyanide was detectable in the reaction mixtures. At this early stage in the reaction even the method of addition does not give highly accurate results, but when the results after subtracting the added concentration are negative, it is safe to say a negligible amount of free cyanide is present. To calculate efficiency in terms of cyanide destroyed, the numbers given above must be multiplied by 12, since the oxidation to cyanate is a two electron, and therefore a two photon reaction. Frank and Bard⁵ reported an efficiency of 0.06 for the reaction of cyanide on TiO₂. Peral et al.⁷⁸ found 0.08. (They appear to have neglected the factor of two electrons.) Rose and Nanjundiah²⁹ found 0.25 for platinized P25 powder. The efficiency for the lowest light intensity in this work
and the 0.0096 M sol is 0.30. At intensities probably nearer to those in the large reactor, 0.16 to 0.18 are obtained.

Conclusions

All the complexes observed, including the mercury complex, give evidence of being susceptible to photooxidation by TiO₂. The rate of oxidation of cyanide was found to be independent of the complex with which it was associated, when measurement was possible. It was faster at a pH lower than 13. It was also apparently independent of the concentration of cyanide, except at low concentrations. This observation is compatible with the expected saturation kinetic expression for \( k_{\text{obs}}[\text{CN}^-] \gg 1 \).

Adsorption of the metal ion onto TiO₂, when it occurred, did not observably affect the rate of oxidation of cyanide. This last is a surprising finding that confirms that this reaction is potentially useful in the presence of various metals.

Suggestions for Further Work

Two possible digressions into coordination chemistry were not pursued, but could have been: 1) Equilibrium constants for the replacement of CN⁻ by OH⁻ in the zinc cyanide complex could easily have been obtained had a pH electrode been available. Analogous constants for the replacement of NH₃ by CN⁻ are known.²⁵ 2) According to Sharpe,⁸⁵ there is no evidence for the existence of iron cyanide complexes of coordination number higher than six. However, when a solution 0.0002 M in both K₃Fe(CN)₆ and KCN is prepared,
the amount of CN⁻ ion detected is substantially less than 0.0002 M. The simplest explanation would be that some fraction of the iron ions are coordinating seven cyanide ions, at least on a very short time scale. If there is some other explanation, it might also be worth knowing.

Questions of more pertinence to the applicability of TiO₂ photocatalysis to waste disposal could also be pursued: 1) It has not been demonstrated that the nickel cyanide complex is as effectively decomposed as the more stable octahedral complexes. It is not obvious whether this is a consequence of the conditions under which the reaction was observed, or whether the square planar geometry is more resistant to oxidation by TiO₂. If it were, it might give some unique insight into the mechanism of the reaction. 2) The cobalt cyanide reaction could be more thoroughly studied. It may have direct photochemistry which should be taken into account. 62 The stable Co(III) complex(es) produced by photocatalysis were not identified. They might include cyanide ligands or not. If not, the indication would be that cyanide was decomposed more quickly in the presence of cobalt than in any other case. Since Co(II)(CN⁻)₅⁻³ is a likely intermediate and has catalytic properties of its own, including the the generation of peroxide and H₂ in water,⁸⁵ some form of co-catalysis could be occurring. 3) A complete accounting for the fate of nitrogen is probably not possible without analysis for N₂. So far, nothing has been published on the factors that favor production of N₂ over NO₃⁻ or NH₃; in fact, no study involving nitrogen has been able to analyse all three. Since, for many applications, N₂ would be a preferable product, a knowledge of the factors that control the fate of nitrogen in photocatalytic reactions would be worthwhile.
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