guanine amino group, with loss of nitrogen.

Each of the oligonucleotide peaks from the DNA–nitrous acid reaction was further hydrolyzed ith spleen phosphodiesterase and alkaline phosphatase. The hydrolysates were fractionated by anion exchange high pressure liquid chromatography. By this procedure, a second cross-linked nucleoside product, IIb, was obtained (yield 5 A_{310} units). This compound did not reduce with sodium dithionite and had the following ultraviolet spectrum: λ_{max} 306 nm (pH 6); λ_{max} 258, 301, 344 nm (pH 10.5), $pK_a = 7.9$. Mass spectra of the trimethylsilylation[11] and N,O-permethylation[15] (CD_3) products of II showed molecular weights (933 and 603, respectively) consistent with combined molecules of deoxyguanosine and deoxyadenosine minus NH_3. Exact mass measurement of the base–base + 2H ion (*m/e* 303.1454 found, 303.1445 calcd for $C_{12}H_5N_9OD_6$) confirmed the presence of the latter structural unit. Similar to the case of Ib, principal fragment ions showed retention of base–base units with typical sugar fragmentation.[14,15] The structure shown for II is based upon the above data, and analogy to I.

We believe that our results demonstrate the possibility of direct isolation and determination of the structures of DNA cross-links. (It should be noted that the conditions used above, and by others[1,2] for the study of cross-linking by nitrous acid involve a greater extent of reaction than those employed for mutagenesis. It is possible that other chemical transformations may predominate under the latter set of conditions.) Our isolation method, which will be published in detail elsewhere, should be applicable to other cross-links of interest.[17]

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Heterogeneous Photocatalytic Oxidation of Cyanide Ion in Aqueous Solutions at TiO_2 Powder

Sir:

There has been much recent interest in photoelectrochemical processes at single-crystal and polycrystalline TiO_2 electrodes and those of other semiconductors.[1-3] While the photoinduced oxidation of water to oxygen has been the subject of most investigations, oxidations of other species, such as I^-, Br^-, hydroquinone, and *p*-aminophenol at TiO_2 have also been demonstrated.[4,5] We were intrigued by the possibility that TiO_2 power could be employed as a heterogeneous photocatalyst for useful chemical processes and that the principles and measurements obtained with photoelectrochemical studies at semiconductor electrodes could be applied to these systems as well. Most studies of semiconductor photocatalysis have been concerned with gas phase reactions;[6] solution studies are much less common. An excellent review of this field has been given by Freund and Gomes.[7]

We report here the photocatalyzed oxidation of cyanide ion, a frequent industrial pollutant, with oxygen in the presence of TiO_2 in both the anatase and rutile forms. The reaction was studied at several cyanide concentrations and with illumination from either a 450-W xenon lamp, a 2.5-kW mercury–xenon lamp, or unfocused sunlight; under all conditions the reaction proceeded at a measurable rate. The general procedure involved irradiation of 10-ml solution samples of 0.1 M KOH containing 1 mM to 0.1 M KCN and 0.05 to 0.2 g of TiO_2 in quartz tubes with continuous bubbling of oxygen. The amount of cyanide which reacted was determined by potentiometric titration with a standard silver nitrate solution.[8] Typical results are given in Figure 1 and Table I. All TiO_2 was prepared from Matheson, Coleman and Bell reagent powder, with a particle size below 1 µm.

Four forms of TiO_2 were investigated: undoped anatase (the white form of the untreated commercial material), anatase reduced in a hydrogen gas stream at 700 °C (causing conversion to the black doped form containing about 5% rutile), anatase converted to about 70% rutile by heating in air at 1200 °C, and 70% rutile reduced in H_2 at 700 °C (resulting in doping, and conversion to about 90% rutile). The results were essentially independent of the amount of TiO_2 employed in the 0.05–0.2 g range, but were highly dependent upon the placement of the sample tube in the light beam. Control experiments with irradiated solutions in the absence of TiO_2, or TiO_2 containing solutions in the absence of irradiation showed that no or very little oxidation of CN^- occurred under these conditions. When nitrogen was bubbled through the solution during irradiation, the rate of CN^- oxidation decreased to less than 10% of the value found with oxygen bubbling.

The results shown in Figure 1 for high intensity radiation show that the rate of CN^- disappearance was essentially in-

Table I. Percent CN^- Removed by Illumination of Oxygen Saturated Solutions[a]

TiO_2 sample	Light source	Illumination time	% removed
Undoped anatase	450-W xenon	30 min	54
Doped anatase			31
Rutile			9
Doped rutile			9
No TiO_2			<1
Undoped anatase	Sunlight	2 days	>99
Doped anatase			>99
No TiO_2			<1

[a] 10 ml of 1 mM KCN in 0.1 M KOH solutions contained in quartz tube. Essentially the same results are obtained without KOH.

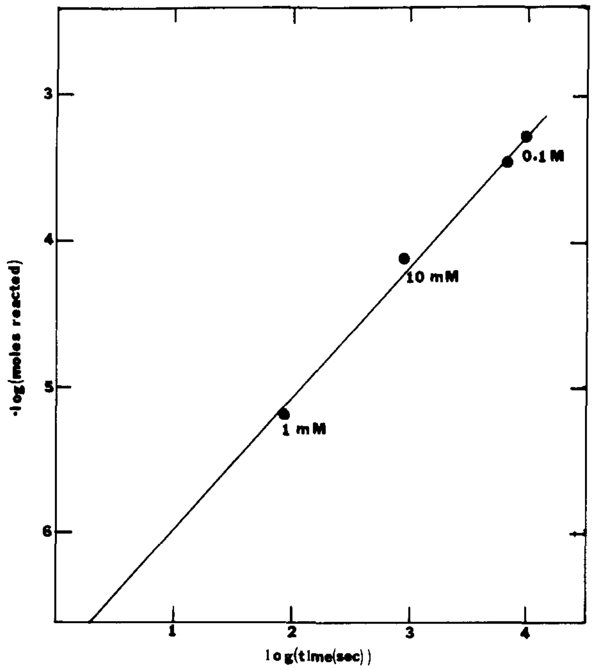

Figure 1. Amount of cyanide reacted following illumination with a 2.5-kW mercury-xenon lamp in 0.1 M KOH in the presence of doped anatase and oxygen. Solution volume was 10 ml. The illumination time and cyanide concentration are shown.

dependent of the CN^- concentration. A spot test for cyanate[9] showed the presence of CNO^- in solution after irradiation. The studies of different forms of TiO_2 with irradiation for 30 min with the 450-W Xe lamp (Table I) demonstrated that the undoped anatase was the most active form. From the known quantum efficiency and current characteristics of a rutile electrode with this lamp,[10] a quantum efficiency for CN^- oxidation of at least 0.06 is calculated assuming a two-electron reaction and absorption of only radiation beyond 3.0 eV (the TiO_2 band gap). Previous studies[11] have shown that the lamp output in this region is three to five times that of mid-day sunlight. When quartz sample tubes containing oxygen-saturated solutions of 1 mM CN^- were placed where they were exposed to sunlight and left for 2 days, essentially complete oxidation of CN^- was found with the tubes that contained TiO_2 and no reaction was found in tubes where TiO_2 was absent.

A mechanism for the process can be proposed based on the known operation of TiO_2 electrodes. Irradiation of a TiO_2 particle with light of energy greater than the band gap causes excitation of an electron to the conduction band leaving a hole in the valence band. Apparently these electrons and holes can be trapped in surface levels with recombination being sufficiently slow that the electron transfer processes can occur. The conduction band electrons reduce oxygen while the valence band holes cause the oxidation of CN^-:

$$CN^- + 2OH^- + 2p^+ \rightarrow CNO^- + H_2O$$

Further oxidation of CNO^- is possible, as is the intermediacy of H_2O_2 from the reduction of oxygen, but we have no evidence for these processes. Since the extent of band bending that exists at a TiO_2 photoanode in the usual electrochemical cell and which assists in the separation of the photogenerated electrons and holes is probably larger than at the surface of a single TiO_2 particle, recombination effects, and hence lower quantum efficiencies, are expected with particles. Indeed the efficiencies found here are lower than those found for photoassisted electrolysis at a polycrystalline TiO_2 electrode coupled to a Pt cathode but are still respectable. The higher efficiency of undoped anatase can perhaps be attributed to a lower recombination rate in it compared to the doped or rutile forms.

Although this process uses only a small fraction of the available sunlight, it does show promise as a catalytic method for removal of cyanide from waste streams. Cyanide is a rather frequent pollutant, for example in rinse waters following steel surface hardening treatments, and is currently removed at considerable expense by chemical or electrolytic means.[12] Heterogeneous photocatalytic processes employing other semiconducting materials and for the oxidation or reduction of other solution species also appear promising and are currently under investigation in this laboratory.[13]

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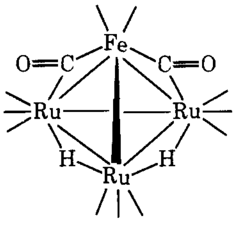
The Designed Synthesis of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$. The First Examples of Clusters Comprised of Three Different Transition Metals

Sir:

The current interest in transition metal cluster chemistry has illustrated the need for the development of general synthetic methods for the designed synthesis of mixed-metal clusters. Carbonylmetalates have been widely used as synthetic reagents in cluster chemistry and a number of interesting compounds have been prepared.[1-8] Several of the reported reactions appear to be adaptable to design, especially those of Knight and Mays[7] who prepared a series of group 7-group 8 tetrameric mixed-metal clusters through the addition of a carbonylmetalate to a closed $M_3(CO)_{12}$ trimer. Employing a similar reaction, we have synthesized the known cluster $H_2FeRu_3(CO)_{13}$, whose structure **1** has been determined by x-ray crystallography,[9] by the reaction of $Ru_3(CO)_{12}$ with $Na_2[Fe(CO)_4]$. Our synthetic yield of 49% represents a fivefold improvement over the previously reported[10,11] pyrolysis procedures. As a test of the potential for designed synthesis using this carbonylmetalate approach, we set out to prepare



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