on oxygen.[11] Further evidence for the existence of the η^2-COH species is provided by the observation of ^{1}H NMR resonances of δ 13.2 and −26.5 which are assigned to an oxygen-bound proton and a bridging metal hydride, respectively.

The ^{13}C NMR spectrum in the terminal CO region is more complicated, but comparison of the spectra of I–III shows consistent trends. The ^{13}CO resonances of II display an intensity pattern of 1:2:1:1:2:2:2:2, consistent with the symmetry found in the crystal structure. That of III is similar, 1:2:2:2:2:2:2:2 (Figure

I, X = H
II, X = e⁻
III, X = CH₃
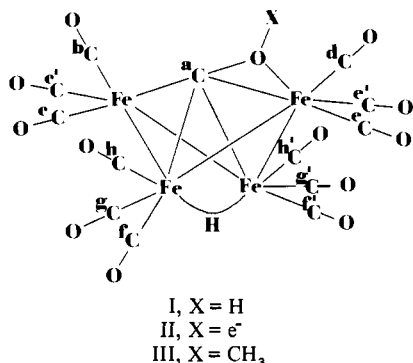
2). In the case of III, two of the unique CO's, b and d, have accidental, near degeneracy. This is supported by the slight splitting in the peak at 212.5 ppm. Compound I shows a pattern of 1:2:1:2:3:4. The resonance of area three is assigned to one of the unique CO's (b or d) which has achieved accidental degeneracy with two other carbonyls. It also is possible that upon protonation a fluctional process causes rapid interchange of these three carbonyls; however, the first hypothesis is more consistent with observations for II and III. The feature of area 4 is assigned to two resonances of area 2, indicated by the asymmetry. These are also unresolved for II on the 20-MHz instrument.[12]

As found for $(\mu\text{-H})\text{Fe}_3(\text{CO})_{10}(\mu\text{-COH})$, $(\mu\text{-H})\text{Fe}_4(\text{CO})_{12}(\eta^2\text{-COH})$ is highly unstable at room temperature in CH₂Cl₂ solution. Reexamination of the product reported earlier as $\text{H}_2\text{Fe}_4(\text{CO})_{13}$[7] leads us to question the original formulation. When $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ was treated with a large excess of aqueous 6 M HCl according to the method of Hieber and Werner[7] and then dried over Na₂SO₄ overnight, the resulting infrared spectrum showed bands characteristic of $[\text{HFe}_4(\text{CO})_{13}]^-$ and H₂O or H₃O⁺·nH₂O (intense broad bands around 3450 and 1630 cm⁻¹). In a different attempted preparation of H₂Fe₄(CO)₁₃, addition of a small excess of concentrated hydrochloric acid to an ether slurry of $[\text{PPN}]_2\text{-}[\text{Fe}_4(\text{CO})_{13}]$ produced a precipitate of 2 equiv of [PPN]Cl. The carbonyl stretching region of the spectrum was again identical with that of $[\text{HFe}_4(\text{CO})_{13}]^-$. Therefore this product is formulated as $[\text{H}_3\text{O}\cdot n\text{H}_2\text{O}][\text{HFe}_4(\text{CO})_{13}]$, which is analogous to the previously isolated $[\text{H}_3\text{O}\cdot n\text{H}_2\text{O}][\text{HFe}_3(\text{CO})_{11}]$.[3] When dried under vacuum a brown solid results which display a complex ^{13}C NMR spectrum, indicating the presence of a mixture of iron carbonyls (IR:ν_{CO} (hexane) 2045 vs, 2020 s, 1998 m, 1985 sh, 1980 sh, 1894 w, 1865 w cm⁻¹). An identical IR spectrum is obtained for "H₂Fe₄(CO)₁₃" when the synthesis is attempted at room temperature under anhydrous conditions. Thus we conclude that the original "H₂Fe₄(CO)₁₃" was a complex mixture.

Isotope labeling experiments demonstrated that when III undergoes proton-induced reduction the carbon monoxide being reduced is derived from the η^2-COCH₃ moiety.[10] By analogy it was proposed that I is an intermediate when $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ is exposed to strong acid,[13] but firm evidence for the existence of

Table I. Proton-Induced Reduction Reactions with and without Added Reducing Agents[a]

iron complex	amount of complex used, mol	CH₄	CO	H₂
[PPN]₂[Fe₄(CO)₁₃]	1.14 × 10⁻⁴	0.56	2.2	0.20
[PPN]₂[Fe₂(CO)₈]	8.14 × 10⁻⁵	trace	2.2[b]	0.57[b]
{[PPN]₂[Fe₄(CO)₁₃]	1.97 × 10⁻⁴}	0.76	2.2	0.37
{[PPN]₂[Fe₂(CO)₈]	7.65 × 10⁻⁵}			
{[PPN]₂[Fe₄(CO)₁₃]	1.09 × 10⁻⁴}	1.0	3.0	0.37
{[PPN]₂[Fe₂(CO)₈]	6.29 × 10⁻⁵}			

[a] Yields, after three days reaction, are given in mol/mol of Fe₄ cluster. [b] Yield based on moles of Fe₂(CO)₈²⁻.

a four-iron butterfly with an η^2-COH was lacking. The present characterization of I adds credence to the original proposal. The conversion of I to another reaction intermediate, HFe₄(CO)₁₂-(η^2-CH) (eq 2), requires 2 equiv of protons and electrons. The

$$\xrightarrow{2\text{H}^+,\ 2\text{e}^-} \quad + \ \text{H}_2\text{O} \quad (2)$$
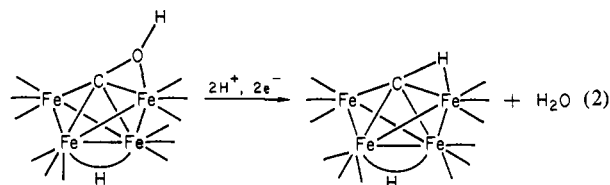
latter appears to be supplied by sacrificial oxidation of an iron species, because addition of $[\text{Fe}_2(\text{CO})_8]^{2-}$, which does not produce CH₄ upon reaction with HSO₃CF₃, increases the yield of CH₄ (Table I).

In summary, the present results provide an example of a new type of protonated carbon monoxide ligand and indicate that the protonation of a carbon monoxide ligand activates CO toward C–O bond scission and reduction.

(11) The shift to lower field in the ^{13}C NMR signal of a bridging carbonyl upon complex formation of the CO oxygen with an electrophile is well documented. See J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, *118*, 199 (1976); H. A. Hodali and D. F. Shriver, *Inorg. Chem.*, **18**, 1236 (1979).

(12) Because of the instability of $(\mu\text{-H})\text{Fe}_4(\text{CO})_{12}(\eta^2\text{-COH})$, its ^{13}C NMR spectrum was obtained at Northwestern University where only a 20-MHz instrument was available. The 90-MHz spectra were obtained at the NSF Regional NMR Facility at the University of Illinois, Urbana, IL.

(13) E. M. Holt, K. Whitmire, and D. F. Shriver, *J. Organomet. Chem.*, *213*, 125 (1981).

Photocatalytic Oxidations of Lactams and *N*-Acylamines

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Although there is considerable interest in the use of semiconductors in photovoltaic cells and in the synthesis of high-energy compounds as potential fuels,[1] their use as photocatalysts in organic synthesis has received much less consideration.[2] As part of our program to explore the utility of semiconductors in synthetic organic photochemistry, we wish to report that the 5- and 6-membered lactams and *N*-acylamines undergo photocatalytic oxidation to the corresponding imides upon irradiation in the presence of oxygenated aqueous suspensions of TiO₂.

Irradiation of 10 mL of 0.2 M aqueous solutions of amides **1–6** in the presence of 100 mg of suspended unreduced anatase TiO₂
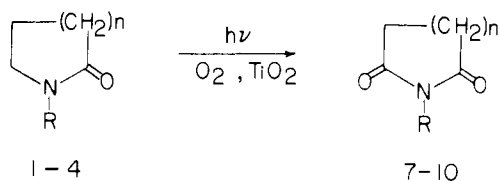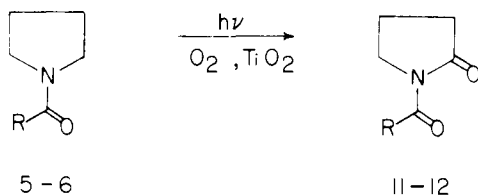
(1) See, for example: Heller, A.; Miller, B.; Lewerenz, H. J.; Bachmann, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 6555. Wrighton, M. S. *Acc. Chem. Res.* **1979**, *12*, 303. Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5985 and references therein.

(2) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, 467.

1,7 : n = 1 , R = H

2,8 : n = 1 , R = CH₃

3,9 : n = 2 , R = H

4,10: n = 2 , R = CH₃

5,11 : R = CH₃

6,12 : R = CH₃CH₂

under a constant stream of oxygen led to the formation of imides **7–12**.[3,4] Although the yields of these reactions were not maximized, Table I shows the quantity of each imide formed after 48 h of irradiation. Product isolation was accomplished by preparative GLC, and structures were rigorously confirmed by direct comparison of their spectroscopic properties with authentic samples.

1,7 : n = 1 , R = H

2,8   n = 1 , R = CH₃

3,9   n = 2 , R = H

4,10   n = 2 , R = CH₃

5,11 . R = CH₃

6,12 R = CH₃CH₂

5   13

Table I

compd	reactant consumed, mmol	product formed, mmol
1	1.0	0.9
2	1.7	1.0
3	1.9	0.9
4	1.3	0.6
5	1.1	0.9
6	1.0	0.6

Control experiments confirm that oxidation of amides to imides requires light, TiO_2, and oxygen. Thus, no consumption of the reactants was observed when the irradiations were carried out in either the absence of TiO_2 or the presence of nitrogen-purged suspensions of TiO_2. Furthermore, when the aqueous suspension of TiO_2 containing lactam **1** was irradiated for 6 h in a closed system under an initial oxygen pressure of 400 torr, 4.7×10^{-5} mol of imide **7** was formed and 3.7×10^{-5} mol of oxygen was consumed. Within the limits of our experimental error, this suggests a 1:1 stoichiometry of imide formation and oxygen consumption.

When an unbuffered aqueous suspension of TiO_2 containing lactam **1** was irradiated for 10 h under a constant stream of oxygen, 3.7×10^{-4} mol of imide **7** was formed while the initial pH of 5.2 decreased to 4.5. This is essentially equal to the pH of an aqueous solution of the imide at that concentration, suggesting that the hydrogen lost from the α carbon is ultimately consumed—presumably during the reduction of oxygen. Although the formation of imides also occurs upon irradiation of amides in oxygenated acetonitrile suspensions of TiO_2, the yields of imides increase upon addition of water to the reaction medium. Finally, the use of reduced anatase TiO_2, formed by heating the catalyst at 700 °C for 6 h in a hydrogen atmosphere, had little effect on the yield of amide oxidation.[5]

While the presence of oxygen is clearly required for imide formation, Cu(II) can also be employed as an oxidant. Thus, when 10 mL of a deoxygenated aqueous solution which was 0.2 M in both *N*-acetylpyrrolidine (**5**) and copper sulfate was irradiated for 6 h in the presence of 100 mg of TiO_2, 1.0×10^{-4} mol of Cu(II) was reduced to Cu metal and an equimolar quantity of **5** was consumed. GC analysis of the resulting solution led to the detection and isolation of *N*-acetyl-2-pyrroline (**13**), which was identified on the basis of its spectroscopic properties.[6,7]

5   13
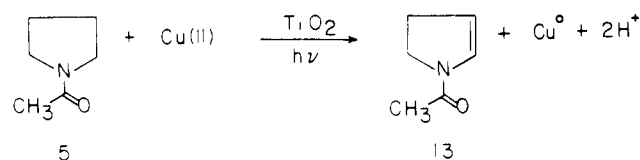
Although the complete mechanistic details of these reactions are not yet clear, these results suggest direct oxidation of the amide by the photoexcited semiconductor. Thus, according to the Gerischer model,[8] excitation of TiO_2 with light of energy equal to or greater than the band-gap energy of 3.23 eV[9] is accompanied by promotion of an electron from the valence band ($E = +2.35$ V) to the conduction band ($E = -0.88$ V), generating a positive

(3) All compounds were irradiated with Pyrex filtered light from a 200-W high-pressure Hg lamp.

(4) The TiO_2 was obtained from J. T. Baker. X-ray diffraction showed only the anatase form present. Electron micrographs revealed a particle size of <1 μm, and BET measurements gave a surface area of ~8 m² g⁻¹.

(5) Treatment of anatase TiO_2 under these conditions results in oxygen deficiencies in the crystal lattice. No conversion to rutile under these conditions could be detected by X-ray diffraction.

(6) IR (CCl₄) 3100, 2980–2870, 1650 (amide carbonyl), 1610 (C=C), and 1420, and 1355 (C—N) cm⁻¹; 60-MHz (CDCl₃) δ 2.04 s and 2.10 s (total 3 H), 2.60 (m, 2 H), 3.80 (t, 2 H), 5.20 (m, 1 H), 6.40 m and 6.90 m (total 1 H). For a comparison with the spectral properties of other 2-pyrrolines, see: Wong, C. M.; Buccini, J.; Schwenk, R.; TeRaa, J. *Can. J. Chem.* **1971**, *49*, 639. Baggidini, E.; Buscheid, H. G.; Bozzato, G.; Cavaliciu, E.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1971**, *54*, 428.

(7) The obvious synthetic utility of this reaction is under current investigation.

(8) Gerischer, H. *J. Electroanal. Chem.* **1975**, *58*, 263.

(9) Pak, V. N.; Ventov, N. G. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1975**, *49*, 1489.

hole in the valence band.[10,11] Since secondary and tertiary amides are oxidized at 1.8 and 1.2-1.5 V, respectively,[12] electron transfer from amide to semiconductor would be thermodynamically possible.

Since the reactants are inert to photolysis in the absence of a suitable oxidant such as O_2 or Cu(II), these reagents presumably serve as electron acceptors to maintain the charge neutrality of the semiconductor. Considering the potential of the conduction band electron, the reduction of oxygen to H_2O ($E = 0.57$ V), H_2O_2 ($E = 0.024$ V), or O_2^- ($E = -0.39$ V)[13] are all thermodynamically possible. Since the latter two reduction products are oxidizing agents, it is at least plausible that these reagents serve to oxidize the organic reactant rather than the excited semiconductor. The following facts, however, are not consistent with this interpretation.

First, H_2O is known to rapidly quench O_2^- and indeed, where photocatalytically generated O_2^- has been implicated in hydrogen abstraction, the rate of oxidation was observed to decrease significantly upon addition of H_2O to the suspension.[14,15] Accordingly, the observed increase in amide oxidation upon addition of H_2O to acetonitrile suspensions of TiO_2 is inconsistent with significant oxidation by this species. Second, although the reduction of O_2 to H_2O_2 is thermodynamically favorable, its formation has only been observed upon irradiation of reduced TiO_2 powders[16,17] —conditions which do not enhance the rate of amide oxidation. Furthermore, control experiments in the presence of added H_2O_2, but in the absence of TiO_2, or in the presence of TiO_2 but without irradiation were accompanied by a 10-fold decrease in imide formation. Accordingly, direct oxidation by photocatalytically generated H_2O_2 is, at most, a minor pathway in these reactions. Finally, oxidation of **5** with concomitant reduction of Cu(II) confirms that oxidizing agents photocatalytically generated from added molecular oxygen are not a prerequisite for amide reaction.

The increase in oxidation upon addition of H_2O to the reaction medium might also suggest that H_2O is scavenging valence band holes to generate HO· or H_2O· radicals which are, in turn, responsible for amide oxidation. Although such radicals have been detected during irradiation of aqueous TiO_2 suspensions and have been implicated in the photocatalytic hydroxylation of benzene,[18,19] such species do not appear to be responsible for amide oxidation in the present case. Thus, when a nitrogen-purged 0.2 M aqueous solution of Cu(II) containing 100 mg of suspended TiO_2 was irradiated for 6 h in the absence of amide **5**, no reduction of Cu(II) could be detected. Accordingly, the rate at which water scavenges valence band holes cannot account for the yield of reaction in the presence of amide **5**. Similarly, although Bard and colleagues have observed only very low yields of Cu(II) reduction after 24 h of irradiation at much higher light intensities, the reaction yield was greatly enhanced by the addition to the solution of acetate, a species known to efficiently scavenge valence band holes.[20]

As revealed by the mass balance shown in Table I, these photocatalytic reactions show a high degree of selectivity for oxidation at the carbon α to the amide nitrogen. Although in this respect they resemble direct electrochemical oxidations at platinum surfaces[21] and benzophenone sensitized oxidations,[22] reactions at

TiO_2 do not yield mixtures of imides and hydroxy lactams as are obtained in the former reactions. Further work directed toward the mechanistic details and synthetic applications of these photocatalytic oxidations is in progress.[23]

Mechanistic Features of the Semiconductor Photocatalyzed Olefin-to-Carbonyl Oxidative Cleavage

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We wish to report our mechanistic investigation of a high-yield selective oxidation of organic olefins which occurs upon irradiation of platinized or metal-free TiO_2, ZnO, or CdS. Our approach combines photoelectrosynthesis[1] (semiconductor band theory[2]) with recent developments in synthetic applications of photoinduced electron-transfer reactions.[3] Our work is the first clear demonstration that sensitized organic photoxidations do, in fact, occur at the semiconductor-liquid interface rather than in bulk solution.

Tokumaru and co-workers recently described the irradiation of TiO_2 or CdS suspended in solutions containg 1,1-diphenylethylene or its simple derivatives [2-methyl-1,1-diphenylpropene or 2-methoxy-1,1-diphenylethylene] which afforded the corresponding epoxides and benzophenone.[4] Our own studies extend these results to other arylated and nonarylated olefins, delineate the mechanistic possibilities for these conversions, and allow for cleaner preparation of carbonyl derivatives than found under the previously described conditions.[4]

Typically, the semiconductor powder (ca. 5 mg) in its native[5] or platinized[6] form was suspended in a solution of olefin (ca. 200 mg, 0.01 M) in a dry acetonitrile-trifluoroethanol (20:1) mixture. The stirred suspension was irradiated under a slow, constant stream of air bubbles at room temperature at 350 ± 30 nm. Under these conditions, essentially no direct excitation of the organic molecules occurs (<1% of incident light). Product formation was monitored by gas-liquid chromatography (GLC) or high-pressure liquid chromatography (HPLC). Parallel results were obtained usually with ZnO and CdS, and relative rates and yields for the oxidation of 1,1-diphenylethylene as a function of semiconductor catalyst and catalyst type were identical within a factor of 2. A typical conversion is shown in eq 1.

If neat acetonitrile is used as solvent, additional oxidation product(s) were formed. For **1**, for example, irradiation with suspended TiO_2 (an air-saturated 0.01 M solution of **1** in acetonitrile) gave rise to a mixture of benzophenone ($\sim$64%), 1,1-diphenyloxirane ($\sim$32%), and 2,2-diphenylacetaldehyde ($\sim$4%) at 50% conversion of starting material. Upon prolonged irradiation, these products were converted, essentially quantitatively, to benzophenone. Product distributions obtained in acetonitrile with several other olefins are shown in Table I. Here, too, prolonged irradiation and/or the use of $CH_3CN-CF_3CH_2OH$ solvent mixture leads to carbonyl compounds in high yield.

We consider first the possibility that the observed oxygenation occurs by generation of an active specie or species at the photoexcited catalyst surface which desorbs into solution where reaction occurs. Band gap irradiation of TiO_2 in acetonitrile causes

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(5) The semiconductor powders were dried overnight at 110 °C before use (TiO_2: Matheson-Coleman-Bell technical grade, powder).

(6) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.