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Supplementary Material Available: Tables giving final atomic parameters, anisotropic thermal parameters, structure factor amplitudes, and selected interatomic distances and angles (13 pages). Ordering information is given on any current masthead page.

Effect of Semiconductor on Photocatalytic Decomposition of Lactic Acid

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Photocatalytic reactions of particulate semiconductors have been investigated not only from the viewpoint of solar energy conversion but also from that of organic synthesis. From this viewpoint, the specificity of the photocatalyst to a given reaction is important to control the reaction. Here we report the dependence of the photocatalytic reaction of lactic acid on the kind of semiconductor. Platinized TiO₂ and CdS were found to decompose lactic acid very efficiently. The quantum yield of hydrogen production amounts to 71% (at 360 nm) for Pt/TiO₂ and 38% (at 440 nm) for Pt/CdS. Interestingly, a clear difference was observed in the reaction products, depending on the kind of semiconductor. For Pt/TiO₂, the main products are H₂, CO₂, and acetaldehyde, whereas for Pt/CdS they are H₂ and pyruvic acid. Photocorrosion of CdS was found to be suppressed during the reaction and the photocatalytic activity was maintained for more than 300 h of irradiation.

As powdered semiconductors, cadmium sulfide (Katayama Kagaku Co., cubic and average size 0.6 μm) and titanium dioxide (Furuuchi Chem. Co., rutile, and average size 0.5 μm) were used. Platinized TiO₂ (Pt/TiO₂) was prepared by depositing Pt photochemically on the surface of TiO₂.¹ Pt/CdS was prepared by mixing CdS with 5% Pt black.² Each photocatalyst was suspended in a lactic acid-water mixture (1:10 in volume) and irradiated after evacuation with a 1-kW Xe lamp (under 500-W operation). After irradiation the gaseous reaction products were trapped and analyzed by a quadrupole mass spectrometer (Anelva, AGA-360) as described previously.² The yield of gaseous products was determined from the pressure measured by a pressure gauge (Datametrics). The liquid reaction products were analyzed by a steam carrier gas chromatograph (Ohkura Denki, Model 103) and a liquid chromatograph (Shimadzu, LC-4A).

In each case, when the glass bulb containing the photocatalyst suspended in the lactic acid solution was irradiated with white light from the Xe lamp, gas bubbles evolved vigorously. The gaseous products were H₂ and CO₂ for Pt/TiO₂ and only H₂ for Pt/CdS. The quantum yields of H₂ production are quite high as shown in Table I. The wavelength dependence of the quantum yield indicated that the band-gap excitation of the semiconductor is essential to the reaction. Since a clear difference was observed in the gaseous products for Pt/TiO₂ and Pt/CdS, the reaction

Table I. Quantum Yields for H₂ Production from Lactic Acid-Water (1:1 vol) Solution^a

cat.	wavelength/nm	quantum yield
Pt/TiO ₂	420	0.03
	400	0.43
	380	0.64
	360	0.71
Pt/CdS	520	0.08
	500	0.12
	480	0.21
	460	0.26
	440	0.38

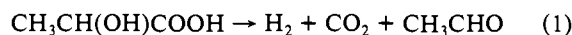
^aQuantum yields were based on incident photon flux, which was measured by a thermopile (Eppley Lab. Inc.).

Table II. Photocatalytic Reaction Products from Lactic Acid-Water (1:10 vol) Solution^a

cat. ^b	prod./mmol					
	H ₂	CO ₂	CH ₃ CHO	C ₂ H ₅ OH	CH ₃ -COOH	CH ₃ -COCOOH
Pt/TiO ₂	1.21	1.43	1.08	0.047	0.151	0.02
Pt/CdS	1.20	0.015				0.80

^aIrradiated with 1-kW Xe lamp (under 500-W operation) for 4 h. ^b300 mg of catalyst was used. In the case of Pt/CdS, the photocatalyst prepared by photochemical deposition of Pt showed a poorer activity than the photocatalyst by mechanical mixing. Therefore, in the present experiment the photocatalyst prepared by the latter method was used. There was no dependence of the distribution of the reaction products on the preparation method.

products in aqueous medium were also analyzed. Table II shows the results after 4 h of irradiation. Since a large excess of lactic acid, about 30 mmol, was used as the reactant, the result in this table should be considered as for an initial stage of the reaction. As shown in this table, for Pt/TiO₂, the amounts of H₂, CO₂, and CH₃CHO are nearly equal. This result suggests that the following reaction takes place:



Ethanol, acetic acid and pyruvic acid were produced as minor products. The production of ethanol and acetic acid can be explained by decarboxylation of lactic acid and the oxidation of acetaldehyde in water, respectively.³ On the other hand, for Pt/CdS, the main products are hydrogen and pyruvic acid. Only a trace amount of CO₂ was produced and no acetaldehyde was detected, which is in strong contrast with the case of Pt/TiO₂. Since the products were quite different from that for Pt/TiO₂, we cannot apply reaction 1 to this system. The following reaction is proposed for Pt/CdS:



The ratio of the yield of H₂ to that of pyruvic acid is a little larger than the ratio (1.0) expected from reaction 2. Liquid chromatography indicates that some unidentified compounds are produced as minor products together with pyruvic acid, which might explain the above discrepancy. The decomposition of pyruvic acid produced from reaction 2 can be discounted because of the small yield of CO₂.⁴

The anodic current due to the oxidation of lactic acid begins to rise at about 1.1 V vs. SCE at a glassy carbon electrode in 0.5 M K₂SO₄ solution. Since the valence band edge of CdS is located at 1.6 V vs. SCE,⁵ lactic acid can be oxidized with CdS as well as TiO₂. A clear difference in the reaction can be explained by the difference in oxidation power of the hole in the valence band. It is known that ethanol can be decomposed efficiently with both of these two semiconductor photocatalysts. However, acetic acid is decomposed with TiO₂ but not with CdS,⁶ because the oxidation

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potential of acetic acid is located more positively than the valence band edge of CdS. The situation in the case of lactic acid looks similar to the case of acetic acid. Because the valence band of TiO₂ is located deeply enough to oxidize carboxylate, decarboxylation could occur for TiO₂. On the other hand, the valence band of CdS is located less deeply than that of TiO₂. Therefore CdS photocatalyst could oxidize only the OH group of lactic acid. At the present stage of research this is an assumption, but it seems reasonable. In addition to the above reason, the difference in the adsorption properties of lactic acid to the surface of TiO₂ and CdS would also be important. Anyway, the above results suggest the possibility of controlling photocatalytic reactions by selecting a semiconductor with a suitable oxidizing power and adsorption property.

It is known that CdS suffers corrosion under irradiation.⁷ In order to determine the amount of CdS dissolved during the photocatalytic reaction, cadmium was analyzed by atomic absorption spectroscopy. In the sample before irradiation, 0.1 mmol of Cd was detected. This quantity was not changed even after 130 h of irradiation. Since 28.3 mmol of hydrogen was produced during the reaction, more than 99.6% of the photogenerated holes were consumed for the photocatalytic reaction even if all of 0.1 mmol of Cd was assumed to have been produced from the photocorrosion.⁸ In the analysis by polarography, the amount of Cd²⁺ was smaller than 3.6 μmol. These results indicate that the photocorrosion of CdS is negligibly small in the present reaction, suggesting a very rapid and efficient oxidation of lactic acid.

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Registry No. TiO₂, 13463-67-7; CdS, 1306-23-6; Pt, 7440-06-4; lactic acid, 50-21-5.

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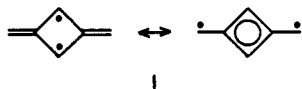
2,4-Dimethylene-1,3-cyclobutadiyl

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We report herein the direct observation of 2,4-dimethylene-1,3-cyclobutadiyl (**1**, alternatively 1,3-dimethylenecyclobutadiene) by ESR spectroscopy.

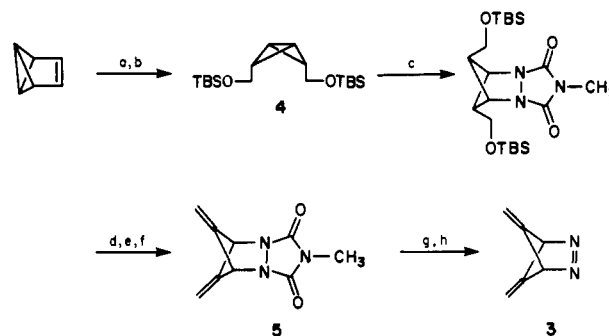


Biradical **1** is a non-Kekulé² C₆H₆ alternant hydrocarbon, which

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Scheme 1^a



^a (a) O₃, -78 °C; LiAlH₄, THF, -30 °C. (b) *t*-BuMe₂SiCl, imidazole, CH₂Cl₂. (c) MTAD, *hν*, pentane. (d) *n*-Bu₄N⁺F⁻, THF. (e) *o*-NO₂PhSeCN, *n*-Bu₃P, THF. (f) O₃, CHCl₃, -65 °C; *i*-Pr₂NH, CCl₄, Δ. (g) KOH, Me₂SO/H₂O. (h) Nickel peroxide, CH₂Cl₂, -78 °C.

has been predicted by both simple³ and sophisticated⁴ theoretical models to possess a triplet ground state. Its covalent isomer, **2**,



is highly strained, and thus a significant barrier to ring closure could exist for both triplet and singlet **1**. This, in turn, could allow thorough spectroscopic and chemical characterization of this novel species.⁵

Diazene **3** is a logical precursor to **1**,⁶ and its synthesis is shown in Scheme I. The key step in this sequence is the stereospecific photochemical addition⁷ of *N*-methyltriazolinedione (MTAD) across the strained central bond of bicyclobutane derivative **4**.⁸ Thus, the photochemical attack of MTAD occurs from the sterically congested endo face, as is the case for the thermal addition to the parent bicyclobutane.⁹ Apparently, photochemical excitation enhances the reactivity of MTAD, since **4** is completely inert toward thermal addition. Subsequent removal of the protecting groups¹⁰ and *o*-nitrophenyl selenoxide elimination¹¹ efficiently afforded diene **5**.¹² Although standard hydrolysis/oxidation procedures were unsuccessful, diazene **3** could be prepared by a novel two-step sequence involving first a partial hydrolysis of **5** to the semicarbazide.¹³ Treatment of this compound with

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(12) Isolated as a white solid, mp ca. 150 °C dec, after chromatography: ¹H NMR (C₆D₆) δ 4.50 (s, 2 H, CH), 4.37 (s, 4 H, CH₂), 2.50 (s, 3 H, NCH₃); ¹³C NMR (CDCl₃) δ 161.6 (C=O), 137.4 (quat C), 100.9 (CH₂), 68.9 (CH), 25.9 (NCH₃); mass spectrum, *m/e* 191 (36), 134 (35), 106 (33), 78 (55), 52 (100). Anal. (C₉H₉O₂N₃) C, H, N.

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