16.0 Hz, 1 H), 2.87 (dd, $J = 5.4$, 16.0 Hz, 1 H), 3.19 (m, 1 H), 4.04 (m, 4 H), 7.16 (q, $J = 1.3$ Hz, 1 H).

Method B. Direct Thermolysis of 3E-R. A solution of 25.2 mg (0.080 mmol) of tertiary alcohol **3E-R** in 3 mL of dry, degassed mesitylene was treated with 6 mg of $NaHCO_3$, and the resulting mixture was heated at reflux for 24 h under N_2. Concentration under reduced pressure and purification by preparative TLC then afforded 13.0 mg (60%) of **7**α, identical with that prepared by Method A above.

(±)-Gnididione (1). A solution of 27.2 mg (0.094 mmol) of gnididione ketal (7) in 4 mL of acetone was treated with ~2 mg of *p*-toluenesulfonic acid at room temperature with stirring. After stirring for 15 min, the reaction was quenched with 10 mL of saturated $NaHCO_3$ and extracted with 3 × 5 mL of CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by preparative TLC to afford 22.5 mg (98%) of 1 as a colorless cyrstalline solid, R_f 0.55 (silica gel, ether), which had identical NMR, IR, UV, mass spectral, and TLC behavior as an authentic sample.[20] Recrystallized from MeOH, synthetic 1 had mp 108–09 °C (lit. mp 102–03 °C, synthetic;[5b] 110–11 °C, (+)-1[1]).

(±)-Isognididione (2). A solution of 12.9 mg (0.045 mmol) of isognididione ketal (7α) in 2 mL of acetone was treated with ~2 mg of *p*-toluenesulfonic acid at room temperature with stirring. After stirring for 1 h, the reaction was quenched with 10 mL of saturated $NaHCO_3$ and extracted with 3 × 5 mL of CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by preparative TLC to afford 10.5 mg (96%) of 2 as a colorless, crystalline solid, R_f 0.50 (silica gel, ether), which had identical NMR, IR, UV, mass spectral, and TLC behavior as an authentic sample.[1,20] Recrystallized from ether/petroleum ether, synthetic 2 had mp 130–31 °C (lit. (–)-2,[1] amorphous solid).

Acknowledgment. Financial support of this work by the National Science Foundation, Grants No. CHE-8108984, CHE-8408158, and CHE-8711922, is gratefully acknowledged.

Registry No. (±)-1, 89999-21-3; (±)-2, 89999-22-4; (±)-**3*Z*-*R***, 123597-42-2; (±)-**3*E*-*R***, 123621-26-1; (±)-**3*Z*-*S***, 123597-43-3; (±)-**3*E*-*S***, 123597-44-4; (±)-*S*, 89999-23-5; (±)-**5**α, 89999-24-6; (±)-**7**, 89999-25-7; (±)-**7**α, 89999-26-8; (±)-**13**, 81159-11-7; **15**, 123597-45-5; (±)-**16**, 123597-46-6; (±)-**17**, 123597-47-7; (±)-**18**, 123597-48-8; (±)-**19**, 123597-49-9; (±)-**20**, 89999-31-5; (±)-**21**, 123597-50-2; (±)-**23*Z*-*R***, 123597-51-3; (±)-**23*E*-*R***, 123621-27-2; (±)-**23Z-*S***, 123597-52-4; (±)-**23E-*S***, 123597-53-5; (±)-**24*Z***, 89999-33-7; (±)-**24*E***, 89999-34-8; (±)-**25-*R***, 89999-35-9; (±)-**25-*S***, 89999-36-0; (±)-**26**, 89999-37-1; CH_3NC, 593-75-9.

Selective Photoelectrochemical Oxidation of Vicinal Cyclohexanedicarboxylic Acids: A Mechanistic Study

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Received December 28, 1988

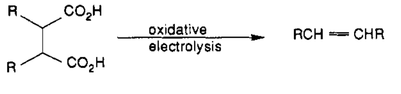
The course of photooxidation of vicinal diacids on irradiated TiO_2 suspensions proceeds via one-electron oxidative decarboxylation rather than two-electron oxidative bis-decarboxylation (which occurs on poised metal electrodes). The formation of a monocarboxylic acid as the major product indicates that trapping of an intermediate radical is competitive with further oxidation. The observed regiochemical preference in unsymmetrical diacids is rationalized by the conformational preference of the diacid adsorbed onto the photoactivated catalyst surface.

Introduction

The semiconductor-mediated photocatalyzed oxidation of many organic substrates proceeds through interfacial electron transfer, with an appropriate adsorbate trapping the photogenerated hole.[1-3] In several cases, clear evidence exists for surface-confined organic cation radicals formed in this manner.[4,5] Since the occurrence of single vs multiple electron transfer redox reactivity remains one of the pressing problems in synthetic organic electrochemistry, we sought to determine whether photoelectrochemical methods using semiconductor powders could be used to selectively achieve a desired single-electron oxidative route.

Photoexcitation of semiconductor particles such as titanium dioxide with light of energy greater than the band gap produces electron-hole pairs[2] (Figure 1). These electrons and holes serve as reductants and oxidants, respectively, for compounds adsorbed to the semiconductor surface. Chemical selectivity of these photoelectrochemical transformations is influenced by three different factors: (1) the accessible electrochemical potentials (defined by the potential of the band edges of the semiconductor); (2) preferential adsorption of donors and/or acceptors to the catalytic surface; and (3) the rate at which charge carriers (electrons and holes) are delivered to the adsorbed donor or acceptor. All three effects have demonstrable consequence in the selectivity observed in this study.

We report herein our investigation of the TiO_2-photocatalyzed oxidation of several vicinal dicarboxylic acids. Mild two-electron oxidation of these compounds at an inert electrode causes bis-decarboxylation, producing an alkene, eq 1.[6] In contrast, we find that in several cases photoe-



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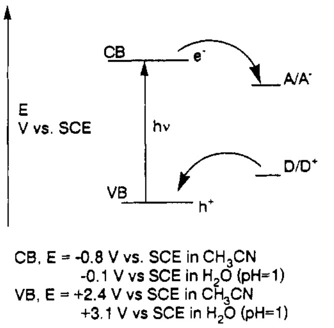


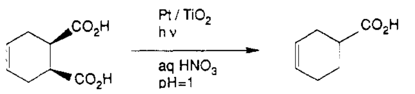
Figure 1. Photoinduced electron transfer at an excited TiO_2 semiconductor particle to an adsorbed donor (D) or acceptor (A).

Table I. Effect of Purging Atmosphere on Selectivity Attained in the Photoelectrochemical Decarboxylation of 1[a] on 10% Pt/TiO_2

reactant	atm	rel rate (±15%)	selectivity[b] (2/3)
cis-1	O_2	1.00	0.7 ± 0.3
	air	0.66	1.8 ± 0.8
	N_2	0.41	2.7 ± 0.4
	degas		18 ± 6
trans-1	O_2	0.90	1.1 ± 0.1
	air	0.45	4.3 ± 1.2
	N_2	0.40	3.5 ± 1.1
	degas		28 ± 8

[a] Five milligrams of 10% Pt/TiO_2, 50 mL of 0.01 M diacid, pH = 1 in aqueous nitric acid, blazed at 350 nm. [b] Reported values are averages of three separate determinations and are corrected for relative GC response.

lectrochemical oxidation results in monodecarboxylation in several cyclohexane diacids, consistent with trapping of a single-electron oxidized intermediate, eq 2.[7] The novel



(2)

photoelectrochemistry we observed on irradiated semiconductor powders provides a selective route to products not observed on poised metal electrodes.

Results

Cyclohexane-1,2-dicarboxylic Acids 1. Long wavelength ultraviolet irradiation of native or platinized[8] TiO_2 powders suspended in a dilute solution of the diacid in aqueous nitric acid (pH = 1) under a slow stream of nitrogen, air, or oxygen initiates the loss of CO_2, which is trapped as barium carbonate by passing the effluent gas stream through a $Ba(OH)_2$ trap. Acidic conditions have been chosen because the TiO_2-catalyzed photo-Kolbe reaction proceeds most efficiently in acid.[9,10] The faster rate in acid has been attributed to changes both in adsorption equilibria[9] and in semiconductor energetics.[10] Nitric acid has been used to control the pH of the reaction mixture, because nitrate competes less effectively for TiO_2 adsorption sites[11] and is not itself photocatalytically active (as is HCl).

Table II. Effect of Platinum Loading Level on Selectivity Attained in the Photoelectrochemical Decarboxylation of 1[a] on Irradiated TiO_2 Powders under N_2 and O_2 Purging Gases

reactant	Pt loading level (wt %)	selectivity (2/3)[d]	
		N_2	O_2
cis-1	10%[b]	8.1 ± 2.3	1.1 ± 0.4
	0.5%	3.0[c]	2.0 ± 0.1
	native (0%)	2.1 + 1.0	0.4 ± 0.2
trans-1	10%[e]	20.2 ± 6.5	1.9 ± 0.5
	0.5%	6.4[c]	1.9 ± 0.3
	native (0%)	1.3 ± 0.1	1.8 ± 0.7

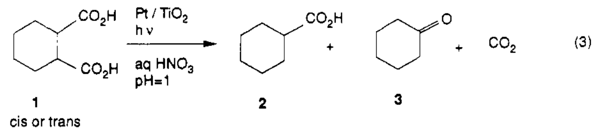
[a] Five milligrams of TiO_2 catalyst, 50 mL of 0.01 M diacid, pH = 1 in aqueous nitric acid, blazed at 350 nm. [b] Representative yields of monoacid are 77% under N_2 and 6% under O_2, based on starting material consumed. [c] Single determination. [d] Reported values are averages of three determinations and are corrected for relative GC response. [e] Representative yields of monoacid are 76% under N_2 and 6% under O_2, based on starting material consumed.

Table III. Effect of Catalyst Aging and Pretreatment on Selectivity Attained in the Photoelectrochemical Decarboxylation of 1[a] on 10 % Pt/TiO_2

reactant	cat.	selectivity[b] (2/3)		
		N_2	Air	O_2
cis-1	fresh[c,d]	8.1 ± 2.3	3.0 ± 0.4	1.1 ± 0.4
	aged[e]	1.9 ± 1.0	1.2 ± 0.5	
	pretreated[f]		2.7 ± 0.6	
trans-1	fresh[c,g]	20 ± 6	7.0 ± 1.6	1.9 ± 0.5
	aged[e]	6.1 ± 1.9	2.2 ± 0.6	
	pretreated[f]		5.5 ± 2.7	

[a] Five milligrams of TiO_2 catalyst, 50 mL of 0.01 M diacid, pH = 1 in aqueous nitric acid, blazed at 350 nm. [b] Reported values are averages of three determinations and are corrected for relative GC response. [c] Freshly prepared 10% Pt/TiO_2 prepared as in Experimental Section and stored under air. [d] Representative yields of monoacid are 77% under N_2, 24% under air, and 6% under O_2, based on starting material consumed. [e] Ten percent Pt/TiO_2 as in c except stored under air for 6 months before use. [f] Aged 10% Pt/TiO_2 from d, pretreated under H_2 at 450 °C and stored under Ar. [g] Representative yields of monoacid are 76% under N_2, 27% under air, and 6% under O_2, based on starting material consumed.

cis- and *trans*-1 were studied in parallel reactions. The TiO_2-mediated photooxidation of either the cis or trans isomer of cyclohexane-1,2-dicarboxylic acid (1) gives cyclohexanone (3), cyclohexanecarboxylic acid (2), and CO_2 as the only observed products (eq 3). Cyclohexene, the



(3)

possible bis-decarboxylation side product, was not detected by gas-liquid chromatography in any of the reaction mixtures. Because of the difficulty in reproducing absolute product yields on such heterogeneous suspensions, we have reported the ratio of product yields, which were reliable and reproducible, for reactions run under nitrogen, air, or oxygen with differing platinum loadings, Tables I and II. At conversions lower than 50%, these ratios do not change with changing percent conversion of starting material.

While the absolute yields of monoacid varied from run to run, nearly equal amounts of monoacid were observed for parallel experiments with *cis*- and *trans*-1 as substrate. The cis diacid, however, formed more cyclohexanone (3) and CO_2 than did the trans isomer under all the conditions tested. Thus, its monoacid/ketone ratio (a measure of reaction selectivity) is lower. Decreased selectivity for monoacid formation is observed upon increasing oxygen availability, Table I. Platinization increases the overall rate of reaction and changes the product distribution. With heavier platinum coverages, greater selectivity for

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Table IV. Regio- and Chemoselectivity in the Photoelectrochemical Decarboxylation of 4 on 10% Pt/TiO_2[a]

	regio-selectivity		chemoselectivity[b]	yields[b]			
atm	(6/5)[b]	(7/8)[b]	(5+6/7+8)	5	6	7	8
air	2.0	2.6	3.5	53	25	15	5
air	1.7	2.7	12.4	56	37	6	2
N_2	1.3	>10[c]	46.0	55	44	2	0

[a] Five milligrams of 10% Pt/TiO_2, 50 mL of 0.01 M diacid in 5% H_2O/CH_3CN, blazed at 350 nm. [b] Ratios and yields are reported as uncorrected GC areas. [c] Only one isomer could be detected, because of the low yield.

monoacid formation is observed, Table II. Attainable selectivity is quite sensitive to catalyst pretreatment, Table III.

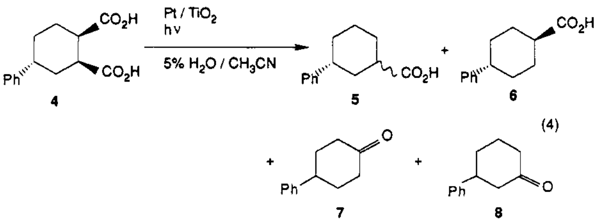
CO_2 trapping has been used in experiments comparing the initial rate of evolution of CO_2 from the cis and trans diacids 1. These experiments reveal that the cis diacid reacts approximately 50% faster than the trans diacid. Some of the diacid is degraded beyond bis-decarboxylation, since 2.72 mol of CO_2 are formed (for every mole of diacid starting material) at long irradiation periods, even while some diacid still remains unreacted. Attempted CO_2 trapping has also been used in control experiments to verify that no decarboxylation proceeded in the absence of light, TiO_2, or diacid.

The photocatalytic decomposition of the monodecarboxylation product, cyclohexanecarboxylic acid (2), has been studied. The monoacid produces cyclohexanone (3) about 4.7 times more slowly than does the diacid.

The reaction of trans diacid 1 has been studied in anhydrous acetonitrile under air (using freshly prepared catalyst, described below) in order to determine whether H_2O participates in cyclohexanone (3) formation. In this medium, the reaction is much slower. Upon prolonged irradiation (3 days), the starting material decomposes to yield monoacid 2 and ketone 3 together with a wide array of side products, probably a result of competing oxidative decomposition of the ring.

Rigorous degassing of an aqueous reaction suspension has been performed (with freshly prepared catalyst described below) to determine whether atmospheric oxygen is responsible for formation of cyclohexanone (3). This resulted in a dramatic increase in the monoacid/ketone ratio for both cis and trans isomers, Table II.

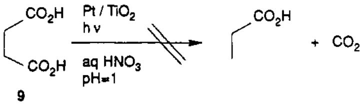
***trans*-4-Phenyl-*cis*-1,2-cyclohexanedicarboxylic Acid (4).** Analogous photocatalytic oxidation of 4 in 5% H_2O/CH_3CN with 10% Pt/TiO_2 produces 3-phenylcyclohexanecarboxylic acid (5),[12] *trans*-4-phenylcyclohexanecarboxylic acid (6), 4-phenylcyclohexanone (7), and 3-phenylcyclohexanone (8), eq 4.[13]



4 5 6 7 8 (4)

The 4-substituted acid 6 is formed in preference to the 3-substituted acids 5 and the ratio of acid to ketone changes with dissolved gas, Table IV. The monoacids could be obtained almost quantitatively, to the nearly complete exclusion of the two ketones, i.e., (5 + 6)/(7 + 8) = 46, by proper control of the reaction conditions, i.e., under N_2. When the photocatalyzed oxidation of substituted diacid 4 was attempted on irradiated native (unplatinized) TiO_2, only unreacted starting material is observed by gas chromatography.

Succinic Acid (9). Photocatalyzed decarboxylation of succinic acid (9) exhibits very different reactivity, with no propanoic acid having been observed, eq 5. In a reaction run in aqueous nitric acid with 0.5% Pt loading at 60% conversion, the CO_2 trapped from this reaction corresponds to about 1.6 molecules of CO_2 for each diacid molecule consumed. No other organic products could be observed, implying that the production of other volatile organic products lost in the purging gas stream may have occurred. Had bis-decarboxylation occurred, ethylene would have been lost in the purging gas stream. With native TiO_2, the decarboxylation is slower, and unreacted starting material is the only compound observed in the solution after partial decomposition.



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TiO_2 Aging Effects and Pretreatment. After the platinized TiO_2 samples had been stored for prolonged periods (6 months) in vials under air, the catalysts became yellow in color. Repetition of the above photocatalytic oxidations of 1 on samples aged under air indicates that the aged catalysts are less selective than before. The selectivity trends are unchanged, but the distribution of products formed in reactions run under nitrogen and air on aged samples more closely resemble those formed under air and oxygen on unaged samples, Table III.

In order to determine whether this aging is reversible, a catalyst pretreatment was carried out, Table III. The pretreatment consists of heating the catalyst at 450 °C for 2 h under an atmosphere of hydrogen.[14] While the yellow color of the catalyst is not removed by this pretreatment, the reactivity of this catalyst under air resembles that obtained before aging had occurred. Another batch of TiO_2 was platinized (following the same procedure) to insure that the catalyst preparation is reproducible. The trends observed with the freshly prepared catalyst agree with those observed on reactivated platinized TiO_2.

Electrochemistry. An electrochemical control experiment has been performed under conditions that favor radical formation[15] to determine whether monodecarboxylation might be achieved by conventional electrolysis. Analysis of the resulting products by gas-liquid chromatography reveals no monoacid formation nor dimers from monodecarboxylated radicals. Mechanistic electrochemical studies have shown that vicinal diacids sometimes react by intramolecular trapping of the two-electron oxidized intermediate cation by the second acid,[16,17] but they generally show bis-decarboxylation, eq 1.[6]

Discussion

Oxidative Decarboxylation. Photocatalytic decarboxylation (eq 6) of carboxylic acids (the photo-Kolbe

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[12] A mixture of *cis*- and *trans*-3-phenylcyclohexanecarboxylic acids of undetermined ratio was formed.

[13] The solvent composition was changed from previous conditions because of insolubility of 4 in aqueous acid.

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$$RCO_2H \xrightarrow[h\nu]{TiO_2} RH + CO_2 \qquad (6)$$

reaction) on illuminated TiO_2 is one of the first organic photoelectrochemical reactions discovered.[18-21] Although alkyl radicals (formed via decarboxylation of carboxy radicals) have been implicated in this photo-Kolbe reaction,[18c] the photochemical products differ from those obtained by conventional electrolysis of carboxylic acids (the Kolbe reaction, eq 7),[15,22] where radical coupling is the

$$RCO_2H \xrightarrow[\text{electrolysis}]{\text{oxidative}} RR + CO_2 \qquad (7)$$

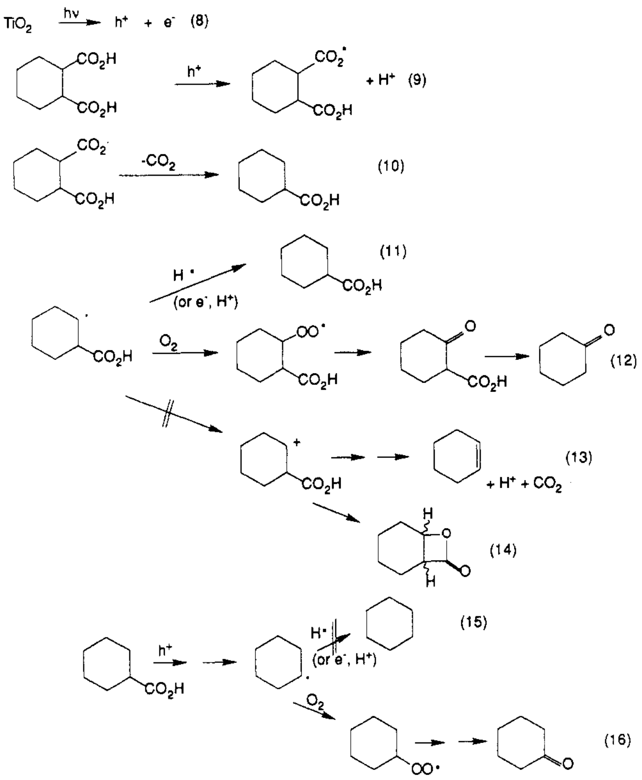
major reaction pathway. In the photoelectrochemical oxidation, the alkyl radicals appear to react with hydrogen atoms accumulated at Pt islands at a rate faster than the radical accumulation rate.

As mentioned earlier, vicinal diacids generally react electrochemically (eq 1) to yield alkenes by bis-decarboxylation.[6] The work of Corey and Casanova indicates the intermediacy of the cation RHC^+CHRCO_2H (or the corresponding carboxylate zwitterion) for both electrochemical- and lead(IV)-mediated oxidations of 1,2-dicarboxylic acids.[23] Electrooxidative monodecarboxylation of vicinal dicarboxylic acids has been reported in special cases[16,17] involving the generation of stable carbocations formed by rearrangement of the initial carbocation (analogous to that implicated by Corey and Casanova). The stabilized cation is then trapped intramolecularly in competition with loss of the second carboxylate group, leading to a lactone monodecarboxylation product.

Diacids 1 and 4 are apparently not predisposed to this efficient intramolecular trapping. Indeed, only bis-decarboxylation was observed upon electrolysis of 1 on a poised metal electrode. We, however, have demonstrated that monodecarboxylation (eq 2) is a major oxidative reaction pathway with TiO_2 as the photocatalyst.[7,24]

Proposed Mechanism for Selective Monodecarboxylation. The proposed reaction mechanism is shown in Scheme I. Band gap excitation forms a surface-confined electron-hole pair, eq 8. From the results discussed above, it is clear that the oxidative potential of a photogenerated hole poised at the valence band edge of TiO_2 is sufficiently active to initiate the observed oxidative photodecarboxylation, thus meeting the first general criterion for observable photoelectrochemistry. The diacid is adsorbed to the catalytic surface at a basic site,[11] thus meeting the second requirement. Reaction of the adsorbed carboxylic acid with a photogenerated hole forms a carboxyl radical (eq 9), which quickly loses CO_2 to form an alkyl radical (eq 10). Although a photogenerated hole in TiO_2 is a highly reactive single-electron oxidation catalyst, the oxidative activity of the photocatalyst is completely switched off after interfacial electron transfer from an adsorbed donor fills the hole, forming an adsorbed oxidized intermediate. This intermediate is not further oxidized, despite its lower oxidation potential, and may then be trapped by other routes, e.g., eq 11 or 12, more rapidly than the photocatalyst can be reactivated by absorption of a second photon at the reactive site. Since the ratio of molecules adsorbed to the surface is higher than the locally accessible number of photogenerated holes, single-electron oxidative routes are likely to predominate. That is, the rate of photooxidation of an adsorbed substrate will be governed by the ratio of rates at which photons are delivered to the surface (i.e., at which oxidative holes are generated) to that at which the oxidized substrate desorbs or is chemically trapped. Thus, the low light flux employed in steady-state irradiations should allow control of the rate of generation of charge carriers and should thus meet the third consideration.

Scheme I. Proposed Mechanism



Several routes are available to the radical intermediate. Since platinum on the catalyst surface accumulates photogenerated electrons, it may facilitate reduction of the radical, leading to monoacid product, eq 11. The radical may also be trapped by oxygen, eq 12, producing a peroxy radical and eventually leading to ketone product. Indeed, acid-catalyzed dehydration of hydroperoxides to the corresponding ketones is well precedented and decarboxylation of the β-keto acids, as formed in this step, can be induced under acidic or basic conditions.[25] Ketone formation has been reported in Kolbe electrolysis reactions run in aerated solutions.[26] A second oxidation of the initially formed radical would produce a cation, which may either rapidly decarboxylate to cyclohexene, eq 13, or be trapped as a β-lactone, eq 14, neither of which was observed under any of our photoelectrochemical reaction conditions. The monoacid, formed in eq 11, may itself decarboxylate to give a carbon radical. This radical might also be converted to cyclohexane (which was not observed, eq 15) or cyclohexanone (eq 16).

The effects of catalyst platinization and atmosphere (Tables I and II) support this proposed mechanism.

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Higher Pt loadings facilitate the reduction of the initially formed alkyl radical (higher monoacid/ketone ratio), eq 11. Higher surface-bound oxygen concentration, which is dependent on oxygen content of the purging gas, on the other hand, promotes oxygen trapping of the alkyl radical (lower monoacid/ketone ratio), eq 12 and 16. The fact that neither cyclohexene nor the β-lactone are observed indicates that the second surface-mediated oxidation is slower than the other trapping reactions of the radical formed in eq 10.

Catalyst aging and pretreatment affect the reaction selectivity. If exposure of the catalyst to oxygen for prolonged periods involves the development of high locally adsorbed oxygen concentrations, the observed effects support the proposed mechanism. Enhanced oxygen adsorption onto the catalytic surface (perhaps as a surface-bound peroxide) should thus favor eq 12 over eq 11 (decreasing reaction selectivity). Pretreatment by reduction of the catalyst under hydrogen, likewise, should produce the opposite effect, i.e., an increase in selectivity, as is observed.

Water is necessary for decarboxylation to proceed efficiently, as the reaction is very slow in anhydrous acetonitrile. This suggests the possible involvement of hydroxy radicals in initiating the photodecarboxylation.

The high monoacid/ketone ratio observed in rigorously degassed solution (freeze–pump–thaw) demonstrates the synthetic utility of this photoelectrochemical reaction. That ketone is observed at all indicates that either adventitious oxygen remains strongly adsorbed to TiO_2 in the deaerated solution (allowing ketone formation) or that H_2O or surface (lattice) oxygen atoms contribute to cyclohexanone formation.

A comparison of the reactions of the cis diacid and cyclohexanecarboxylic acid revealed that the diacid yields cyclohexanone more efficiently than does the monoacid. This slower reactivity probably reflects the weaker adsorption of the monocarboxylic acid to the active photocatalyst surface. This relative reactivity indicates that most of the ketone is probably formed in the primary photocatalytic reaction, via eq 12 rather than an eq 11/eq 16 sequence.

Adsorption Effects. The slight difference in reactivity of the cis and trans isomers **1** may be attributed to small secondary differences in the orientation of the adsorbed diacids. *cis*- and *trans*-**1**, in their most stable conformations,[27] have gauche acid groups. If we assume reasonably that both isomers associate to the photocatalytic surface through both carboxyl groups, we might predict that their adsorption should be similar and their reactivity differences subtle.

Models reveal that *cis*-**1** is oriented with the ring closer to the catalytic surface than is *trans*-**1**, Figure 2. This picture implies that the radicals derived from *cis*- and *trans*-**1** formed via decarboxylative C–C cleavages will be very differently oriented on the surface and perhaps differently exposed to surface-bound oxygen. The proximity of the cyclohexane ring of the cis isomer to the catalytic surface might be expected to facilitate surface oxygen trapping of the initially formed radical (eq 12) relative to hydrogen atom trapping (eq 11). This branching of the pathway between eq 11 and 12 leads to a shift in reaction selectivity for the cis and trans isomers, with cis exhibiting a lower monoacid/ketone ratio than trans.

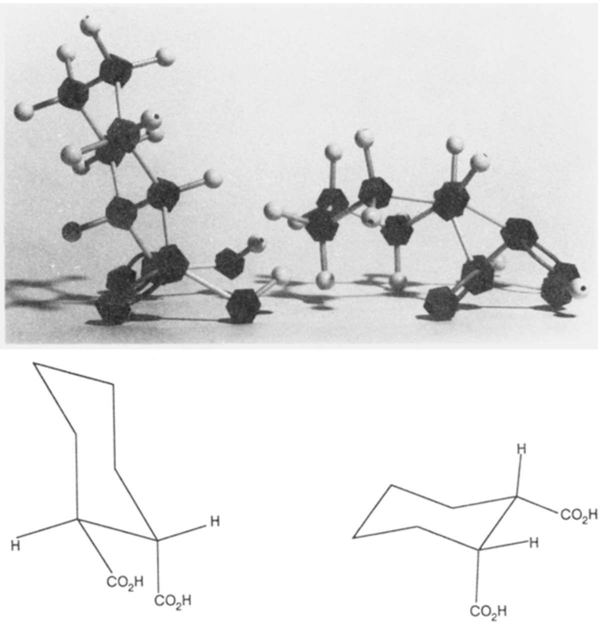

Figure 2. Adsorption geometries for *trans*-**1** (left) and *cis*-**1** (right), assuming primary surface interaction with two carboxylic acids.

The adsorption of the acid functionalities should determine the reactivity of **4** in a similar manner. At first glance, one might expect that a phenyl substituent on the 4-position of the cyclohexane ring would be too far removed from the reaction center to perturb the adsorption enough to influence the regioselectivity of monodecarboxylation. On closer inspection, however, two possible adsorption geometries (Figure 3) are revealed, one involving adsorption by two acid functionalities and the other with the phenyl ring[28,29] and the 2-acid group associated with the surface. Assuming that the surface is reasonably free of deep crevices, the phenyl ring and the 2-acid group cannot both be adsorbed simultaneously.

Although one might not expect the phenyl group to adsorb sufficiently strongly to the metal oxide surface to compete with the acid's adsorption to the TiO_2,[30] it does adsorb strongly enough to metal electrodes to perturb the product distributions in Kolbe reactions on Pt electrodes.[31,32] Because the catalyst used here has a high platinum loading, phenyl adsorption might have a considerable effect on the reactivity. Regioselective product formation may then be attributed to a competition between the two favored adsorption geometries, with the removal of the 2-carboxylate (to preferentially form **6**), Table IV, favored because of its close surface association in either adsorbed state. That the 4-ketone **7** is formed in higher yield than the 3-ketone **8** indicates that eq 11 and 16 are more important as a route to ketone from **4** than is the direct trapping, eq 12. This is consistent with the requirement for π-association of phenyl of **4** with the reducing platinum islands, since these represent sites where efficient reductive radical trapping (via eq 11) might be expected.

Another possible contribution to the observed regioselectivity is thermodynamic. Assuming that the bulky phenyl group will occupy an equatorial position, the removal of the 2-acid group is more thermodynamically fa-

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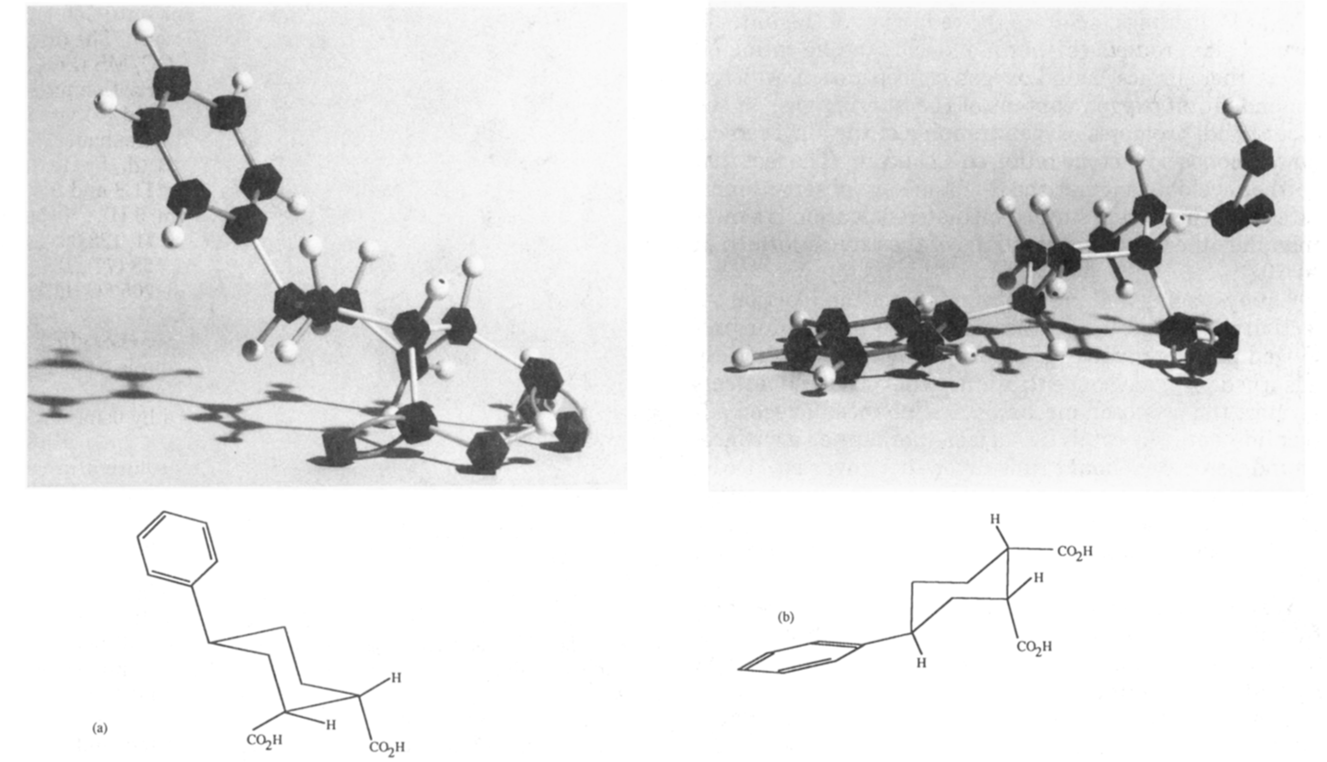

Figure 3. Adsorption geometries of substituted diacid **4** to a metallized semiconductor surface: (a) strong specific molecular interaction of carboxyl groups; (b) weak specific interaction of π bonds with surface with a single associated carboxyl group.

vored because it relieves strain from an axial ring substituent.

Bis-decarboxylation of Succinic Acid (9). This trapping of a one-electron oxidized intermediate from **1** and **4** stands in contrast to the bis-decarboxylation observed with succinic acid (**9**). The thermodynamics for the reactions of each diacid (calculated crudely from Benson's tables[33]) indicate that bis-decarboxylation is the favored reaction, as it is roughly twice as exothermic as monodecarboxylation. An explanation for the observed difference in reactivity of **1** and **9** might lie in differences in their adsorption to the photoactivated catalytic surface. The cyclohexanedicarboxylic acids **1** will have the acid functionalities in a gauche relationship with ring-enforced hindered rotation about the C_1-C_2 bond. The acid moieties on succinic acid (**9**), on the other hand, are relatively free to rotate around the C–C bond. This rotational freedom allows the acid groups to adsorb more readily to the catalytic surface. Because both acid groups may then be expected to be adsorbed in their optimal surface-associated geometry, bis-decarboxylation might be more facile with this diacid. Another possible difference may involve the dissimilarity of the surface interaction with the initially formed radicals.

Conclusions

These results indicate that TiO_2 can photocatalyze the selective oxidation of dicarboxylic acids. The selectivity attained involves chemoselective monodecarboxylation through a one-electron oxidation and the regioselective loss of one acid group in unsymmetrical diacids. The products obtained depend strongly on reaction conditions (solvent, dissolved gas, and platinum loading of the photocatalyst). The product distributions observed may be rationalized by reasonable surface adsorption effects, radical stabilities, and strain energies. Under optimal conditions and with rigorous degassing, monodecarboxylation can be achieved in synthetically useful chemical yields. The sensitivity of product composition to reaction conditions provides a rigorous test for currently accepted mechanism regarding organic photoelectrochemical transformations.

Experimental Section

Materials. Water was purified by a Millipore Milli-Q Reagent Water System. Titanium dioxide (MCB, reagent grade, anatase powder) was used as supplied. Acetonitrile (Aldrich, 99%) was stored over 3-Å molecular sieves for 1 week and distilled from the sieve dust prior to use. $H_2PtCl_6 \cdot 6H_2O$ (Spectrum Chemical), cyclohexanecarboxylic acid (**2**) (Aldrich), and 4-phenylcyclohexanone (**7**) (Aldrich) were used as supplied. *cis*- and *trans*-1,2-cyclohexanedicarboxylic acids **1** (as anhydrides, Aldrich) were used for aqueous experiments. *trans*-1,2-Cyclohexanedicarboxylic acid (Aldrich) was used in acetonitrile experiments.

Instrumentation. Gas–liquid chromatographic (GC) analyses were obtained on a Hewlett-Packard 5890A instrument equipped with a flame ionization detector and a 0.5 mm × 10 m DB-5 capillary column or a thermal conductivity detector and a $^1/_8$ in. × 0.5 m Chromosorb 101 column. High pressure liquid chromatography (HPLC) analyses were performed on a Waters 6000A solvent delivery system, a U6K injector, an R401 differential refractometer, a Hewlett-Packard 3390A integrator, and an Econosil C18 column (10-mm particle size), with 35/65 methanol/water with 1% acetic acid as the mobile phase. Gas chromatography/mass spectrometry (GC/MS) analyses were performed on a Finnigan Model 4023 automated GC/MS instrument equipped with an INCOS data system using a 25-m DB-1 capillary column. Nuclear magnetic resonance spectra were obtained on a General Electric QE300 spectrometer. Irradiations of the semiconductor suspensions were conducted in a Rayonet photochemical reactor (Southern New England Ultraviolet) equipped with low pressure mercury lamps blazed at 350 nm and a cooling fan.

Preparation of TiO_2. Platinized TiO_2 was prepared by a modification of a procedure by Kraeutler and Bard.[8] For 10% Pt/TiO_2, $H_2PtO_6 \cdot 6H_2O$ (Spectrum Chemical, 0.9 g, 1.6 mmol) was combined with distilled H_2O (15 mL) and glacial acetic acid (15

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mL). Na_2CO_3 was added until the solution pH was about 5. TiO_2 (anatase, MCB, 3.0 g) was added. While being stirred in a quartz tube, the mixture was irradiated with a 500-W Xenon lamp for 10 h. The mixture was centrifuged to isolate the solid, which was then washed 4 times with 25 mL of H_2O. The platinized (grey) TiO_2 was dried in an oven (132 °C) overnight. Lower loading levels were attained by a modification of the same procedure.

Photolysis Procedure. TiO_2 (5 mg) was added to a solution of diacid (0.01 M) in 50 mL of aqueous HNO_3 (pH = 1), which was agitated in an ultrasonic bath for 15 min to form a suspension. Magnetically stirred reaction mixtures in Pyrex tubes were irradiated in a Rayonet photochemical reactor (temperature ca. 52 °C) with 350-nm light for 24 h (unless otherwise noted). The reaction mixtures were filtered through a fritted glass filter before being analyzed by GC or HPLC. Products were identified by comparing retention times and fragmentation patterns obtained by GC/MS with authentic samples. Product yields were determined by GC using 2,4,6-trimethylphenol as an internal standard. The diacids were quantified by HPLC (after neutralization of reaction mixture) with a reverse-phase column. Experiments with *trans*-4-phenyl-*cis*-1,2-cyclohexanedicarboxylic acid (prepared via a Friedel–Crafts arylation of *cis*-1,2,3,6-tetrahydrophthalic acid[34,35]) were performed in 5% H_2O/CH_3CN (because of insolubility in H_2O) and the irradiations were carried out for 72 to 144 h, but were otherwise analogous to the reactions of unsubstituted cyclohexanedicarboxylic acids.

CO_2 Trapping Experiments. CO_2 trapping experiments were run by bubbling gas (N_2, air, or O_2) through the reaction mixture during the irradiation. The effluent gas was then passed through a $Ba(OH)_2$ trap, trapping CO_2 as $BaCO_3$ (measured by weight).[8,18d] Barium hydroxide traps were prepared with saturated $Ba(OH)_2$ in 1 M NaOH. The absence of CO_2 in the purging gas stream was ensured by inserting a $Ba(OH)_2$ trap in the line before the purge gas entered the reaction mixture.

Controls were performed by excluding, respectively, light, catalyst, and diacid to verify that no reaction occurred (no CO_2 was trapped) in the absence of any one of these.

Electrochemistry. Preparative electrolyses were conducted with a Princeton Applied Research Model 173 potentiostat equipped with an Electrosynthesis Model 640 digital coulometer using a single compartment electrochemical cell with a Pt foil working anode and a Pt grid cathode. The solution (prepared with 9.9 mmol of *trans*-1,2-cyclohexanedicarboxylic acid and 0.7 mmol of triethylamine in 40 mL of methanol) was cooled in an ice bath, magnetically stirred, and bubbled with nitrogen during electrolysis. The electrolysis was carried out until 300 C had passed (equivalent to 30% monodecarboxylation). The product mixture was analyzed by GC (HP 5890A) and GC/MS (Finnigan 4023), revealing no monoacid formation or dimerization product.

***trans*-4-Phenylcyclohexanecarboxylic acid (6)** was synthesized by using the method of Johnson and Offenhauer.[36] ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (m, 4 H), 2.01 (d, J = 13.3 Hz, 2 H), 2.17 (d, J = 13.6 Hz, 2 H), 2.42 (tt, J = 11.8 and 3.5 Hz, 1 H), 2.54 (tt, J = 11.7 and 3.2 Hz, 1 H), 7.26 (m, 5 H). ^{13}C NMR ($CDCl_3$): 29.11, 33.15, 42.76, 43.51, 126.12, 126.71, 128.39, 146.7, 182.24 ppm. MS: m/z 204 (65, M$^+$), 186 (19), 158 (77), 132 (21), 117 (100), 104 (51), 91 (74), 77 (19). MP: 203–205 °C (lit.[35] mp 203–204 °C).

Mass spectral data of **3-phenylcyclohexanecarboxylic acids 5** were consistent with that of an authentic sample prepared by the method of Rustamov et al.[37]

3-Phenylcyclohexanone (8) was prepared by using a modification of a procedure by House et al.[38] To 5.76 g of CuI (Alfa) was added 30 mL of phenyllithium (2.0 M solution in cyclohexane–ether, Aldrich). The reaction mixture was cooled in an ice bath. A solution of 3.02 g of 2-cyclohexen-1-one (Aldrich) in 50 mL of freshly distilled diethyl ether was added through a dropping funnel so that the temperature never exceeded 10 °C. The mixture was stirred for 15 min after the addition was complete. The reaction mixture was quenched with a solution of saturated aqueous NH_4Cl and ammonia (pH = 8) and air was bubbled through the mixture (to oxidize the insoluble Cu(I) to soluble $Cu(II)NH_3$). The organic layer was combined with the ether extracts of the aqueous layer and was washed with saturated NH_4Cl. The organic layer was dried, concentrated, and distilled at reduced pressure, yielding 0.75 g (13.7%) of 3-phenylcyclohexanone. MS: m/z 174 (100, M$^+$), 131 (75), 117 (89), 104 (56), 77 (13).

Acknowledgment. This work was supported by the U.S. Army Research Office. We gratefully acknowledge the contributions of Drs. Ming-Jang Chen and Koon Ha Park, who did preliminary work with these diacids and provided the phenyl-substituted diacid. We would like to thank Dr. Haruo Ogawa, who provided the 0.5% Pt/TiO_2 samples, and Dr. Phillipe Renaud for help with the electrochemistry.

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Stereoselective Nucleophilic Additions to the Carbon–Nitrogen Double Bond. 3. Chiral Acyliminium Ions

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Received June 7, 1989

(*S*)-(–)-α-Phenethylamine (**3**), (*S*)-(–)-1-(2-chlorophenyl)ethylamine (**4**), (*S*)-(–)-1-(2,6-dichlorophenyl)ethylamine (**5**), and (*S*)-(–)-1-(2,3,4,5,6-pentachlorophenyl)ethylamine (**6**) have been incorporated into acyliminium ions of structural type **1** and **2**. Five-membered ring acyliminium ion **1d** and six-membered ring acyliminium ion **2c** react with allyltrimethylsilane very stereoselectively. The configurations of the product allyl lactams were determined by chemical correlation with (*S*)-(+)-2-pyrrolidinone-5-acetic acid (**17**) and (*S*)-(+)-2-piperidinone-6-acetic acid (**18**). A transition-state model consistent with molecular orbital theory and substrate conformational preferences is proposed to account for the observed reversal of diastereoselection in the series **1a**–**d** and **2a**–**c**.

Acyliminium ions have emerged as an important class of electrophiles which participate in carbon–carbon bond forming reactions.[1] The intramolecular capture of cyclic acyliminium ions by π-bond nucleophiles has proven to be

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