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The Heterogeneous Photocatalytic Decomposition of

Benzoic Acid and Adipic Acid on Platinized TiO$_2$ Powder.

The Photo-Kolbe Decarboxylative Route to the Breakdown

of the Benzene Ring and to the Production to Butane.

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(ABSTRACT)

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(End of Abstract)

Introduction

Semiconductor materials are currently of much interest in electrochemical systems which can utilize solar energy for the production of electricity or useful chemical species. Recently semiconductor powders suspended in solution have been used to carry out heterogeneous photocatalytic and photosynthetic processes.[1] For example, applications of particulate semiconductors, e.g., TiO_2 and ZnO, to photocatalytic oxidation of cyanide,[2,3] sulfite,[3] acetate[4] and other substances[5,6] have demonstrated the versatility and ease of application of these methods. Recent studies from this laboratory have shown that irradiation of reaction mixtures containing suspended platinized TiO_2 (Pt/TiO_2) powders can promote several photocatalytic and photosynthetic reactions, such as the photo-Kolbe reaction, in which acetic acid is decomposed to methane and carbon dioxide,[4,6] and even the photosynthesis of amino acids from methane-ammonia-water mixtures.[7] To extend the scope of synthetic methods at illuminated semiconductor powders, we describe here the heterogeneous photooxidation of benzoic acid on Pt/TiO_2 powders in the presence of oxygen, and also the heterogeneous photocatalytic decomposition of adipic acid in deaerated aqueous solution.

The oxidation of benzoic acid has been demonstrated by the thermal decomposition of the cupric or molybdenum salt to phenol and carbon dioxide,[8] by the radiolysis of aqueous solutions of benzoic acid or benzoate to monohydroxlated compounds and carbon dioxide derived from the carboxyl group,[9-11] and by the Kolbe electrolysis in nonaqueous solvents to products due to the intermediacy of benzoyloxy and/or phenyl radicals.[12] We report here that the photocatalytic oxidation of benzoic acid in aqueous solutions containing suspended Pt/TiO_2 powders involves the breakdown of the benzene ring through the addition of hydroxyl radicals to aromatic rings (unlike the usual electrochemical Kolbe reactions described above).

The electrolysis of dicarboxylic acids in aqueous media has been reported to yield olefins and alcohols, containing two carbons less than the starting material.[13] We report here the heterogeneous photocatalytic decomposition of adipic acid, a six-carbon saturated aliphatic dicarboxylic acid, on Pt/TiO_2 to yield n-butane, valeric acid and CO_2 (eq. 1).

$$HO_2C(CH_2)_4 CO_2H \xrightarrow{-CO_2} CH_3(CH_2)_3CO_2H \xrightarrow{-CO_2} C_4H_{10} \qquad (1)$$
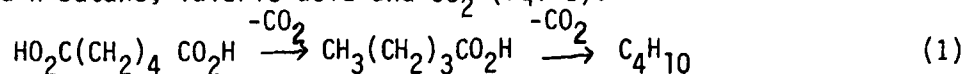
This predominant decarboxylation reaction to yield an uncoupled alkane thus follows previous studies from this laboratory in which unactivated monocarboxylic acids at ambient temperature are decomposed efficiently to the corresponding alkanes in a reaction pathway different from the electrochemical one.

Experimental Section

Materials. Benzoic acid (reagent grade, Matheson, Coleman and Bell), salicylic acid (reagent grade, Baker and Adamson), sodium hydroxide (analytical reagent grade, Mallinckrodt Chemicals), barium hydroxide (reagent grade, MC & B) and adipic acid (reagent grade, Baker Chemical Co.) were used without further purification. Triply distilled water was used to prepare aqueous solutions. All solvents and other chemicals used were reagent or spectrophotometric grade and were used without further purification. The cation exchange resin (Dowex 50W-X8, Baker Chemical Co.) was used after swelling with triply distilled water and exchanging Na^+ ions with H^+ ions. The platinized TiO_2 powders were made by photodecomposition of hexachloroplatinic acid onto TiO_2 powders (reagent grade, Matheson, Coleman and Bell, 125-250 μm) and contained 10% platinum by weight.[14]

Apparatus. A 2500 W Xe-Hg lamp (Model UF30KK, Christie Electric Corp., Los Angeles, Calif.), operated at 1600 W, was used as the light source for all preparative runs; a 450 W Xe lamp with Model 6242 power supply (Oriel Corp., Stamford, Conn.) served in several analytical runs. The reaction cell with a flat window for irradiation and the water bath were both of Pyrex; the bath temperature usually was set to $27\pm1^{\circ}C$. Irradiation was performed by illuminating the

sample (a stirred suspension of typically 100 mg of powder in 25 mL solution) through the water bath and the reaction cell. GC-Mass spectra of reaction gases were obtained with an automated Gas Chromatograph/EI-CI Mass Spectrometer System (Finnigan, Model 2000). Infrared spectra were taken on a Beckman IR-9 spectrophotometer. UV-visible spectra were recorded with a Cary Model 14 spectrophotometer. Electrochemical experiments were performed using PAR Model 173 Potentiostat (Princeton Applied Research, Princeton, NJ) and a PAR Model 173 Universal Programmer. Fluorescence measurements were made with an Aminco-Bowman spectrophotofluorometer.

Product Analysis. (a) A typical preparative experiment for the photooxidation of benzoic acid consisted of illuminating 25 mL of a solution containing 0.305 g (0.10 M) benzoic acid, 10 mL of 0.20 M NaOH, distilled water and 100 mg of 10% platinized TiO_2 powder kept in suspension by bubbling oxygen through the solution. The gases produced during the irradiation under O_2 were collected in a mercury-containing gas volumetric apparatus.[15] After termination of photolysis, a directly attached, evacuated gas sample cell for use in analysis by GC-Mass spectrometry was filled with the gas mixture in the volumetric apparatus. The rate of carbon dioxide evolution was determined gravimetrically in another preparative run. The reaction gases were swept out of the reaction vessel with a stream of oxygen and were bubbled through a saturated solution of $Ba(OH)_2$ in 0.2 M sodium hydroxide. The precipitated $BaCO_3$ was filtered off, washed with distilled water, dried at $120^\circ C$, and weighed. The reaction mixture, that had a yellow-brown color after irradiation, was brought to pH 10 with 0.2 M NaOH and then extracted with ether. No neutral material and organic bases resulted from the ether layer. The aqueous layer was then extracted with carbon tetrachloride after being acidified to pH 1-2 with 1 M HCl. A small amount of resinous brown solid (solid (1)) formed at the interface between the CCl_4 and aqueous layers. The carbon tetrachloride layer was dried over Na_2SO_4 and carefully removed under reduced pressure at room temperature to give unreacted benzoic acid with m.p. $119-121^\circ C$ ($122-123^\circ C$ for

standard sample). The aqueous layer was extracted again with ether. The ether layer obtained here was treated by the same procedure as that of the CCl_4 layer described above to give a resinous yellowish solid (solid (2)). Na^+ ions in the aqueous layer were exchanged with H^+ ions through a column of cation exchange resin, and a resinous shiny brown solid (solid (3)) was obtained. For the determination of hydroxylated intermediates, a fluorimetric method was employed, as follows. The reaction mixture was extracted with carbon tetrachloride after being acidified to pH 1-2 with 1 M HCl to remove colored products into the aqueous layer. The CCl_4 layer was extracted with 5 wt % sodium bicarbonate and then the aqueous layer, adjusted to pH 5, was examined in the spectrophotofluoro-meter.

(b) Fenton Reactions: The reaction between Fenton's reagent and benzoate were carried out as described by Cier, et. al.[16] 5 mmol benzoic acid and 5 mmol NaOH were dissolved in 75 mL of H_2O. The reaction chamber was a one-compartment cell fitted with three side-arms (one for nitrogen gas input, one for gas output and the other with a septum for injecting reagents). The aqueous benzoate solu-tion prepared above was put in the reaction chamber and deaerated for 30 min. 5 mmol of $FeSO_4$ was then added to the solution. After the solution became clear, 10 mmol H_2O_2 ($\sim$1.13 mL of 30% H_2O_2) was injected slowly into the reaction chamber with a syringe. After a reaction time of $\sim$30 h, the CO_2 gas generated and the product mixture were collected, separated and analyzed as described above.

(c) A typical experiment for the photooxidation of adipic acid was performed as follows. In a Pyrex cell connected to a gas volumetric system, 25 mL of a mixture of 0.365 g (0.10 M) adipic acid, 12.5 mL of 0.2 M sodium hydroxide, triply distilled water and 100 mg of 10% platinized TiO_2 powder was irradiated with a 2.5 KW Xe-Hg lamp (operated at 1.6 KW) while stirring at $45^\circ C$. Before and during irradiation the mixture was deaerated with purified nitrogen. After

irradiation for 40 h,   the gaseous products, which were collected in a gas
buret, were analyzed by GC-Mass spectrometry. The identities of the products
were confirmed by comparison with a standard sample. The yield of CO_2 was determined
quantitatively by trapping as $BaCO_3$ in a separate experiment. After irradiation
the colorless reaction mixture, which had an unpleasant odor, was adjusted to
pH 10 with 0.2 M NaOH and extracted with ether. The aqueous layer was acidified
to pH 1-2 with 1 M HCl and then extracted with a large amount of benzene. The
aqueous layer was further extracted with ether to yield unreacted adipic acid
(m.p. 148-150°C compared to 149-151°C for a standard sample).[17] The benzene layer
was dried over Na_2SO_4 and evaporated under reduced pressure at 40°C to give a
liquid product. The infrared spectrum of the liquid product was identical to
that of a standard sample of valeric acid with strong absorption at wave numbers
(cm^{-1}) of 530-560, 950, 1120, 1235, 1295, 1430, 1735, and 3000.

Results

Photocatalytic Decarboxylation of Benzoic Acid on Platinized TiO_2 Powders.
Illumination of suspensions of platinized TiO_2 powders in aqueous benzoic acid/
sodium benzoate mixtures in the presence of oxygen leads to the observable
evolution of carbon dioxide. After the illumination was stopped, the gaseous
products, which were collected in a gas volumetric system, were analyzed by
GC-Mass spectrometry. The mass spectrum: m/e, (rel intensity) consisted of
signals due to CO_2, 44 (44.9%), 16 (11.5%) with background signals due to O_2,
32 (100%); and air contaminents, nitrogen, 28 (27.9%); and water, 18 (4.9%).
No benzene signals were obtained. The only gaseous product evolved under illumina-
tion was thus CO_2. The CO_2 yield (determined as $BaCO_3$) as a function of the time
of illumination at 27±1°C, as shown in Fig. 1, gives a CO_2 evolution rate of
0.05 mmol/h. From the yellow-brown reaction mixture the unreacted benzoic acid was
recovered by the separation procedure described in the experimental section. The

amount of the unreacted benzoic acid was also determined by titration of the solution. Following the procedure of Kaeding,[18] the CCl_4 layer obtained in the separation procedure was titrated to the thymol blue end point with a standard solution of 0.2 M NaOH. The results from the gravimetric and titrimetric methods agreed to within ∼10%. The mole ratio of the CO_2 evolved to the benzoic acid consumed (from the titration results) is shown in Fig. 1. It increased from the value of ∼1.8 after 3 h illumination to values above 4. Three kinds of resinous solids (1) - (3) were also obtained in the separation of the reaction mixture. Analysis of these products produced after 3 days illumination of benzoic acid/benzoate solution with Pt/TiO_2 powders showed that the 1.76 mg of yellowish solid (2) was soluble in ether and the 23.2 mg of shiny brown solid (3) was soluble in water and methanol. All resinous products were insoluble in CCl_4. The infrared spectra of thin films of these solids showed the OH frequency at 3480 cm^{-1}, accompanied by two broad absorption waves at 2700 cm^{-1} and 3120 cm^{-1}, and the >C=O frequency at 1725 cm^{-1} with a shoulder at 1630 cm^{-1}.[19] The infrared spectrum was very similar to that of phenolic resin[20] particularly in the region of wave numbers higher than 1100. Thus the resinous products all appear to be the same kind of hydroxylated polymer containing carbonyl groups.

In a separate experiment, the yellow-brown reaction mixture after acidification was directly extracted with ether. After being dried over sodium sulfate and careful removal of most of the solvent, the concentrated ether solution was examined by gas chromatography (SE-30 column). No peaks corresponding to benzene, biphenyl, or phenyl benzoate were obtained.

A fluorimetric technique was used to identify and determine any hydroxylated benzoates.[9] The reaction mixture, after removal of the brownish resinous products, showed an excitation spectrum maximized at 303 nm and an emission peak at 408 nm. The positions of the peaks and the shapes of the spectra are identical to those of

standard salicylic acid solutions.   No p-hydroxybenzoate was found. The
fluorescence spectrum of salicylic acid was shown to be unaffected by the presence
of unreacted benzoic acid, so that the concentration of salicylic acid in an
illuminated sample could be derived from the maximum fluorescence emission intensity
relative to that of the standard sample. The yield of salicylic acid thus obtained
is shown in Fig. 2. The initial formation rate (for ~30 min) of salicylic acid
was 0.5 μmol/h.mL; this rate decreased to about one-fifth of the initial value at
longer times.

Several control experiments were carried out to eliminate possible effects
of sample contamination and to investigate other paths for photodecarboxylation
of benzoic acid under O_2. Passing oxygen for 72 h in the dark through the same
solution with Pt/TiO_2 under otherwise identical conditions as the irradiation
experiments showed only a negligible amount of CO_2 production (less than 5.1×10^{-3}
times that under the illumination, see Table I). A 58 h illumination under the
same conditions but under nitrogen also produced a negligible amount of carbon
dioxide (8.2×10^{-3} times of that under oxygen). Two experiments in nonaqueous
solvents were performed as follows. A solution of benzoic acid in benzene under
oxygen was illuminated and produced only a trace amount of CO_2 ($\sim 10^{-2}$ times that
in water). However, a solution of benzoic acid/tetra-n-butylammonium benzoate in
acetonitrile under illumination yielded a small amount of CO_2 (12.7% of that in water).

When potassium ferricyanide was added to the deaerated aqueous solution containing benzoic acid/benzoate and Pt/TiO_2, which was then illuminated under nitrogen, CO_2 was produced in an amount ∿15.1% of that under oxygen. Thus the photodecomposition rate under nitrogen increased by 18.4 times when potassium ferricyanide was present in the solution. Preliminary experiments concerning the reactions between Fenton's reagent, which produces hydroxyl radicals, and benzoate showed that carbon dioxide, phenol, and hydroxylated benzoate were the major products (Table 1). This demonstrates the possibility of at least the initial stages of the photodecomposition process occurring by attack of ·OH on benzoic acid and intermediates.

Photocatalytic Decarboxylation of Adipic Acid on Pt/TiO_2 Powders. Similar to the behavior of benzoic acid mentioned above, illumination of suspension of Pt/TiO_2 powders in aqueous adipic acid solutions leads to the observable evolution of CO_2. After irradiation for 40 h, the gaseous products were analyzed by GC-Mass spectrometry. The mass spectrum for the separated gas components showed signals corresponding to carbon dioxide, m/e = 44; n-butane, m/e (rel intensity) = 43(100), 41(31.8), 42(15.1), 58(14.0), 39(11.7); and hydrogen, respectively. The identity of n-butane was confirmed by comparison with a standard sample [43(100), 41(27.2), 42(12.8), 58(16.8), 39(9.6)]. No additional gaseous reaction products such as cyclo butane or butene were obtained. The amount of CO_2 evolved (determined as $BaCO_3$ in a separate experiment) as a function of time of irradiation is shown in Fig. 3. The rate of production of CO_2 was constant at 50 μmol/h. After irradiation the colorles reaction mixture was analyzed as mentioned in the experimental section. Only adipic acid and valeric acid were present in significant amounts. An analysis of the products showed that the ratio of adipic acid reacted : CO_2 evolved : valeric acid produced : n-butane produced was 1.0 : 1.75 : 0.25 : 0.76. Several control experiments in the absence of Pt/TiO_2 and without irradiation[21] under similar conditions as described above resulted in only minute amounts of CO_2 corresponding to ∿6 μmol/h.

Electrochemical Measurements. As shown in previous studies,[4,6] the photocatalytic activity of suspended powders can be correlated with the behavior of semiconductor electrodes in photoelectrochemical (PEC) measurements.[4,6] The current-potential (i-V) behavior of a rutile single crystal electrode in an aqueous solution (pH ~ 5) containing 20 m$\underline{M}$ benzoic acid, 80 m$\underline{M}$ sodium benzoate, and 0.5 $\underline{M}$ sodium perchlorate as the supporting electrolyte is shown in Fig. 4. In the dark, only a very small anodic current was observed on TiO_2 electrodes both in deaerated and in oxygen-saturated solutions (curves 1 and 2). Note, however, that in oxygen-saturated solutions, the TiO_2 electrodes showed higher cathodic background currents than in deaerated solutions, presumably because of oxygen reduction. Under illumination, the anodic current was substantially enhanced. The onset potential, V_{on}, of the photocurrent and the shape of the anodic photovoltammetric curves were essentially unaffected by the absence or the presence of oxygen or the benzoic acid/benzoate mixture (curves 3-5), with V_{on} ~ -0.30 V vs. SCE. Following the principles for photocatalyst design discussed previously,[1b,1c] where the rate of reaction at the catalyst powder is determined by the system operating at a potential where the anodic and cathodic currents are equal in magnitude, TiO_2 powder alone, even in the presence of oxygen, is not expected to be a very efficient catalyst. The role of Pt was examined by observing the i-V curves of a Pt electrode in these solutions. The reduction of protons on Pt in the presence of benzoic acid occurs at potentials more negative than -0.40 V vs. SCE (curve 6), so that H^+ reduction, even at Pt, is not a useful photocatalyst half reaction, as opposed to the results on aliphatic carboxylates. The reduction of oxygen on Pt (curve 7) occurs at potentials much more positive than either V_{on} or the potentials at which reduction of oxygen on TiO_2 occurs. Thus, the photocatalytic activity of TiO_2 powder for the oxidation of benzoic acid is substantially enhanced by the presence of Pt and oxygen.
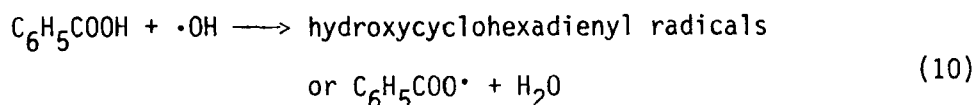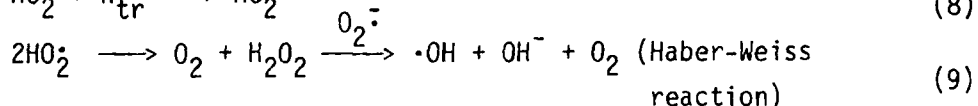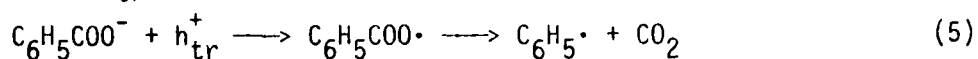
The current-potential behavior of a rutile single crystal electrode in an aqueous solution (pH $\sim$ 5) containing 0.10 $\underline{M}$ adipic acid half-neutralized with NaOH and 0.5 $\underline{M}$ sodium perchlorate as the supporting electrolyte is shown in Fig. 5. Thus, the photo-induced oxidation of adipic acid (presumably as the adipate ion) on an illuminated n-type TiO_2 rutile single crystal electrode takes place at slightly more negative potentials than the reduction of protons on platinum (see curves 1 and 3). Therefore, the photooxidation of adipate ions on n-type TiO_2 and the reduction of protons on platinum can easily take place simultaneously at the two electrodes under short circuit conditions, i.e., without applied potential. Moreover, the photooxidation of n-valeric acid, the intermediate in the photo-oxidation of adipic acid to n-butane, on TiO_2 and the reduction of protons on platinum can also be rationalized by similar voltammetric curves. Thus, as in previous studies,[4,6] the Pt/TiO_2 powders act as a multitude of small, short-circuited electrode systems.

Discussion

In the presence of oxygen, several n-type semiconductor powders have been shown to behave as photocatalysts and promote the oxidation of sub-strates.[1-6] Irradiation of a semiconductor with light of energy higher than the band gap results in creation of holes in the semiconductor valence band (VB) and electrons in the conduction band (CB) followed by trapping of the separated charges in shallow traps (tr) at the powder-solution interface.

$$(TiO_2) + h\nu \longrightarrow e_{CB}^- + h_{VB}^+ \qquad (2)$$

$$e_{CB}^- \longrightarrow e_{tr}^- \; ; \; h_{VB}^+ \longrightarrow h_{tr}^+ \qquad (3)$$

As recently discussed in connection with the photo-Kolbe reaction at Pt/TiO_2 powder,[4] adsorbed species, e.g., OH^-, could also provide a site for trapping of the holes. These trapped carriers can recombine or the h_{tr}^+ can be scavenged by oxidizable species (for example, H_2O, H_2O_2, $C_6H_5COO^-$, or adipate ion), and e_{tr}^- by reducible species (for example, O_2 or H^+) in the solution. Thus the following reactions appear reasonable for the photooxidation of benzoic acid (adsorption of intermediates on the powder surface is possible, but is not specifically indicated in the equations below):

$$OH^- + h_{tr}^+ \longrightarrow \cdot OH \tag{4}$$

$$C_6H_5COO^- + h_{tr}^+ \longrightarrow C_6H_5COO\cdot \longrightarrow C_6H_5\cdot + CO_2 \tag{5}$$

$$H^+ + e_{tr}^- \longrightarrow H\cdot \tag{6}$$

$$O_2 + e_{tr}^- \longrightarrow O_2\cdot \xrightarrow{-H\cdot} HO_2^- \tag{7}$$

$$HO_2^- + h_{tr}^+ \longrightarrow HO_2\cdot \tag{8}$$

$$2HO_2^- \longrightarrow O_2 + H_2O_2 \xrightarrow{O_2^{\cdot-}} \cdot OH + OH^- + O_2 \text{ (Haber-Weiss reaction)} \tag{9}$$

$$C_6H_5COOH + \cdot OH \longrightarrow \text{hydroxycyclohexadienyl radicals}$$
$$\text{or } C_6H_5COO\cdot + H_2O \tag{10}$$

The electrochemical measurements suggest that the reduction of H^+ on Pt and the reduction of O_2 at TiO_2 do not occur at a high enough rate at the potentials where photooxidation of benzoate takes place for these to be effective half reactions at the catalyst particle. The role of the Pt for this reaction is thus to provide a site for the more efficient reduction of O_2 (eq. 7). In fact the photodecarboxylation of benzoate does not occur to an appreciable extent in deaerated solutions containing Pt/TiO_2 (Table I).[22] The addition of ferricyanide to a deaerated solution to provide an alternate species which can be reduced causes decomposition of benzoate, but at a much smaller rate than in the presence of O_2. Thus, intermediates that form during the reduction of O_2 may also play a role in the oxidation process, as shown in reactions (7) - (9). Recent experiments involving spin trapping and electron spin resonance
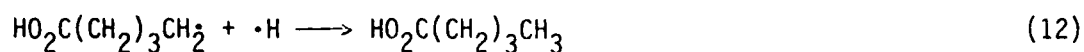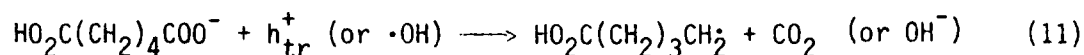
spectroscopic detection of intermediates formed during irradiation of Pt/TiO_2 in aqueous solutions have demonstrated the intermediacy of $\cdot OH$ and $HO_2 \cdot$.[23]

Since the mole ratio of CO_2 evolved to benzoic acid consumed is much larger than 1 (Fig. 1), breakdown of the benzene ring must be occurring. This possibility has been confirmed by experiments on the photooxidation of aerated solutions of benzene, where CO_2 production has been established. Detailed studies of the photocatalytic decomposition of hydrocarbons at Pt/TiO_2 have been reported.[24] The mode of decomposition of the benzene ring has not been established. However, the detection of salicylic acid in the experiments described here suggests that attack by $\cdot OH$ radicals is a likely route. The probable role of $\cdot OH$ in these reactions is also supported by experiments showing the reaction of benzoic acid with Fenton's reagent as well as earlier studies on the radiolysis of benzoic acid solution.[10,11] The shape of the concentration-time profiles for salicylic acid production (Fig. 2) can be qualitatively explained. The salicylic acid, which results from attack on the parent benzoic acid by $\cdot OH$, builds to a steady concentration, since it is produced from the benzoic acid whose concentration does not change significantly, and is also converted to more highly oxidized products (ultimately CO_2) by reaction with $\cdot OH$, holes, or other intermediates.

Note that the photocatalytic decarboxylation of benzoate differs from that found with acetate[4] and adipate under similar conditions (pH ~5), where decomposition even in the absence of O_2 occurs. This implies that reaction (6) might be more favorable with aliphatic carboxylic acids than with aromatic acids. Although the observed onset potential for oxidation of adipic acid at $n-TiO_2$ is slightly more negative than for benzoic acid, this effect alone is probably insufficient to account for this difference in behavior. At this stage the most likely explanation is that aromatic intermediates in the benzoate system adsorb on the

Pt sites and decrease the rate of the hydrogen evolution reaction. It is well-known that many adsorbed organic species can "poison" Pt electrodes towards proton reduction.[25] Note that only a small increase in the hydrogen overpotential can cause a significant decrease in the reaction rate at the Pt/ TiO_2 powders. The lower molecular weight intermediates of adipic acid may never leave the TiO_2-sites and are less likely to poison the proton reduction reaction. Oxidation of adipic acid might take place through the following reactions:

$$HO_2C(CH_2)_4COO^- + h_{tr}^+ \text{ (or } \cdot OH) \longrightarrow HO_2C(CH_2)_3CH_2^{\cdot} + CO_2 \text{ (or } OH^-) \quad (11)$$

$$H^+ + e_{tr}^- \longrightarrow H\cdot \quad (6)$$

$$HO_2C(CH_2)_3CH_2^{\cdot} + \cdot H \longrightarrow HO_2C(CH_2)_3CH_3 \quad (12)$$

The breakdown of valeric acid then follows a similar route, leading to butane.

The products found for the adipic acid oxidation are useful in providing information about the path of the photo-Kolbe reaction, since several possible routes are possible, as shown in the scheme below:

General scheme of adipic acid decarboxylation
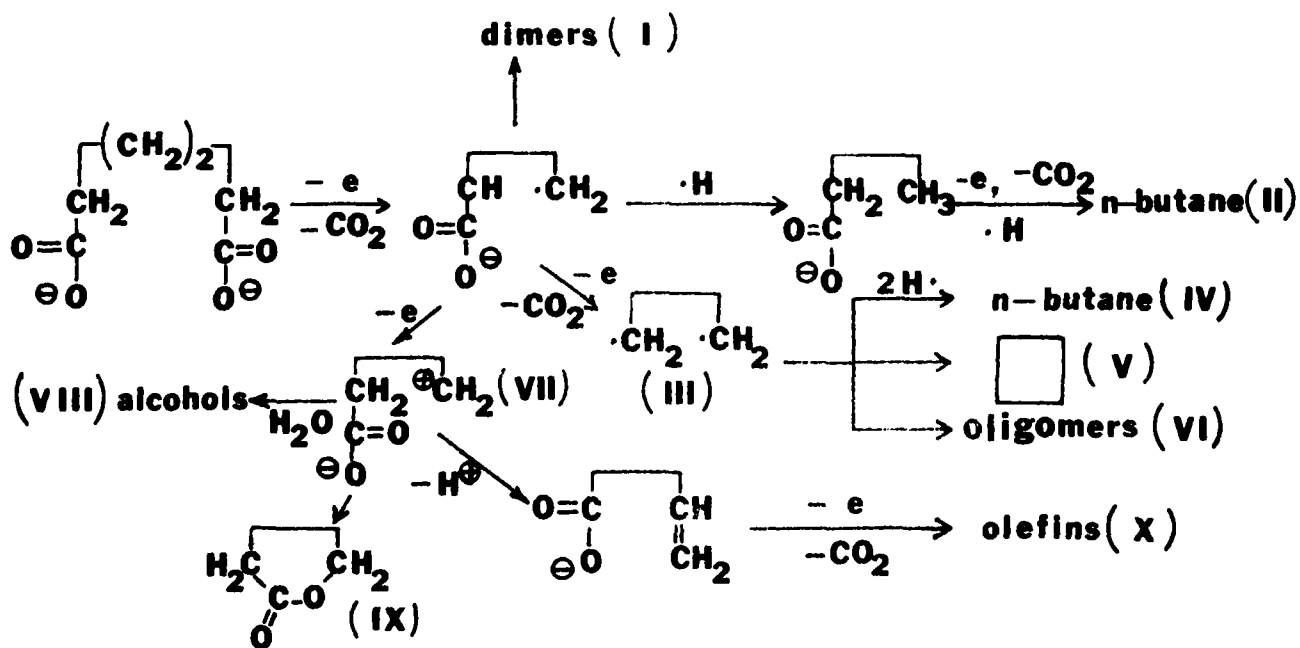
The Kolbe electrolysis of dicarboxylic acids has been reported to occur via carbonium ions (VII) and to produce alcohols (VIII), lactones (IX), and olefins (X).[13,26] Homogeneous photochemical reactions of dicarboxylic acids either in $FeCl_3$ solution [27a] or with uranyl salt as a sensitizer[27b] usually produce monocarboxylic acids. The results reported here showed that n-butane (II) was the predominant product during the photocatalytic decarboxylation of the adipic acid on Pt/TiO_2 with no cyclobutane (V) or oligomers (VI) obtained. This suggests that the diradical (III) was not formed. Whether any dimers (I) were formed is still not clear and bears further investigation. However their yield is very low, consistent with previous findings that radical intermediates react with H· or are reduced before extensive dimerization occurs. This probably can be attributed to the rather low surface density of adsorbed alkyl radicals at the prevailing light flux and catalyst surface area. The density of active sites on the catalyst powders may also be quite small.[28] The lifetime of these adsorbed radicals is also sufficiently small that further oxidation to the carbonium ion by another photogenerated hole does not occur. This accounts for the difference between the products of the electrochemical Kolbe reaction (olefins and alcohols)[13] or oligomers (e.g. the Brown-Walker reaction)[29] and those of the photo-Kolbe reaction. The absence of appreciable amount of intermediates (e.g. valeric acid in the case of adipic acid and salicylic acid in the case of benzoic acid) in the oxidative breakdown probably indicates they largely remain adsorbed on TiO_2 sites on the particles and are decomposed before they escape to the bulk solution.

Because the predominant photocatalytic breakdown of benzoic acid forms CO_2, and not the usual electrochemical Kolbe type intermediates, e.g., biphenyl and phenyl benzoate, such a process may be of use in the treatment of waste streams containing this intermediate, as has been suggested previously for removal of cyanide, sulfite[3] and aliphatic carboxylates.[4]

Acknowledgment

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19. Except for these absorption peaks, some distinct absorption peaks were also observed at 660, 725, 785, 1135, 1250, 1295, 1400 and 1445 cm^{-1}.

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21. The control experiment in the dark was carried out with bubbling N_2 for one day. No CO_2 was precipitated as $BaCO_3$.

22. A negligibly small amount of CO_2 may result from the adsorbed oxygen on powders.

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28. Photoelectrophoresis experiments on anatase powders have shown that the photogenerated positive charge carriers, presumably trapped at the interfacial sites, were ∼3500 electronic charges on a powder of diameter ∼ 1μm. (See Takahashi, A.; Aikawa, Y.; Toyoshima, Y.; Sujigara, M. _J. Phys. Chem._ 1979, 83, 2854; Dunn, W. W.; Aikawa, Y.; Bard. A. J.; manuscript in preparation.

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Table I. Heterogeneous photocatalytic carbon dioxide evolution under illumination at platinized TiO_2 powder and control experiments.

Pt/TiO_2 Powder	Solution Composition	Conditions	Amount of CO_2 evolved, mmole	Rate of CO_2 evolved, mmole/h
Yes	0.020 M HBz [a] 0.080 M NaBz in water	3-96 h illuminated under O_2	0.350 - 4.10	$\sim 5.0 \times 10^{-2}$
Yes	0.020 M HBz 0.080 M NaBz in water	72 h in the dark under O_2	0.0182	2.5×10^{-4}
Yes	0.020 M HBz 0.080 M NaBz in water	58 h illuminated under N_2	0.0238	4.1×10^{-4}
Yes	0.10 M HBz in benzene	72 h illuminated under O_2	0.162	2.3×10^{-3}
Yes	0.125 M HBz 0.125 M tetra-n-butylammonium benzoate in acetonitrle	48 h illuminated under O_2	0.304	6.3×10^{-3}
Yes	0.020 M HBz 0.080 M NaBz 0.10 M $K_3Fe(CN)_6$ in water	19.5 h illuminated under N_2	0.147	7.54×10^{-3}
No [b]	0.060 M NaBz in water	Fenton's reagent	0.40	---

[a] HBz is benzoic acid; NaBz is sodium benzoate.

[b] With Fenton's reagent (0.06 M $FeSO_4$ and 0.12 M H_2O_2). In addition to CO_2 0.12 mmol phenol and 6.8×10^{-3} mmol of salicylic acid were formed.

Figure Captions

Fig. 1 CO_2 yield (circles) and the mole ratio of CO_2 evolved to benzoic acid consumed (triangles) as functions of the time of illumination. Oxygen-saturated aqueous solutions containing 20 m$\underline{M}$ benzoic acid and 80 m$\underline{M}$ sodium benzoate with 100 mg of suspended 10% platinized anatase powder were irradiated with a 2.5 kW Xe lamp (operated at 1.6 kW) at 27°C.

Fig. 2   Salicylic acid yield as a function of the time of illumination. Experimental conditions same as in Fig. 1.

Fig. 3 CO_2 yield as a function of the time of illumination of 37.5 mL 0.067 $\underline{M}$ deoxygenated adipate solutions with 100 mg of suspended 10% platinized anatase powders irradiated with a 2.5 kW Xe lamp (operated at 1.6 kW) at $\sim 40^{O}$C.

Fig. 4   Voltammetric curves at Pt and n-type TiO_2 single crystal electrodes. A 450-W Xe lamp with a water filter was used as the light source. Scan rate, 100 mV/sec. Initial potentials at positive extremes.

1. TiO_2 in the dark under N_2; 0.5 $\underline{M}$ $NaClO_4$ containing 20 m$\underline{M}$ benzoic acid and 80 m$\underline{M}$ sodium benzoate.

2. TiO_2 in the dark under O_2; same solution as in 1.

3. TiO_2 in the light under N_2; same solution as in 1.

4. TiO_2 in the light under O_2; same solution as in 1.

5. TiO_2 in the light under N_2; 0.5 $\underline{M}$ $NaClO_4$.

6. Pt; under N_2; same solution as in 1.

7. Pt; under O_2; same solution as in 1.

Fig. 5   Current-potential curves at Pt and n-TiO_2 single crystal electrodes in 0.5 $\underline{M}$ $NaClO_4$ solutions containing 0.10 $\underline{M}$ adipic acid half-neutralized

with NaOH.   A 450 W Xe lamp fitted with a water infrared filter was the light source.   Scan rate, 100 mV/sec.

1.   On Pt; Initial potential, 0.20 V vs. SCE.

2.   On n-TiO$_2$ in the dark; Initial potential, -0.31 V vs. SCE.

3.   On n-TiO$_2$ in the light; Initial potential, -0.31 V vs. SCE.

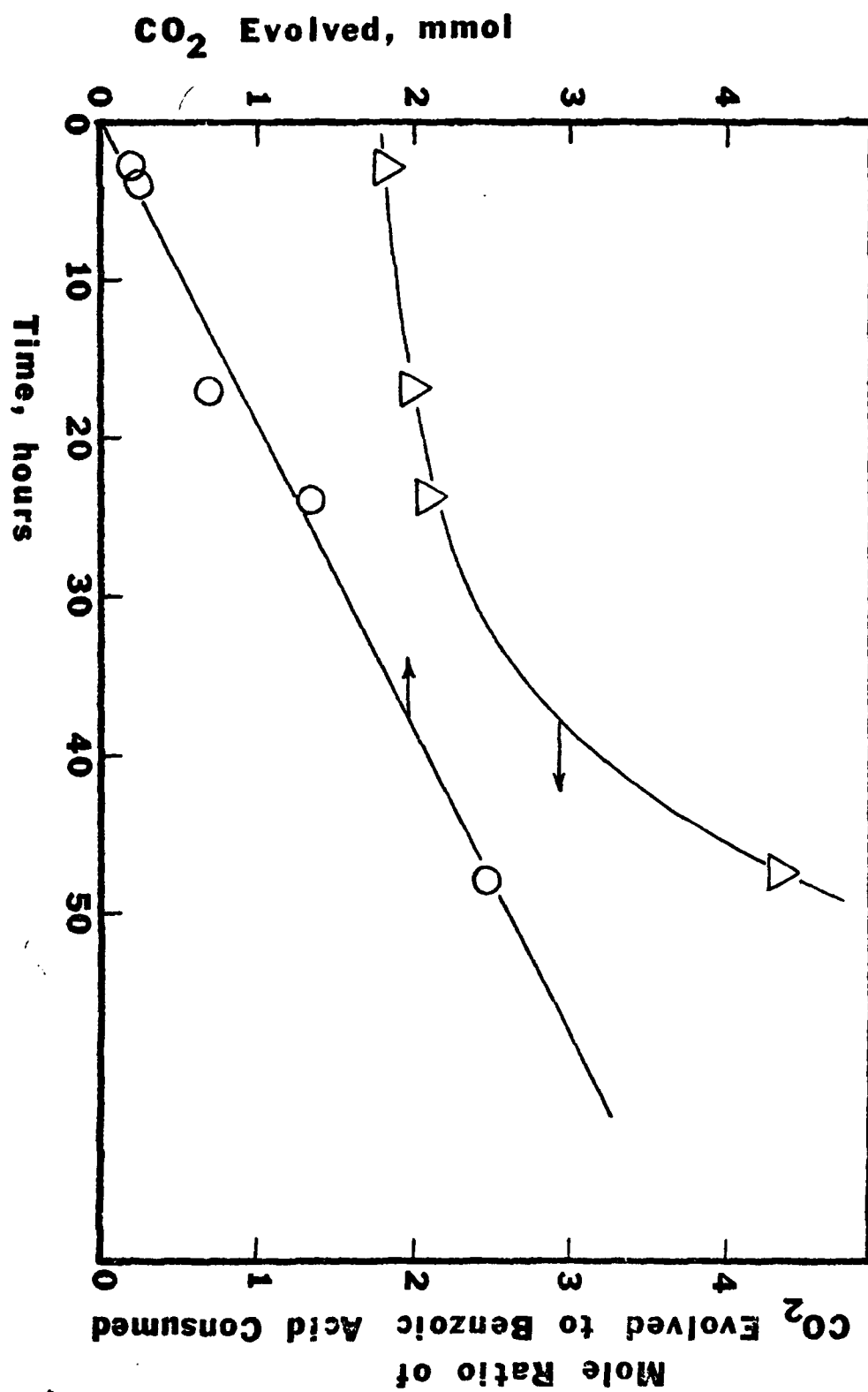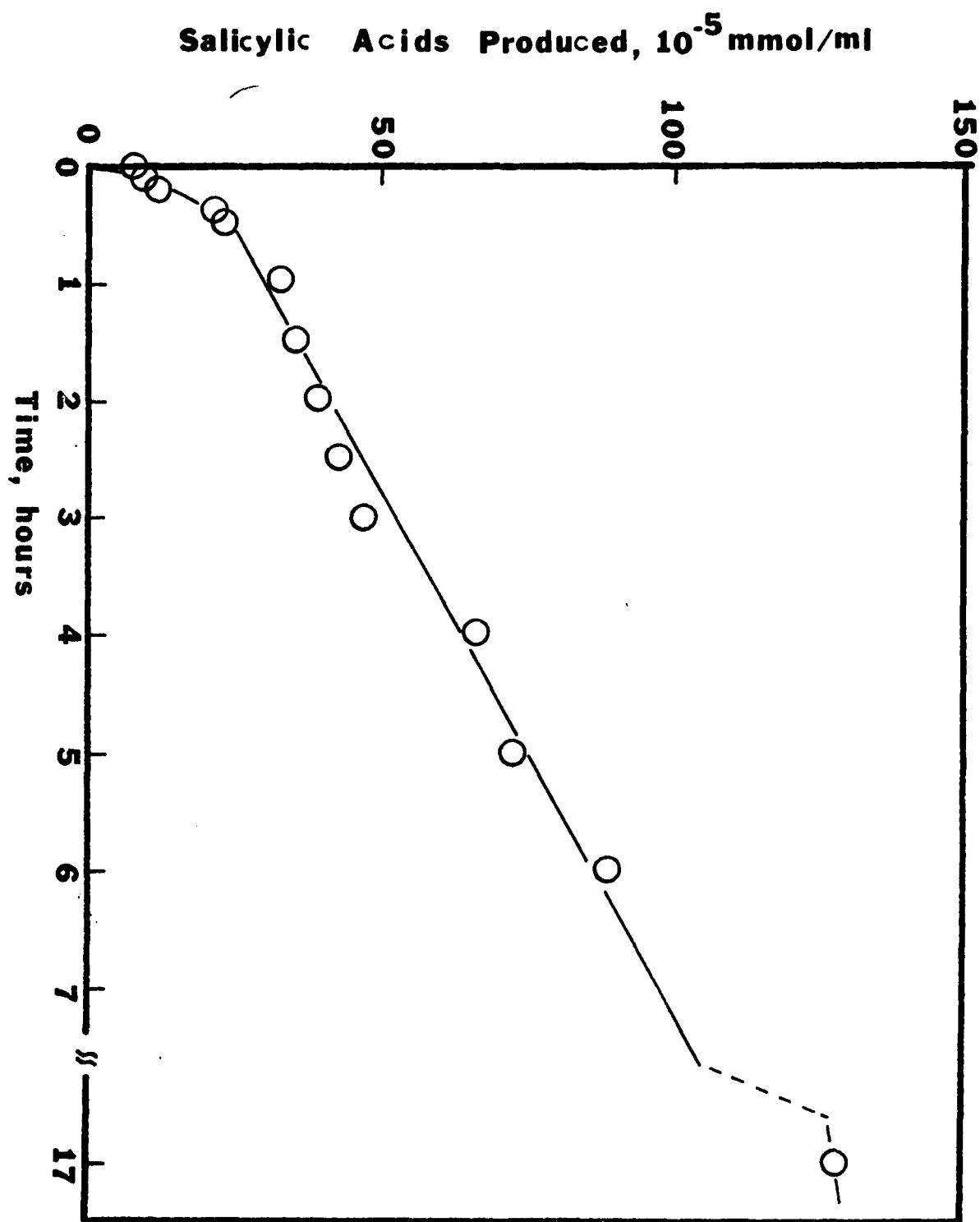Curves 2 and 3 use the left-handed current scale and curve 1 uses the right-handed scale.
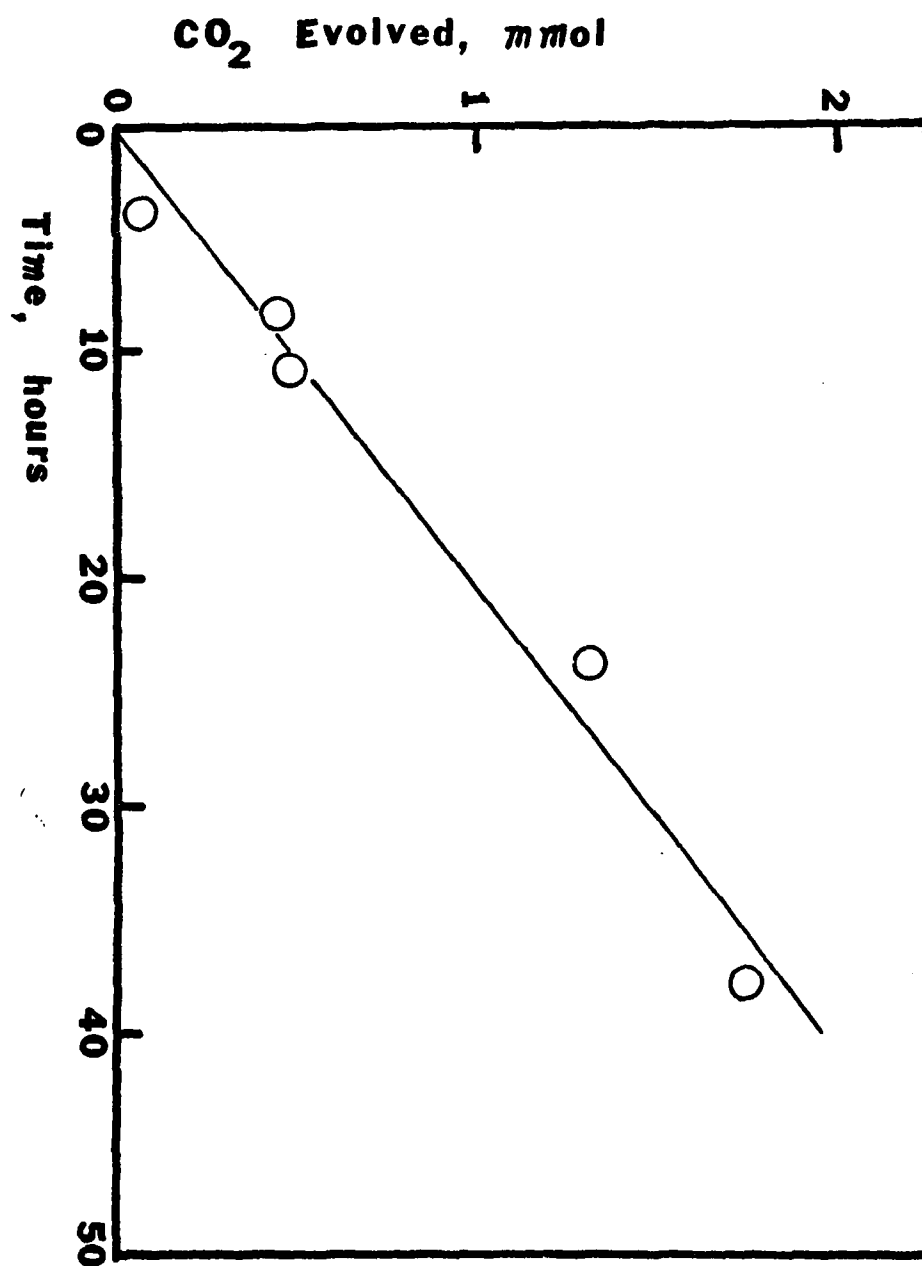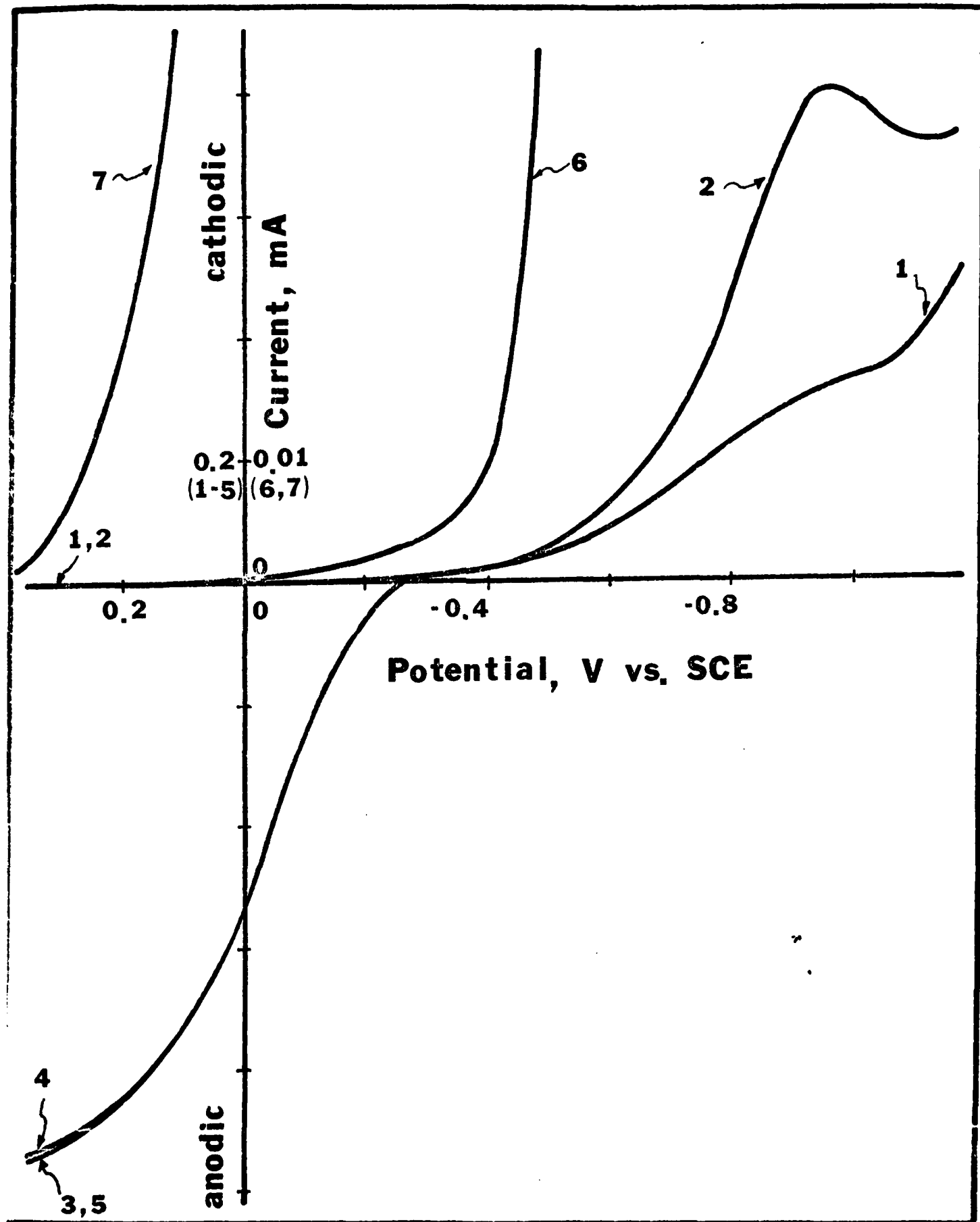
Fig 1

Fig 2

Fig 3

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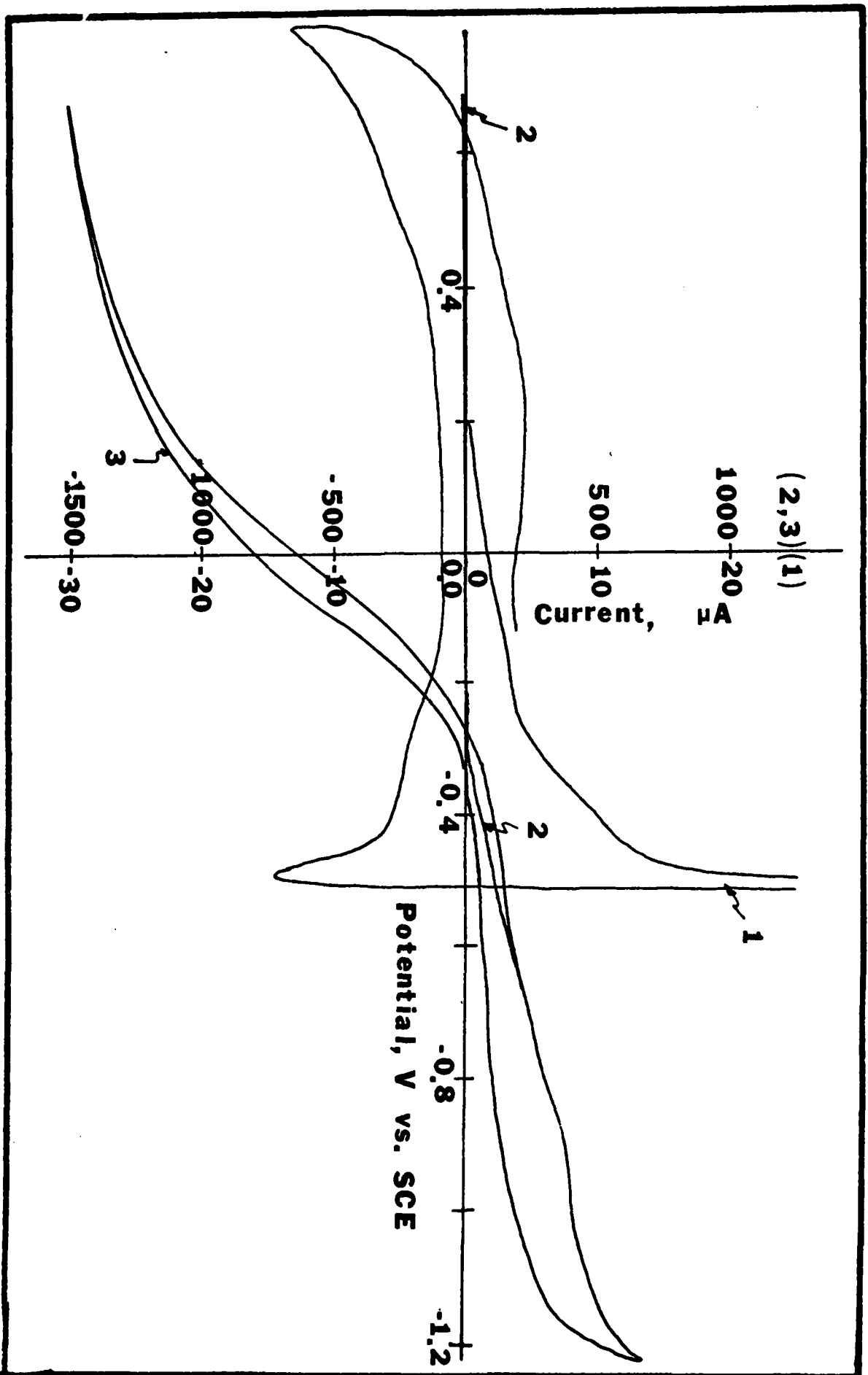
Fig 5

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