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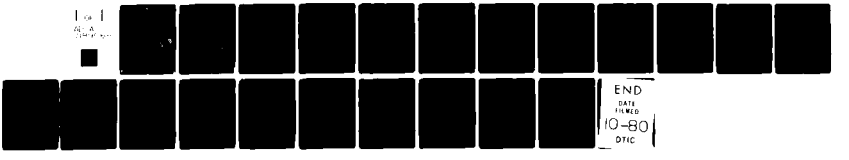

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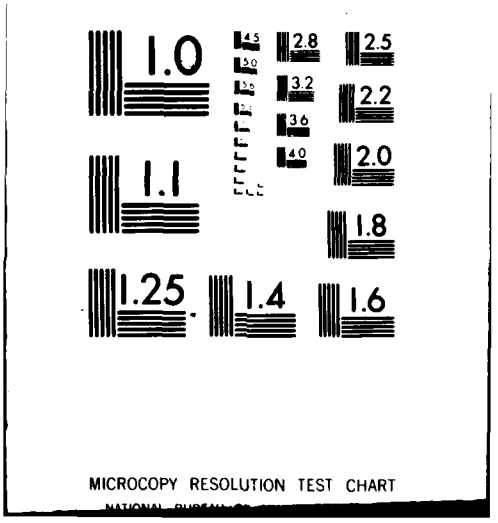
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The Heterogeneous Photocatalytic Oxidation of Hydrocarbons on Platinized TiO_2 Powders

by

Ikuichiro Izumi, Wendell W. Dunn, Keith O. Wilbourn,

Fu-Ren F. Fan, and Allen J. Bard

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The Heterogeneous Photocatalytic Oxidation of Hydrocarbons on Platinized TiO_2 Powders.

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(ABSTRACT)

The photodecomposition of hydrocarbons in oxygen-containing solutions at platinized TiO_2 yields predominantly CO_2 as the reaction product, with intermediate production of hydroxylated compounds. A mechanism for the reaction based on photogeneration of hydroxyl radicals at the TiO_2 surface is proposed.

(End of Abstract)

Introduction

Recent investigations from this laboratory have described the application of platinized titanium dioxide powders (Pt/TiO_2) to heterogeneous photocatalytic and photosynthetic processes, such as the photo-Kolbe reaction, in which aliphatic mono-[1] and di-[2] carboxylic acids are decomposed to give the corresponding alkane as the main product, as well as other reactions[3]. These investigations have clearly demonstrated the usefulness of Pt/TiO_2 in photoelectrochemical experiments and the potential for the accomplishing reactions requiring highly oxidizing conditions. In previous works we found that the decarboxylation of benzoic acid at Pt/TiO_2 involved the preceding hydroxylation of the benzene ring to form hydroxylated benzoates as reaction intermediates.[2] However, the main product of this reaction was CO_2, suggesting that photodecomposition of hydrocarbon intermediates was possible. Thus in this paper we extend these studies to the photocatalyzed decomposition of hydrocarbons at Pt/TiO_2. Phenol is shown to be a reaction intermediate for the photodecomposition of benzene, with the final product, CO_2. This unusual and efficient photocatalyzed breakdown of benzene at room temperature to yield CO_2 thus provides a possible pathway in the decarboxylation mechanism proposed for the photooxidation of benzoic acid.[2] We also describe the photodecomposition of several aliphatic hydrocarbons, in which alcohols have been detected as intermediates.

Experimental Section

Materials. Benzene [reagent grade, Matheson, Coleman and Bell (MCB)], hexane (MCB, 99$^+$ mol %), cyclohexane (spectrophotometric grade, MCB), heptane (reagent grade, Eastman), nonane and decane (Fisher Certified), barium hydroxide (reagent grade, MCB) and phenol (reagent grade, Fisher) were used without further purification. Decanol, nonanol, heptanol, hexanol, and cyclohexanol

(reagent grade, Eastman) were used as received for standards in GC-Mass spectroscopic analysis. The kerosene was extracted repeatedly with distilled water prior to illumination to simplify subsequent analysis of the aqueous phase. All solvents and other chemicals were reagent or spectrophotometric grade and were used without further purification. The platinized TiO_2 powders were prepared by photodecomposition of hexachloroplatinic acid onto TiO_2 powders (reagent grade, MCB, 125-250 μm) and contained 10 % platinum by weight.[4]

Apparatus. The irradiation source for the photodecomposition of aliphatic hydrocarbons was an Atlas Weatherometer, Model 6000, equipped with a 6000 W Xe lamp. The described experiments were performed at an unfocused power output of 5000 Watts, which corresponds to a total radiant intensity of $\sim$ 35 mW/cm^2 at the location of the reaction cell. The Xe lamp was jacketed with a water cooling cell to remove infrared irradiation. A constant reaction temperature was maintained with a large water bath fitted with a coil for water cooling. A 2500 W Xe lamp (Model UF 30 KK, Christie Electric Corp., Los Angeles, Calif.) operated at 1600 W, was used as the light source for all preparative runs in the photodecomposition of benzene. The reaction cell with a flat window for irradiation and the water bath were both of Pyrex. A 450 W Xe lamp with Model 6242 power supply (Oriel Corp., Stamford, Conn.) served in the photoelectrochemical measurements. Mass or GC-Mass spectra of reaction gases were obtained with an automated Gas Chromatograph/EI-CI Mass Spectrometer System (Finnigan, Model 2000). UV-visible spectra were recorded with a Cary Model 14 spectrophotometer. Electrochemical experiments were performed using a PAR Model 173 Potentiostat (Princeton Applied Research, Princeton, NJ) and a PAR Model 173 Universal Programmer.

Product Analysis. (a) Aliphatic Hydrocarbons: In a typical experiment, 200 mg of the photocatalyst powder was suspended by magnetic stirring in a two-phase system composed of 5 mL water and 5 mL of the hydrocarbon. The reaction cell was maintained at 36 ± 1 °C. The sweep gas, N_2 or O_2, was first passed through $Ba(OH)_2$ to remove any traces of CO_2 in the cylinder gas and then into the reaction cell. The gas was then passed through a large volume cell cooled at -56 °C to condense volatile organic chemicals, and then into a $Ba(OH)_2$ solution for determination of CO_2 as precipitated $BaCO_3$. Solar experiments were conducted in a Pyrex flask with a liquid surface area of approximately 700 cm^2 using 1.0 g of the photocatalyst. The condensed volatile organic chemicals were analyzed by a GC-Mass spectrometer. For hydrocarbon analysis, the columns used were a 6 m capillary of OVI and a 36 cm OVI column. Relative concentrations of trace impurities were compared by integration of ion current peaks and calibrated with standard samples. Investigation of the more polar constituents was performed with a Carbowax column. Identification of intermediate products was based on comparison of retention times and mass spectra of sample and standards. A detection limit of 2 ppm (equivalent to ~ 12 μM) was established for heptanol under these conditions.

The gas products not condensed at -56 °C were collected in a gas buret and were analyzed by a mass or GC-Mass spectrometer.

(b) Fenton's Reagent Reaction of Heptane: 5 mL heptane suspended in 100 mL 0.64 M $FeSO_4$, was purged with N_2 to remove CO_2. 5 mL H_2O_2 was added while the system was swept with N_2. After 12 hours, an additional 3 mL of H_2O_2 was added to ensure complete reaction. The evolved CO_2 was precipitated as $BaCO_3$ from a saturated $Ba(OH)_2$ solution.

(c) Benzene: In a Pyrex cell, a stirred suspension of 100 mg of Pt/TiO_2 in an emulsion of 5 mL benzene and 20 mL distilled water held at 27 ± 1 °C was illuminated under oxygen with white light from a 2500 W Xe lamp (operated at 1600 W). The gases produced during the irradiation were collected in a mercury-containing gas volumetric apparatus, as reported previously.[1] After termination of photolysis, the mixture in the gas buret was transfered to an evacuated gas sample cell which attached to the mass spectrometer for gas analysis. The average rate of CO_2 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 °C, and weighed. The colorless reaction mixture after filtering off the photocatalyst powders was analyzed by UV-visible absorption.

Results

Photocatalytic Decomposition of Benzene on Platinized TiO_2 Powders.

Illumination of suspensions of platinized TiO_2 powders in aqueous benzene mixtures in the presence of oxygen produced observable evolution of gaseous CO_2. After illumination, the gaseous products were analyzed by mass spectrometry. The mass spectra [m/e (relative intensity)] consisted of signals of CO_2, 44 (44.9 %), 16 (11.5 %) with background signals due to O_2, 32 (100 %); N_2, 28 (28 %); benzene, 78 (12 %); and water, 18 (5 %). Thus the only significant gaseous product of photooxidation of benzene in water was CO_2. The yield of CO_2 determined gravimetrically in another series of experiments is shown in Table I. The UV spectrum of the colorless reaction mixture showed absorption maxima at 2390, 2720, and 2780 Å with a shoulder at 2670 Å. The product was identified as phenol by comparing its UV spectrum with that of a standard

phenol solution. The concentration of phenol given in Table I was determined by UV spectroscopy. The results of some control experiments are also summarized in Table I. As shown in experiment 4, the photodecomposition of benzene requires the presence of catalyst. Platinized anatase has a higher efficiency than plain anatase powder (see experiments 2 and 7). The results shown in experiments 3 and 6 show that the presence of oxygen promotes the photodecomposition of benzene. Particularly interesting, the addition of water, compared to a system containing only benzene, promotes the photodecomposition of benzene (see experiments 2 and 5). As shown in experiments 1 and 2, substantial amounts of phenol were isolated as an intermediate product. These results suggest that the photooxidation of benzene on platinized TiO_2 powders suspended in H_2O probably proceeds via the hydroxylation of benzene to form phenols as the intermediate.[5,6] Moreover, the results are different from those for the electrolysis of aqueous benzene solutions in which p-benzoquinone is the predominant product.[7-9] No p-benzoquinone or p-hydroquinone were obtained in the present experiments.

Photocatalytic Decomposition of Aliphatic Hydrocarbons on Pt/TiO_2 Powders. Illumination of a suspension of Pt/TiO_2 in aqueous aliphatic hydrocarbon mixtures in the presence of oxygen also leads to the observable evolution of CO_2. The yields of CO_2, which was the only significant gaseous product (not condensed at -56 °C), are shown in Table II.

Extensive analysis for intermediates revealed a detectable level of only the alcohols (see Table II), except in the case of decane, where trace amounts of 2-, 4-, and 5-decanone were identified. The concentrations of lower molecular weight hydrocarbon impurities remained essentially unchanged before and after reaction, demonstrating that the cleavage of the alkanes does not result in the formation of shorter-chain hycrocarbons.

The reduction in the rate of photocatalytic oxidation with increasing molecular weight is coincident with an increase in the viscosity of the hydrocarbons. An exception to this trend is cyclohexane; however, in this case an emulsion of the three phases (photocatalyst powder, H_2O, and hydrocarbon) occurs. Addition of an emulsifying agent, IGEPAL-560 (nonionic nonyl phenoxy polyoxyethylene ethanol, GAF Corp.) to a suspension of decane was found to increase the rate of CO_2 production from 34.0 μmole/hr to 75.0 μmole/hr, confirming that the enhanced rate for cyclohexane oxidation is probably due to improved phase mixing.

The reaction between heptane and Fenton's reagent, which produces hydroxyl radicals, also produced a considerable amount of CO_2 (Table II). This demonstrates the possibility that at least in the initial stages of the photodecomposition process, the attack of ·OH on hydrocarbons and intermediates occurs.

Electrochemical and Photoelectrochemical Measurements. The photocatalytic activities of suspended platinized anatase powders were correlated with the behavior of TiO_2 single crystal electrodes in photoelectrochemical (PEC) measurements as shown in Figure 1. The current-potential behavior of a rutile single crystal electrode was examined in an aqueous solution containing 1 M $NaClO_4$ as the supporting electrolyte. In the dark, only a very small anodic current was observed on a TiO_2 electrode both in deoxygenated and in oxygen-saturated solutions, with or without benzene. In oxygen-saturated solution, however, the TiO_2 electrodes showed a reduction peak at -1.16 V vs. SCE (curve 2); this peak can be attributed to the reduction of oxygen, since it disappeared when the solution was thoroughly deoxygenated (curve 1). These voltammetric curves were essentially unaffected by saturating the solution with benzene (curves 5 and 6). Under illumination, an appreciable anodic

current was observed. The on-set photopotential, V_{on}, was essentially unaffected by the presence of oxygen or benzene, and was about -0.35 V vs. SCE for all cases. The presence of oxygen did not change the magnitude of the photocurrent, however, the presence of benzene caused a slight reduction in the photocurrent (curves 7 and 8), probably due to the absorption of some of the incident light by benzene and phenols generated. On the other hand, proton reduction on a platinum electrode in the presence of benzene occurred at potentials more negative than -0.4 V vs SCE (curve 9). However, oxygen reduction on platinum occurred at potentials much more positive than either the on-set photopotential or the reduction potential of oxygen on TiO_2 (curve 10). Thus, the presence of platinum on the TiO_2 powder could promote the photocatalytic activity of TiO_2 compared to TiO_2 alone. Also, the photocatalytic activity of platinized TiO_2 powder would be substantially enhanced by the presence of oxygen. These results at a rutile electrode are thus qualitatively consistent with the powder results. The role of oxygen in PEC and the accompanying photocatalytic reactions on TiO_2 have also been demonstrated by Korsunovskii.[10]

Discussion

In the presence of oxygen, several n-type semiconductor powders have been shown to behave as photocatalysts and promote the oxidation of substrates. Irradiation of a semiconductor with light of energy higher than the band gap results in the creation of holes in the valence band and electrons in the conduction band of the semiconductor. These charge carriers can recombine or the holes can be scavenged by oxidizable species (for example, H_2O, H_2O_2, or hydrocarbons (RH)), and electrons by reducible species (for example, O_2 or H^+) in the solution.

$$(TiO_2) + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \quad (2)$$

$$H^+ + e^- \rightarrow H\cdot \quad (3)$$

$$O_2 + e^- \rightarrow O_2^{\cdot-} \xrightarrow{H\cdot} HO_2^- \quad (4)$$

$$HO_2^- + h^+ \rightarrow \cdot HO_2 \quad (5)$$

$$2\cdot HO_2 \rightarrow O_2 + H_2O_2 \xrightarrow{O_2^{\cdot-}} \cdot OH + OH^- + O_2$$

(Haber-Weiss reaction) (6)

$$RH + \cdot OH \text{ (or } \cdot HO_2) \xrightarrow{-H\cdot} ROH \quad (7)$$

$$RH + h^+ \rightarrow RH^{+\cdot} \xrightarrow{h^+} RH^{++} \quad (8)$$

The electrochemical and photoelectrochemical measurements suggest that the reduction of H^+ on Pt and the reduction of O_2 on TiO_2 do not occur at an appreciable rate at the potentials where significant anodic photocurrent on TiO_2 is observed. However, the reduction of O_2 on Pt occurs at these potentials and this represents a viable half-reaction at the photocatalyst particle. The role of the Pt for this reaction is thus to provide a site for the more efficient utilization of the photogenerated electrons in the reduction of O_2 (e.g., eq. 4), in agreement with the finding that the photooxidation of hydrocarbons in deoxygenated solutions does not occur to an appreciable extent (Tables I and II). It is also possible that intermediates formed during the reduction of O_2 play an important role in the oxidation process, as suggested by reactions (4) - (6). 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 $HO_2^{\cdot}$.[17] The very slow rate of CO_2 production in pure benzene (see Exp. 5 in Table I), the lack of the intermediates other than hydroxylated compounds, and the dependence of the CO_2

evolution rate on the degree of phase mixing (Table II) suggest that the photogenerated holes are scavenged by water (eq. (2)) rather than by hydrocarbons (eq. (8)). These would form ·OH or $\cdot HO_2$, and lead to the hydroxylation of hydrocarbons and eventually the complete oxidation. The mode of the complete decomposition of the hydrocarbons has not been established. However, the detection of phenol for the case of benzene and alcohols for the cases of aliphatic hydrocarbons suggests that attack by ·OH or HO_2^- radicals is a likely first step. The probable role of ·OH in these reactions is also supported by the reaction of benzoic acid[2] and hydrocarbons with Fenton's reagent.

Thus the heterogeneous photooxidation of hydrocarbons in suspensions with Pt/TiO_2 can be explained by a mechanism similar to that invoked for benzoic acid, that is, the photooxidation proceeds via hydroxylated intermediates. In both experiments it is of importance that hydrocarbons, which are unattacked by most oxidizing agents, readily react with ·OH to form the final product CO_2. Since aliphatic hydrocarbons are themselves the products of the photo-Kolbe reaction,[1,2] their isolation in experiments involving the photodecomposition of organic acids suggest that they are capable of escaping from the powder surface. They then are swept from the reaction medium or react with ·OH less readily than the organic acid precursor. The destruction of hydrocarbons by the photocatalytic reaction described here might be useful in the treatment of waste streams or spills involving these materials.

Acknowledgment

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TABLE I. Photocatalytic Oxidation of Benzene on Platinized Anatase or Anatase Powders.[a]

Exp. No.	Catalyst	Time of illumination hrs	Conditions	CO_2 generated mmol	Phenol generated mmol
1	10% platinized anatase	4	illuminated, O_2 saturated	0.13	0.10
2	10% platinized anatase	18.5	illuminated, O_2 saturated	0.72	0.41
3	10% platinized anatase	40	illuminated, O_2 saturated	1.85	---
4	none	72	illuminated, O_2 saturated	0.03	---
5[b]	10% platinized anatase	19	illuminated, O_2	0.10	---
6	10% platinized anatase	43	illuminated, deoxygenated	0.15	---
7	anatase	14	illuminated, O_2 saturated	0.38	---

[a]If not otherwise mentioned, the solution was composed of 5 mL of benzene suspended in 20 mL of H_2O. 100 mg of catalyst was employed.

[b]25 mL of benzene was used as the reacting solution.

TABLE II. Photocatalytic Oxidation of Aliphatic Hydrocarbons on Platinized Anatase Podwers.

Alkane	Weight Powder (g)	Time of illumination (hr)	Rate CO_2 production (μmol/hr)	Rate of oxidation (μmol/hr)	Alcohol generated (μmol)
Hexane	0.199	24	53.7	8.95	
	0.200	12	30.9	5.2	0.55
	0.200	24	65.2	10.9	
Cyclohexane	0.200	24	86.4	14.4	6×10^{-5}
Heptane	0.200	48	60.4	8.6	0.650
	0.201	24	61.1	8.7	
	0.201	24	45.3	6.5	
	[a]0.0	18	14.4	2.1	
Nonane	0.200	24	41.4	4.6	0.220
	0.200	46	65.6	7.3	
	[b]1.430	24	54.6	6.1	
Decane	0.200	67	14.8	1.5	
	0.201	291	34.1	3.4	0.105
	[c]0.0	30	0.0	0.0	
	[d]0.200	24	0.0	0.0	
	[e]0.200	6	75.0	7.5	
Kerosene	0.200	72	17.2	---	---

[a]Performed with Fenton's Reagent, see exp. section.

[b]Solar experiment.

[c]Control experiment, no catalyst added.

[d]N_2 substituted for O_2.

[e]Emulsifying agent added (0.25 mL IGOPAL - 560)

FIGURE CAPTION

Fig. 1 Voltammetric curves at platinum and single crystal rutile electrodes in solution containing 1 M $NaClO_4$ as the supporting electrolyte. Scan rate 100 mV/sec. Initial potential at the positive extremes.

Curve 1: In the dark; on TiO_2; under N_2; solution without containing benzene.

Curve 2: In the dark; on TiO_2; oxygen saturated; without benzene.

Curve 3: Under illumination; on TiO_2; under N_2; without benzene.

Curve 4: Under illumination; on TiO_2; under O_2; without benzene.

Curve 5: In the dark; on TiO_2; under N_2; benzene saturated solution.

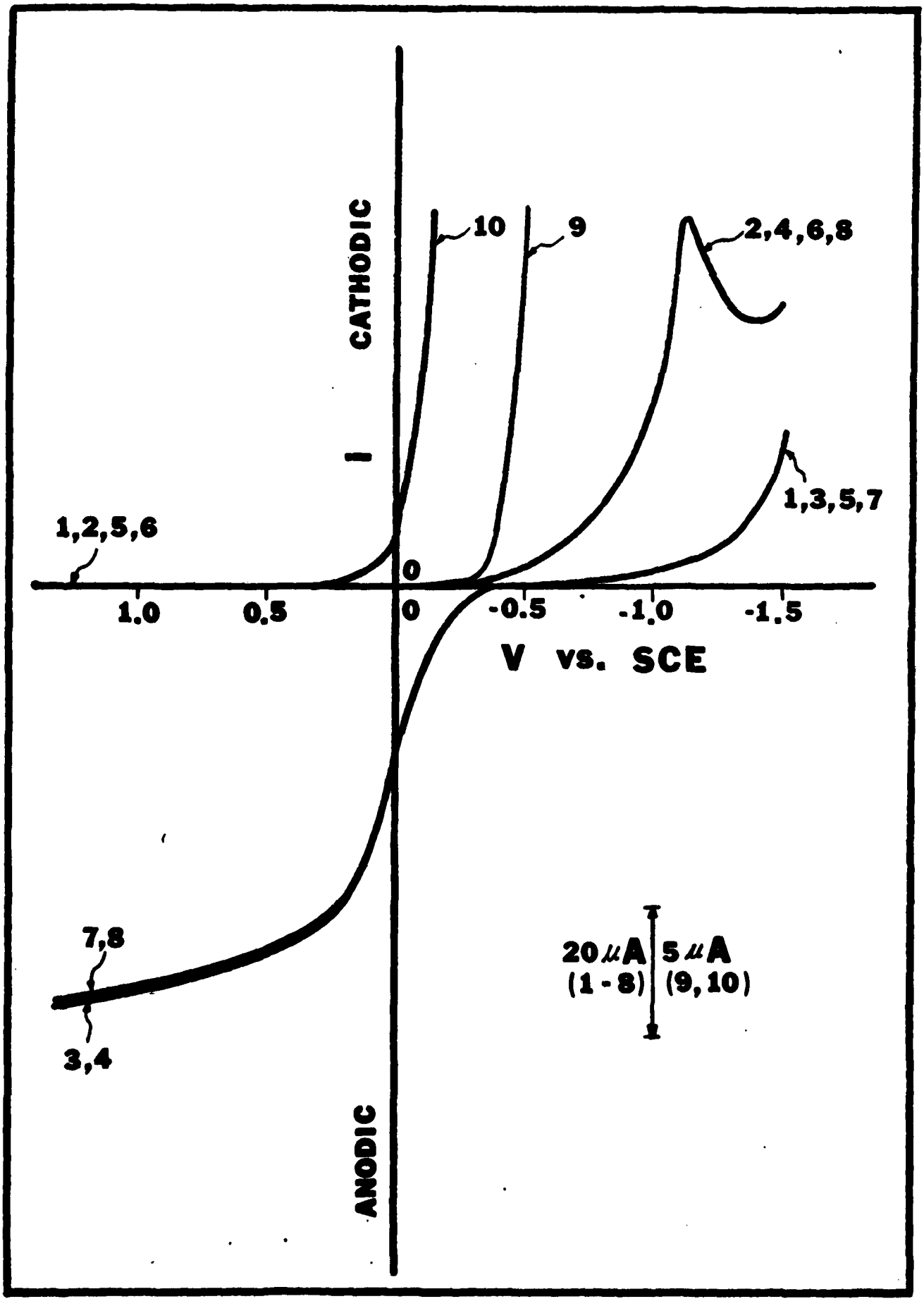
Curve 6: In the dark; on TiO_2; oxygen and benzene saturated solution.

Curve 7: Under irradiation; on TiO_2; under N_2; benzene saturated solution.

Curve 8: Under irradiation; on TiO_2; oxygen and benzene saturated solution.

Curve 9: On Pt; under N_2; benzene saturated.

Curve 10: On Pt; oxygen and benzene saturated.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