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Catalytic Oxidation of Organic  
Compounds in Waste Water

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F I N A L   R E P O R T

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ABSTRACT

CATALYTIC OXIDATION OF ORGANIC COMPOUNDS IN WASTE WATERS

Water pollution is rapidly becoming a major problem. Through studies of the effect of ultrasound on catalysts it has been found that certain water pollutants can be oxidized or modified. This synergetic effect between ultrasound and certain heterogeneous catalysts, sonocatalysis, is demonstrated qualitatively for a number of organic compounds (anilines, stilbestrol, orthochloronitrobenzene and phenol) and quantitatively for the oxidation of iodide ion. The technique shows promise as a tertiary treatment of municipal waste water.

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# SONOCATALYSIS

by

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## INTRODUCTION

Heterogeneous catalysts increase the rates of chemical reactions by gathering reactants in close proximity and furnishing new, lower energy pathways. In spite of this common surface ability to collect molecules, high energy barriers preclude the ready occurrence of many reactions. Usually heat is supplied to surmount high energy barriers, but, in principle, other forms of energy may be used. For example, electrical energy is used in electrochemical reactions, and both high energy particles and electromagnetic radiations have imparted extra energy to surfaces. We have discovered that ultrasonic irradiation may be another energy source for certain catalytic reactions.<sup>1,2</sup> In this and the following papers, we present evidence for sonocatalysis, the synergetic effect between certain catalysts and high frequency ultrasound, and discuss its possible mechanisms and implications.

## APPARATUS AND PROCEDURES

The standard experimental apparatus was simply a large flat-bottomed glass tube (2½ x 16 inches) positioned a few millimeters above an 800 KHz submersible piezoceramic transducer (Macrosonics Inc.), both of which were immersed in a cooling water bath. The bottom of the reactor tube was usually glass; however,

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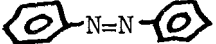



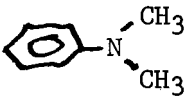
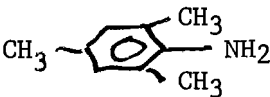


in some experiments aluminum foil and Cuprophan (150PT-M) membrane were used. Aluminum foil worked very well for short periods but developed holes after several hours. The special Cuprophan (150PT-M) membrane worked well. Gases were introduced through glass tubes extending to within a few millimeters of the bottom and optimum insonation was estimated by adjusting variables, e.g. reactor/transducer positions, for maximum liquid jet height at each energy input. Other details of the apparatus and procedures were as previously described except where noted.

## RESULTS

### Oxidative Dehydrogenation of Certain Anilines

In six hours at 120°C. (boiling petroleum ether) aniline is converted to azobenzene in 87% yield over activated  $\text{MnO}_2$ .<sup>3</sup> At room temperature and in aqueous solution, the reaction is not readily detected; however, insonation at 800 KHz yields azobenzenes and other unidentified products for certain anilines. Results from these qualitative experiments are tabulated in Table I. Since experiments were conducted for the purpose of detecting a reaction, not all products were isolated and identified. Azobenzene and p,p'-dimethoxyazobenzene were isolated and identified by mass spectrometry.

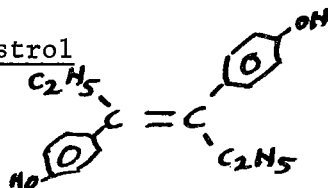
TABLE I: OXIDATIVE DEHYDROGENATION OF AQUEOUS SOLUTIONS OF  
ANILINES BY SONOCATALYSIS WITH  $MnO_2/800\text{ KHz}$

<u>COMPOUND</u>	<u>PRODUCTS/RESULTS<sup>a</sup></u>
	 + at least four others
	 + six others
	trace of product, possibly the azobenzene
	no products detected
	no products detected
	no products detected
	no products detected

a) reaction mixtures were filtered, extracted with acetone, evaporated to dryness and analyzed by thin-layer-chromatography.

### Epoxidation of Stilbestrol

Stilbestrol,



, is oxidized to the epoxide by

peracids. We have identified the epoxide in the reaction mixture obtained from a six-hour irradiation of a mixture of 200 mg of stilbestrol, 200 ml of water, and 500 mg of  $MnO_2$  catalysts.

The product isolated by preparative thin-layer-chromatography (TLC) matched exactly (TLC, I.R., N.M.R.) an authentic sample of the epoxide prepared from stilbestrol by epoxidation with m-chloroperbenzoic acid.

### Attempted Sonocatalytic Oxidations of Steroids

Insonation of water is believed to produce  $H_2O_2$  as a principle product.<sup>4</sup> However, since peracid is required for the conversion of stilbestrol to the epoxide, our finding of stilbestrol epoxide points to the presence of a more powerful oxidizing agent than  $H_2O_2$ . To attempt to identify the relative potency of the oxidizing agent in insonated water we subjected a variety of steroids to sonocatalytic oxidation using  $MnO_2$ . Compounds tested were progesterone, cholesterol, stigmasterol, testosterone and lanesterol. No products could be detected.

### Sonocatalytic Reactions of Orthochloronitrobenzene

Orthochloronitrobenzene is a known water pollutant which can be removed only by charcoal filtration. It was of interest, therefore, to test the applicability of the sonocatalytic technique to the destruction of orthochloronitrobenzene. Initially, a variety of catalysts were tried,  $PtO_2$ , Pd/C,  $MnO_2$ , Pt/C, Rh/C with air, oxygen or oxygen/ozone mixtures, but no reactions were detected. Products were obtained, however, with aluminum powder or Raney-nickel catalysts with air, oxygen or oxygen/ozone mixtures. These experiments are described and discussed in progress reports to the FWQCA and in later papers in this series. Several products were formed in six hours and the three isolated were typical nitrobenzene reduction products. When a saturated aqueous solution of orthochloronitrobenzene is submitted to sonocatalytic ozonation for 24 hours, neither starting material nor products can be detected.

### The Silver Mirror Phenomenon

During the studies with orthochloronitrobenzene silver oxide,  $\text{Ag}_2\text{O}$ , was tested as a potential catalyst. No change in orthochloronitrobenzene occurred, but a silver mirror formed on the walls of the reaction vessel, Plate 1. Since no mirror formed in the absence of orthochloronitrobenzene, but the silver was reduced by ultrasound, we assume that a complex between  $\text{Ag}^+$  and/or  $\text{Ag}^0$  and orthochloronitrobenzene adjusts the silver concentration to that favorable for forming the mirror. As can be seen in the upper portion of Plate 1, the distance between rings of silver is approximately 1mm, about the wavelength of insonation.

### Sonocatalytic Oxidation of Phenol

Previously, we reported preliminary results of our studies on sonocatalytic oxidation of phenol.<sup>1</sup> Complete details of more extensive studies are included in reports to the FWQCA and a later paper in this series.

Although phenol can be oxidized under the influence of ultrasound alone, it is not readily oxidized by catalysts and air at room temperatures. The combination of ultrasound and certain catalysts, however, causes the concentration of phenol to decrease faster than does ultrasound alone.

### Sonocatalytic Oxidation of Potassium Iodide

Aqueous solutions of potassium iodide (0.1M, 200 ml) were oxidized either by high (800 KHz) or low (55KHz) frequency ultrasound or by various catalysts and ultrasound. Tables II - VI compare the experimental results at high and low frequencies. The values for liberated iodide appear to be reproducible to within  $\pm 10\%$  of the number and were determined by titration with an 0.05 N solution of  $\text{Na}_2\text{S}_2\text{O}_3$ .

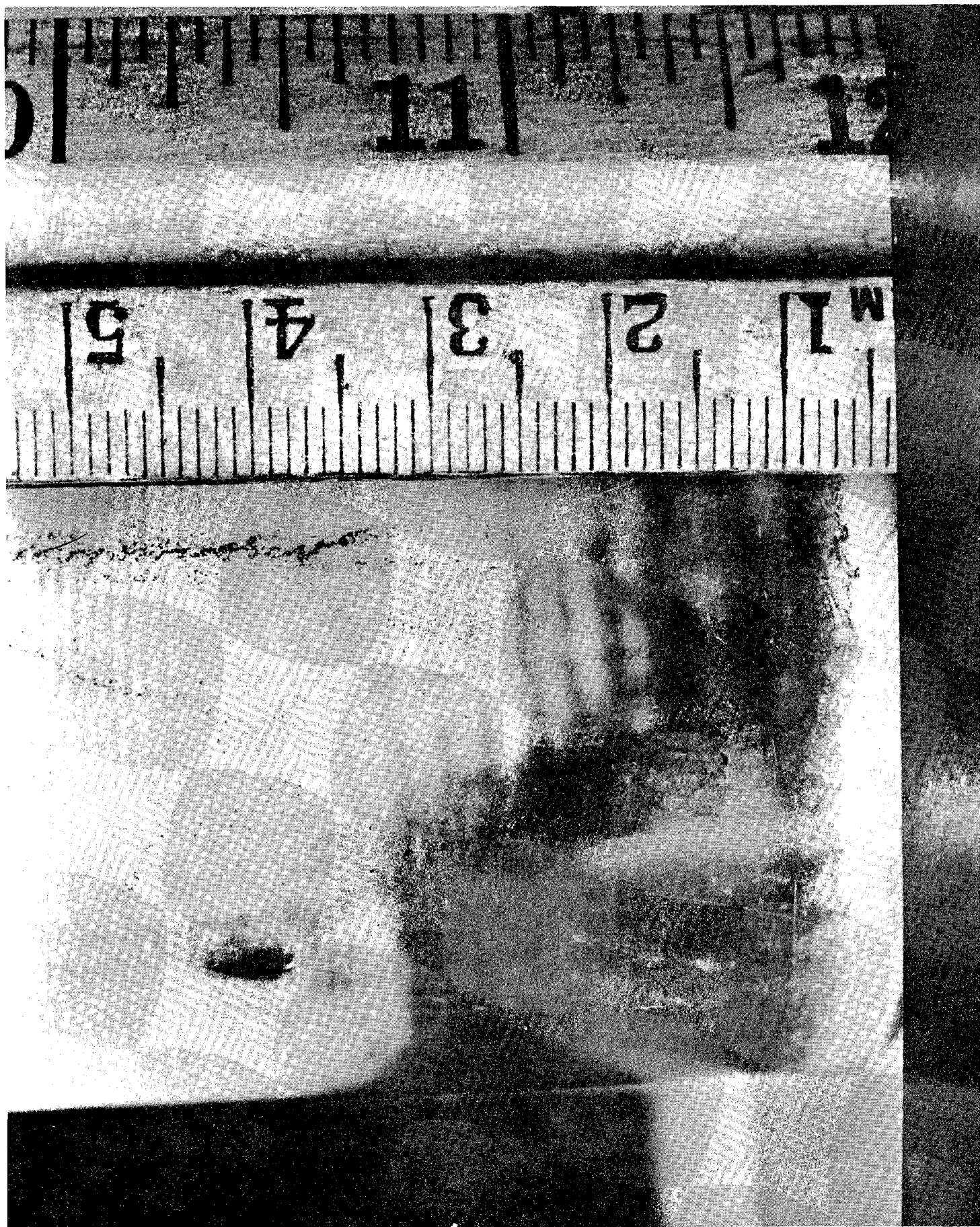


Plate 1: Sonodeposition of silver mirror from aqueous solution of orthochloronitrobenzene containing solid silver oxide.



TABLE II: OXIDATION OF IODIDE ION TO IODINE AT HIGH FREQUENCY

<u>CATALYST<sup>a</sup></u>	<u>0.0 Hz<sup>b</sup></u>	<u>800 KHz<sup>b</sup></u>	<u><math>\Delta</math><sup>c</sup></u>
Ru <sub>2</sub> O <sub>3</sub>	204	415	+23
MnO <sub>2</sub>	116	260	-40
PtO <sub>2</sub>	51	240	+1
V <sub>2</sub> O <sub>5</sub>	20	290	+82
PdO <sub>2</sub>	0	170	-18
CuO/Al <sub>2</sub> O <sub>3</sub>	0	210	+22
MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0	270	+82
108 G(F.-T.)	0	225	+37
Chalk	0	193	+5
Ru/C	0	0	-188
Ru/C+Ru <sub>2</sub> O <sub>3</sub> <sup>d</sup>	0	0	-188
None	0	188	0

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a) 0.50 grams

b) mg/liter of I<sub>2</sub> liberated in 3 hours from 0.1M I<sup>-</sup>

c) (ultrasound and catalyst)-(ultrasound without catalyst)-188 =  $\Delta$

d) 0.50 grams each catalyst

TABLE III: OXIDATION OF IODIDE ION TO IODINE AT LOW FREQUENCY

CATALYST <sup>a</sup>	0 Hz <sup>b</sup>	55 KHz <sup>b</sup>	$\Delta^c$
MnO <sub>2</sub> <sup>d</sup>	51	103	+4
Ru <sub>2</sub> O <sub>3</sub>	206	257	+3
Ru/C	0	0	-48
V <sub>2</sub> O <sub>5</sub>	19	128	+61
CuO/Al <sub>2</sub> O <sub>3</sub> <sup>e</sup>	0	10	-38
None	0	48 $\pm$ 3	0

a) 0.50 grams except for MnO<sub>2</sub> and CuO/Al<sub>2</sub>O<sub>3</sub>

b) mg/liter of I<sub>2</sub> liberated in three hours from 0.1 M I<sup>-</sup>

c) (ultrasound and catalyst)-(ultrasound without catalyst)-48 =  $\Delta$

d) 0.200 grams

e) 1.00 grams

TABLE IV: OXIDATION OF IODIDE ION TO IODINE  
AS A FUNCTION OF AMOUNT OF MnO<sub>2</sub>

GRAMS MnO <sub>2</sub>	0 Hz		800 KHz	
	<u>a</u>	<u>b</u>	<u>a</u>	<u>c</u>
0.00	0	0	188	159 <sup>b</sup>
0.05	15	-	260	190
0.20	58	32	276	159
0.50	116	140	257	216
1.00	193	272	193	343
1.50	280	394	289	439
2.00	353	483	360	447

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- a) catalyst activated according to reference 2, i.e. dried at 125°C for 24 hours
- b) catalyst activated according to reference 3.
- c) catalyst activation same as in b but a different batch

TABLE V: OXIDATION OF IODIDE TO IODINE AS A  
FUNCTION OF AMOUNT OF  $V_2O_5$

<u>GRAMS <math>V_2O_5</math></u>	<u>0 Hz</u>	<u>800 KHz</u>	<u><math>\Delta</math></u>
0.50	19	290	+83
1.00	26	630	+416
1.50	(38) <sup>a</sup>	218	-8
2.00	58	135	-111

a) determined graphically

TABLE VI: OXIDATION OF IODIDE ION TO IODINE UNDER SPECIAL CONDITIONS

CAT/gms	0 KHz	55 KHz	800 KHz
MnO <sub>2</sub> /0.20 <sup>a</sup>	0	5	--
None <sup>a</sup>	--	12.8	--
MnO <sub>2</sub> /0.20 <sup>b</sup>	39	32	--
MnO <sub>2</sub> /1.50 <sup>c</sup>	0	--	0
MnO <sub>2</sub> /1.50 <sup>d</sup>	330	--	360
MnO <sub>2</sub> /0.20 <sup>e</sup>	109	--	283

- a) irradiated for three hours then added enough KI solution to make 0.1M. after ten minutes centrifuged and titrated for I<sub>2</sub>. In case of no catalyst, solid KI was added after irradiation
- b) irradiated only fifteen minutes
- c) solution made basic by adding 0.2 grams KOH to 200 m. 0.1 M KI solution
- d) solution made acidic by adding two drops 6M HCl to 500 ml 0.1M KI solution

## DISCUSSION

Sonocatalysis

There is a synergetic effect, sonocatalysis, between certain catalysts and high frequency sound. This effect is measured quantitatively in the experiments with potassium iodide and qualitatively in the other experiments. In some cases, a reaction appears to go faster in the presence of both a catalyst and ultrasound than in the presence of either one alone; in other cases, in which reaction does not occur under the experimental conditions, reactions are sonocatalyzed, e.g. epoxidation of stilbestrol. We believe the effect is real and have sought a rational explanation.

Physical vs. Chemical Effects

A very good way to start is to decide whether the effect is physical or chemical in nature. Table VII lists a variety of potential physical and chemical effects.

That certain catalysts are colloidized during insonation is shown by experiments with  $PtO_2$ . Sonocatalysis of aqueous phenol with  $PtO_2/800$  KHz causes changes in the phenol as detected by ultraviolet spectroscopy. Using this as a rough guide to disappearance of phenol, it was found that irradiated aqueous suspensions of  $PtO_2$  were active for oxidation of phenol. For example, when 0.2 gms  $PtO_2$  in 100 ml of water is irradiated one hour and 100 ml of 0.01 M phenol solution is added after the irradiation is stopped, a large decrease in the phenol U. V. band (70% decrease) occurs. Apparently the catalyst was colloidized by the irradiation; the catalyst passed through filter paper, exhibited a Tyndall effect and could be removed only by ultracentrifugation.

The cleaning ability of ultrasound occurs by cavitation at high intensity/frequency ratios.<sup>5</sup> Since most of our experiments were conducted at high frequency, 800 KHz, and low intensities, 33 watts/cm<sup>2</sup> maximum possible but probably about 5

TABLE VII: POSSIBLE PHYSICAL AND CHEMICAL  
EFFECTS CAUSING SONOCATALYSIS

PHYSICAL	CHEMICAL
<p>I. Increasing surface area</p> <p>A. Fracturing Catalyst (colloid; create more pores)</p> <p>B. Cleaning surface (destroy thick absorbed layers)</p> <p>II. Increasing rate of diffusion</p> <p>A. Bulk diffusion</p> <p>B. Pore diffusion</p> <p>III. Deform double layer</p> <p>IV. Catalyst serving as nuclei for cavitation</p>	<p>I. Effecting substrate-catalyst bonding</p> <p>A. Energy absorbed by substrate-catalyst complex</p> <p>B. Energy absorbed by catalyst and then transferred to substrate</p> <p>    i. heating of catalyst</p> <p>    ii. electric (piezo)</p> <p>C. Energy absorbed by solvent or gas and then transferred to substrate-catalyst complex</p> <p>II. Changing solvent into reactive species</p> <p>A. <math>\text{H}_2\text{O}_2</math></p> <p>B. <math>\cdot\text{OH}</math>, <math>\text{H}\cdot</math></p> <p>III. Changing gas into reactive species</p> <p>A. <math>\text{O}_2</math> (singlet oxygen)</p> <p>B. <math>\text{O}_3 \longrightarrow \text{O}\cdot + \text{O}_2</math> (singlet or triplet)</p>

watts/cm<sup>2</sup> under actual conditions, liquid phase cavitation was probably not occurring. At different kinds of surfaces, however, some cavitation may occur at intensity/frequency ratios lower than required in the liquid phase and lower than required for some surfaces. Such surface cavitation could provide physical disturbances of adsorbed poisons or thick adsorbed layers of molecules or could deform double layers of any ions present. Because of our high intensity/frequency ratios it does not seem likely that cavitation is significant. In several phenol oxidation experiments Adams platinum oxide catalyst was replaced by powdered activated charcoal to test the possibility that small catalyst particles were serving as nuclei for cavitation. Other than an initial and rapid adsorption of phenol by the charcoal no further decrease in phenol concentration occurred during insonation.

Supermixing resulting from acoustic streaming could remove diffusion control either in the bulk phase or in catalyst pores. We did not test for either of these possibilities; however, chemical evidence, such as the changes in orthochloronitrobenzene and stilbestrol which do not occur under the same conditions in the absence of ultrasound, seem to preclude removal of diffusion control as a significant factor in our experiments.

It seems generally accepted that ultrasound causes chemical changes in various substances. In water, for example, it is believed that hydrogen peroxide is formed.<sup>4</sup> Our sonoepoxidation of stilbestrol, however, suggests a somewhat more powerful oxidizing agent than hydrogen peroxide. Such an agent might be  $\cdot\text{OH}$ , singlet oxygen or some oxygen species absorbed on the catalytic surface.

An exciting possibility is that ultrasonic energy is used by the catalyst (or catalyst-substrate complex) to surmount energy barriers for reactions. Such a possibility offers the potential for selectively catalyzing **one** reaction in preference to others.



Bond energies are altered in catalyst-substrate complexes. Substantial pressures and motions are created by insonation at 800 KHz<sup>6</sup> and such effects may be enough to rupture weakened bonds. Long organic molecules, for example, are ruptured by the rapid motions caused by high frequency irradiation<sup>7</sup> and conformational equilibria are disturbed by insonation.<sup>8</sup> In a similar way the energy of certain molecules in solution could be raised such that absorption on the catalyst surface causes bond rupture or ready interaction with other absorbed molecules.

Conversion of ultrasonic energy into heat energy at the catalyst surface would provide a means of surmounting certain energy barriers. Among other things, absorption of ultrasound by solids depends upon anisotropic crystalline grains which would be present in catalysts. Likewise, if the catalyst is a piezoelectric substance, the ultrasonic waves may be either attenuated or amplified. This, of course, could not occur in our experiments since none of our catalysts were piezoelectric substances.

#### Sonocatalytic Oxidation of Iodide

Although the exact nature of the mechanism of sonocatalysis is uncertain, some of the gross character of the effect is clear. For example, it might be expected that a reaction either initiated by ultrasound or catalyzed by a solid would, under the simultaneous influence of both, proceed at a rate approximately equal to the sum of the two independent rates. In fact, this does not happen as shown in Figure 1. Plotting the data from Table IV in Figure 1 reveals an interesting phenomenon. At small amounts of catalyst the liberation of iodine is greater than expected from the addition of amounts liberated by ultrasound alone and activated manganese dioxide alone, i.e. sonocatalysis. However, as more and more catalyst is added the amount of iodine liberated becomes less and less until it equals that liberated by activated manganese dioxide alone. Apparently the increasing quantities of catalyst particles disperse and reflect the ultrasonic waves so badly

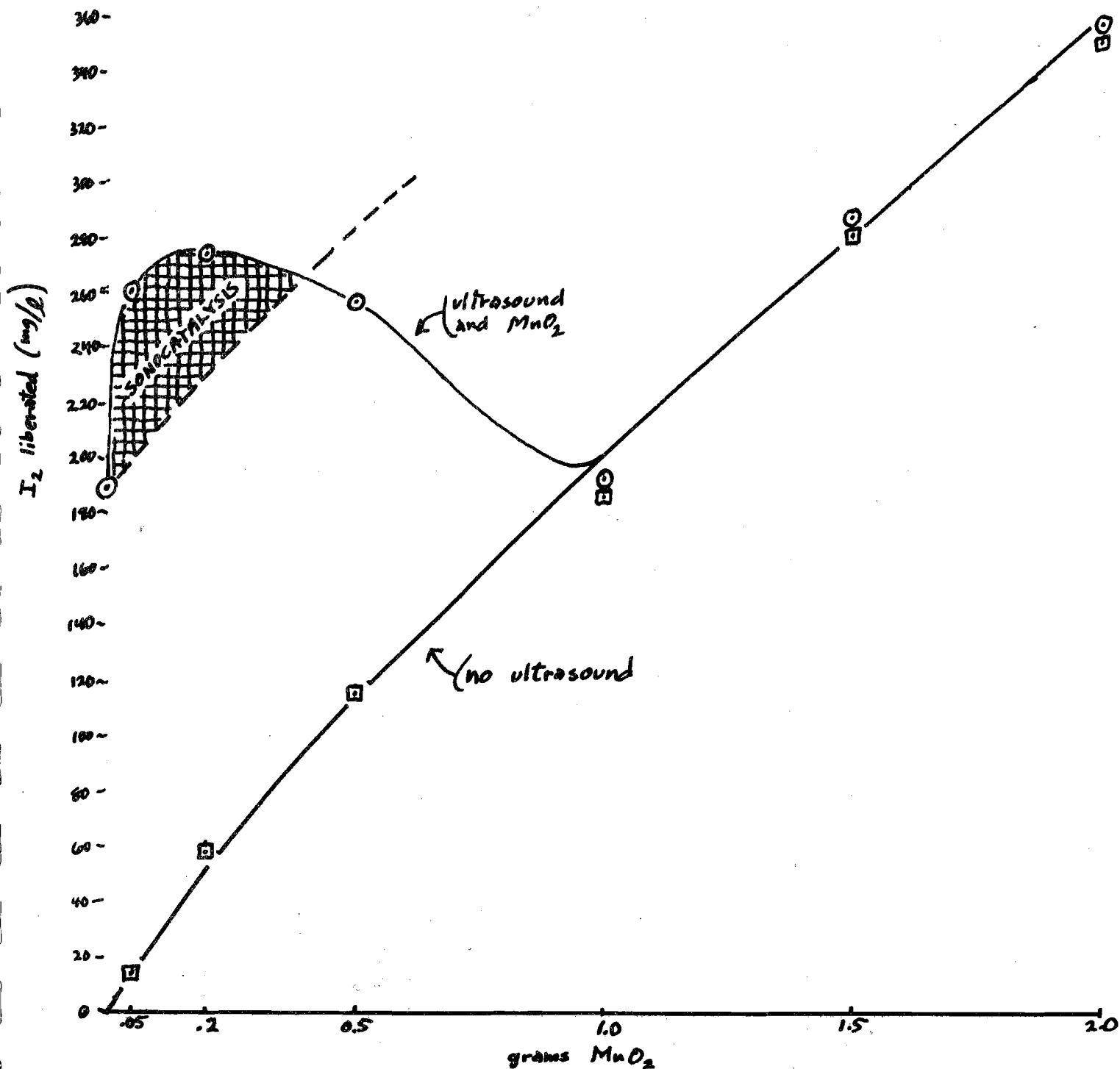


Figure 1: Sonocatalytic oxidation of  $I^-$  to  $I_2$  over activated  $MnO_2$  with and without insonation (800 KHz)

that the ultrasound induced reaction and sonocatalytic reaction cannot occur. A similar but greater effect can be seen in the data for  $V_2O_5$  in Table V.

Excellent experimental agreement for this damping effect is seen in recent work which was apparently conducted simultaneous to ours. By measuring the decomposition of hydrogen peroxide by ultrasound (550 KHz,  $4-5 \text{ W cm}^{-2}$ ) as a function of increasing amounts of catalysts, data plotted in Figure 2 were obtained.<sup>9</sup> Although we were not able to extract the datum for ultrasound and no catalyst, the damping effect is obvious. Data for rhodium and palladium did not so clearly demonstrate the effect.

Evidently sonocatalysis is limited by this damping effect. Reactor design can probably overcome some of the effect but large amounts of catalyst will decrease rates on a per gram basis. This will apply to reactions which are sonolytically induced as well as reactions which are sonocatalyzed.

#### ACKNOWLEDGEMENTS

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We appreciate Mr. Michael Beckett increasing our confidence in certain data through repeat experiments.

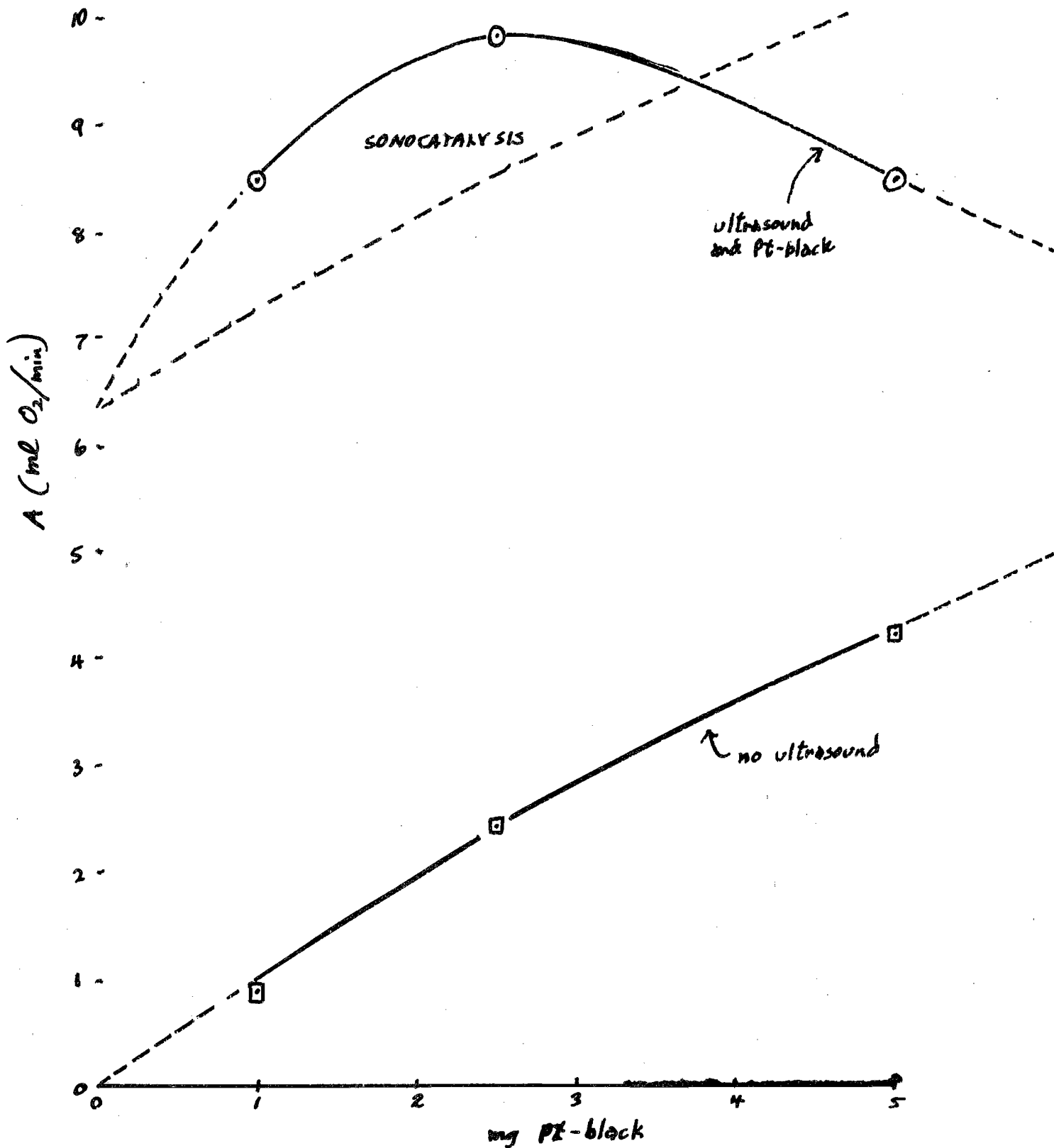


FIGURE 2: SONOCATALYTIC DECOMPOSITION OF  $H_2O_2$  over Pt-black with and without insonation (550 KHz), see reference 9.

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