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## The Photochemistry of the Nitrite Ion

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# The Photochemistry of the Nitrite Ion

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Chemistry 499 Thesis  
Illinois Wesleyan University  
May 13, 1994

Approval Page  
"The Photochemistry of the Nitrite Ion"  
by Deborah Anne Cull


A PAPER SUBMITTED IN PARTIAL FULFILLMENT OF  
THE REQUIREMENTS FOR CHEMISTRY 499 AND  
HONORS IN CHEMISTRY.

Approved, Honors Committee:



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Dr. Timothy R. Rettich, Research Advisor



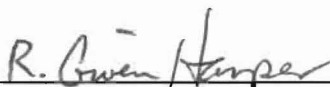
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Illinois Wesleyan University  
1994

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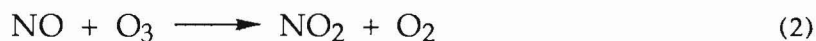
## Abstract

The photolysis of aqueous nitrite ion,  $\text{NO}_2^-$ , yields the free radicals nitric oxide,  $\text{NO}\cdot$ , and hydroxyl radical,  $\cdot\text{OH}$ . It has been found by Treinin and Hayon<sup>1</sup> and supported in this laboratory that no net reaction occurs when nitrite is photolyzed in pure water. Zafirou<sup>2</sup> has extensively studied the solar photolysis of nitrite-containing seawater, and has detected increased partial pressures of  $\text{NO}\cdot$  during the day, as well as decreased nitrite concentrations, which both suggest that net photolysis of nitrite has occurred.

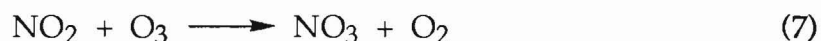
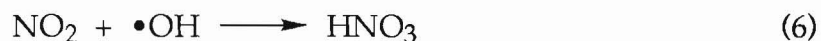
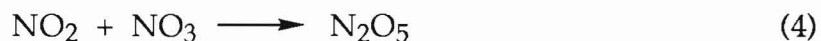
In pure water, the  $\cdot\text{OH}$  and  $\text{NO}\cdot$  radicals produced from the photolysis of  $\text{NO}_2^-$  presumably recombine and ultimately reproduce  $\text{NO}_2^-$ . In the presence of benzene, a known radical scavenger, this process is interrupted and net photolysis of nitrite is observed. This particular scavenging process is of primary interest to this research. Aqueous nitrite saturated with benzene has been photolyzed at 366nm, a wavelength present in solar radiation at which nitrite absorbs. The effect of varying the pH as well as the solvent for maximal extraction of the scavenger product has been studied. Ideally, the identity of the product will be obtained, leading to the quantification of the scavenging process. The reaction has been monitored both spectrophotometrically as well as by a nitrite-specific electrode. In addition to the photochemical reaction, the thermal reaction of nitrite in the presence of benzene has been tested. The scavenging of the hydroxyl radical by benzene has also been studied by producing  $\cdot\text{OH}$  via hydrogen peroxide and a catalyst. Long range goals include the determination of the quantum yield with respect to nitrite disappearance, with the results compared to the photolysis of nitrous acid, a process that occurs in polluted atmospheres.

## Introduction

Today, with an ever-increasing population comes ever-increasing ramifications of human activities, otherwise known as environmental degradation. Much of the harm to the environment, and especially the atmosphere, is the result of releasing unnaturally high levels of chemicals into the environment. One of the most common families of pollutants are the various nitrogen oxides, which are the result of the combustion of fuels in air. Nearly 100 million tons of nitrogen dioxide (NO<sub>2</sub>) are emitted annually as a result of the combustion of fossil fuels<sup>3</sup>, initially forming primarily nitric oxide (NO), which is rapidly converted into a myriad of nitrogen oxide compounds in the troposphere, some of which are shown below.<sup>3</sup>



The amber haze observed as one flies over a polluted city includes nitrogen dioxide, NO<sub>2</sub>. However, nitrogen dioxide also reacts in the atmosphere to form nitric acid or to deplete ozone.<sup>3</sup>



The reactions presented above are only a few of the many reactions which occur with nitrogen oxides. These reactions exemplify a "double attack" on ozone by both nitric oxide (reaction 2) and nitrogen dioxide (reaction 7), both resulting from the combustion of fuels. It has been hypothesized that a fleet

of 500 supersonic Concorde-type aircraft *could* reduce the ozone layer by as much as 5% due to the high levels of nitrogen oxides emitted during flight, which would increase UV radiation by 10%.<sup>4</sup> Also shown is the formation of nitric acid, a component of acid rain, which results from several different reactions (reactions 4 & 5, 6). Paramount to this research is the formation of nitrous acid,  $\text{HNO}_2$  which forms in the moist atmosphere via the following reaction.<sup>5</sup>

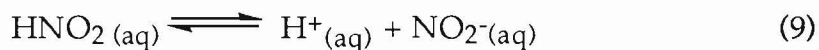


Nitrous acid can enhance the formation of secondary photooxidants, such as ozone, hydroxyl radical, and hydrogen peroxide.<sup>6</sup> In the troposphere, the layer of the atmosphere closest to the earth, ozone is harmful and therefore another atmospheric pollutant resulting from nitrogen oxides.

In the night, it is thought that gaseous nitrous acid builds up to concentrations as high as 8 ppb, which subsequently contributes to early morning hydroxyl radical formation and initiates atmospheric photochemical reactions.<sup>6</sup> The elusive nature of nitrous acid has limited the understanding of it. Because  $\text{HNO}_2$  contributes to photochemical smog through the formation of  $\cdot\text{OH}$ , recent studies have focused on nitrous acid, its mechanisms and properties. It is speculated that an important pathway to  $\text{HNO}_2$  are the reactions of  $\text{NO}\cdot$  and  $\text{NO}_2$  with water, followed by diffusion from the aqueous to the gaseous phase.<sup>6</sup> It is the purpose of this research to study aqueous nitrite,  $\text{NO}_2^-$ , the conjugate base of nitrous acid, and the scavenging of free radicals produced from the photolysis of nitrite.

### Equilibrium of $\text{HNO}_2$ :

Nitrous acid, a weak acid, undergoes dissociation into its conjugate base in an aqueous medium.



$$K_a = 7.1 \times 10^{-4} \text{ ref. } 7$$

$$\text{p}K_a = 3.15$$

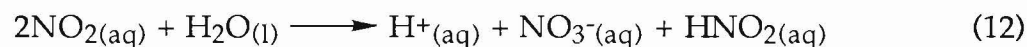
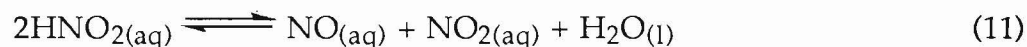
This reaction is pH controlled, with an acidic solution obviously favoring the formation of nitrous acid and an alkaline solution forming nitrite ion.

Applying the Henderson-Hasselbach equation

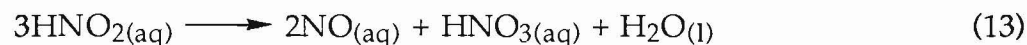
$$\text{pH} = \text{p}K_a + \log [\text{base}]/[\text{acid}] \quad (10)$$

a solution of nitrite at pH=12 will have a nitrite concentration  $7 \times 10^8$  times that of nitrous acid. In this research, it is assumed that reactions run at pH=12 will provide an adequate isolation of  $\text{NO}_2^-$ .

Another equilibrium of nitrous acid includes the first step of a two-part thermal decomposition reaction, as proposed by Park and Lee.<sup>6</sup>

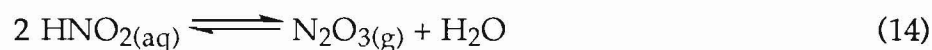


The sum of these two reactions yields the overall decomposition reaction,<sup>7</sup>



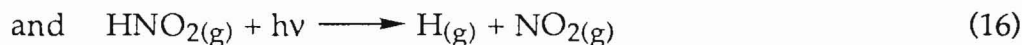
The rate of decomposition depends on the temperature, the nitrous acid concentration, as well as the hydronium ion concentration.<sup>9</sup> However, regardless of the conditions when quantifying the photochemical disappearance of  $\text{HNO}_2$ , the thermal decomposition must also be recognized and accounted for due to the relatively speedy rate of decomposition, with a half life of 14 hours at  $0^\circ\text{C}$ .<sup>10</sup> Because of this "short" half-life, and the volatile nature of the  $\text{NO}$  and  $\text{NO}_2$  formed as intermediate and product, nitrous acid is elusive and difficult to study.

A solution that contains nitrous acid may be bubbled with nitrogen gas to remove it, shown below in the degassing reaction.

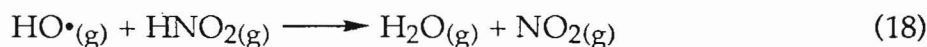
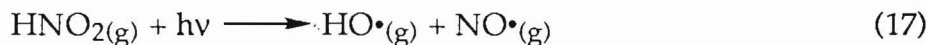


### Photochemical decomposition:

Both nitrous acid and nitrite ion undergo photochemical reactions. Two primary processes of the photodissociation of nitrous acid have been proposed by Cox and Atkins<sup>11</sup>, with equation (15) thought to be far more important.

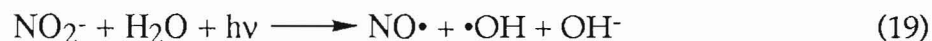


However, Nash<sup>12</sup> proposed a slightly different sequence of events for the gas phase photolysis of nitrous acid, which includes only reaction 15 as the primary photolysis step.

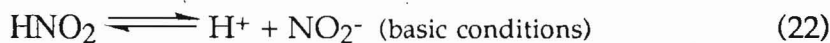
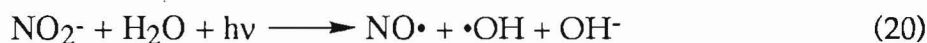


In either case, the reactive hydroxyl and nitric oxide free radicals are formed, which may further react as in reactions 2, 3, 6, and 8. Some reactions of these radical species with aromatic compounds, the focus of this research, are forthcoming.

As previously mentioned, the nitrite ion also undergoes a photochemical reaction. Zafiriou<sup>13</sup>, a prominent scientist in the area of  $\text{NO}_2^-$  photochemistry of natural waters, supports the work of Treinin and Hayon<sup>1</sup>, who set out to clarify the reaction mechanisms surrounding the nitrogen oxides, which, although obscure, are of utmost importance in air pollution. It was uncertain if any photochemical reaction of nitrite took place, even though  $\text{NO}_2^-$  absorbs in the near UV,  $\lambda_{\text{max}} \sim 350\text{nm}$ . Treinin and Hayon proposed the following overall primary reaction via flash photolysis findings:<sup>1</sup>



It is still believed and supported in this research that under normal conditions, this reaction is part of a cycle that results in no *net* photolysis. The entire cycle follows: primary reaction, recombination of free radicals and reformation of  $\text{NO}_2^-$  (due to basic conditions created in the primary reaction).<sup>1</sup>



However, one of the frustrations surrounding the chemistry of the nitrogen oxide family is the myriad of reactions that can occur. Depending on the conditions, the following may compete against the cyclical reaction above:<sup>1</sup>



The  $\text{NO}_2$  formed can dimerize to yield yet another nitrogen oxide:



It becomes obvious that the chemistry occurring in these reactions is not simple.

Reaction 20 is of great importance to this research, which focuses on photolyzing aqueous nitrite ion in a strongly basic medium. Also present in this research is a radical scavenger, benzene, which will trap either or both of the free radicals,  $\cdot\text{OH}$  and  $\text{NO}\cdot$ , resulting in a net photolysis. This will be discussed further.

The work of Zafiriou et. al.<sup>14</sup> focuses on the processes of the photic zone, the surface layer of the ocean which receives sunlight and is therefore especially active and diverse. It is this region of the water where aquatic primary productivity is more intense than other areas. In addition to being a "zone of life," this photic zone is also the receptacle for many liquid, solid and



airborne wastes<sup>14</sup>. As previously stated, nitrogen oxides constitute a significant fraction of known pollutants. Therefore, if nitrite is present in ocean water, it may undergo the primary photochemical reaction of Treinin and Hayon via solar radiation, forming free radicals which may harm the very important primary producers such as plankton. Zafiriou's study focuses greatly on steady state detection of  $\text{NO}\cdot$ , which has a daytime concentration of  $>10^{-11}\text{M}$  and a lifetime of 10 to 100 seconds.<sup>15</sup> Contrarily, the less stable  $\cdot\text{OH}$  radical has a lifetime of  $<10^{-6}$  second before reacting.<sup>15</sup>

Zafiriou has proposed a rather elaborate mechanism for the photolysis of nitrite in ocean water, of which some highlights follow.<sup>13</sup>



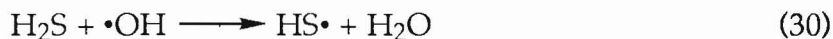
In this mechanism, the square brackets represent a solvent-cage. In reaction 27, a certain number,  $n$ , of water molecules surround the  $\text{NO}$  and  $\text{O}^-$ , which react fast enough in reaction 28 such that they do not diffuse out of the solvent cage. The formation of the two radicals and hydroxide species require one of the solvent cage water molecules resulting in  $n-1$  water molecules comprising the solvent cage. The products  $\cdot\text{OH}$ ,  $\text{NO}\cdot$ , and  $\text{OH}^-$  diffuse out of the solvent cage and are able to further react in ways which are of primary concern to this research. Other nonconsequential steps include the reformation of nitrite ion and nitrous acid.

### The Hydroxyl Radical:

As implied above, nitrous acid and nitrite ion are major sources of the hydroxyl radical,  $\cdot\text{OH}$ . The reason this is of utmost concern is because the

hydroxyl radical is "the most reactive photochemically produced free radical in the environment".<sup>16</sup> Due to its high electronegativity,  $\bullet\text{OH}$  is a highly reactive oxidizing agent, reactive to organic molecules both in water and the atmosphere.<sup>17</sup> In the atmosphere, there are several sources of the hydroxyl radical, including the photolysis of nitrous acid, nitrite, hydrogen peroxide, ozone, and even water at high altitudes.<sup>3</sup> Just as important as how  $\bullet\text{OH}$  forms is how  $\bullet\text{OH}$  reacts.

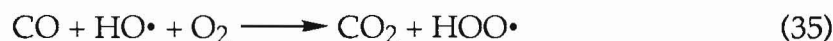
Of environmental interest is how the hydroxyl radical catalyzes the conversion of hydrogen sulfide, primarily from sulfur-containing coal, to sulfur dioxide in the atmosphere.<sup>3</sup>



The sulfur dioxide then further reacts with water or hydrogen peroxide to form sulfuric acid, which can return to the earth in the form of acid rain, acid snow, or acid fog. Another form of acid precipitation can be formed from the hydroxyl radical and nitrogen dioxide, which was previously mentioned.<sup>3</sup>



Two additional pathways of  $\bullet\text{OH}$  are the reactions with ozone and carbon monoxide, the latter being a combustion product.<sup>3</sup>

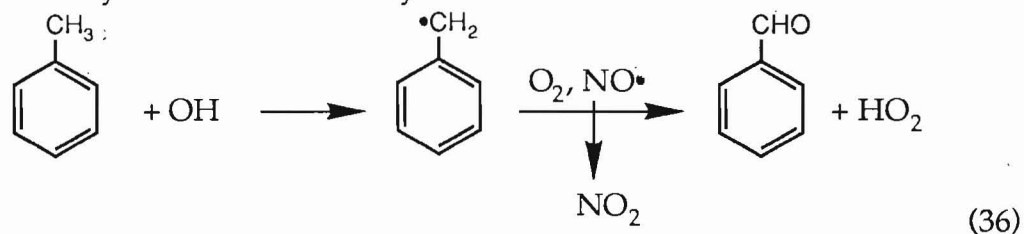


The decomposition of ozone (reaction 34) has negative effects in the stratosphere, but could be a beneficial reaction in the troposphere, where ozone is a toxin. Because of the high levels of CO present in the troposphere, and the presence of  $\bullet\text{OH}$ , reaction 35 is a major contributor to increasing the levels of carbon dioxide, a greenhouse gas. In both reactions 34 and 35, the

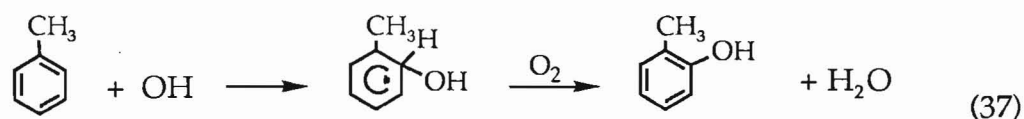
hydroperoxide radical (HOO•) forms, which can further react with NO to reform •OH and NO<sub>2</sub>, perpetuating the cycle. The hydroxyl radical also reacts with aromatic hydrocarbons, which is an important reaction in this research.

#### Reaction of •OH with aromatic hydrocarbons:

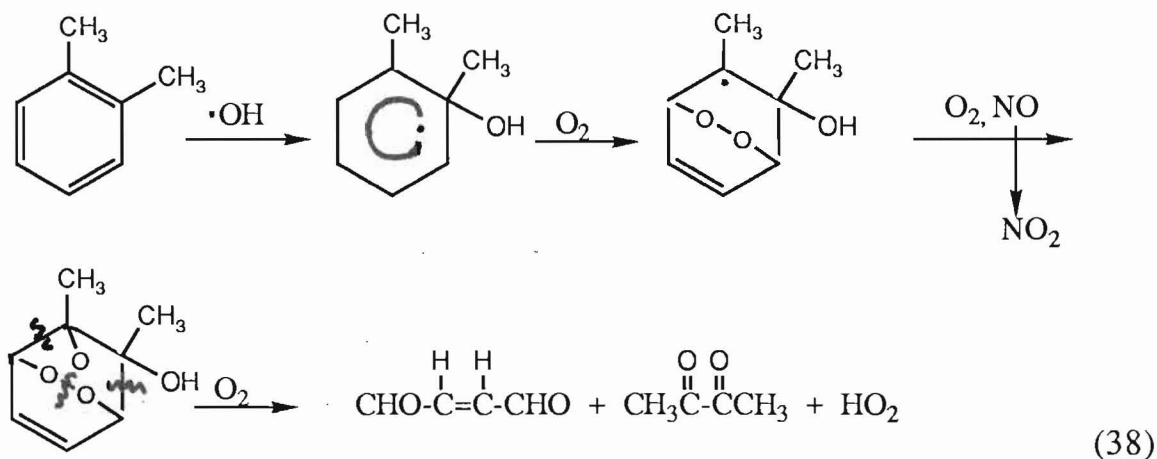
Aromatic hydrocarbons are important constituents of emissions from commercial fuels.<sup>18</sup> These compounds represent a large portion of the reactive hydrocarbons present in urban atmospheres.<sup>19</sup> The reactions of the reactive aromatic compound and the highly reactable hydroxyl radical have two paths: hydrogen atom abstraction from substituent alkyl groups and more importantly, •OH addition to the aromatic ring.<sup>18</sup> The hydrogen abstraction reaction abstracts a hydrogen from a substituent alkyl group, which usually results in an aldehyde.<sup>19</sup>



It has been commonly believed that •OH addition to the ring forms phenolic compounds.<sup>19</sup>



Until recently, the phenol formation and the hydrogen abstraction were considered the only two pathways. However, Atkinson et al.<sup>20</sup> have obtained results indicating the occurrence of ring fragmentation. Shepson, Edney and Corse<sup>19</sup> agree that the ring does fragment and propose the following path for the fragmentation of o-xylene.

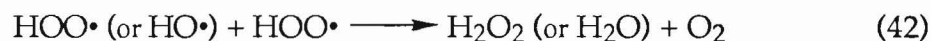


The addition reaction (37) is the most important reaction to consider for this research since reactions 36 and 38 rely on the presence of alkyl substituents. This research focuses on the reaction of free radicals with benzene, which has no alkyl substituents.

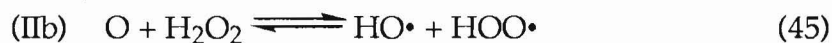
#### Sources of •OH:

The hydroxyl radical can be photochemically generated from nitrous acid and nitrite, as well as photochemically and catalytically from hydrogen peroxide, discussed below. However, alternate sources of •OH do exist in the atmosphere, many of which result from the reaction of a species, such as water or hydrocarbons, with atomic oxygen. The generation of •OH by nitrous acid has been previously discussed.

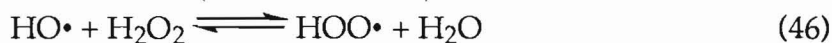
The photochemical production of •OH from hydrogen peroxide is thought to follow a scheme outlined by the Haber-Willstätter reactions:<sup>21</sup>



The wavelengths required for this photochemical reaction to proceed are 300nm or less. However, Hunt and Taube<sup>22</sup> had proposed two alternate mechanisms that concurred with their kinetics study.

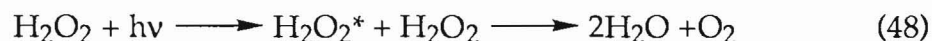


both schemes are followed by



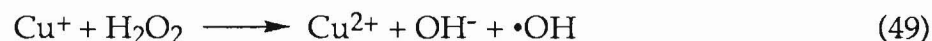
Furthermore, if the formation of hydroxyl radicals are the primary products of the absorption as in mechanism I, Hunt and Taube hypothesized that the radicals could undergo reaction in the solvent cage, resulting in water and atomic oxygen, which are the primary products in mechanism II.

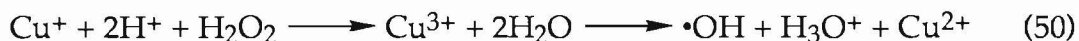
Dainton and Rowbottom<sup>23</sup> found that the photolysis of  $H_2O_2$  had a quantum yield of  $\sim 2$ , and predicted a primary process in agreement with the Haber-Willstätter primary reaction, as well as the primary reaction of mechanism I of Hunt and Taube. However, a different primary process has been proposed by Stern and Volmer which suggests a solvent cage reaction that varies from that of Hunt and Taube.<sup>24</sup>



In this case, hydroxyl radicals are not formed. This raises some doubt regarding this mechanism since phenol-type compounds have been identified in many of the studies as a result of aromatic scavenging.

The catalyzed reactions of hydrogen peroxide to yield the hydroxyl radical often employ a metal species, commonly copper Eberhardt et al.<sup>25</sup> outline two pathways for hydroxyl formation using copper(I) as the catalyst.





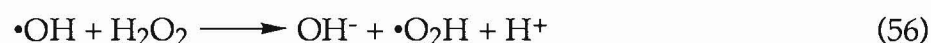
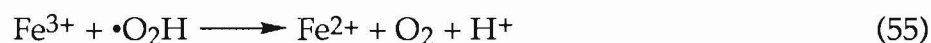
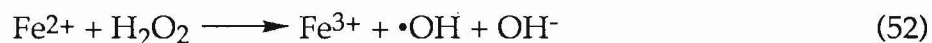
The first reaction is a simple redox reaction in which the copper(I) acts as a reducing agent, becoming oxidized to copper(II). Consequently the peroxide oxygen ( $\text{O}_2^{2-}$ ) will be reduced from the (-1) state to the (-2) state.

Anbar and Pecht<sup>26</sup> supported the formation of  $\bullet\text{OH}$  via copper(III). However, Eberhardt et al. disagree by noting the competing reaction for  $\bullet\text{OH}$  between an aromatic scavenger and  $\text{Cu}^{2+}$ . The copper(II) ion is oxidized by the hydroxyl radical by completing the octet of the oxygen, forming the hydroxide ion.



If copper(III) catalyzes the formation of  $\bullet\text{OH}$ , then an increased concentration of  $\text{Cu}^{2+}$  should not change the concentration of phenol formed from the reaction with benzene. Eberhardt et al.<sup>25</sup> found that increased  $\text{Cu}^{2+}$  concentrations decrease the amount of phenol produced, implying that  $\text{Cu}^{3+}$  does not catalyze hydroxyl radical formation.

These proposed catalytic mechanisms will not explain how copper(II), which is used as catalyst in this research, forms hydroxyl radicals from hydrogen peroxide. Instead they focus on either copper(I) or copper(III) as the catalyst. Brook et. al. <sup>27</sup> studied the hydroxylation of aromatic compounds using hydrogen peroxide generated radicals and an iron species (Fenton's reagent). The mechanism they present for the catalytic formation of  $\bullet\text{OH}$  using iron(II) as the catalyst might be similar to that of copper(II).



## Procedure

### Hydrogen Peroxide Reaction<sup>28,29</sup>:

In a 500mL Erlenmeyer flask, 0.674g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Fisher reagent grade) was added to approximately 30mL  $\text{H}_2\text{O}$ . To this, 75mL benzene (Fisher) was added and stirred on a stir plate for several minutes. With continuing stirring, 50mL 30%  $\text{H}_2\text{O}_2$  (Fisher certified A.C.S.) was added. The solution was stirred for 30 minutes. The solution was transferred to a 250mL separatory funnel and allowed to settle for 20 minutes. The two phases were separated.

To the aqueous phase, 7 drops of 6M  $\text{H}_2\text{SO}_4$  were added after checking that the pH was between 3 and 4. In a 250mL separatory funnel, the aqueous phase was extracted four times with 15mL portions of  $\text{CH}_2\text{Cl}_2$  (Fisher HPLC-GC/MS Grade UV Cutoff 232nm), shaking each portion for 2 to 3 minutes and allowing it to settle for several minutes before separating.

The benzene layer was extracted four times with 20mL 5% NaOH, shaking for approximately one minute. The resulting NaOH solution was acidified with 6M  $\text{H}_2\text{SO}_4$  until pH=2 as checked with indicator paper. The acidified solution was extracted four times with 15mL  $\text{CH}_2\text{Cl}_2$ .

The two  $\text{CH}_2\text{Cl}_2$  extractants were combined and dried with  $\text{Na}_2\text{SO}_4$  (Fisher anhydrous) until no water was visibly floating on top of the  $\text{CH}_2\text{Cl}_2$ . Initial collection efforts involved rotary evaporation under vacuum. Subsequent preparations used the aqueous phase for spectral studies.

### Photolysis of Nitrite:

One liter of a 0.10M solution was prepared from  $\text{NaNO}_2$  (Baker) with a 0.15M NaOH concentration. Approximately 15mL benzene was added and

the two phases were vigorously stirred for 30 minutes to saturate the aqueous phase with benzene.

100mL of this solution was put in a quartz tube with approximately 10mL benzene added to ensure saturation throughout the photolysis. Initially, the solution was photolyzed only 30 minutes. The nitrite levels were monitored via a nitrite specific electrode before and after the reaction (see appendix). Then, the 0.1M solution was photolyzed with 366nm mercury lamps from 7 to 24 hours. The photolysates of these longer reactions were collected and combined in a glass-stoppered jar. To date, the nitrite levels before and after have not been checked.

#### **Extraction of Photolysate:**

In a CH<sub>2</sub>Cl<sub>2</sub> rinsed 2L separatory funnel, approximately 1000mL of the aqueous photolysate was separated from the benzene layer collected from the photolysis. The separatory funnel was rinsed again with CH<sub>2</sub>Cl<sub>2</sub> and the aqueous phase of the photolysate was again placed in the separatory funnel. 50mL CH<sub>2</sub>Cl<sub>2</sub> (Fisher , HPLC/GC-MS Grade UV Cutoff 232nm) was added and the mixture was shaken briefly with venting. Approximately 15mL concentrated H<sub>2</sub>SO<sub>4</sub> were added to the unseparated mixture (until indicator paper showed pH=2 of the aqueous phase). The mixture was again shaken with frequent venting for 10 minutes and then allowed to settle for 10 minutes. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated into a solvent rinsed 250mL Erlenmeyer flask. The solid which was suspended in an emulsion at the interface was also separated into the flask with the organic layer. This was repeated twice more, each with 50mL portions of CH<sub>2</sub>Cl<sub>2</sub> which were collected in the same flask.



If a significant amount of water was present in the extract, this was manually separated in a small separatory funnel. Then, regardless of the presence of water, anhydrous  $\text{Na}_2\text{SO}_4$  was added to the  $\text{CH}_2\text{Cl}_2$  and swirled until no water could be seen floating on top of the organic layer. (Sometimes, several grams of anhydrous sulfate was required.) The  $\text{CH}_2\text{Cl}_2$  was carefully decanted from the solid salt into another solvent rinsed flask. The remaining salt was rinsed with small portions of  $\text{CH}_2\text{Cl}_2$ , which were added to the extract.

The extract was placed in a tared, solvent rinsed crystallization dish or beaker and dried in vacuo with constant pumping for several hours. (This is especially important on humid days, as the coolness of evaporation will cause condensation of water vapor on the dish and  $\text{CH}_2\text{Cl}_2$ .) The dry solid was weighed to obtain the yield.

In a second extraction, the  $\text{CH}_2\text{Cl}_2$  extract was back-extracted into a highly basic aqueous phase (pH=12) by shaking for 10 minutes. This back-extraction was used for spectral analysis.

#### **Thermal Reaction:**

The 0.1M  $\text{NO}_2^-$  solution photolyzed was also subjected to a thermal reaction. 50mL 0.1M  $\text{NO}_2^-$  in basic, saturated benzene water was placed in a 100mL round bottom flask with 5mL benzene on top. A Claisen adapter with thermometer and condenser was attached. The reaction was run at 57°C for 24 hours.

#### **Spectral Analyses: UV-VIS**

$\text{H}_2\text{O}_2$  Reaction: The aqueous phase was analyzed via UV-VIS (Perkin-Elmer 559,  $\lambda=900\text{nm}-190\text{nm}$ ) in both highly basic (pH=12) and highly acidic (pH=2)

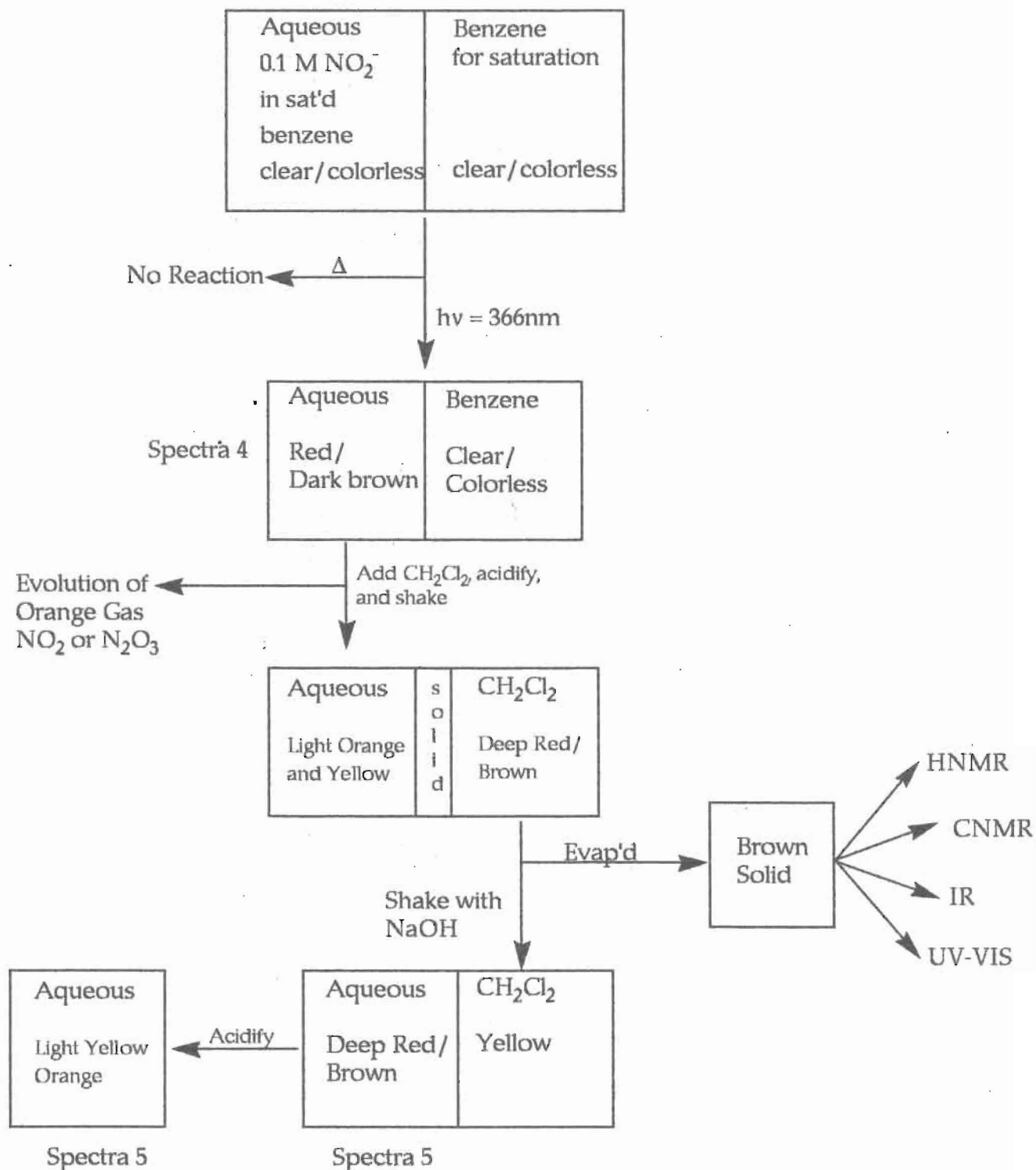
solutions. The pH was adjusted with either NaOH or H<sub>2</sub>SO<sub>4</sub> until the indicator paper showed the correct pH range.

Photolysate: The aqueous phase was analyzed via UV-VIS as above with a water reference. The benzene layer was analyzed with a benzene reference as when the aqueous layer was acidic and basic. The aqueous back-extraction was spectrally analyzed in both acidic and basic media, as above.

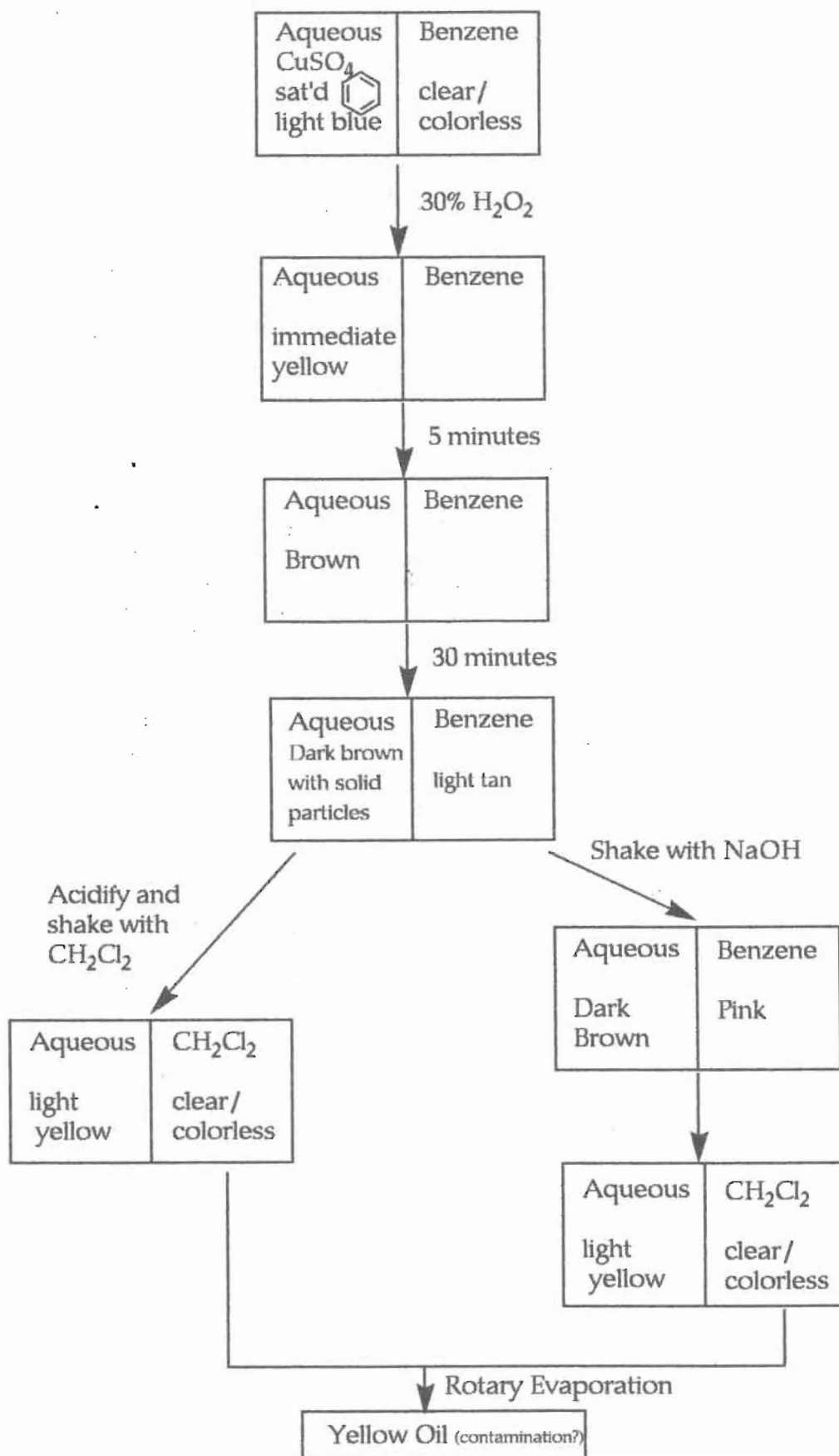
**Comparative Study for Identification of the Photolysis Product:**

Solutions of phenol, catechol, resorcinol, hydroquinone and quinone were made at a concentration of  $1 \times 10^{-3} \text{M}$  in water. Both the acidic and basic UV spectra were taken, often requiring dilutions upto  $1 \times 10^{-5} \text{M}$ . The spectra are only for a qualitative and not quantitative comparison.

# Photolysis Reaction



## Hydrogen Peroxide Reaction



## Results

### Hydrogen Peroxide Reaction:

#### Observations during the reaction:

Table 1

Time of reacting	Appearance
immediate	yellow aqueous; colorless benzene
5 minutes	brown aqueous; colorless benzene
30 minutes	brown aqueous; tan benzene

An emulsion occurred, with brown solid precipitating upon standing for 20 minutes.

#### Observations of H<sub>2</sub>O<sub>2</sub> extraction:

Table 2

	Color of aqueous	Color of organic
CH <sub>2</sub> Cl <sub>2</sub> xtrn from aq.	initial: dark brown final: light yellow	clear/colorless
NaOH xtrn from benzene	dark brown	initial: light tan final: light pink
CH <sub>2</sub> Cl <sub>2</sub> xtrn from NaOH	initial: dark brown final: light yellow	clear/colorless

The acidification of the basic aqueous solution caused it to turn from a light brown to a clear, colorless solution.

To an amateur nose, the resulting yellow oil of the rotary evaporation appeared to have the odor of phenol.

### Spectral Analysis of H<sub>2</sub>O<sub>2</sub> Reaction:

Several minutes after base was added to the aqueous phase (non-extracted), a semi-violent eruption occurred, spewing forth over half of the solution, which was confined to a 2L beaker. A clear solution was obtained with dark brown/black solid suspended in it. Flame tests indicated the presence of copper in the black solid. The solid was also soluble in HCl, a non-reducing acid, implying that the solid was not elemental copper, but perhaps the hydroxide. The clear supernatant was used for spectral analysis.

The acidic and basic UV spectra of the aqueous phase constitute Spectra 1 with the acidic and basic spectra of phenol available for comparison in Spectra 2.

**Photolysis of aqueous nitrite:** basic conditions, benzene scavenger **Table 3**

Time of Photolysis	Aqueous Phase	Benzene Layer	Final Temperature initial = ambient	[NO <sub>2</sub> <sup>-</sup> ] via electrode before	[NO <sub>2</sub> <sup>-</sup> ] via electrode after
30 minutes	light yellow	colorless	41 °C	0.404 mV = ~3.5X10 <sup>-2</sup>	0.402 mV = ~3.5X10 <sup>-2</sup>
> 7 hours	dark red/brown	slightly tan	57°C		

**Thermal reaction:****Table 4**

Time of Reaction	Maintained Temperature	Aqueous Phase	Benzene Layer
24 hours	57°C	clear, colorless	clear,colorless

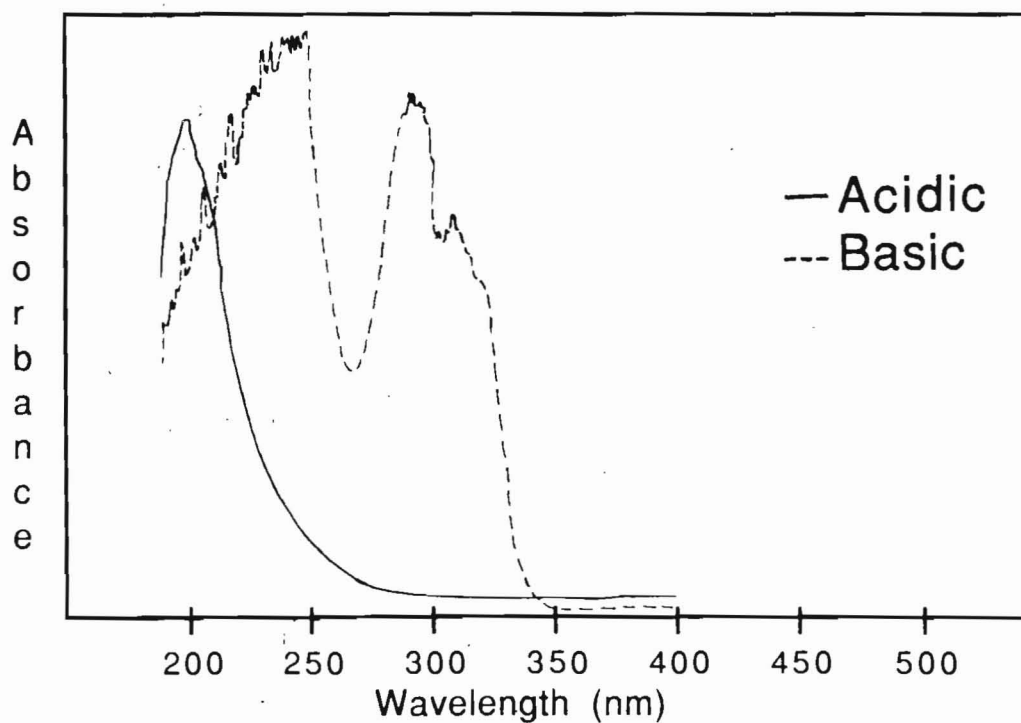
The thermalized solution was not analyzed except for noting that the aqueous phase did not become dark red/brown characteristic of the photolysate.

**Comparison study of possible products:****Table 5**

Compound	Spectra #	Solid	Acidic Solution	Basic Solution
Photolysate	4,5	red/brown		Deep red/brown
Phenol	2	white/colorless	clear/colorless	clear/colorless
p-Nitrosophenol	6	dark purple/black		deep purple/red/brown
Catechol	7	white w/ sparkle	clear/colorless	tan
Resorcinol	8	white crystals	clear/colorless	clear/colorless
Hydroquinone	9	off-white	clear/colorless	tan
Quinone	10		light brown	deep brown

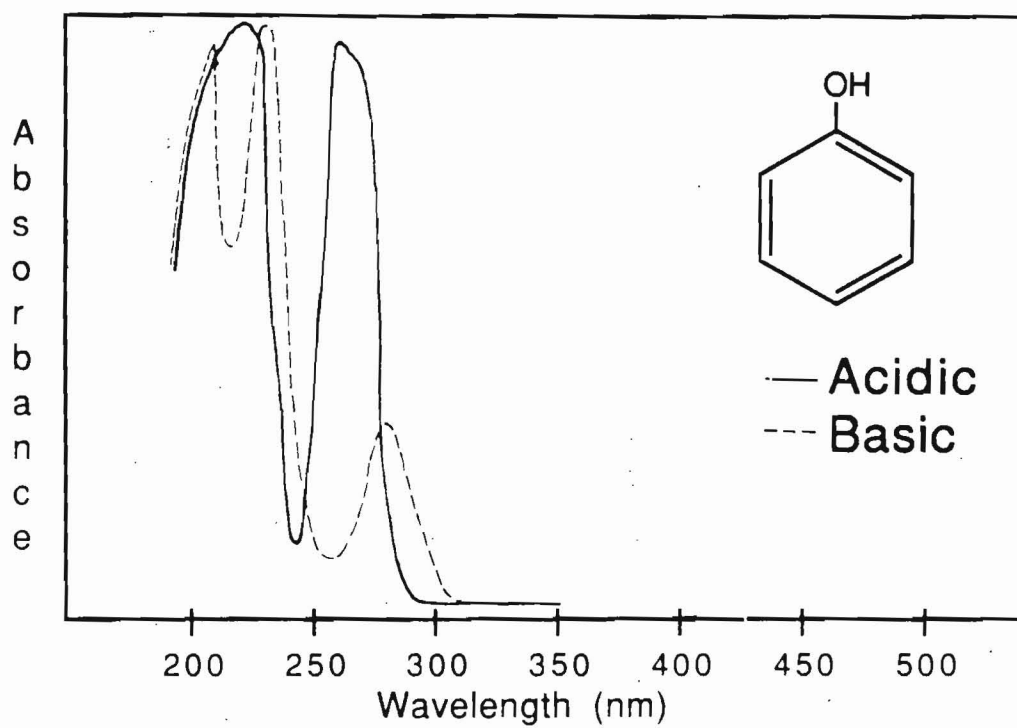
## Spectra 1

### Hydrogen Peroxide Reaction with benzene scavenger Aqueous Phase



## Spectra 2

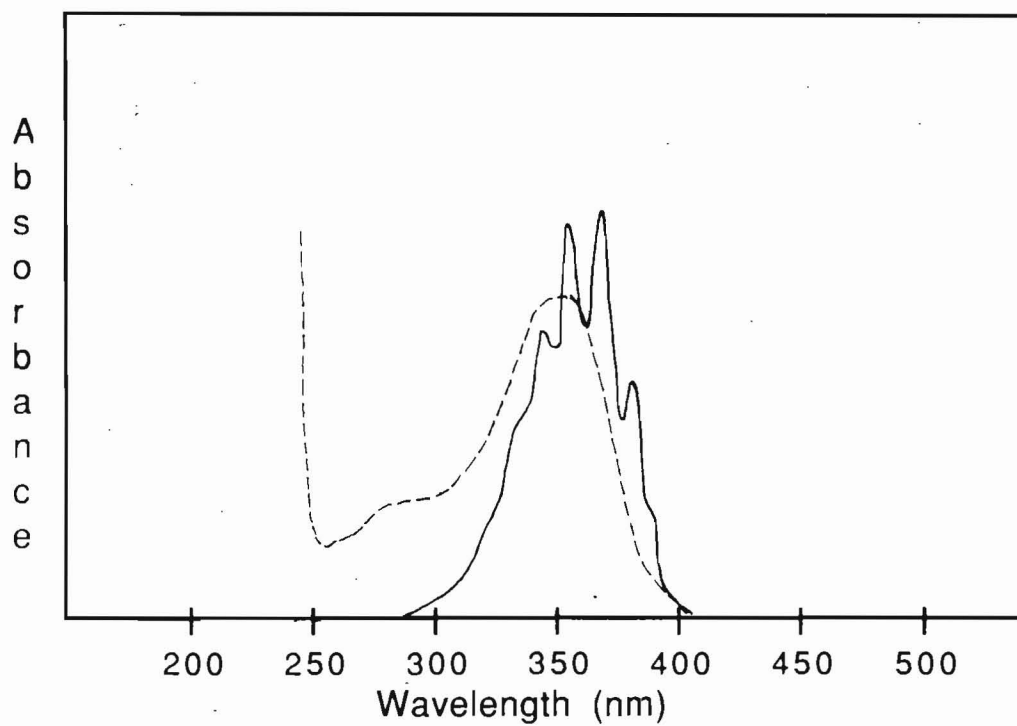
### Phenol Aqueous Phase





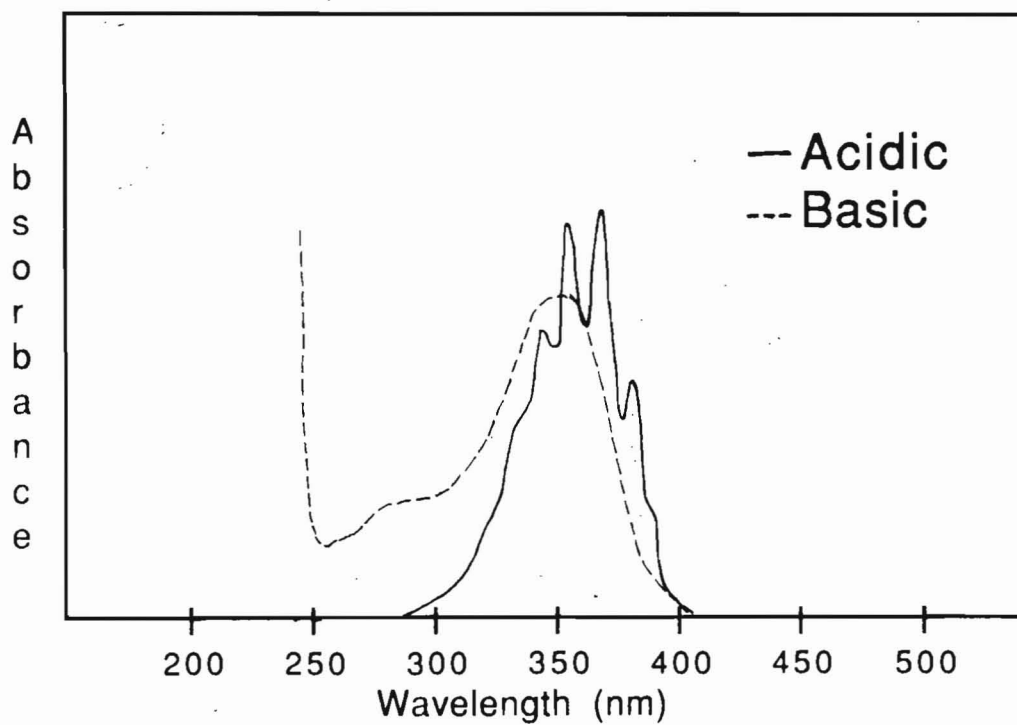
## Spectra 3

### Nitrous Acid and Nitrite Aqueous Phase



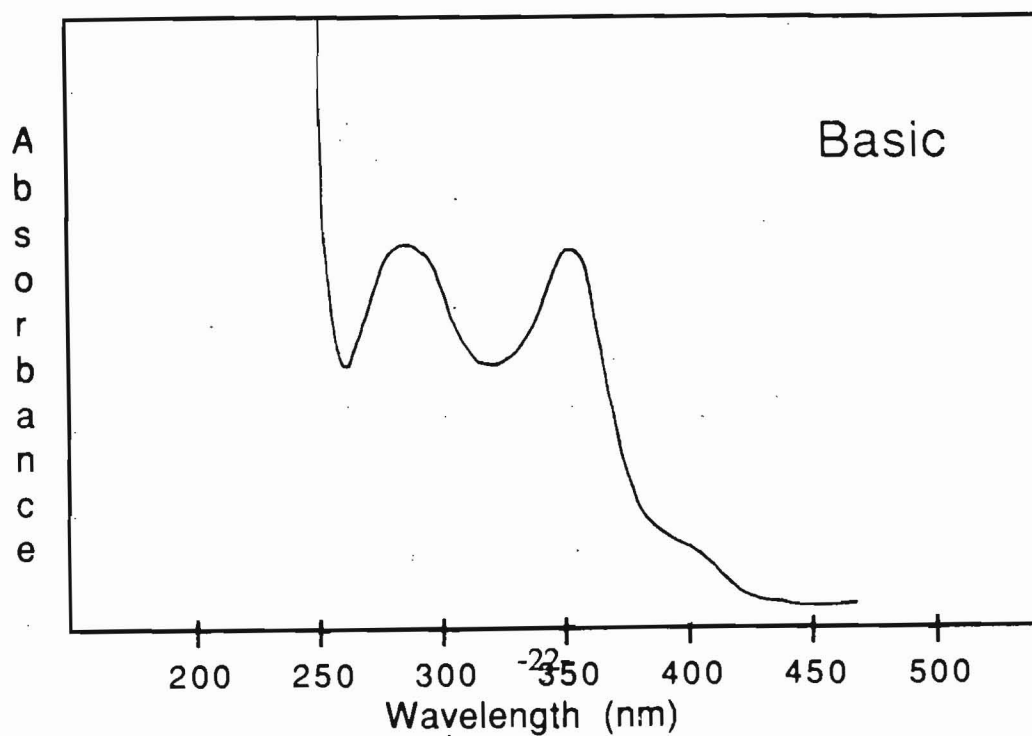
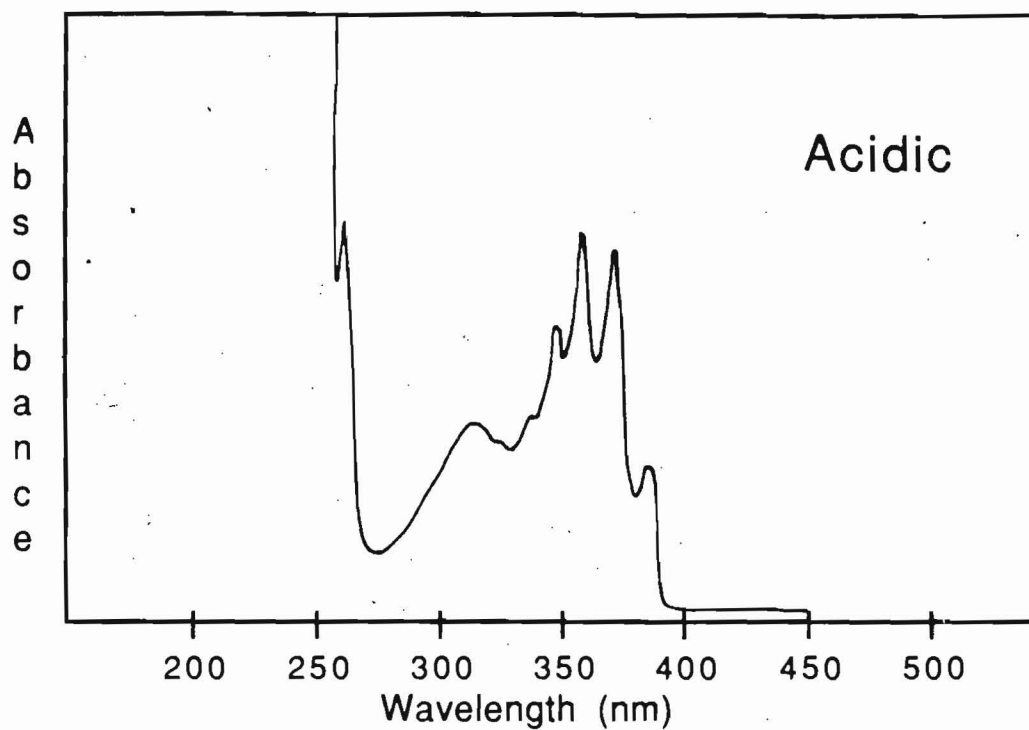
## Spectra 3

### Nitrous Acid and Nitrite Aqueous Phase



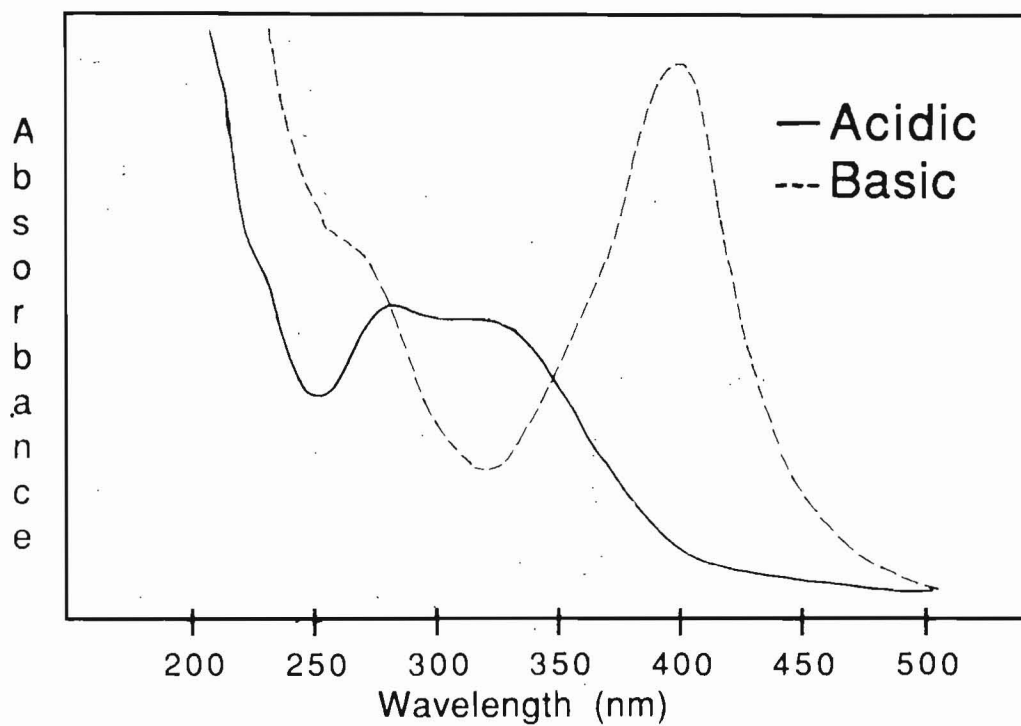
## Spectra 4

### Photolysate Aqueous Phase



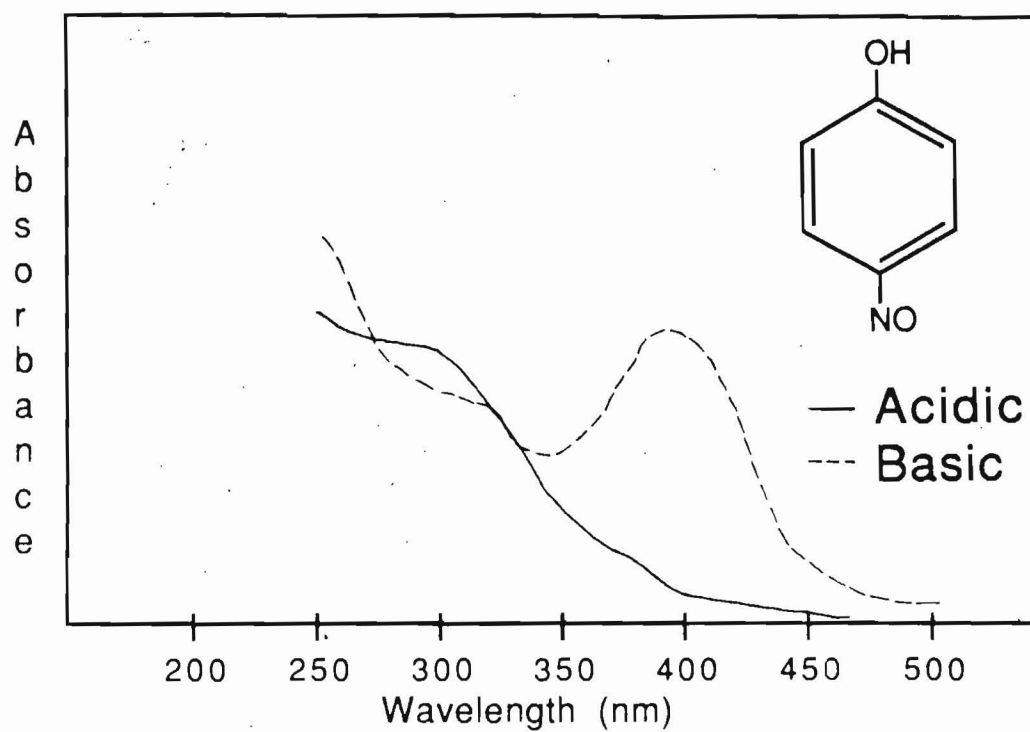
## Spectra 5

### Photolysate Aqueous Phase Back Extraction



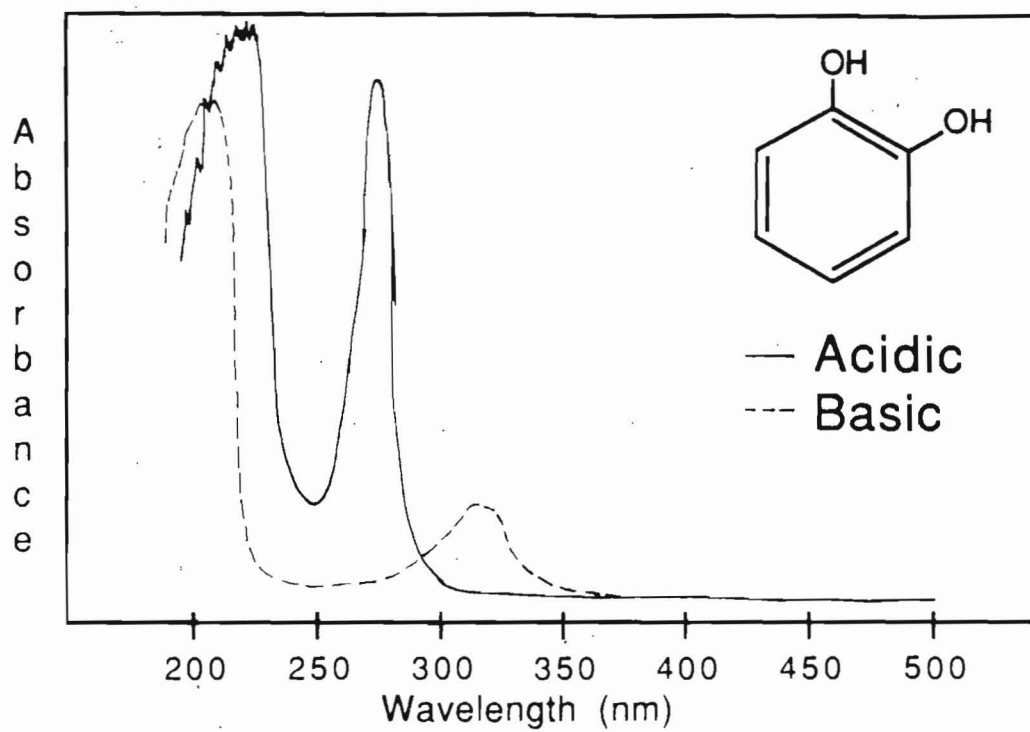
## Spectra 6

### p-Nitrosophenol Aqueous Phase



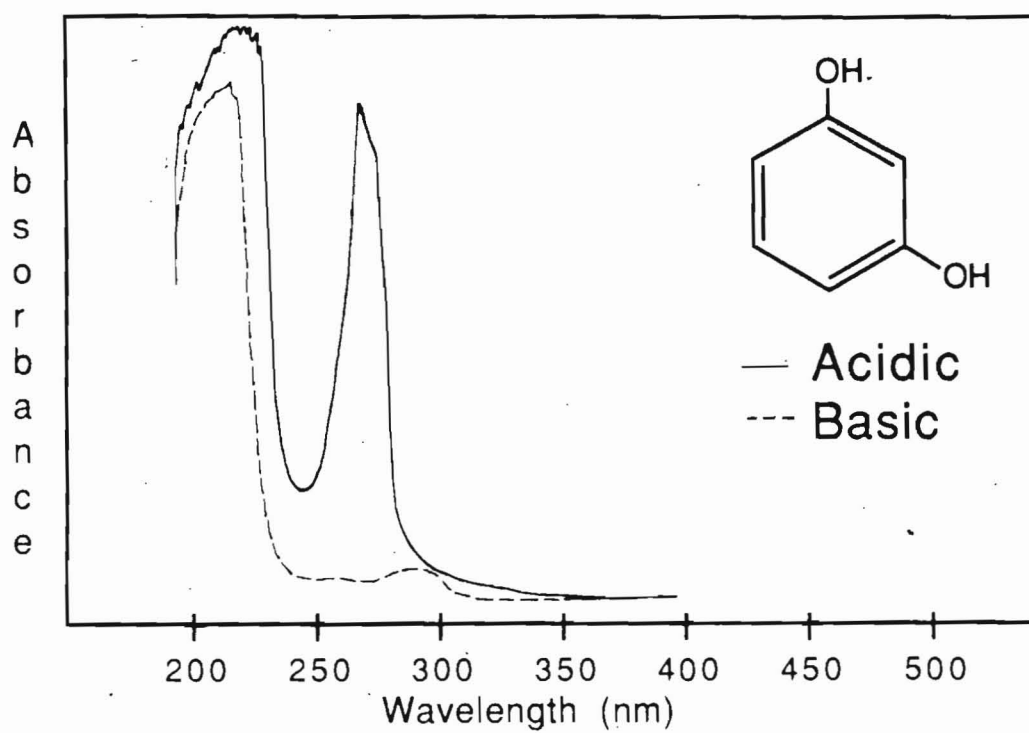
## Spectra 7

### Catechol Aqueous Phase



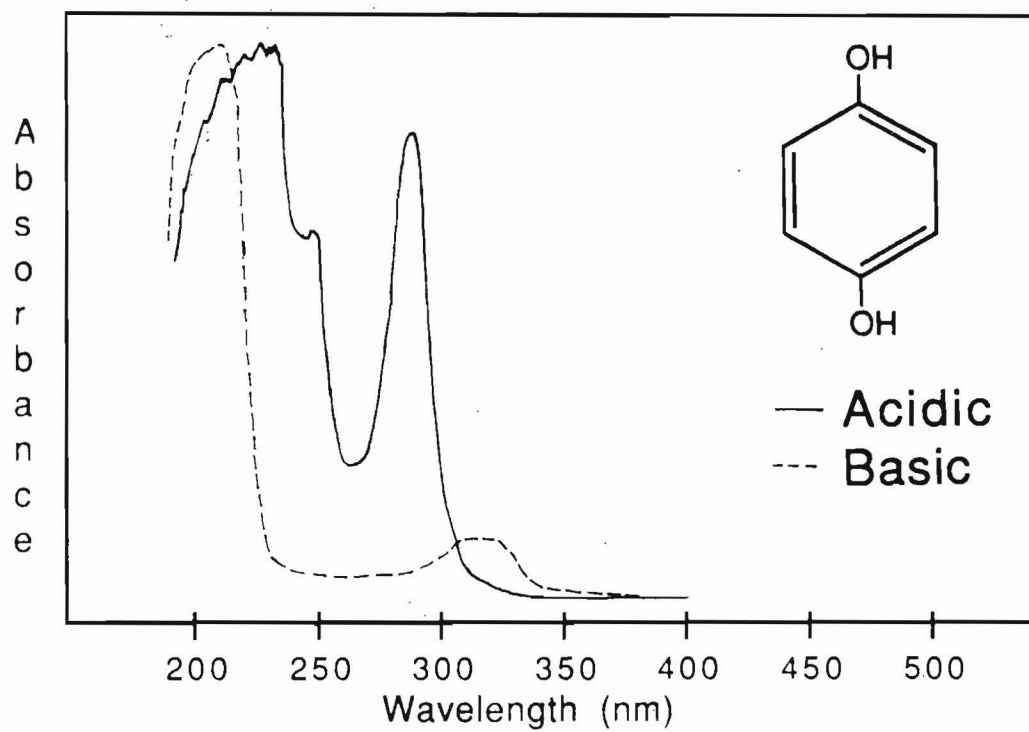
## Spectra 8

### Resorcinol Aqueous Phase



## Spectra 9

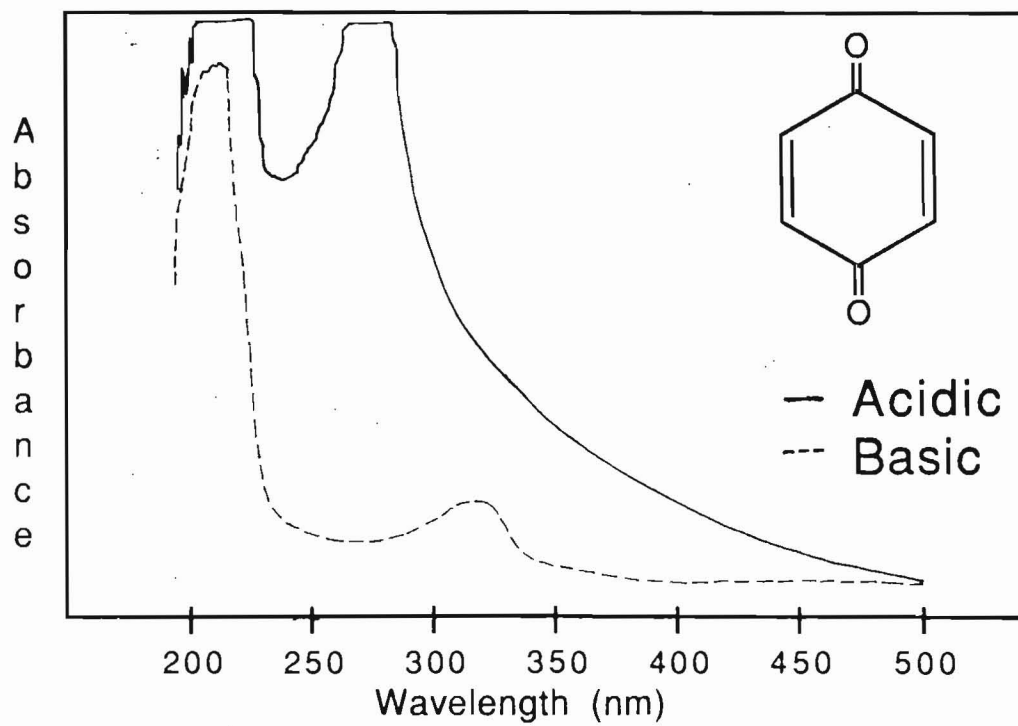
### Hydroquinone Aqueous Phase





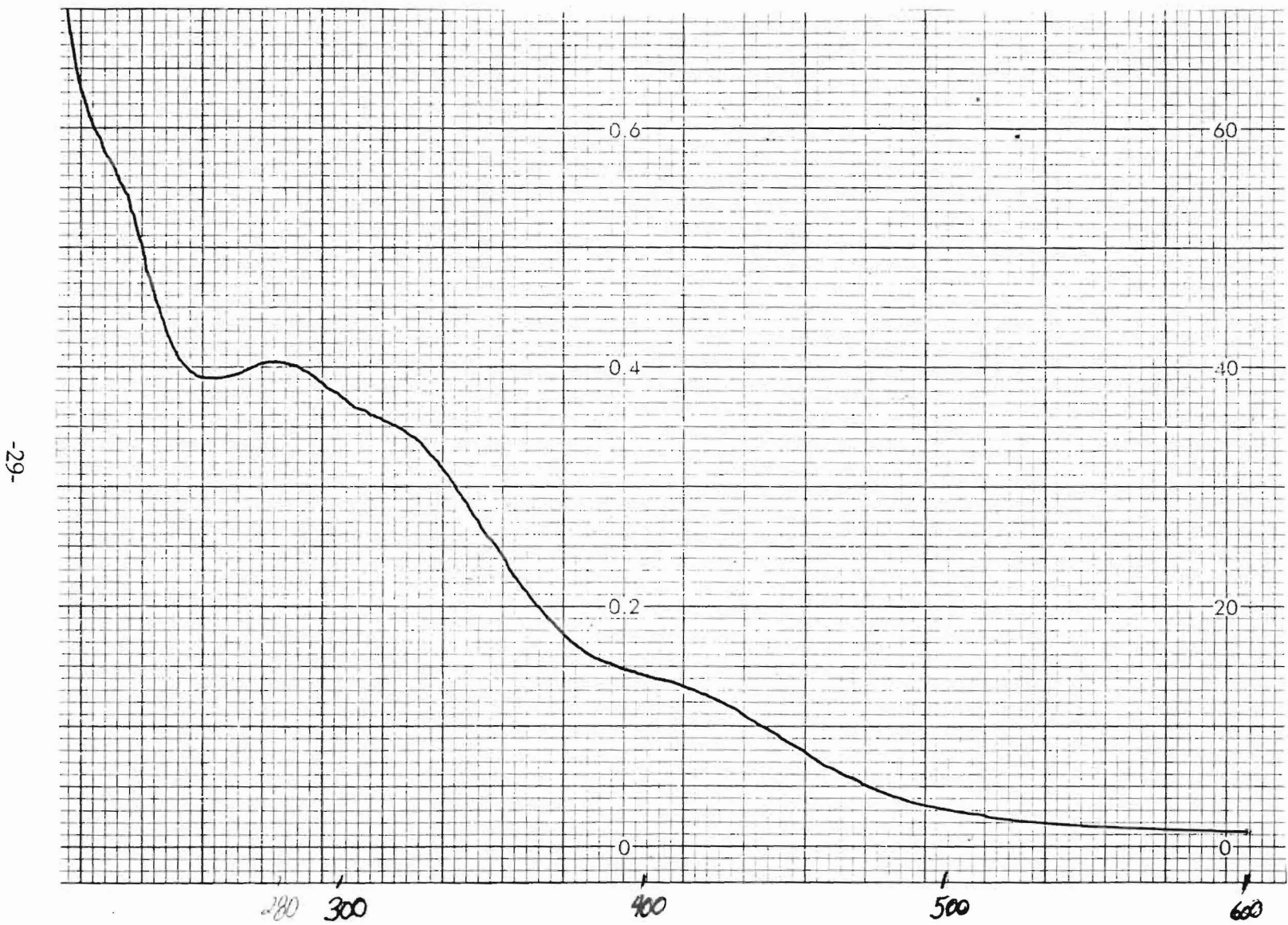
## Spectra 10

### Quinone Aqueous Phase



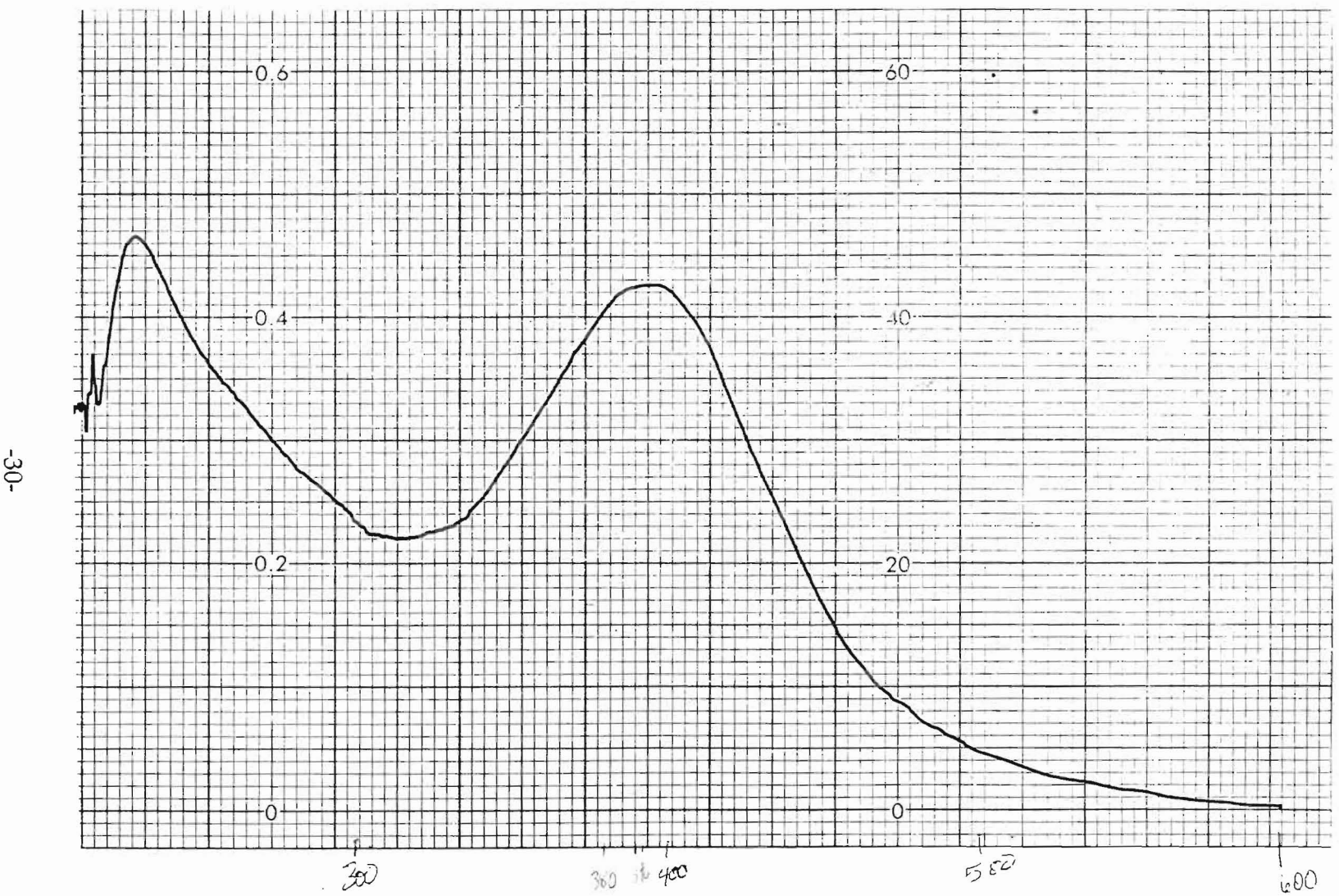
# Spectra 11

UV-VIS of Solid Photolysate (Acidic)



## Spectra 12

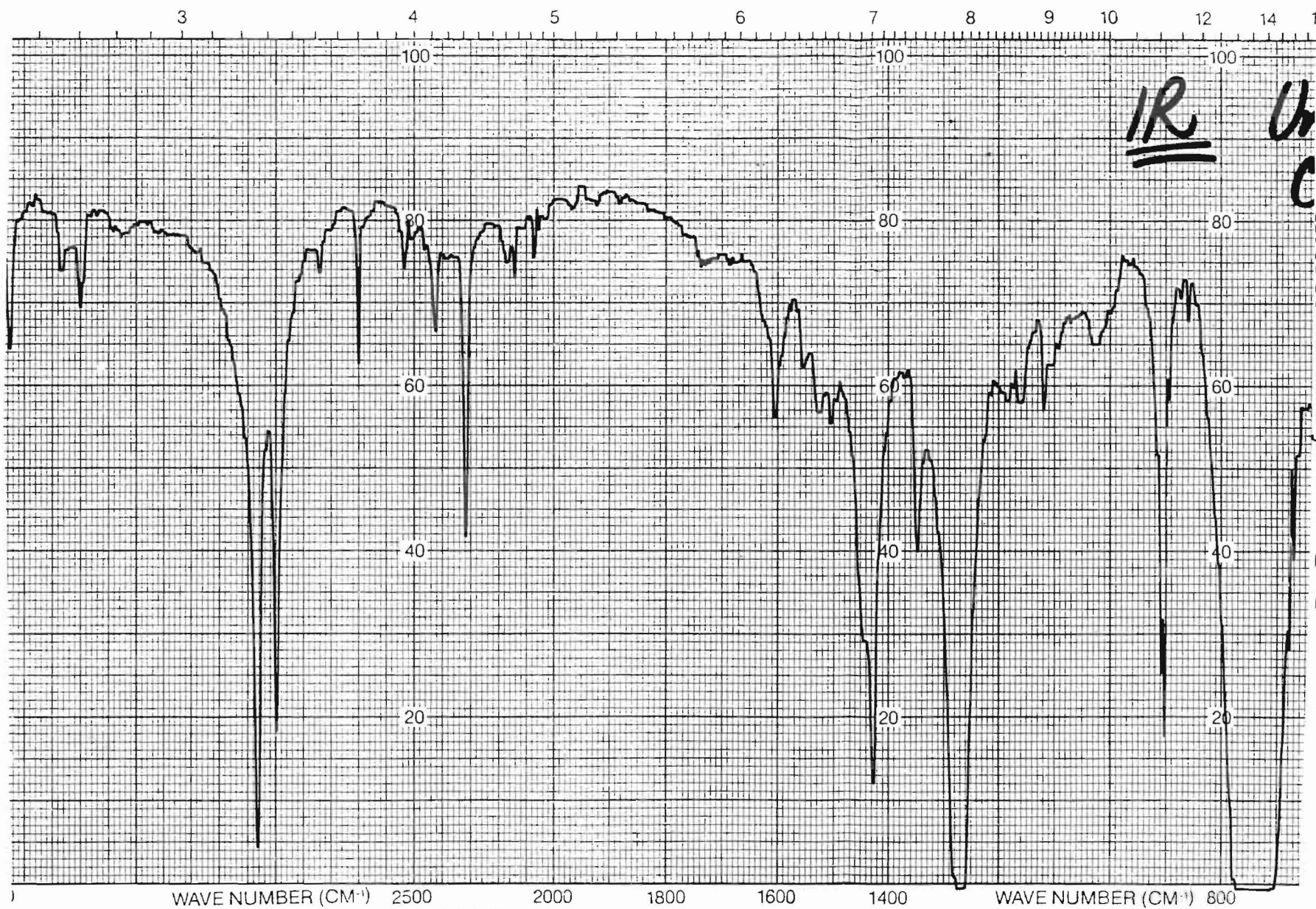
UV-VIS of Solid Photolysate (Basic)



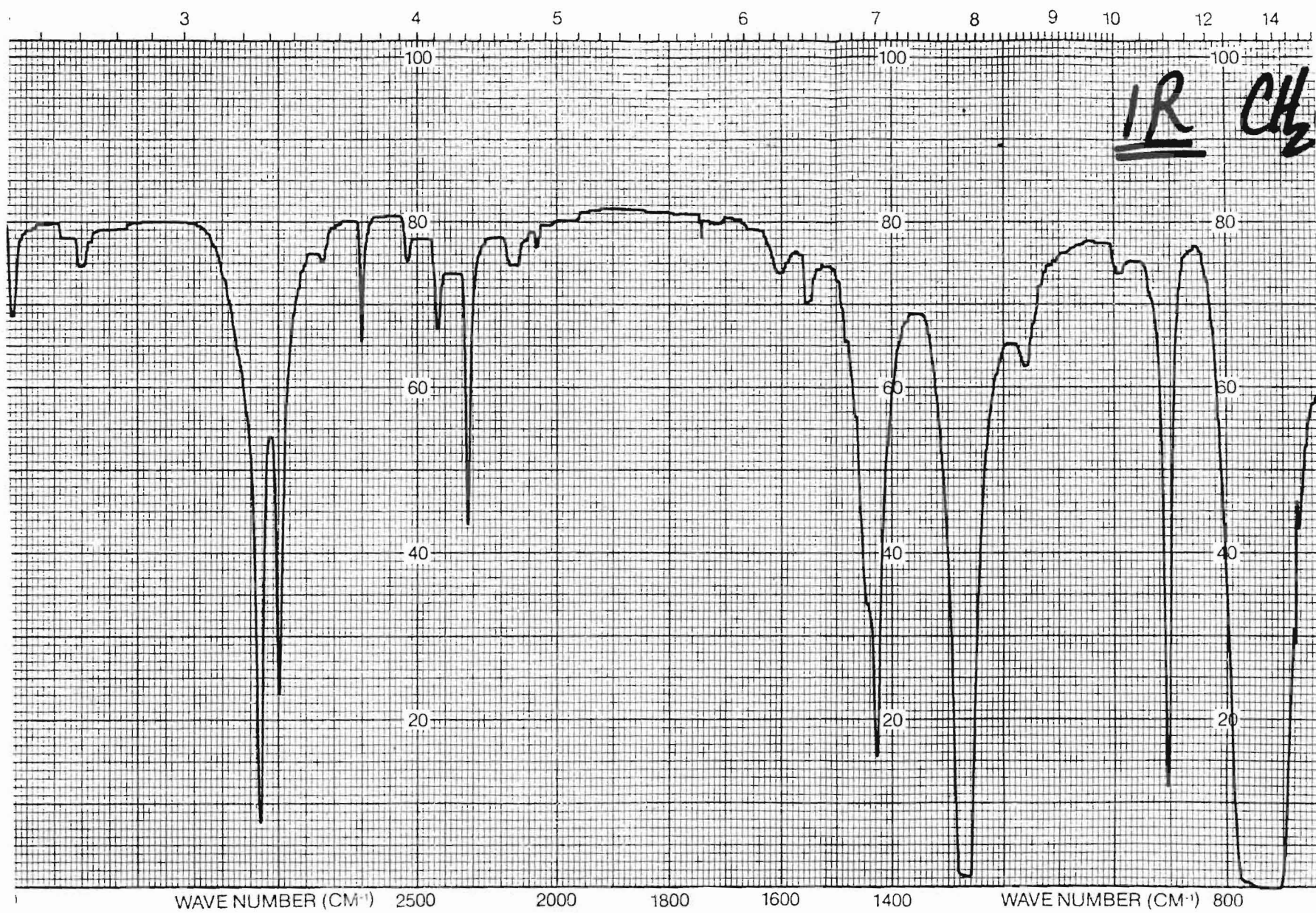
# Spectra 13

IR of Solid Photolysate (CH<sub>2</sub>Cl<sub>2</sub> solvent)

IR 4  
C





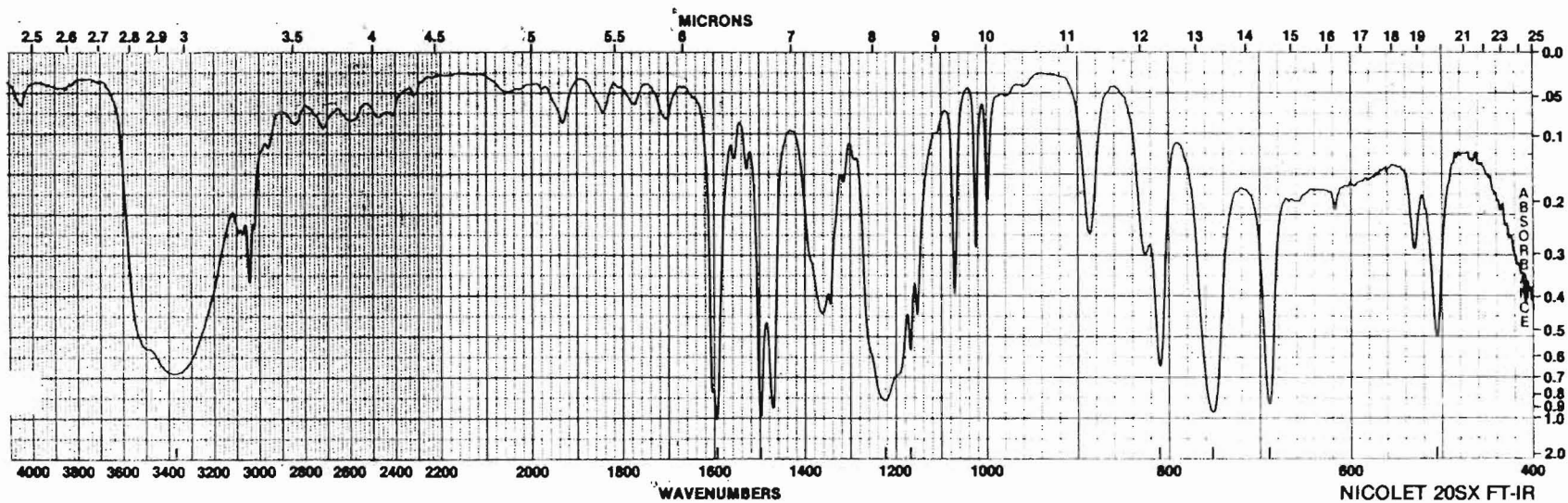


IR of  $\text{CH}_2\text{Cl}_2$  solvent blank

Spectra 14

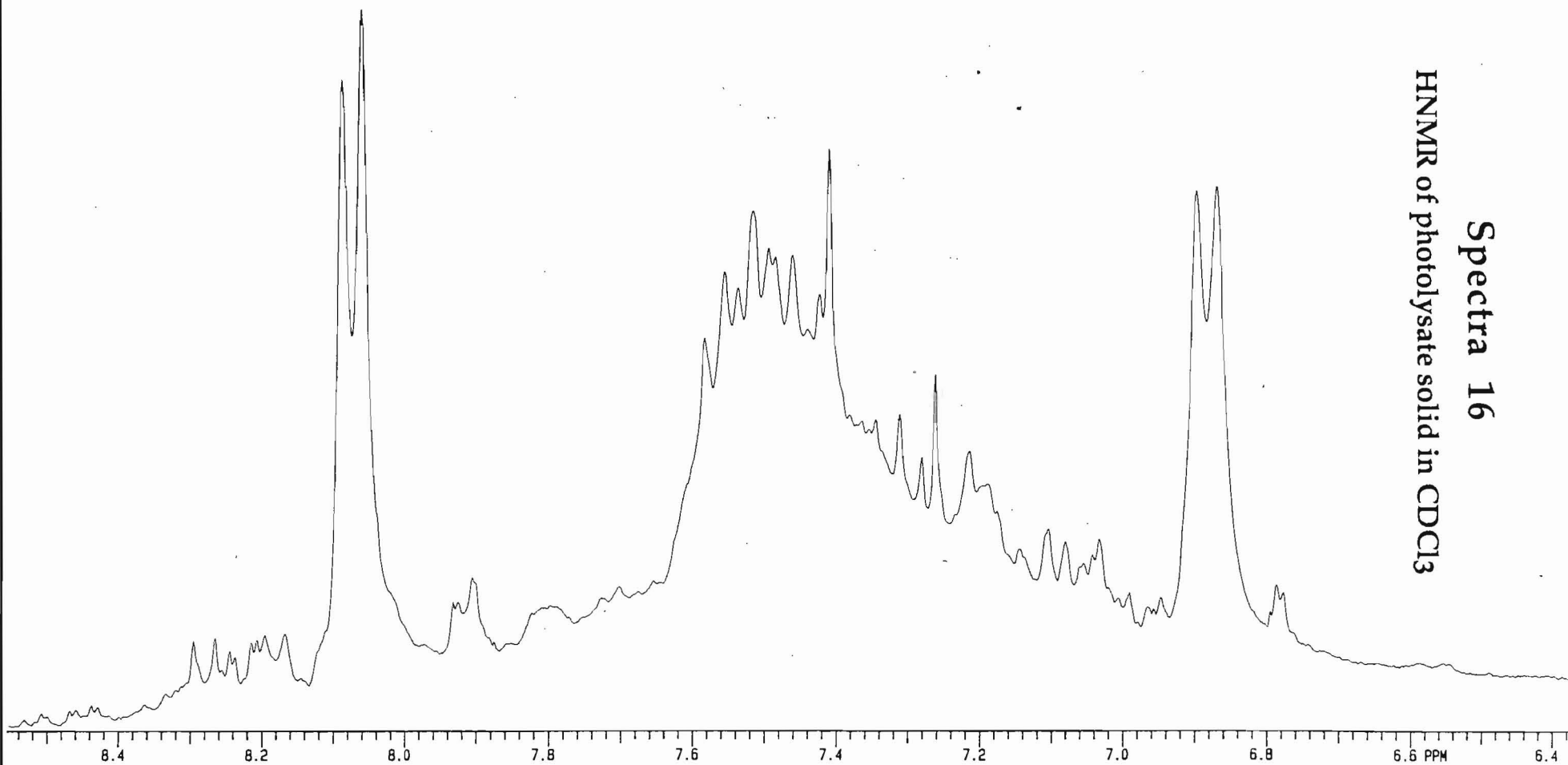
# Spectra 15

Aldrich Known IR of Phenol



# Spectra 16

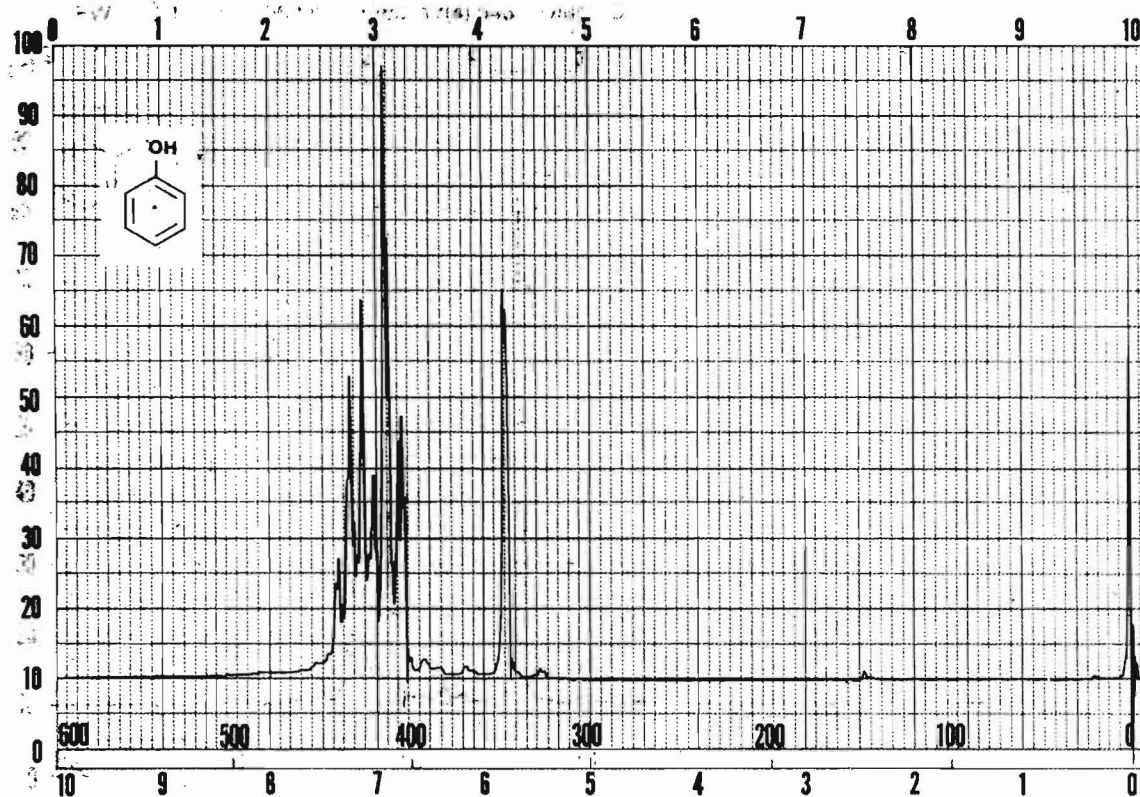
## HNMR of photolysate solid in CDCl<sub>3</sub>



OBSERVE	Nucleus _____	Freq _____ MHz	DECOUPLE	Nucleus _____	Offset _____ Hz	PLOT/PROCESSING	FN _____ K	RE _____ sec	CD _____ sec	EXPERIMENT	Pulse Sequence _____	SAMPLE	Number _____
	Spec. Width _____ Hz	Offset _____ Hz		Mode _____	Power _____ db		LB _____ Hz	AF _____ sec	CCD _____		Tube O.D. _____ mm		File _____
	Acq. Time _____ sec	Delay _____ sec		Modulation Mode _____	Freq _____ Hz		Width _____ Hz/ppm	Start _____ Hz/ppm	Temp _____ °C		Date _____		
	Pulse Width _____ μsec	Transients _____		Pulse Width _____ μsec	Power Mode _____		Reference _____	Solvent _____	XL _____				

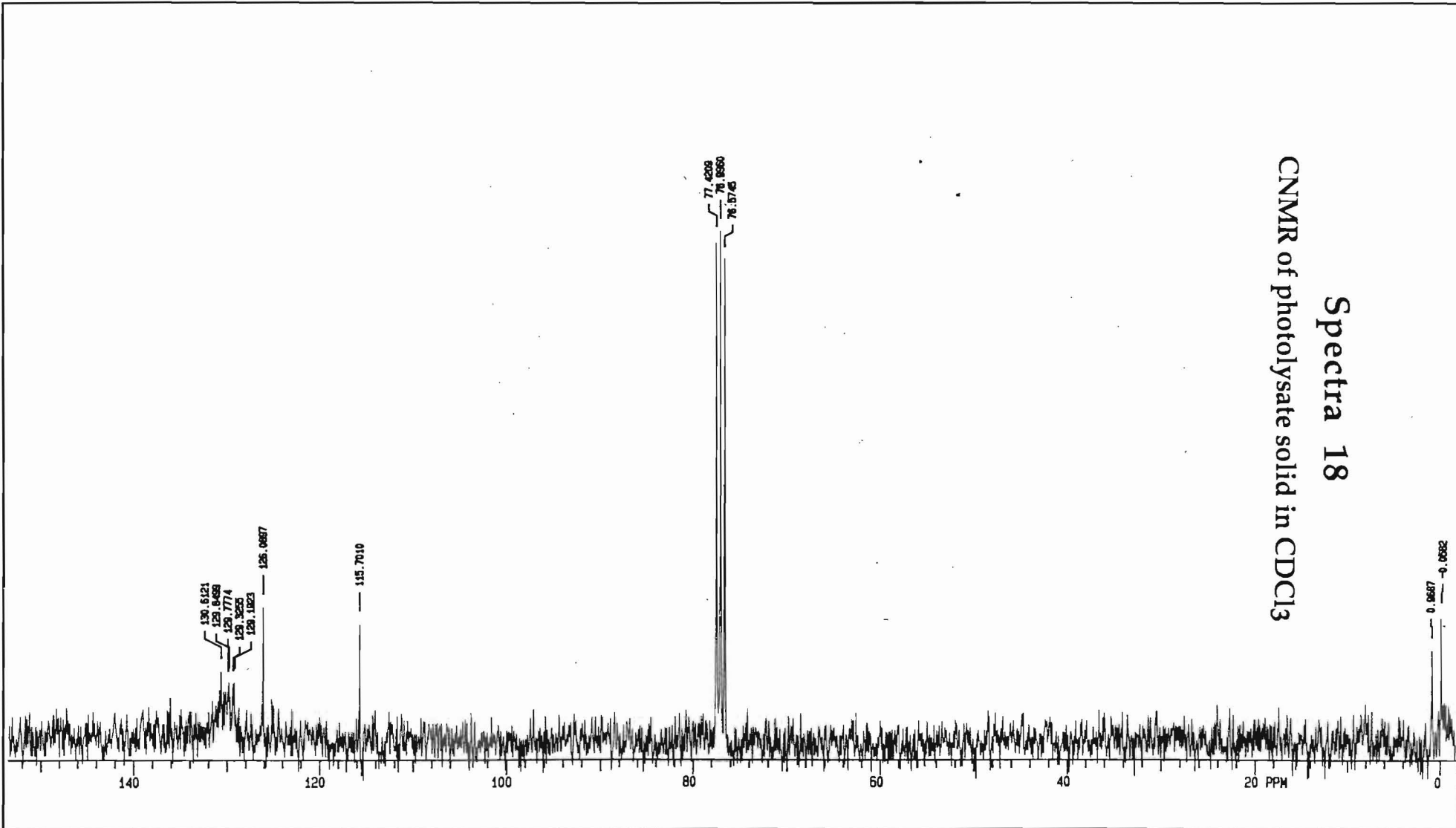
# Spectra 17

Aldrich Known HNMR of Phenol





# Spectra 18



Nucleus 13.000 Freq. 1.5 MHz  
 Spec. Width 1276.1 Hz Offset 0 Hz  
 Acq. Time 0.000 sec Delay 0 sec  
 Pulse Width 13.6  $\mu$ sec Transmits 512

Nucleus 2.777 Offset -156.0 Hz  
 Mode 75 Power 21.0 dB  
 Modulation: Mode N Freq 12800 Hz  
 Pulse Width 13.0  $\mu$ sec Power Mode 47.6

PLOT/PROCESSING  
 FN 32 K RE --- sec CD --- sec  
 LB 3.96 Hz AF --- sec CDD ---  
 Width 4713.4 Hz/ppm Start -134.0 Hz/ppm  
 Reference ---

EXPERIMENT

Pulse Sequence 2500

Tube O.D. \_\_\_\_\_ /mm

Temp. 26.2 °C

Solvent CCl<sub>3</sub>

SAMPLE  
86MNT-300 BB  
STANDARD 13C PARAMETERS

Number \_\_\_\_\_  
File \_\_\_\_\_ C  
Date 01-02-57  
XL- 1957 300

## Discussion

*Much ado about nothing?* I think not. As stated previously, the nitrogen oxide family plays a significant role in the theatrics of the atmosphere. The drama surrounding it becomes more intense as human kind continues to dispose of itself into the atmosphere. But how does the chemistry of a year-long research project fit in?

It seems that many of the components of this research have not been widely studied. The addition of  $\bullet\text{OH}$  to aromatic compounds was not understood kinetically before 1975<sup>30</sup> and as recent as 1993, the following was stated in the *Journal of Organic Chemistry*: "Nitric oxide ( $\bullet\text{NO}$ )... very little fundamental reaction chemistry is known about this molecule".<sup>31</sup> Nitrous acid and nitrite are present where pollution is present and they will photodissociate forming hydroxyl and nitric oxide free radicals. Also present in polluted atmospheres is a significant amount of aromatic hydrocarbons: "examination of the emissions from cars running on regular nonleaded gasoline have shown over 20% of the hydrocarbons emitted were aromatics."<sup>32</sup> If these reactions take place in a micelle of water, such as fog or rain in the atmosphere, then that encompasses aqueous phase chemistry, rather than gas-phase chemistry. One purpose of this research is to identify the product of the photochemical product of the photochemical aqueous reaction of  $\text{NO}_2^-$ ,  $\bullet\text{NO}$ ,  $\bullet\text{OH}$  and benzene, a process which might occur in the environment.

Of significant interest to this research is the primary photochemical reaction of  $\text{NO}_2^-$ , producing the free radicals  $\bullet\text{OH}$  and  $\text{NO}\bullet$ , which can be scavenged by benzene. The scavenging interrupts the cycle outlined in reactions 20-22, resulting in a net photolysis. In previous work at Wesleyan,

photolyses of nitrite in the presence of benzene have not exceeded two hours. This was considered a lengthy period of time and was cited by Johnson<sup>33</sup> as forming a yellow solution. In this research, photolyses of  $\text{NO}_2^-$  in the presence of benzene were reacted from 7 to 24 hours. In this case, a very deep red/brown solution results. The appearance to a layman might be that of strong tea. Previous work by Johnson<sup>33</sup> identified the product as p-nitrosophenol, which would result from the addition of both  $\bullet\text{OH}$  and  $\text{NO}\bullet$  onto the benzene ring. However, spectral studies of the photolysate did not support this identification (compare Spectra 4 and Spectra 6). Efforts commenced to identify the brown species.

A spectral comparison study was initiated based on knowledge of the free radicals produced in the photolysis and how they add. As previously shown, a hydroxyl radical typically adds to form a phenolic compound.<sup>19</sup> Extending that concept, the nitric oxide radical would then add similarly to form a nitroso compound. Additionally, it was hypothesized that  $\bullet\text{OH}$  would result in at least one substituent on the aromatic species. The hydroxyl radical is more highly reactive than nitric oxide, a radical that is relatively stable and exists in the environment. The list of possible products that resulted from this information follows:

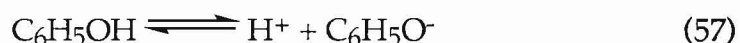
phenol (hydroxybenzene)	Spectra 2
p-nitrosophenol (1-hydroxy-4-nitrosobenzene)	Spectra 6
catechol (1,2-dihydroxybenzene)	Spectra 7
resorcinol (1,3-dihydroxybenzene)	Spectra 8
hydroquinone (1,4-dihydroxybenzene)	Spectra 9
quinone (oxidized form of hydroquinone)	Spectra 10

When comparing the possibilities with the photolysate (Spectra 4), both the acidic and basic spectra were compared. This is important to note because

the combination of the absorption spectra constitutes the hallmark of the compound. Intuitively, it seems likely that the unknown compound has a hydroxyl group as a substituent, due to the reactivity of the hydroxyl radical. Therefore, it is important to understand how the hydroxy group might affect the second or third substitutions as well as the changes a phenol undergoes with varying pH and how that affects the spectroscopy.

First, the hydroxyl group on benzene is considered to be an o,p-director. Typically, an o,p-director is an activating group because it has unshared electrons which resonance stabilize the carbocation intermediate of an aromatic electrophilic substitution.<sup>34</sup> However, benzene is not undergoing electrophilic substitution, but rather attack by a highly reactive hydroxyl radical (presumably) which will "be less picky" with what it "wants" to react (to be anthropomorphic). It is important to understand this tendency, but unclear if the o,p-directing characteristic holds in free radical reactions.

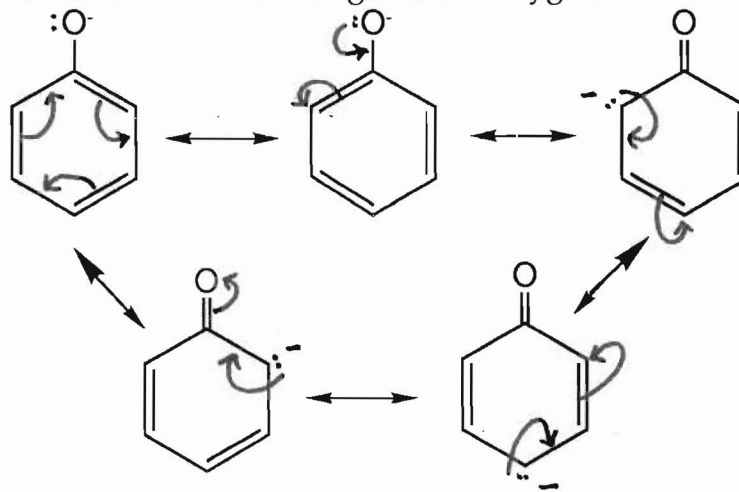
Phenols are acidic compounds due to the C-O bond being relatively strong with respect to the O-H bond, which can be easily broken.<sup>35</sup> The  $pK_a$  of phenol is 10.00, which is stronger than that of water with  $pK_w = 14.00$ ; phenol will dissociate as a weak acid, HA, in an aqueous medium.



If the pH of the solution approaches 12, then Henderson-Hasselbach predicts that the phenoxide ion will have a concentration 100 times that of phenol. Therefore, the acidic spectra is that of phenol, while the basic spectra represents the phenoxide ion.

Looking at Spectra 2, the  $\lambda_{max}$  of the phenoxide ion seems to be shifted red, indicating a lower energy of transition. Comparison of the other known phenolic spectra in a generalized sense seem to exhibit a red shift in the basic

form. The reason that the phenoxo ion of phenol shifts red is due to the resonance stabilization of the charge on the oxygen.



(58)

This delocalization of the charge around the oxygen atom stabilizes the molecule, resulting in a lower energy required for transitions to take place. If the unknown compound is phenolic, then a red shift of the alkaline form might be observed.

Looking at Spectra 4, the unknown peak is represented in the acidic form at 310nm and in the basic form at 278nm. This represents a blue shift of the basic form, something not expected if the unknown is hypothesized to be a phenolic compound. However, the back extraction of the photolysate from CH<sub>2</sub>Cl<sub>2</sub> back to the aqueous phase yielded a different spectrum, both acidic and basic, seen in Spectra 5. The alkaline had the most marked change, from  $\lambda = 278\text{nm}$  to  $\lambda = 400\text{nm}$ . The region of maximum absorption in the acidic form ranges from 280 to 340nm, which is difficult to determine if a change has taken place due to the broadness of the peak. The hump around 340nm may be due to the presence of nitrous acid, making the hump at 280nm representative of the unknown compound. If this is the case, then the back extraction has a strong correlation to p-nitrosophenol, something not seen in

the original photolysate spectra. Has chemistry occurred? Has p-nitroso-phenol been created by the back extraction?

If the photolysis product is the result of hydroxyl addition only, then the reaction of benzene and a hydroxyl radical source might yield the same photolysis product. The hydrogen peroxide reaction tests this hypothesis. Hydrogen peroxide catalytically ( $\text{Cu}^{2+}$ ) decomposes to yield two hydroxyl radicals. Upon the addition of hydrogen peroxide to a copper(II) solution of saturated benzene water, an immediate yellow color forms and eventually becomes dark brown after approximately 5 minutes of reacting. Is this brown color resulting from the same compound which forms from the photolysis of aqueous nitrite in the presence of benzene?

Spectral comparison between the aqueous phase of the hydrogen peroxide reaction and the photolysate (Spectra 1 and 4) show no commonality between acidic forms. The alkaline spectra both have strong absorptions around 280nm. Because both acidic and basic spectra do not match, it is concluded that the product of the hydrogen peroxide reaction is not the same as the product of the photochemical reaction. Phenol is a definite possibility for the identification of the hydrogen peroxide reaction, based on comparing the acidic spectra (Spectra 1 and 2). Additionally, the resulting oil from the extraction had a phenol odor, although the oil was yellow/brown. Perhaps several products formed, including phenol, but TLC trials in acetone, ethyl ether, 95% ethanol, and 5% acetic acid in ethyl acetate only produced "blobs;" no separation of the product occurred.

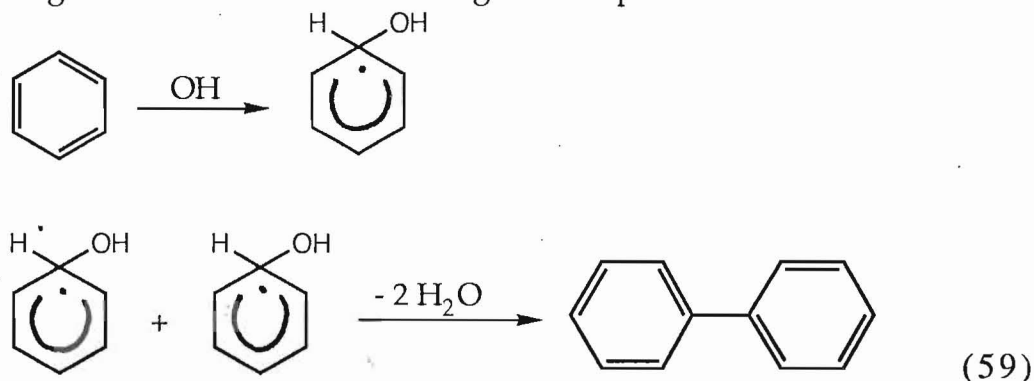
The following is a "best-guess" approach for determining the identity(s) of the photolysate unknown at this stage of research. The first compound

might be p-nitrosophenol, which was alluded to previously, based on the comparison of Spectra 5 (the back-extraction from the organic phase to highly basic aqueous phase) to Spectra 6, that of p-nitrosophenol. This presents a discrepancy in results because p-nitrosophenol was clearly not present in the first spectra of the aqueous photolysate (Spectra 4).

Collaboration with Rettich resulted in an hypothesis that attempts to explain this phenomenon without evidence to support it. Perhaps p-nitrosophenol was initially formed within the first few hours of photolysis, a claim made by Johnson.<sup>33</sup> Then, continuing irradiation caused decomposition or combination into alternate products. The first spectra of this photolysate (Spectra 4) represented the alternate products. However, after the extraction into dichloromethane and back-extraction into basic aqueous phase, absorption spectrum clearly showed a strong 400nm peak. The spectrum of the acidified solution showed absorbance around 300nm. These findings are characteristic of p-nitrosophenol.<sup>9</sup> It is known that the photolysis of nitrous acid and benzene yields p-nitrosophenol. However, if  $[\text{NO}_2^-] = 0.10\text{M}$ , then  $[\text{HNO}_2] = 1.4 \times 10^{-10}\text{M}$ . This is a very low concentration that intuitively should not interfere in the photolysis reaction. Perhaps, even at that low concentration, there is enough nitrous acid present to form p-nitrosophenol.

The extraction techniques employed to extract the photochemical product not only form the acidic form of the unknown, but also form a  $1.4\text{M}$   $\text{HNO}_2$  solution at  $\text{pH} = 2$  (using Henderson-Hasselbach). Both the formation of nitrous acid and the strong acidic conditions may have decomposed the hypothesized "alternate products" back into p-nitrosophenol, which is spectrally seen after the extraction.

A second possible product that is reasoned by literature only with no experimental evidence to support is the formation of biphenyl. Brook et. al.<sup>27</sup> studied the addition of catalyzed  $\cdot\text{OH}$  from  $\text{H}_2\text{O}_2$  and Fenton's reagent to benzene in a benzene medium. Phenol as well as biphenyl were produced in an "analogous manner to Fenton's reagent in aqueous solution."<sup>27</sup>



This product of hydroxyl addition is a candidate for perhaps a minor product of either the photolysis or hydrogen peroxide reactions in this research.

Finally, the last possibility to presently be considered is based on an experimental observation. During the extraction into dichloromethane, emulsions formed. Upon standing, brown solid appeared to be trapped in the emulsion. Some of the solid was collected with the extractant, although some remained clumped on the side of the separatory funnel. The solid was not soluble in dichloromethane, water, or benzene, suggesting that this compound is different than the extracted species. Discussion with Rettich hypothesized the formation of a polymeric species had occurred. No testing of this hypothesis has occurred.

Spectral and other comparison studies, while valuable, can only provide a limited insight on the identity of the photolysate product which can not be determined by speculation alone. The brown photolysate solid was collected only recently via extraction methods. The extraction of 100mL of



aqueous photolysate after 7 hours of irradiation yielded 2.8mg of brown solid. The extraction of 100mL of aqueous photolysate after 24 hours of irradiation yielded 7.8mg of solid. The best method for extraction was determined to be irradiation from 7 and 24 hours with one macro-scale extraction. The extraction of 1000mL photolysate yielded a significantly larger quantity of solid, but the precise amount was mistakenly not determined. Much work lies ahead with this product!

## Future Goals

Because the possibility of the presence of more than one product exists, purity will first be tested with TLC and subsequently with HPLC. The molar absorptivities in acidic and basic aqueous phases as well as  $\text{CH}_2\text{Cl}_2$  will be determined. This work might be completed within the semester.

Future work could involve answering several major questions that arose through this research. First, if the identity of the brown solid is not determined, a sample could be sent off to be analyzed via mass spectroscopy. If only a few compounds constitute the unknown, then the molecular weight of those compounds might be determined. Second, if the compound has only hydroxyl substituents, then the hydrogen peroxide reaction should be further studied. In the photochemical reaction, the nitrite ion and nitric oxide are present in the reaction vessel while these species are not present in the hydrogen peroxide system. These two compounds might affect how the hydroxyl radicals add to the benzene. If the hydrogen peroxide reaction were run with nitrite ion, different results might occur. Problems will exist: nitrite complexes with  $\text{Cu}^{2+}$ , which may inhibit either the catalytic function of  $\text{Cu}^{2+}$  or obscure the true effect of nitrite in the system; the copper complex will interfere in the spectral study below 450nm. Third, different times of photolysis should be studied to answer if secondary products are formed after a certain amount of the primary product is present. This may indicate if side reactions are occurring and may be accomplished by comparing the photolysate solid obtained from macro extractions of exactly 5, 10, 15, 20 and 25 hours. Finally, aromatic compounds other than benzene may be studied, such as simply-substituted benzene compounds. Perhaps more complicated

species, that are specifically present as major constituents in emissions, may be investigated as well.

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## Appendix

### NO Specific Electrode

#### Procedure:

An Orion Nitrogen Oxide electrode model 95-46 was calibrated using aqueous solutions of basic  $\text{NaNO}_2$  (Baker) at concentrations of  $1 \times 10^{-2}$  to  $1 \times 10^{-4}$  M. Additionally, similar solutions were made with saturated benzene water to check the effect of benzene on the electrode. A buffer solution was made by adding 190g  $\text{Na}_2\text{SO}_4$  (Fisher, anhydrous) to 800mL  $\text{H}_2\text{O}$  in a 1L volumetric flask. To this solution, 53 mL concentrated  $\text{H}_2\text{SO}_4$  was added and then diluted to 1L with  $\text{H}_2\text{O}$ . A storage solution was made by diluting 10mL buffer solution to 100mL with  $\text{H}_2\text{O}$ .

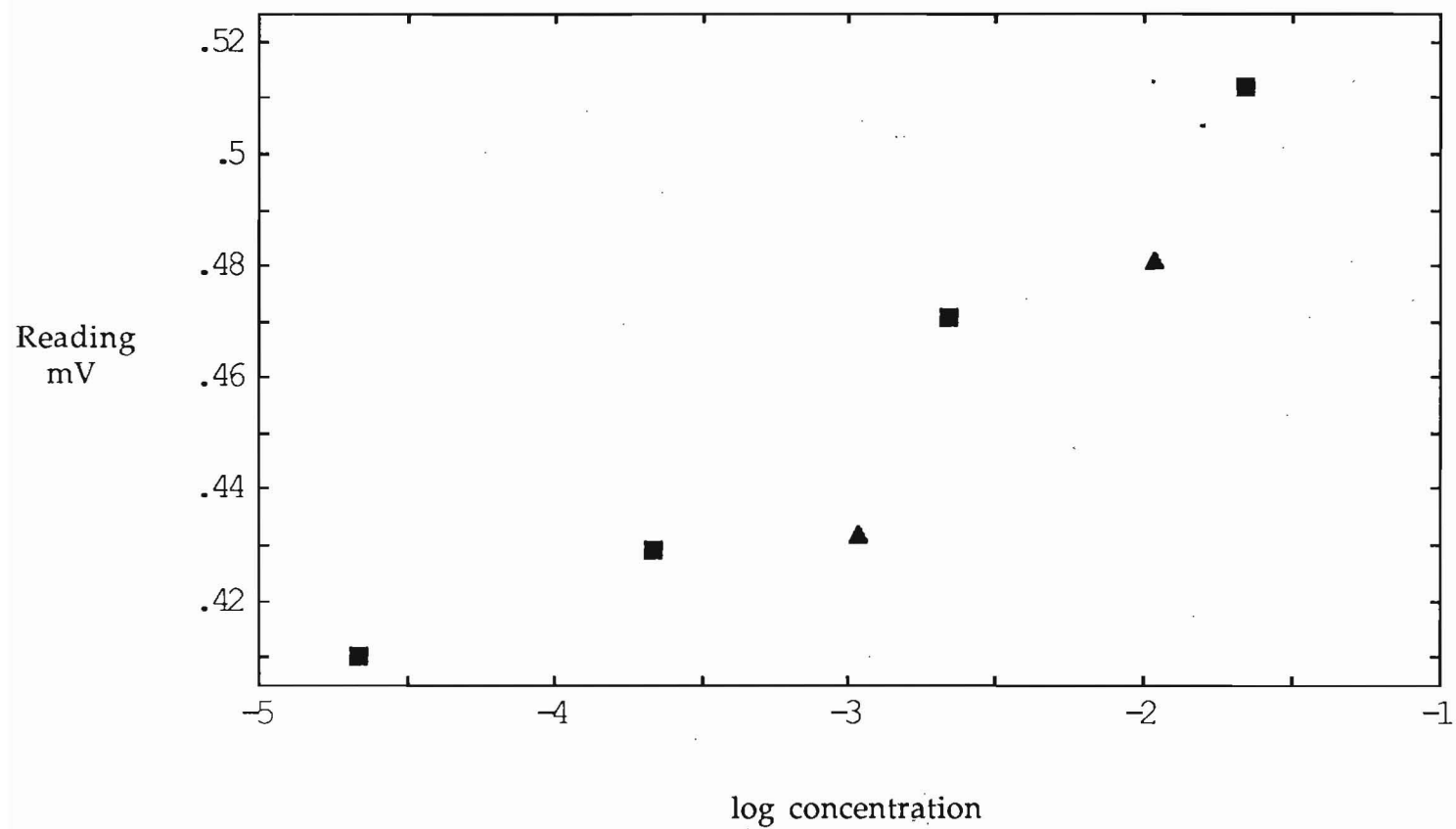
When a measurement was taken, 50.0mL of the solution was adjusted with concentrated  $\text{H}_2\text{SO}_4$  to  $\text{pH}=1.5\text{-}2.0$  with a pH meter calibrated to  $\text{pH}=2.0$ . Immediately, 5mL of the buffer solution was pipetted into the sample and the electrode was immediately placed in the sample after it had been briefly stirred. A reading was taken after approximately 1 minute.

NO Electrode Standardization:

Table 6

Concentration $\text{NO}_2^-$ aqueous	mV	Concentration $\text{NO}_2^-$ sat'd benzene- $\text{H}_2\text{O}$	mV
$2.17 \times 10^{-5}$ <u>M</u>	0.410	$1.08 \times 10^{-4}$ <u>M</u>	0.377
$2.17 \times 10^{-4}$ <u>M</u>	0.429	$1.08 \times 10^{-3}$ <u>M</u>	0.432
$2.17 \times 10^{-3}$ <u>M</u>	0.471	$1.08 \times 10^{-2}$ <u>M</u>	0.481
$2.17 \times 10^{-2}$ <u>M</u>	0.512		

### NO Electrode Standardization Curve



Legend:

- = Nitrite (aq)
- ▲ = Nitrite in sat'd aqueous benzene

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### **Proposal for Research Honors**

This project will examine the production and reactivity of hydroxyl radicals. The radicals may be produced by either thermal or photochemical means, and potential differences in radical reactivity based upon their mode of production may be determined. The mechanism of scavenging reactions which trap the hydroxyl radical will be examined, and characterization, as well as quantification, of the products of these reactions will be attempted.

Title: Investigating the Mechanisms and Reactions of the Hydroxyl Radical