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Photochemistry of the Nitrite Ion

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Photochemistry of the Nitrite Ion

Laura J. Wilson

Chemistry 499 Senior Research Honors Thesis

Research Advisor: Dr. Tim Rettich


Approval Page

"Photochemistry of the Nitrite Ion"

by Laura Jeannine Wilson

A paper submitted in partial fulfillment of the requirements
for Chemistry 499 and Honors in Chemistry

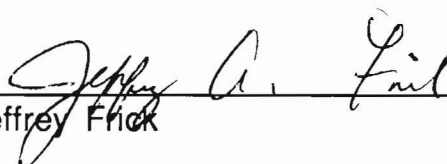
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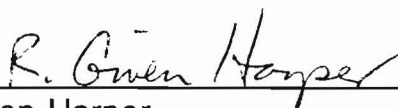
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Index

List of Figures	
List of Tables	
Abstract	1
Theory	2-17
Introduction	2-4
Reactions of nitrous acid and the nitrite ion	4-7
Photochemical reactions of nitrous acid and nitrite	7-11
The hydroxyl radical	11-14
The NO radical	14-15
Dark reaction of phenol and nitrous acid	15-17
Procedure	18-22
Results	23-42
Tables	23-25
Figure	26
Spectra	27-44
Discussion	45-56
Mechanism of addition	45-46
Study of benzene photolysis solution	46-49
Study of phenol photolysis solution	50-53
Possible products	53-54
Oligomer formation	54-55
Conclusion	56
Future Work	57-58
Bibliography	59-60

List of Figures

Spectra 1, IR	KBr pellet of benzene photolysate extract	27
Spectra 2, IR	KBr pellet of phenol extract before photolysis	28
Spectra 3, IR	KBr pellet of phenol photolysate extract	29
Spectra 4, IR	KBr pellet of phenol	30
Spectra 5, IR	KBr pellet of p-nitrosophenol	31
Spectra 6, IR	phenol and p-nitrosophenol	32
Spectra 7, IR	reference of phenol and p-nitrosophenol	33
Spectra 8, IR	reference of catechol and resorcinol	34
Spectra 9, IR	reference of 1,4 biphenol and hydroquinone	35
Spectra 10, HPLC	neutralized aqueous benzene photolysate	36
Spectra 11, HPLC	benzene photolysate spiked with phenol	37
Spectra 12, HPLC	neutralized aqueous benzene photolysate	38
Spectra 13, HPLC	benzene photolysate spiked with phenol	39
Spectra 14, HPLC	neutralized aqueous phenol photolysate	40
Spectra 15, HPLC	nitrite, phenol, and p-nitrosophenol	41
Spectra 16, UV-Vis	aqueous benzene/nitrite photolysate solution	42
Spectra 17, UV-Vis	aq. benzene/nitrite solution before photolysis	43
Spectra 18, UV-Vis	aq. phenol/nitrite solution before and after photolysis	44
Figure 1:	Extraction of Aqueous Photolysates	26

List of Tables

Table 1, Rf values of TLC of extracted benzene photolysate on glass plate	23
Table 2, Rf values of TLC's of extracted benzene photolysate on metal plate	24
Table 3, Rf values of TLC's of extracted phenol photolysate	24
Table 4, possible photochemical products	25

Abstract

Nitrogen containing compounds contribute to many environmental problems such as acid rain, air pollution, groundwater contamination, and smog formation. For example, when the atmosphere is heavily polluted with nitrites and aromatic hydrocarbons, nitrogen compounds can undergo photochemical reactions to produce harmful compounds that can adversely affect the environment. This project studied the photochemistry of the nitrite ion in aqueous basic solution. Both $\cdot\text{OH}$ and $\text{NO}\cdot$ radicals are produced during photolysis, but the two radicals recombine in the presence of pure water causing no net reaction. Aromatic compounds present in the solution being photolyzed can act as scavengers reacting with either one or both radicals to produce different compounds. Two scavengers, benzene and phenol, were studied in the basic nitrite solution. Photolysis for 24 hours at 366 nm caused both solutions to darken considerably. The benzene solution changed from clear to brown/orange, and the phenol solution changed from yellow to dark brown. Thermal reactions for the same amount of time yielded no such results. Methylene chloride preceded by acidification of the aqueous solution was used to extract the photolysate, although some question of this method does exist. The attempt at separation of products contained in the photolysate included the following techniques: TLC, HPLC, and column chromatography. UV-vis spectroscopy, FTIR, and HPLC were used in the attempt to characterize the products formed. Products that are most likely to be present include p-nitrosophenol and phenol (from the benzene photolysate).

Introduction

Environmental problems plague society. From the highest reaches of the atmosphere where ozone depletion raises utmost concern to below the earth's surface where all kinds of post-consumer waste is stored, civilization has affected nature; and now nature is affecting us. Pollution and the depletion of natural resources such as ozone create health problems for many and destroy the ecological balance. By attempting to understand how pollution affects the environment, society comes closer to repairing the damage it has done and to preventing further problems.

Nitrogen containing compounds play a large role in both the natural environment and pollution. The atmosphere consists of about 78% nitrogen and 21% oxygen gas.¹ Various nitrogen containing compounds are present in the atmosphere as well. Nitrous oxide, N_2O , is a colorless, nonflammable, nontoxic gas with a sweet taste and odor that originates mainly from bacterial activity.¹ Nitric oxide, NO , is also a colorless, nonflammable gas, but it is odorless and toxic. Not only natural sources such as lightning but pollutants also produce this gas.¹ Nitrogen dioxide, NO_2 , is a nonflammable, toxic, reddish brown gas that possess a strong choking odor and originates from pollution.¹ Nitric oxide and nitrogen dioxide are the nitrogen containing compounds directly involved in air pollution with 23 million tons of these two compounds being released annually from human activities, most of which involve fuel combustion.¹

Both diatomic nitrogen and oxygen are quite stable in the earth's atmosphere. However, at high temperatures, oxygen can

oxidize the nitrogen to form nitric oxide.¹



Temperatures high enough for this oxidation to occur are reached by fuel combustion, especially from the engines of supersonic jets.²

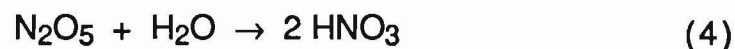
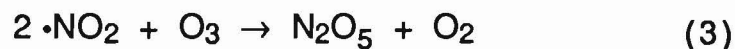
The nitric oxide that is produced from the above reaction can undergo a variety of reactions which will be presented later.

The environmental effects of the NO_x compounds are threefold: the depletion of the ozone layer, the production of acid rain, and the contribution to general air pollution.² Nitric oxide reduces ozone to form nitrogen dioxide and diatomic oxygen. (Eq. 2)



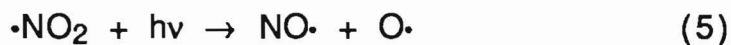
As a result, a toxic gas has now been formed in the atmosphere, and an essential natural resource has been depleted.

Acid rain, another environmental hazard, consists of sulfuric and nitric acids.³ The formation of the nitric acid from nitrogen dioxide is a two step process involving the intermediate N_2O_5 .¹



The NO_x compounds, which are free radicals themselves, will also react photochemically by either dissociating or scavenging to produce additional free radicals and whose end contribution is air

pollution in the form of photochemical smog. In the absence of organic compounds, nitrogen dioxide undergoes a cyclic photolytic process as follows¹:



(same as 2)

Here, the NO_2 is merely recycled back to itself. However, the types of hydrocarbons produced from unburned fuel in exhaust emissions and from petroleum refineries¹ disrupt this cycle creating smog by scavenging the radicals produced in equation 5.

Photochemical smogs consist of a wide variety of organic compounds which are created through the competition of hydrocarbons reacting with the $\text{O}\bullet$ radical in the nitrogen dioxide photochemical cycle.³ Organic free radicals are produced by this competing reaction causing the formation of a host of organic compounds (some that are fairly toxic) to form.¹

Reactions of nitrous acid and the nitrite ion

In aqueous solution, nitrous acid exists in equilibrium with the nitrite ion as illustrated in equation 8:



$$K_a^4 = 7.1 \times 10^{-4}$$

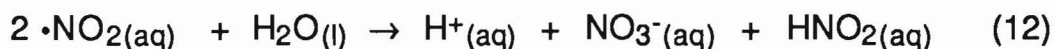
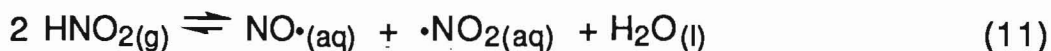
$$\text{p}K_a = 3.15$$

The pH will influence which side of the equilibrium will prevail. In very basic conditions, the nitrite ion will predominate and in acidic, the nitrous acid. For example, seawater is slightly basic, and therefore the nitrite ion will be much more prevalent than nitrous acid in the ocean.

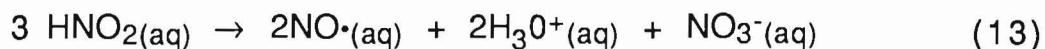
Park and Lee gave two possible reactions for the formation of nitrous acid ⁵; one involves the combination of nitric oxide, nitrogen dioxide, and water and another consisting only of nitrogen dioxide and water to produce two moles of nitrous acid (Eq. 9). The other reaction includes the combination of 2 moles of nitrogen dioxide with water and results in the formation of 1 mole of nitrous acid and 1 mole of nitric acid (Eq. 10).



Nitrous acid is quite unstable and tends to decompose, thus making this acidic compound difficult to study. The decomposition mechanism occurs as reported in Park and Lee's research.⁵ (Eq.'s 11 & 12)

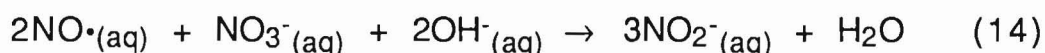


The overall decomposition reaction of the nitrous acid is included in Rettich's paper as follows⁶: (Eq. 13)

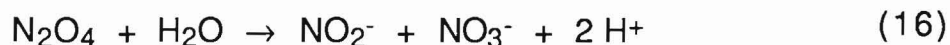
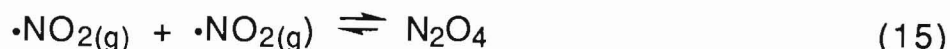


According to Montemartini, at low concentrations of HNO_2 , the decomposition reaction is first order.⁷ Temperature and pH also play a role in the rate of this reaction.⁶ As pH increases, the nitrous acid equilibrium (Eq. 8) shifts to the formation of the nitrite ion (to the right) thus affecting how much nitrous acid will be present to decompose.

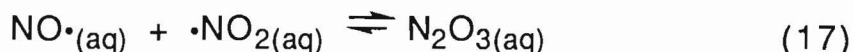
The products of the nitrous acid decomposition also undergo further reaction. For example, nitric oxide and the nitrate ion can combine with hydroxide to produce nitrite and water.⁸ (Eq. 14)



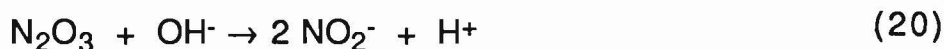
Treinin and Haynon report an additional gaseous NO_2 reaction where nitrogen dioxide combines with itself to form N_2O_4 (Eq. 15) which then decomposes to nitrate and nitrite (Eq. 16).⁹



Nitric oxide, nitrogen dioxide, and nitrous acid systems exist in equilibrium with N_2O_3 as shown in equations 17 and 18.



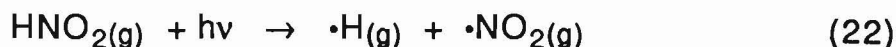
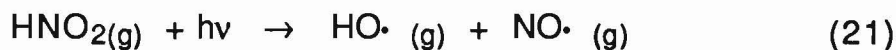
N_2O_3 also reacts with both water (Eq. 19) and the hydroxide ion (Eq. 20) to produce nitrite.⁹



Thus, in an aqueous, basic environment, nitrite becomes an important end product which in turn can play a large role in photochemical reactions.

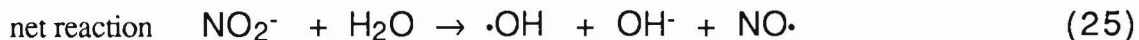
Photochemical reactions of nitrous acid and nitrite

Nitrous acid also decomposes photochemically in two primary processes as reported by Cox and Atkins.¹⁰



The first reaction, which produces the hydroxyl and nitric oxide radicals is favored.¹⁰ Rettich has reported the quantum yield of nitrous acid decomposition to range from zero at zero concentration of nitrous acid to .14 at a .14 M concentration of the acid.⁶

The nitrite ion also undergoes photolysis reactions and absorbs in a 300 nm to 410 nm band and maximally at 356 nm.¹³ Treinin and Hayon extensively studied the photochemistry of the nitrite ion in 1970 and reported the following set (Eq.'s 23-25) of photolysis reactions⁹:



The radicals formed in this primary process can react to reform the nitrite ion.⁹ (Eq's 26-28)



The $\cdot\text{OH}$ and $\text{NO}\cdot$ radicals can also recombine (Eq. 29) to produce nitrous acid.⁹



Of course, nitrous acid is in equilibrium with the nitrite ion. Thus, the chemical reactions that occur after the photolysis of the nitrite ion eventually reform the nitrite ion. Thus, no net photolysis occurs.

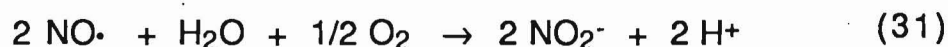
Zafiriou has also studied the photochemistry of the nitrite ion, but in a more natural setting-the ocean. Nitrite rich water found in the central equatorial Pacific Ocean occurs from pollution, waste from microorganisms, etc.¹¹ Sunlight can photolyze nitrite to produce $\text{NO}\cdot$ and $\cdot\text{OH}$ radicals since the nitrite absorbs strongly at around 350 nm which corresponds to the near-visible spectrum range of the sun.¹³ This emphasizes the relevance of the photochemical reactions of nitrite in the environment. The nitrite

photolysis occurs only at the upper few meters of the surface of the ocean where the greatest amount of sunlight reaches.¹² According to Zafiriou, reactions with nitrite in the ocean are analogous to reactions occurring with nitrite in the troposphere.¹¹ The daytime concentration of steady state $\text{NO}\cdot$ (formed from the photolysis of NO_2^-) is greater than 10^{-11} M with a lifetime ranging from 10 to 100 seconds.¹¹ In contrast, the $\cdot\text{OH}$ radical reacts within a lifetime of 10^{-6} seconds. Although both radicals are formed, the longer lifetime of $\text{NO}\cdot$ make it easier to study.¹³ The sea is thus a source of nitric oxide for the atmosphere as opposed to a sink which would take away the $\text{NO}\cdot$ radical.¹¹

Zafiriou has proposed a reaction scheme (Eq. 30) for the photolysis of the nitrite ion in water that is quite similar to Treinin and Hayon's.¹³

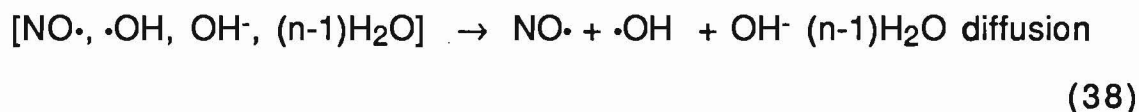
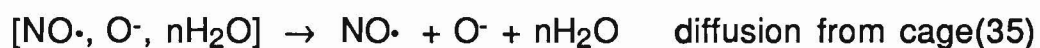


Cyclic regeneration of the $\text{NO}\cdot$ radical results in the reformation of the nitrite ion.¹³ (Eq. 31)



If other radical species are present, the $\text{NO}\cdot$ radical can react as a scavenger—a compound that will combine with a radical in a termination step. The $\cdot\text{OH}$ radical also reacts with many constituents of seawater including all halides except fluorine, almost all organic compounds, and most heavy metal ions.¹² Therefore, both radicals produced upon photolysis of nitrite possess

the potential to react with other species thus causing a net photolysis to occur (since nitrite will not be reforming). However, in order for the $\text{NO}\cdot$ or $\cdot\text{OH}$ radical to react with a species that is not present in the nitrite photolysis cycle, several obstacles must be overcome. Potential radical scavengers are normally present in such minute quantities that it will take longer for a minor substituent to react with $\cdot\text{OH}$ or $\text{NO}\cdot$ than for these same radicals to react with a constituent of the NO_2^- photolytic cycle.¹² The trace compounds must "diffuse in" to where the radicals are present in the aqueous environment. If nitrite and water are surrounding the newly formed radical species, they will most likely immediately react with those compounds producing no net photolysis. Zafiriou describes the primary photolysis product formation as a caged radical pair process (Eq.'s 32-38) and has developed a mechanism for the photolysis reaction based on this solvent cage.¹⁴



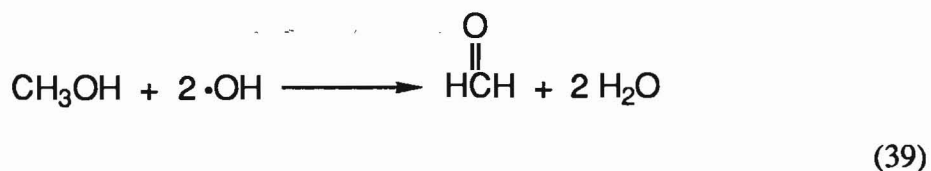
The first step in the solvent cage mechanism involves the photochemical excitation of the nitrite ion (Eq. 32). The S_1 and S_2

functions represent various transitions that the nitrite undergoes at different frequencies.¹⁴ The square brackets indicate caged radical species. Once nitrite has been photochemically excited, two reaction schemes may occur; the excited nitrite might fall back down to its ground state level by emitting heat (Eq. 33), or the excited nitrite might dissociate into the primary photochemical products thus producing a solvent cage containing $\text{NO}\cdot$ and $\text{O}\cdot$ surrounded by water molecules (Eq. 34). The species in the solvent cage can either diffuse out of the cage (Eq. 35), recombine to form nitrite (Eq. 36), or react further within the cage by proton transfer from water to produce a hydroxyl radical and ion (Eq. 37). Once again, these products can leave the solvent cage by diffusion or by forming nitrous acid. Thus, the overall cage mechanism produces no net photolysis.

A median net nitrite loss in the ocean of 10% per day has been observed, which Zafiriou attributes to secondary reactions with the $\text{NO}\cdot$ radical.¹⁴ In other words, diffusion of the nitrite photolysis products out of the solvent cage has occurred and these products scavenge or are scavenged by other compounds present in the ocean. These scavenging reactions are the primary focus of this research.

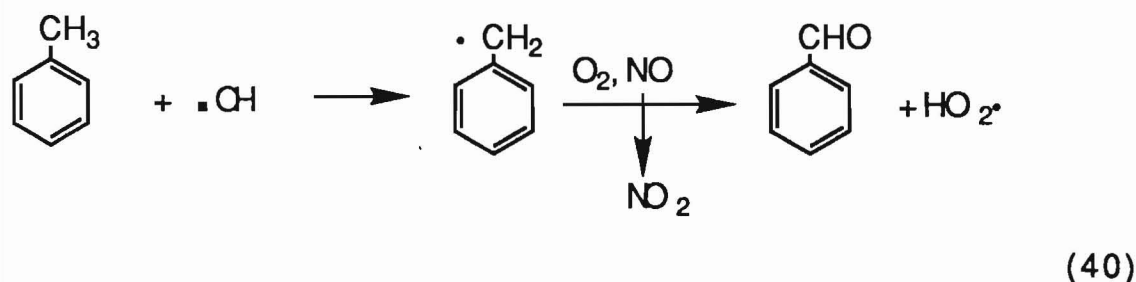
The hydroxyl radical

The hydroxyl radical is the most reactive photochemically produced radical in the environment¹⁵ and will scavenge a myriad of compounds. For example, methanol undergoes hydrogen abstraction in the presence of hydroxyl radical to form formaldehyde.¹⁵

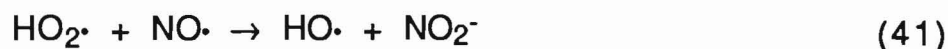


The photolysis of nitrite provides a source for these hydroxyl radicals. The quantum yield of $\cdot\text{OH}$ radical from NO_2^- photolysis was found to be $.046 \pm .003$ at a wavelength of 351 nm, pH of 8, and at 298 K.¹⁶ These conditions are analogous to those found in the ocean environment. When nitrite is photolyzed with 2-propanol, acetone is produced thus illustrating that the $\cdot\text{OH}$ radical from the nitrite will be scavenged by other species.¹⁶

Aromatic compounds also undergo scavenging reactions with the hydroxyl radical. Since automobile emissions contain various aromatic hydrocarbons¹⁷, these $\cdot\text{OH}$ scavenging reactions are quite prevalent in urban environments. Shepson et al. have proposed a possible way for the hydroxyl radical to add to an aromatic ring.¹⁸ (Eq. 40) Hydrogen abstraction from a substituent methyl group produces an aldehyde as shown in reaction 40.

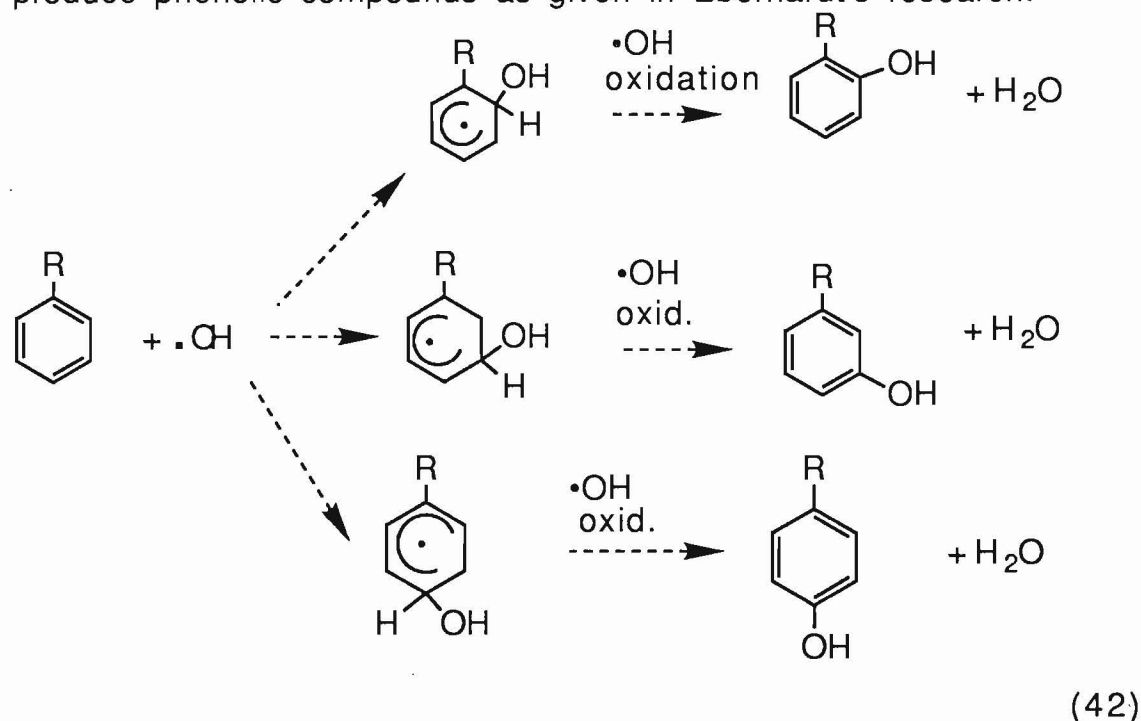


Oxidation of the radical occurs as the $\text{NO}\cdot$ radical is cycling back to nitrite (Eq. 40). Another radical, $\text{HO}_2\cdot$ is produced which reacts with $\text{NO}\cdot$ to produce more hydroxyl radical and nitrite.



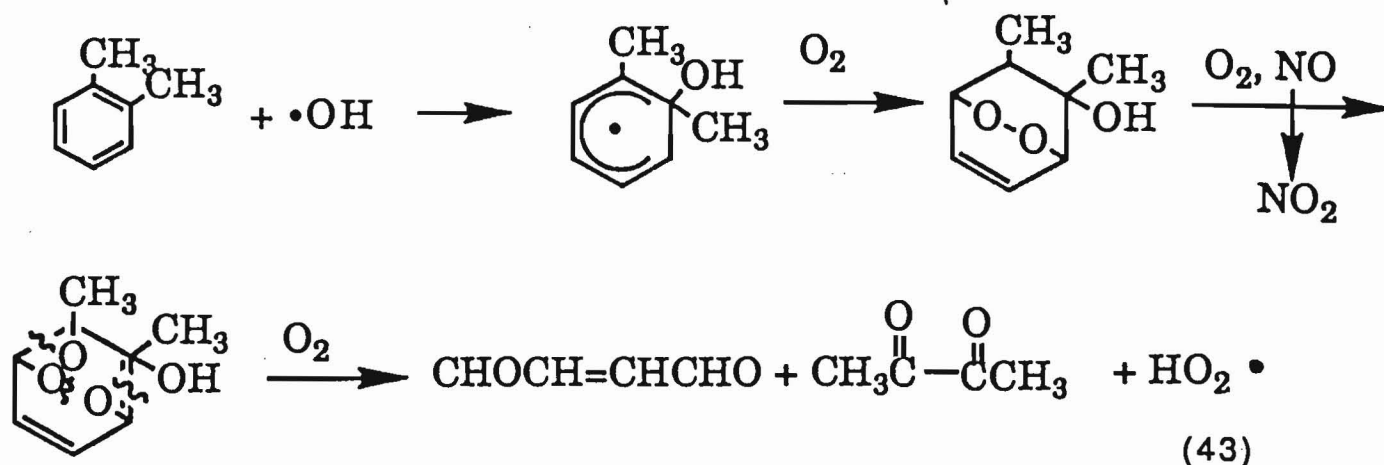
Thus, more hydroxyl radicals can be produced than the number that originated from the original photolysis.

Another possible mechanism is $\cdot\text{OH}$ addition to the ring to produce phenolic compounds as given in Eberhardt's research.¹⁹



Here R represents an alkyl group. Of prime concern to this work is whether the hydroxyl radical can add to benzene ($\text{R} = \text{H}$). Although benzene does not possess a high solubility in water (only 1.77 g/L at room temperature)²³, Warneck and Wurzinger found that phenol evolved upon a one hour photolysis of the nitrite ion in an aqueous benzene-saturated solution.²² (Here, the nitrite was the source of the hydroxyl radicals.)

Ring cleavage is another interesting phenomenon that can occur. The hydroxyl radical can add onto the aromatic ring and then cleavage can occur as illustrated below.¹⁸

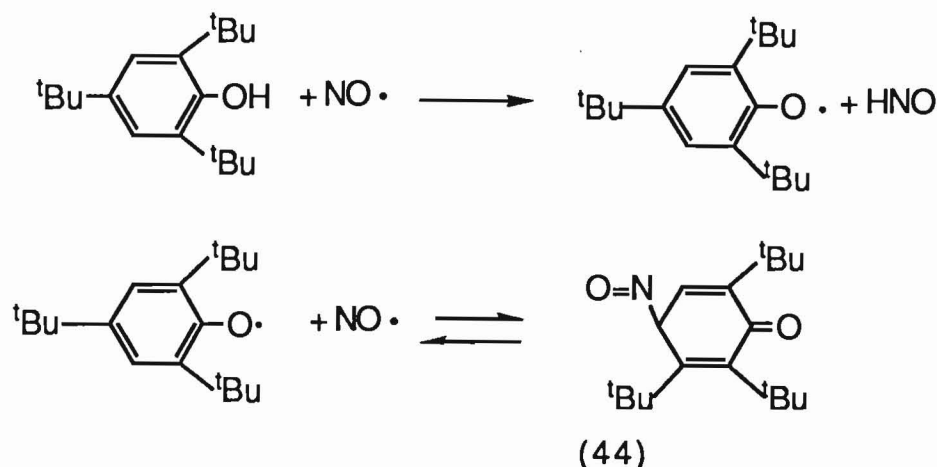


This cleavage reaction is quite important in the fact that it opens a whole new realm of possible products resulting from an aromatic ring in the presence of $\cdot\text{OH}$ radical.

The NO radical

Obviously, the $\cdot\text{OH}$ radical is very reactive, but in the nitrite photolysis an $\text{NO}\cdot$ radical is also produced. Perhaps this radical possesses reactive capabilities similar to $\cdot\text{OH}$.

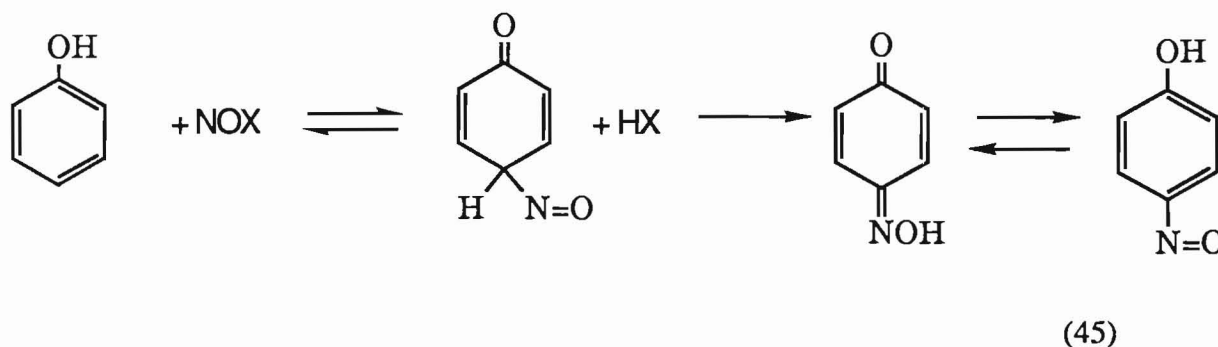
Janzen, Wilcox, and Manoharan studied the reaction of $\text{NO}\cdot$ radical with sterically hindered phenols. They discovered that both phenoxyl radicals and nitroso compounds were produced.¹⁹ The proposed reaction scheme consists of the phenoxyl radical being produced and then reacting with the $\text{NO}\cdot$ radical to produce various nitroso compounds.²⁰



Once the phenoxyl radical is formed, the $\text{NO}\cdot$ radical will attack at the ortho and para positions since OH is an ortho-para director.²⁰ The phenoxyl radical is the predominate product when excess $\text{NO}\cdot$ is removed thus suggesting that this coupling radical reaction is reversible.

Dark Reaction of Phenol and Nitrous Acid

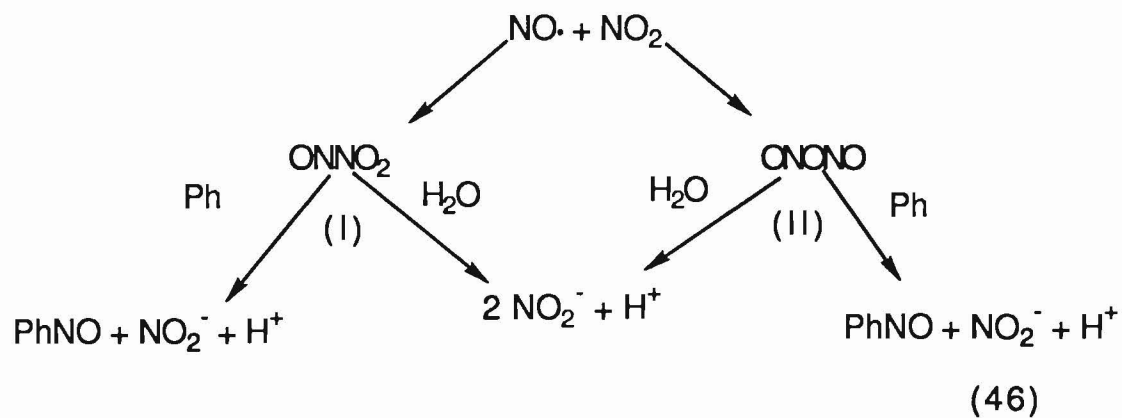
Not only does the possibility exist for phenol to participate in photochemical reactions in the presence of nitrite, but phenol can also undergo "dark" reactions to form p-nitrosophenol. According to Virk and Issenberg, the nitrosation of phenol readily occurs in acidic solutions of NaNO_2 producing primarily p-nitrosophenol with a rate constant of $1.16 \text{ M}^{-1} \text{ min}^{-1}$.²⁴ This dark reaction might possibly interfere with any photochemical reactions that occur in an aqueous phenol/nitrite system. Challis and Higgins found that nitrosation of phenol in .2M H_2SO_4 yielded at least 95% p-nitrosophenol with the remainder being the ortho isomer.²⁵ They have also proposed a reaction scheme of the nitrosation of phenol in water (Eq. 45).



In this reaction, XNO is the nitrosating agent with X being some moiety to which the nitroso group is attached. The rate determining step in the given reaction is a proton rearrangement to form quinone monoxime from the dienone intermediate which converts to p-nitrosophenol.

Pines, Rossi, and Ross suggest that phenol nitrosation in basic solutions with a pH of 12 lead to rapid formation of the 4-nitrosophenylate anion (via N_2O_3 reagent).²⁶ Contrary to this claim, Challis and Higgins mention that the formation of p-nitrosophenol becomes very slow in weakly acidic conditions (pH of 5)²⁵ meaning that the anion of phenol would not be easily nitrosated.

A reaction scheme for the nitrosation of phenol has been proposed using N_2O_3 as the intermediate in this dark reaction.²⁶ Therefore, X (from equation 45) is equal to NO_2 in the reaction scheme shown below: (Eq. 46)



It is thought that route II occurs more rapidly.

Perhaps N_2O_3 will also play a role in the photochemical reactions that an aromatic ring can undergo with nitrite.

Procedure

Solution Preparation and Photolysis

Benzene scavenged solution (0.1M NaNO_2 aq) - Approximately 6.9g of sodium nitrite (NaNO_2 , Merck, 97% pure, MW=69.005 g/mole) was dissolved in approximately 1 L of distilled water, and 50% NaOH was added to make the solution basic to a pH of 13 with indicator paper. Excess benzene (15 ml, Fischer Scientific, purified grade, MW=78.11 g/mole) was added to the solution to ensure saturation, and the aqueous solution, with a layer of benzene on top, was then stirred for 30 minutes.

Phenol scavenged solution (0.1M NaNO_2 aq) - A solution of 50% NaOH was added to 200 ml of distilled water until the solution reached a pH of 13 as determined using pH indicator paper. Approximately 20g of phenol (Aldrich, MW=94.11 g/mole) was added to this solution in small portions adjusting the pH to 13 after each addition which consumed a total of 25 ml of 50% NaOH. (About 10 ml of water was used to rinse the excess phenol from the beaker from which it was being added.) NaNO_2 (1.6g) was finally dissolved into the aqueous phenol solution.

Photolysis procedure - A 42.6 cm quartz tube with a 2 cm diameter was rinsed with the solution being photolyzed, and then 100 ml of that solution were poured into the tube. For benzene solutions, a benzene layer of approximately 1 inch thick was poured on top of the solution to ensure benzene saturation. The solution was then photolyzed at 366 nm for about 24 hours with a Rayonet

photochemical reactor (model #RPR 100) with Rayonet UV lamps #RPR 3500 A.

Extraction of Photolysate

Micro-extraction of phenol - About 50 ml of phenol photolysate solution and 15 ml of methylene chloride (Fischer Scientific, 99.9% pure, MW=84.91 g/mole) were placed into a CH₂Cl₂ rinsed 125 ml separatory funnel which was shaken and vented. Approximately 95 drops of concentrated H₂SO₄ (12 M, Fischer Scientific, 95-98% pure) were added to acidify the solution to a pH of 2. The solution was shaken and vented for approximately 8-9 minutes and allowed to sit for 10 minutes. The methylene chloride layer was then drained into a CH₂Cl₂ rinsed beaker and the pH of the aqueous layer checked to make sure it remained at 2. Another 10 ml of CH₂Cl₂ was added to the aqueous layer, and the separatory funnel shaken and vented for 8-9 minutes, allowed to sit for 10 minutes, and drained. A third extraction was performed identical to the second one. Any aqueous layer accidentally drained was separated from the extracted methylene chloride solution via another CH₂Cl₂ rinsed separatory funnel. The combined methylene chloride extracts were dried using 18 g of anhydrous sodium sulfate until no clumping was observed and then decanted into a pre-weighed, CH₂Cl₂-rinsed beaker. Five 5 ml portions of methylene chloride were used to rinse the anhydrous NaSO₄, and these rinses were added to the previous extracts. The photolysate extract was then evaporated under the hood and placed under vacuum for further analysis.

Macro-extraction of benzene photolysate - The micro-extraction procedure was used for the macro-extraction process except that approximately 1000 ml of photolysate was extracted with 50 ml portions of methylene chloride in a 2 L separatory funnel. The benzene layer on top of the photolysate had to be separated from the aqueous layer before methylene chloride and sulfuric acid were added in order to prevent extraction of excess benzene into the organic layer. Approximately 15 ml of concentrated H_2SO_4 were used to lower the pH of the photolysate to 2.

TLC Analysis

Onto a silica gel metal plate, the extracted photolysate solution in CH_2Cl_2 , a phenol solution in CH_2Cl_2 , and a p-nitrosophenol solution in CH_3OH were all singly spotted and developed using methylene chloride. Other solvents that were used in the phenol photolysate analysis include the following: methanol, 1-propanol, ethyl ether, and methyl iso-butyl ketone. The concentrated benzene photolysate extract CH_2Cl_2 solution was spotted along an entire glass TLC plate, which then was eluted with methylene chloride in a large developing tank. The bands of the benzene photolysate were then scraped from the glass plate and individually placed into small beakers pre-rinsed with CH_2Cl_2 , and small amounts of methylene chloride were added to extract the photolysate products from the silica gel. The methylene chloride extracts were then decanted into other CH_2Cl_2 rinsed beakers and the silica gel underwent a second extraction which was added to the same beakers. Once the methylene chloride had evaporated and the fractions had remained in a vacuum desiccator

for at least 24 hours, a KBr pellet was made (if enough of a fraction was present) and an IR spectrum was measured with an ATI Mattson Genesis Series FTIR.

Column Chromatography

A glass column of a diameter from 2 - 4 cm filled with silica gel and covered with a thin layer of sand was used to separate both benzene and phenol photolysates. The extracted photolysate was added as a slurry with methylene chloride and silica gel. Both photolysates were initially eluted with methylene chloride followed by methanol as their final eluent. Fractions were collected in CH_2Cl_2 or CH_3OH rinsed beakers, evaporated under the hood, and stored in a vacuum desiccator for FTIR analysis.

HPLC Analysis

Small portions of both benzene and phenol photolysates (unextracted) were neutralized with sulfuric acid to a pH of 7 and syringe filtered with aqueous Waters filters. Solutions of phenol, benzene, p-nitrosophenol, sodium nitrite, and various combinations were prepared using distilled water at a pH of 7. All of these solutions were also filtered. Portions of the filtered photolysate solutions were spiked with filtered solutions of phenol, p-nitrosophenol, and benzene. These solutions were then analyzed with Waters Associates HPLC in 10 μl and 15 μl portions with pure methanol and methanol/water/acetic acid mixtures (with a Water Automated Gradient Controller) on a 30 cm Micro Bondapak C_{18} column. The pumps used were Waters Associates Pump Model #'s

6000A and M-45. The Waters Associates Absorbance Detector Model 441 detected at a wavelength of 254 nm.

Results

TLC plates

Table 1: R_f values from glass plate of extracted benzene photolysate developed with CH₂Cl₂

R _f value range	color of band
0-.01	brown
.01-.03	tan/brown layer in between orange line, purple layer above band
.03-.06	yellow
.06-.07	fine brown line
.07-.19	yellow
.19-.22	bright orange
.22-.27	yellow with fine purple line above band
.27-.34	bright yellow
.34-.44	pale yellow
.44-.55	bright yellow with fine purple line above band
.55-.63	bright yellow
.63-.77	pale yellow
>.77	orange (seen on 2nd glass plate)

Table 2: R_f values of TLC's of Extracted Benzene Photolysate

compound	R_f in CH_2Cl_2	R_f in methanol
phenol	.27	.74
p-nitrosophenol	0	.78
benzene photolysate	0 - .13, .22, .31, .53, .59, .70, .77	.54, .63, .88

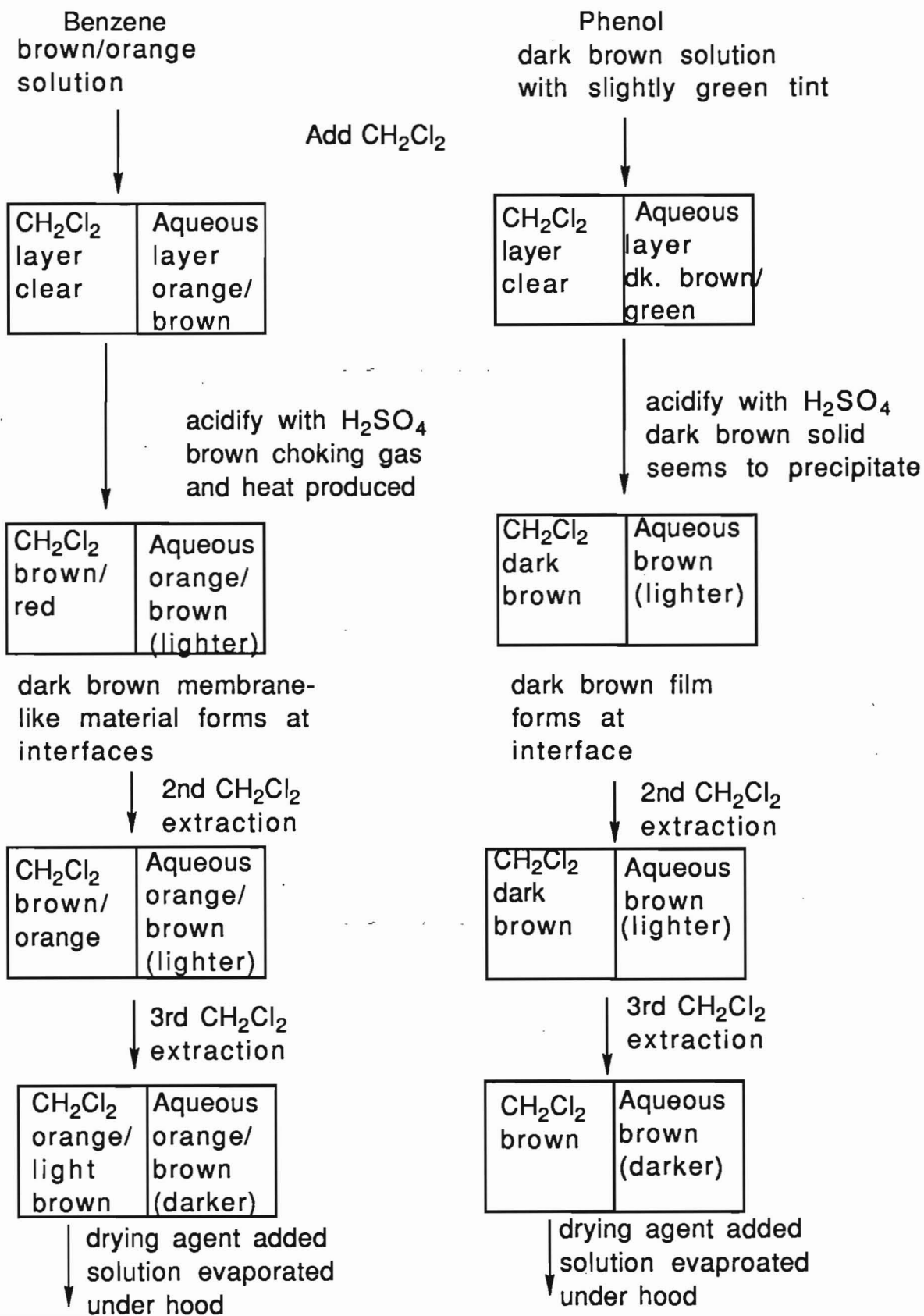
Table 3: R_f values of TLC's of Extracted Phenol Photolysate

R_f values (range)			
solvent used in elution	phenol	p-nitrosophenol	photolysate
methanol	.74 (.65-.84)	.78 (.72-.82)	.76 (.67-.84)
ethyl ether	.66	.01	.67
methyl-isobutyl ketone	.71 (.64-.80)	streak to .93	streak to .93
propanol	.83 (.76-.87)	streak to .84	streak to .85
methylene chloride	.32 (.22-.43)	0	0

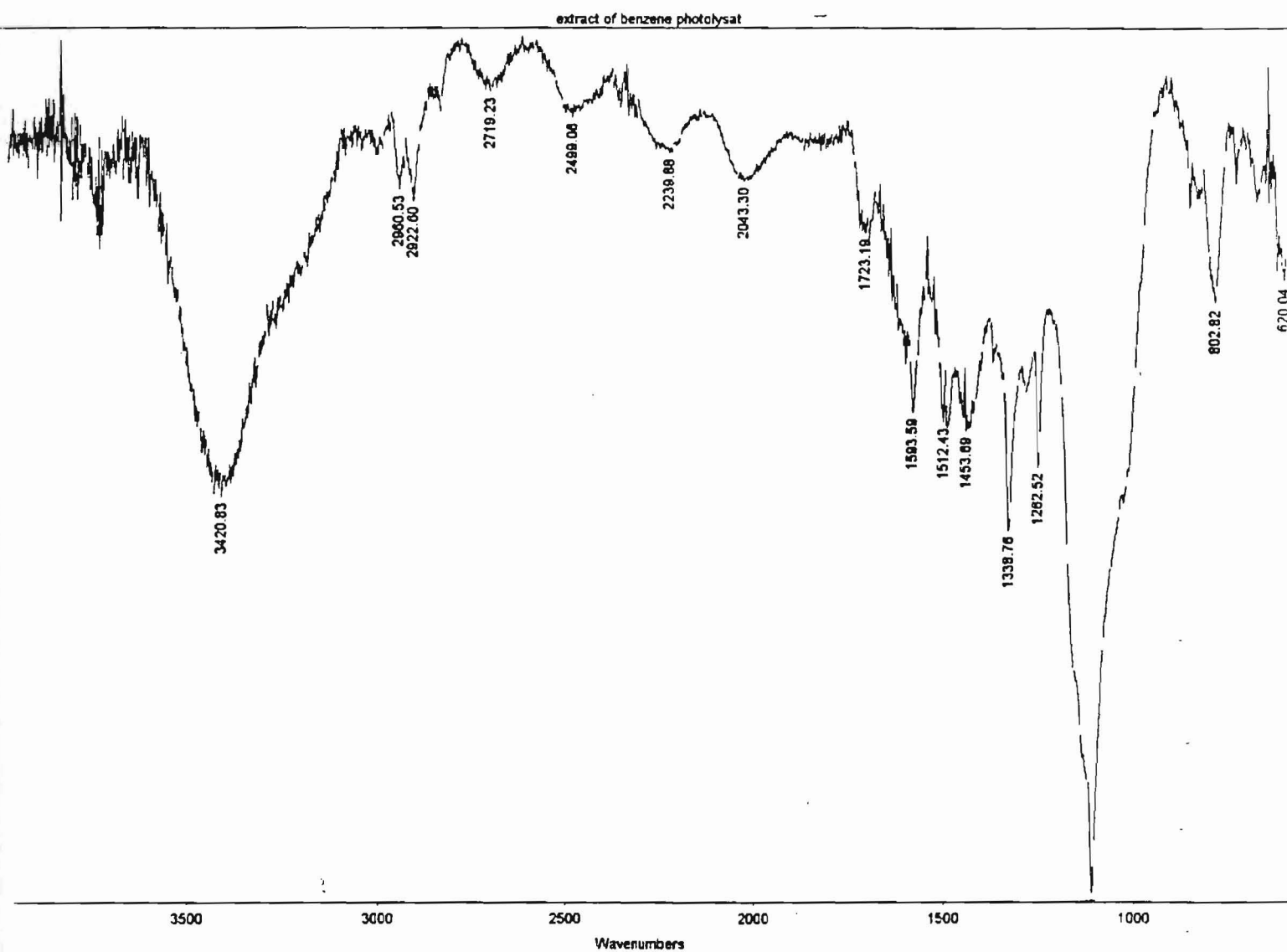
Table 4: Possible Photolysis Products^{23,27,28,29}

compound	solubility	color/form
phenol MW = 94.11 g/mole m.p. = 43°C pKa=9.89	87 g/L in water sol. in alcohols, ether, acetone, benzene, chloroform	clear crystals
nitrosobenzene MW = 107 g/mole m.p. = 67.5-68.0°C	insol. in water, NH ₃ slightly sol. in lign sol. in alcohols	white crystals as dimer green in solution
catechol MW = 110 g/mole m.p. = 110°C pKa1=9.12 pKa2=12.1	sol. in water, diethyl ether, benzene, alkalis, alcohols	colorless
resorcinol MW = 110 g/mole m.p. = 111°C pKa1=9.1 pKa2=11.32	sol. in water, alcohol, ether, acetic acid mod. sol. in chlrm spar. sol. in benzene	solution turns brown in air
hydroquinone MW = 110 g/mole m.p. = 172°C pKa1=9.91 pKa2=12.0	sol. in water, alcohol, ether, acetone	
quinone MW = 108 g/mole m.p. = 117°C	spar. sol. in water sol. in ethanol, diethyl ether, hot water, hot ligroin	yellow crystals forms 1:1 complex with hydroquinone to produce red/brn ned.
p-nitrosophenol MW = 123.11 g/mole decomp. at 144°C pKa=6.48	water: pH=6,.28g/L pH=12,4.4g/L, sol. in dil. alkalis, sol. in alcohol, ether, acetone insol. CH ₂ Cl ₂	pale yellow needles brown-green solution with alkalis pH=6, faint brn color pH=12 dk. opaque brn.
4-nitrosocatechol MW = 139 g/mole decomp. on heating	sol. in alkalis, ethanol, benzene	red solution in alkalis
2-nitrosoresorcinol MW = 139 g/mole m.p. = 102°C	sol. ethanol, ethyl ether, benzene	yellow needles
4-nitrosoresorcinol MW = 139 g/mole decomp. at 150°C	sol. ethanol, acetone, chloroform less sol. water, ethyl ether	yellow needles + H ₂ O from water brown needles from chloroform

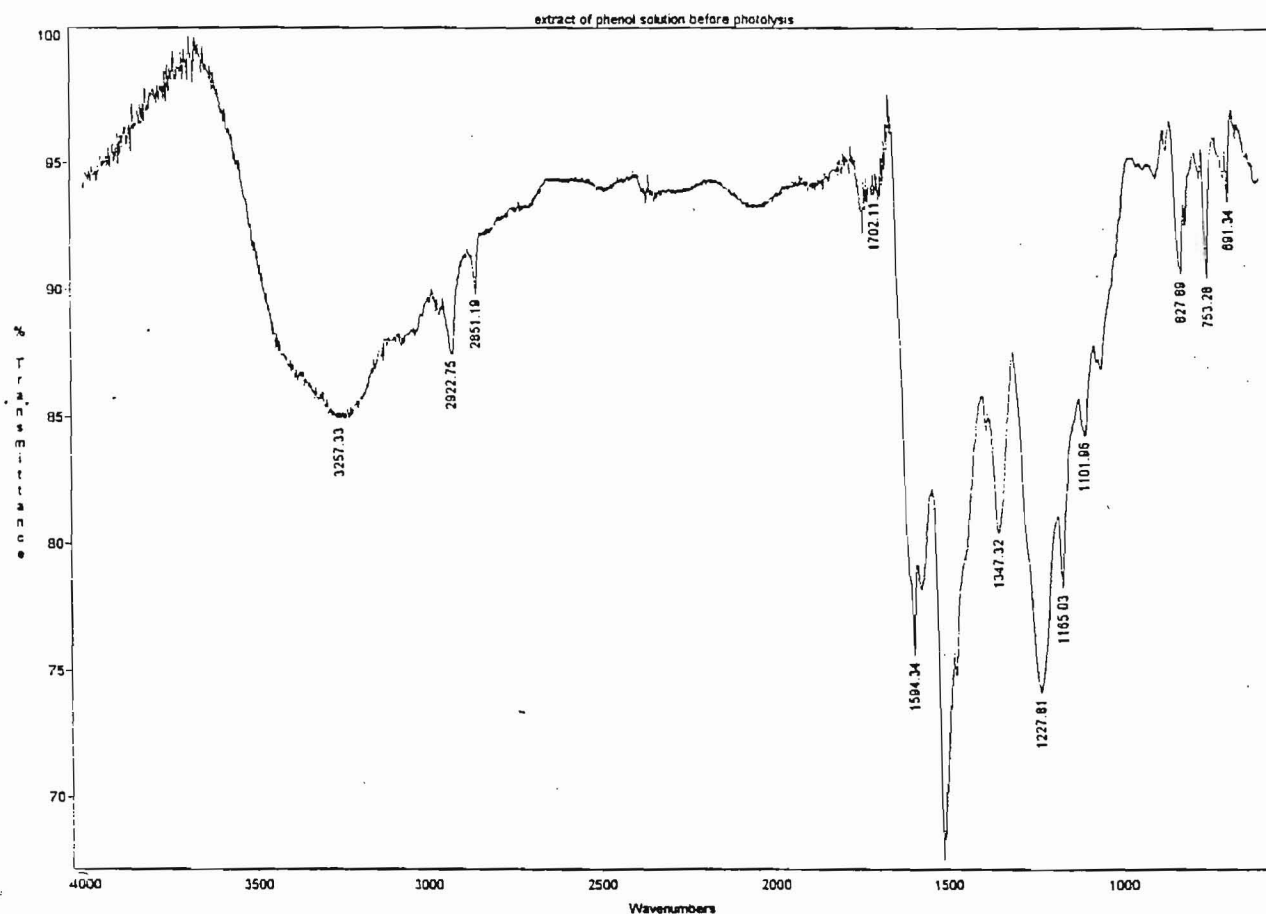
Figure 1: Extraction of Aqueous Photolysates



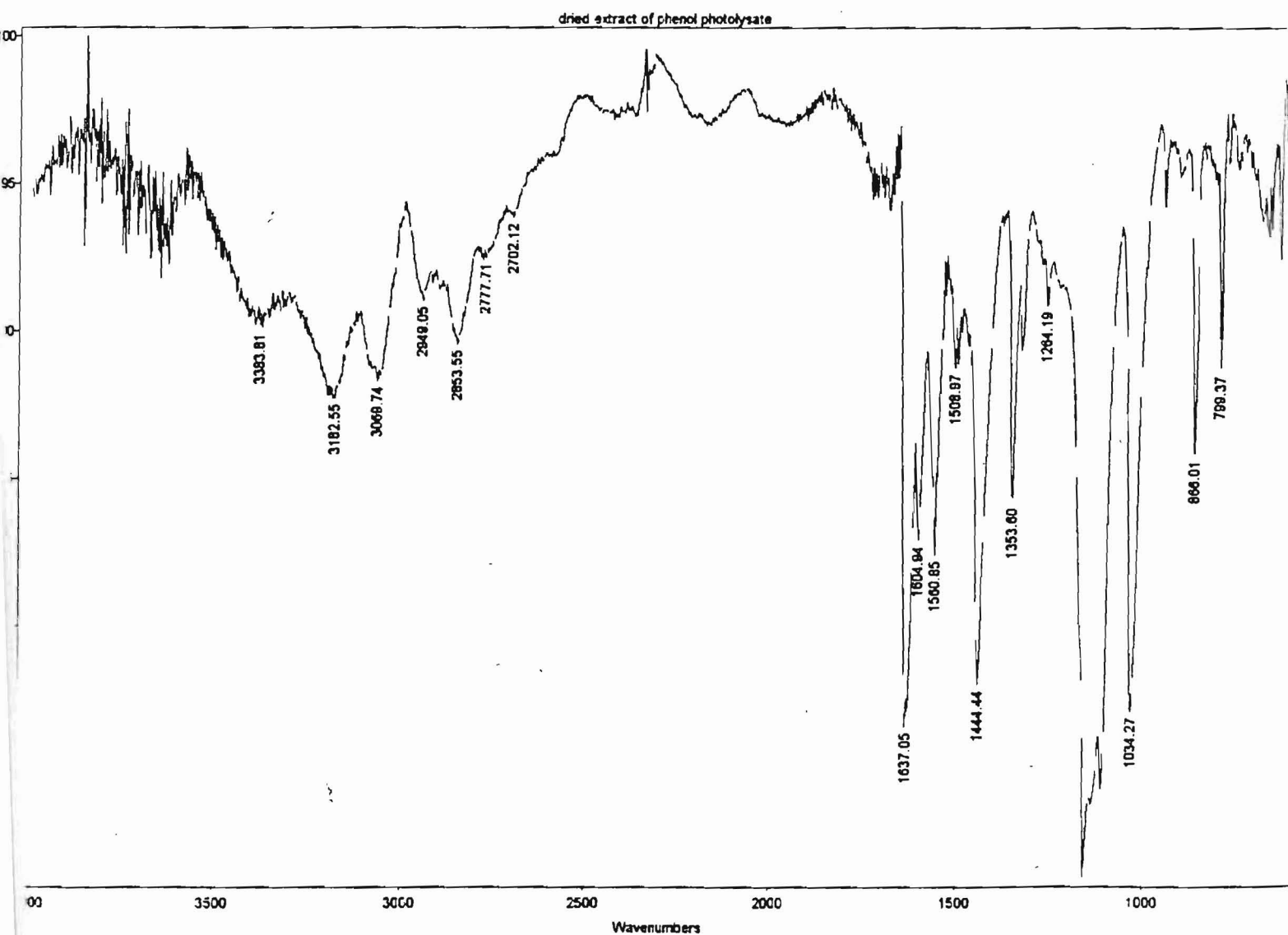
Spectra 1: IR of KBr Pellet of Benzene Photolysate Extract
x axis=wavenumbers, y axis=% transmission



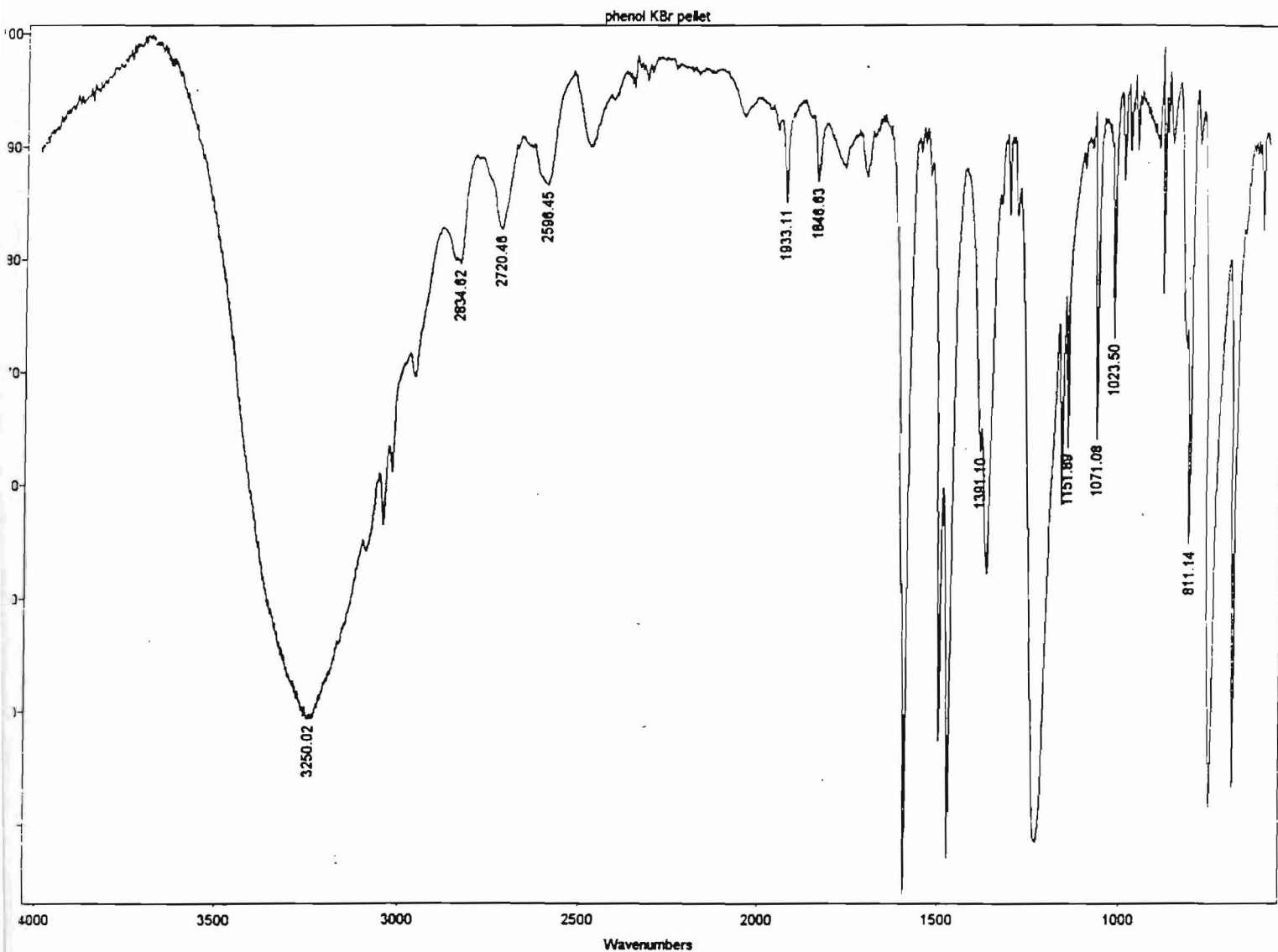
**Spectra 2: IR of KBr Pellet of Phenol Extract
Before Photolysis**
x axis=wavenumbers, y axis=% transmission



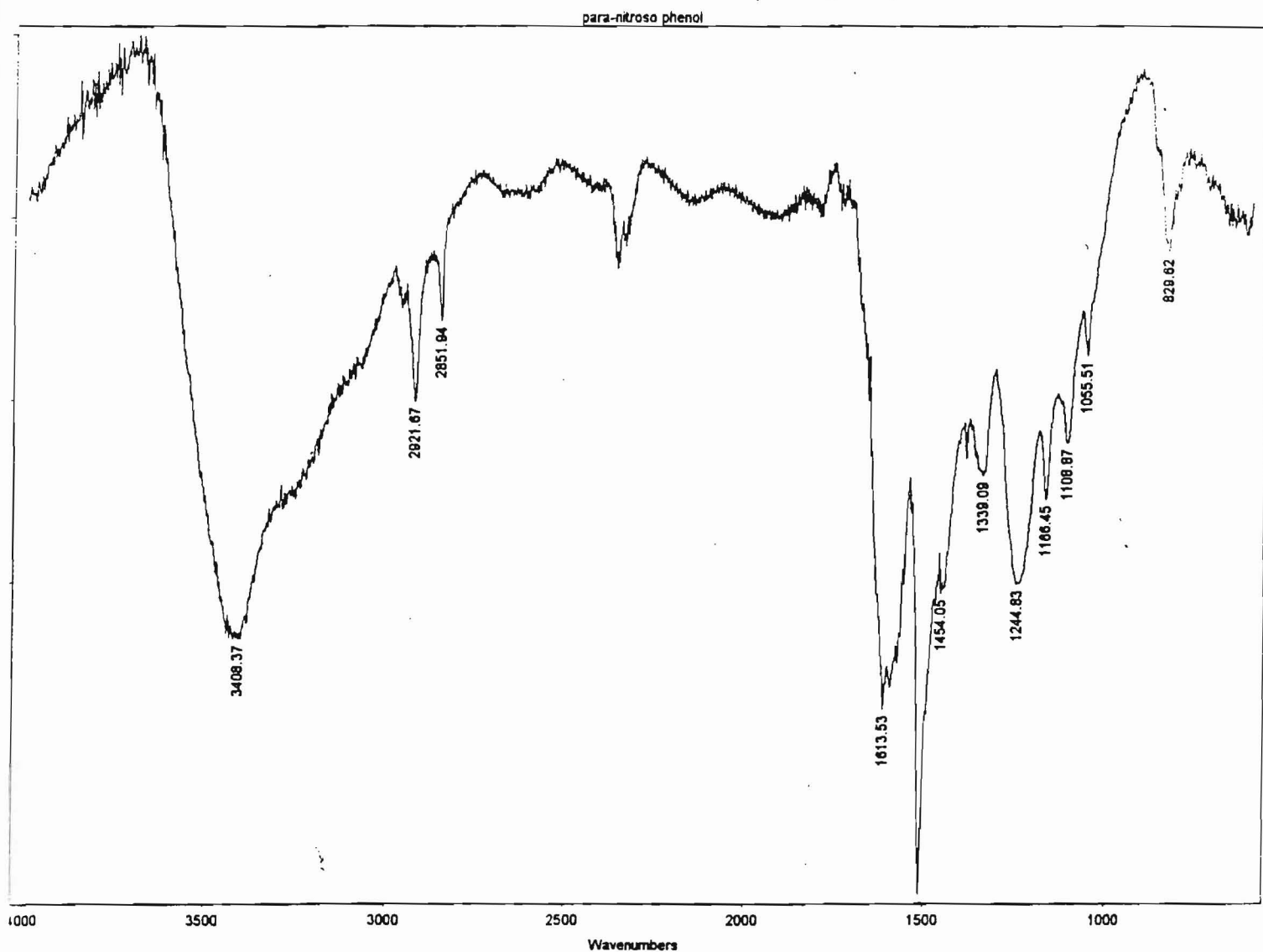
Spectra 3: IR of KBr Pellet of Phenol Photolysate Extract
x axis=wavenumbers, y axis=% transmission



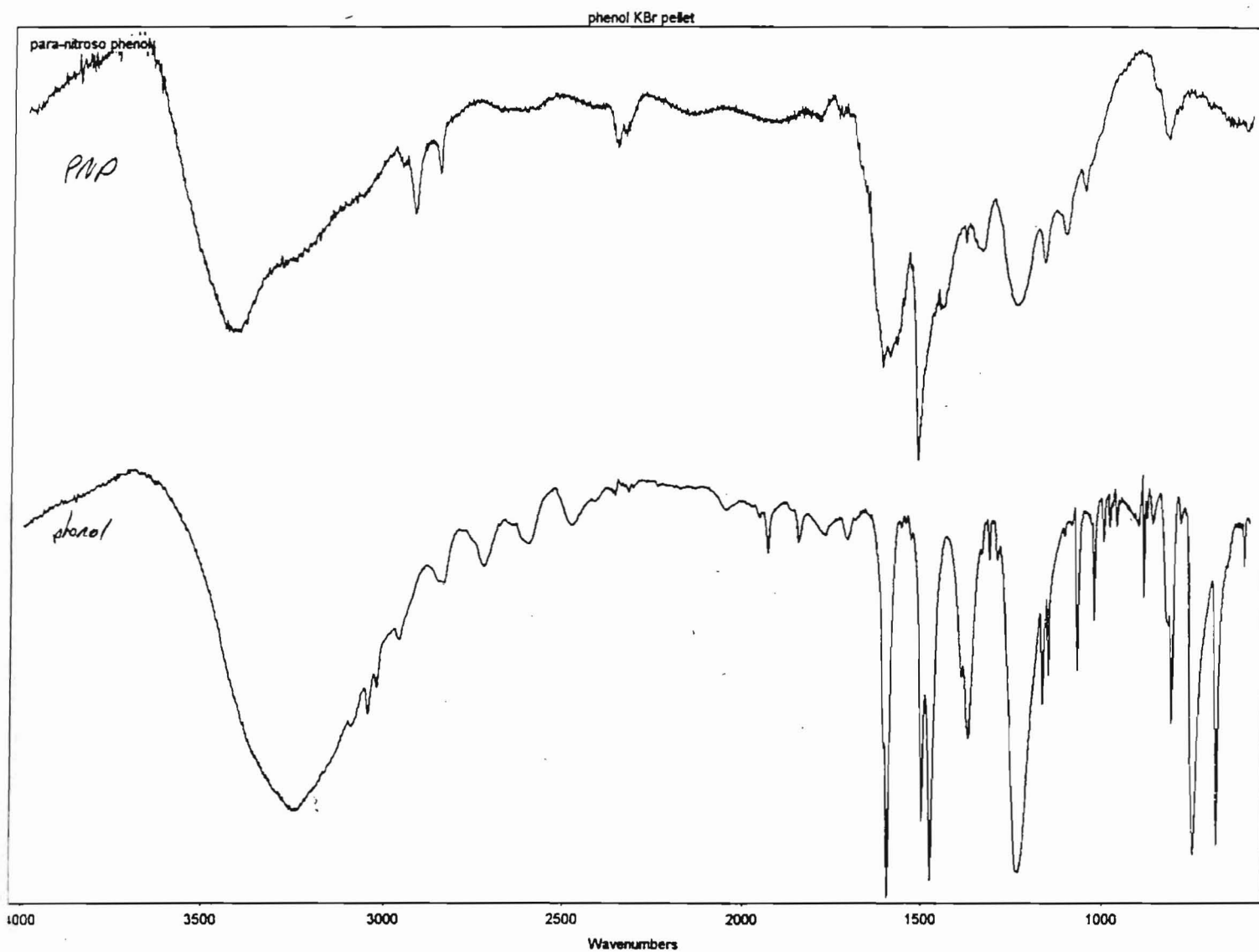
Spectra 4: IR of KBr Pellet of Phenol
x axis=wavenumbers, y axis=% transmission



Spectra 5: IR of KBr Pellet of p-Nitrosophenol
x axis=wavenumbers, y axis=% transmission



Spectra 6: IR of Phenol and p-Nitrosophenol
x axis=wavenumbers, y axis=% transmission



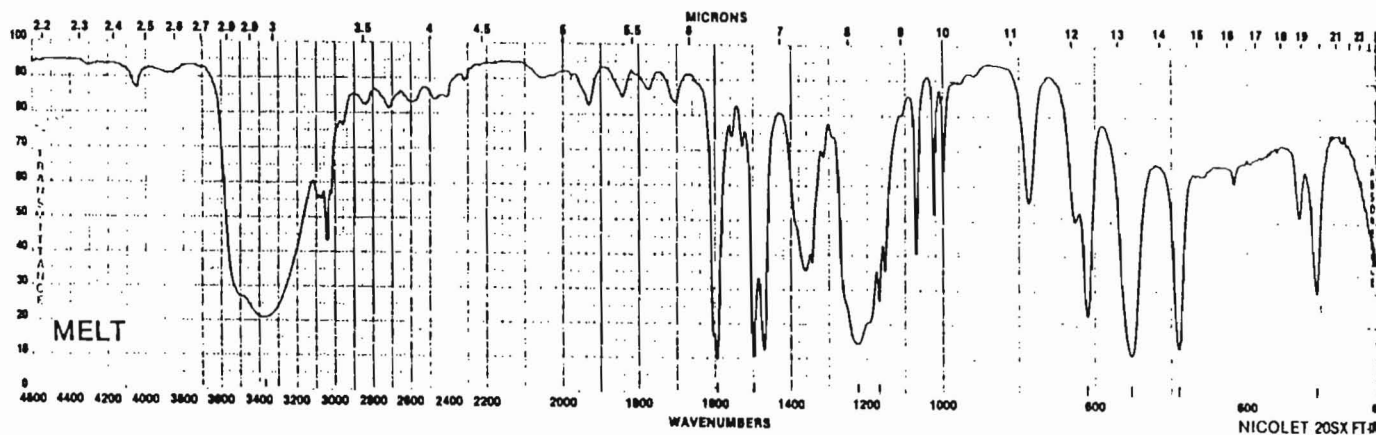
18545-0 CAS [108-95-2]
Phenol, 99 + %

FW 94.11
mp 39.5-41.5°C
bp 181°C

d 1.071
Fp 175°F

IR III, 644A
Merck 10,7115

3372.6	1224.4	751.8
1595.3	1168.0	689.8
1498.9	809.8	506.0

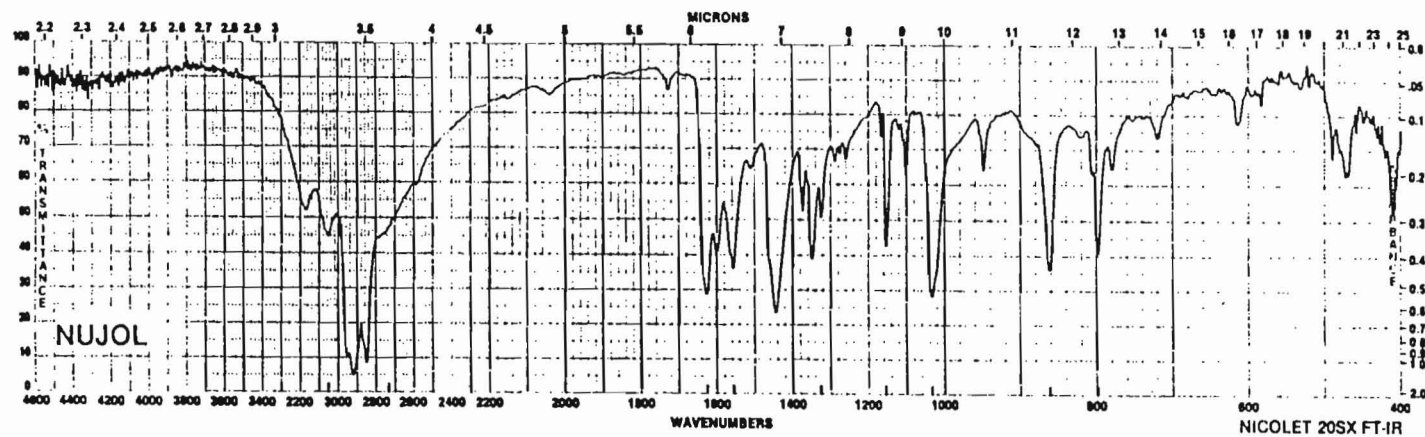


11709-9 CAS [104-91-6]
4-Nitrosophenol

FW 123.11
mp 132°C (dec.)

IR III, 801G
NMR II, 1,1128A
Merck 10,6488

3055.7	1559.9	1037.2
2737.2	1330.0	862.9
1630.4	1158.8	799.8



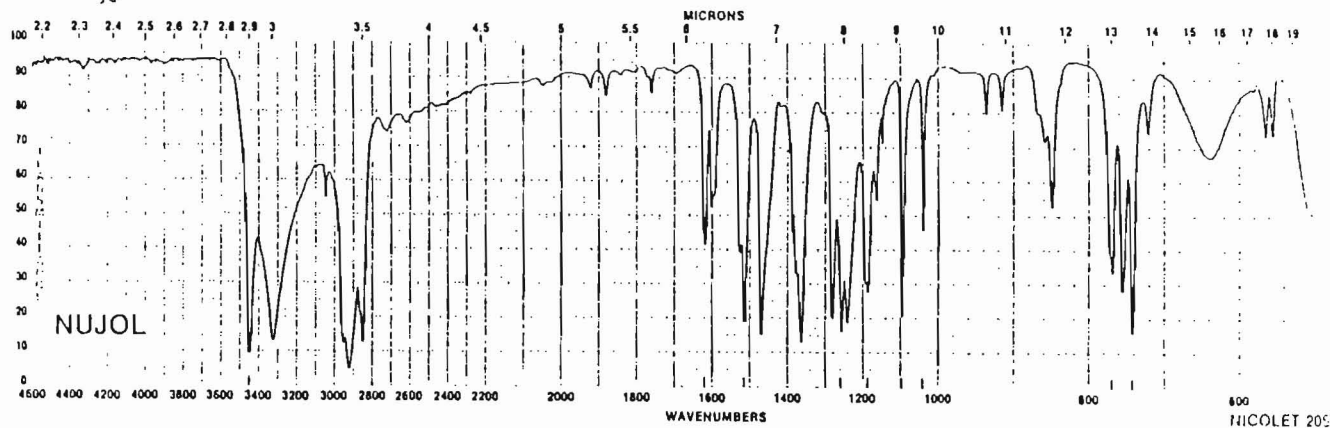
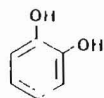
13501-1 CAS [120-80-9]
Catechol, 99 + %

FW 110.11
mp 104-106°C
bp 245°C

Fp 279°F

IR III, 662A
NMR II, 1,870B
Merck 10,7897

3450.4 1256.5
1619.5 1187.4
1513.8 1096.4



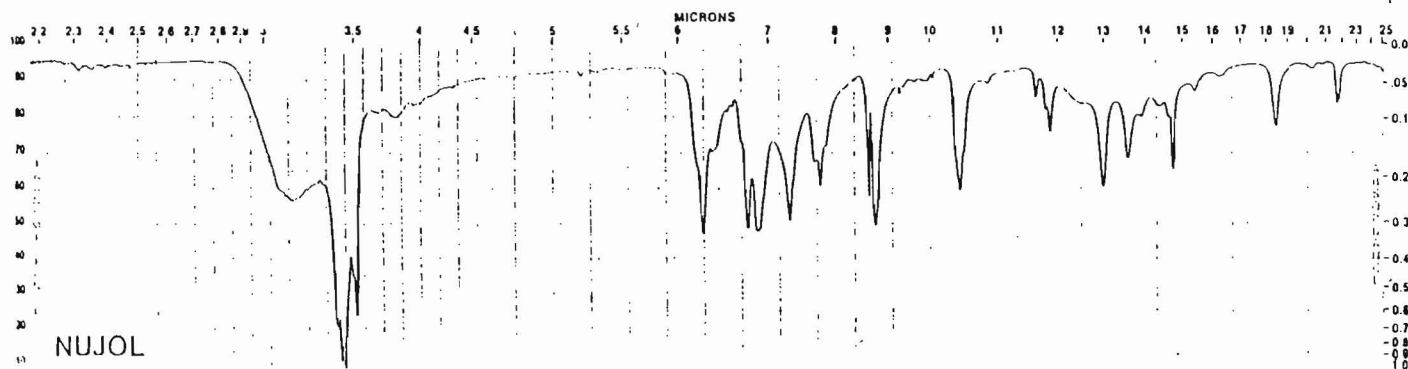
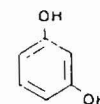
R40-6 CAS [108-46-3]
Resorcinol, 98%

FW 110.11
mp 109-110°C
bp 178°C/16mm

Fp 340°F

IR III, 664D
NMR II, 1,898C
Merck 10,8056

3184.1 1296.8 772.9
1607.1 1150.5 740.2
1489.0 962.3 680.1



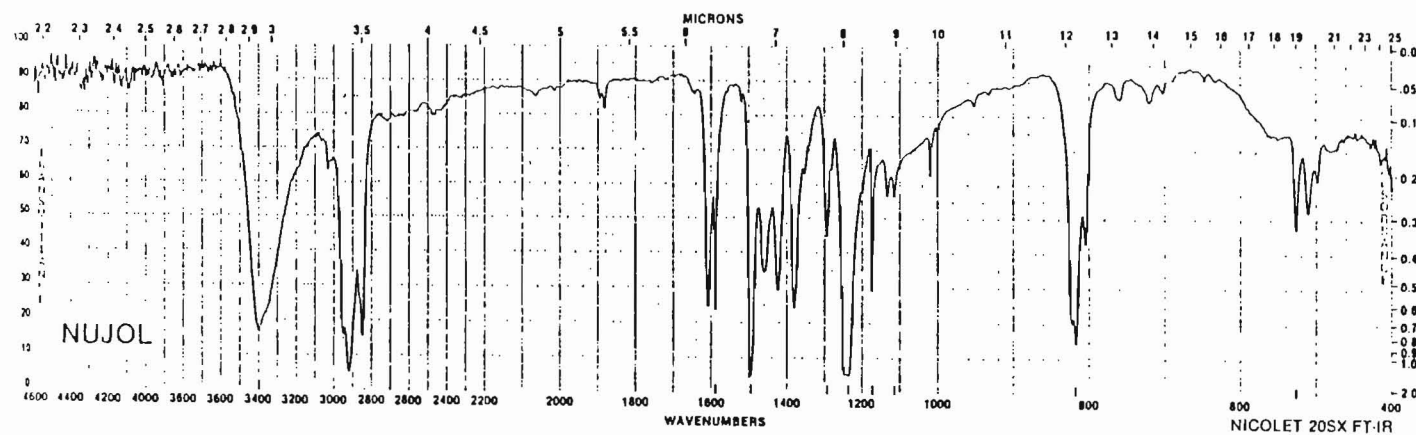
Spectra 9: Reference IR of 1,4 Biphenol and Hydroquinone30

16873-4 CAS [92-88-6]
4,4'-Biphenol, 97%

FW 186.21
mp 278°C (dec.)

IR III, 670H
NMR II, 1,907C

3399.5	1295.8	1116.7
1591.6	1238.4	818.8
1498.4	1176.1	528.4

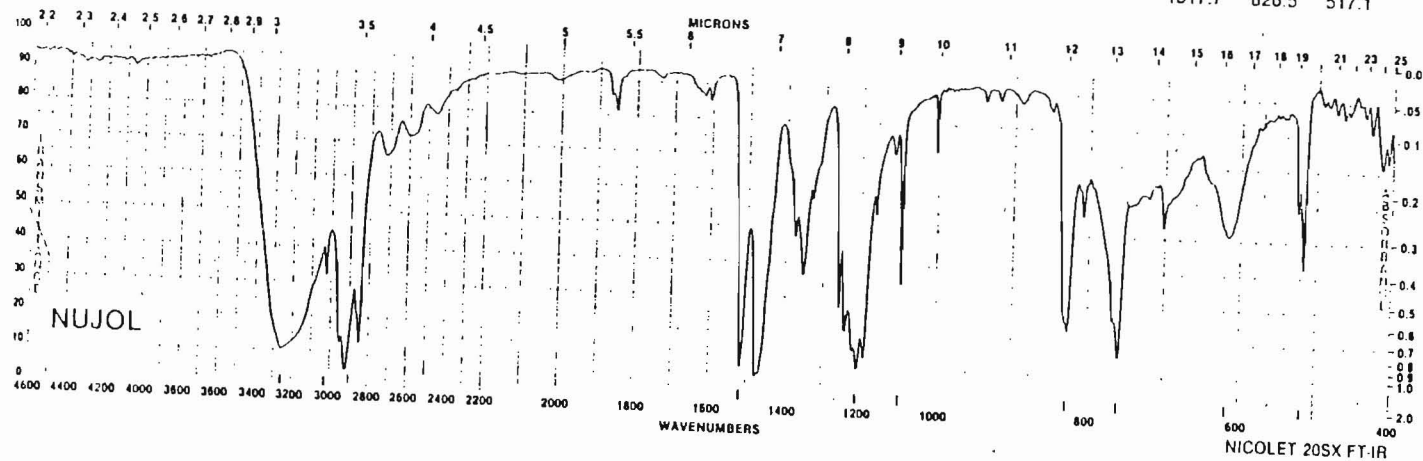


24012-5 CAS [123-31-9]
Hydroquinone, 99 + %

FW 110.11
mp 172-175°C
bp 285°C

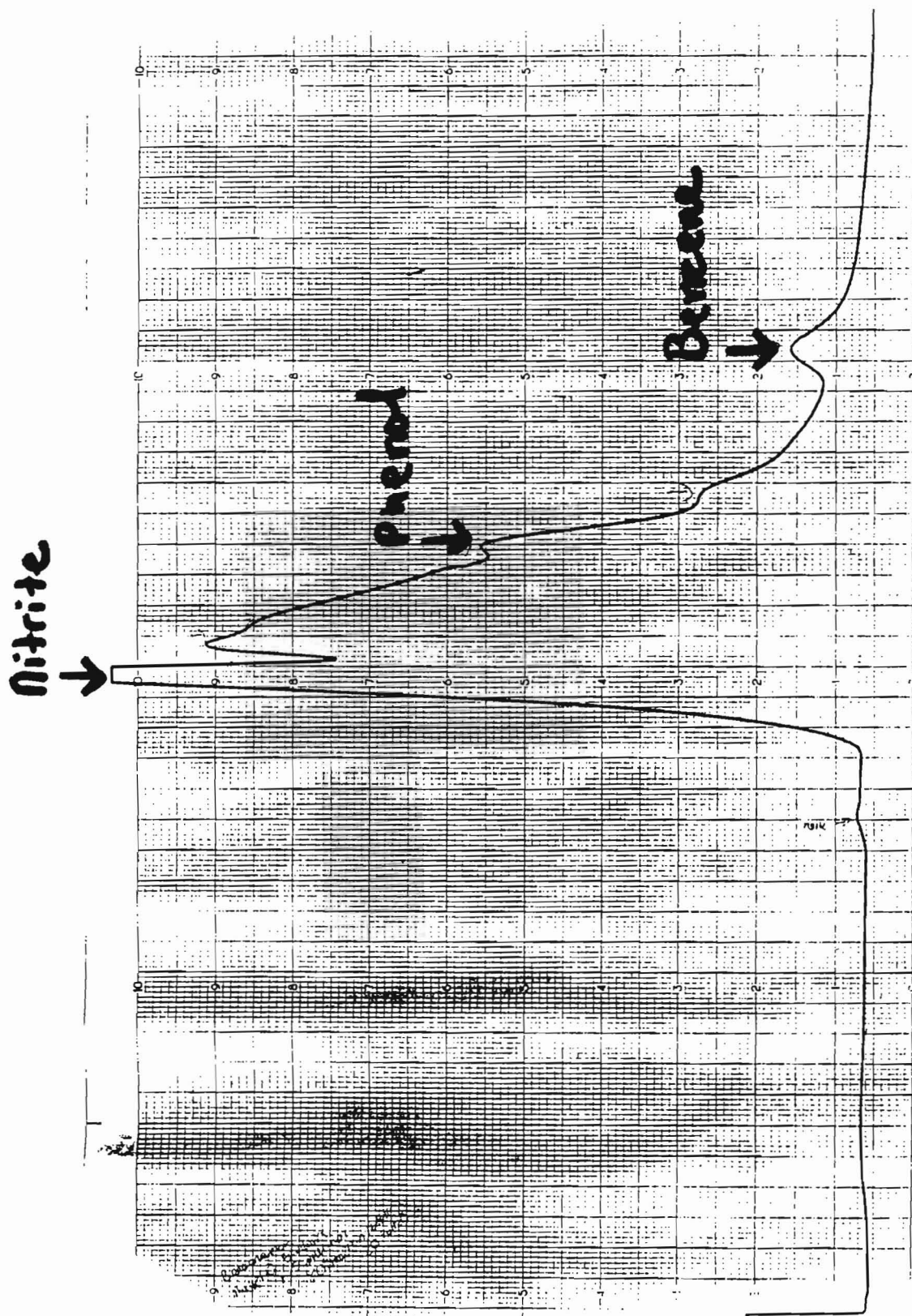
IR III, 666C
Merck 10,4719

3259.5	1209.9	758.9
3030.2	1097.0	615.6
1517.7	826.5	517.1



Spectra 10
HPLC Chromatogram of Neutralized Aqueous Benzene
Photolysate

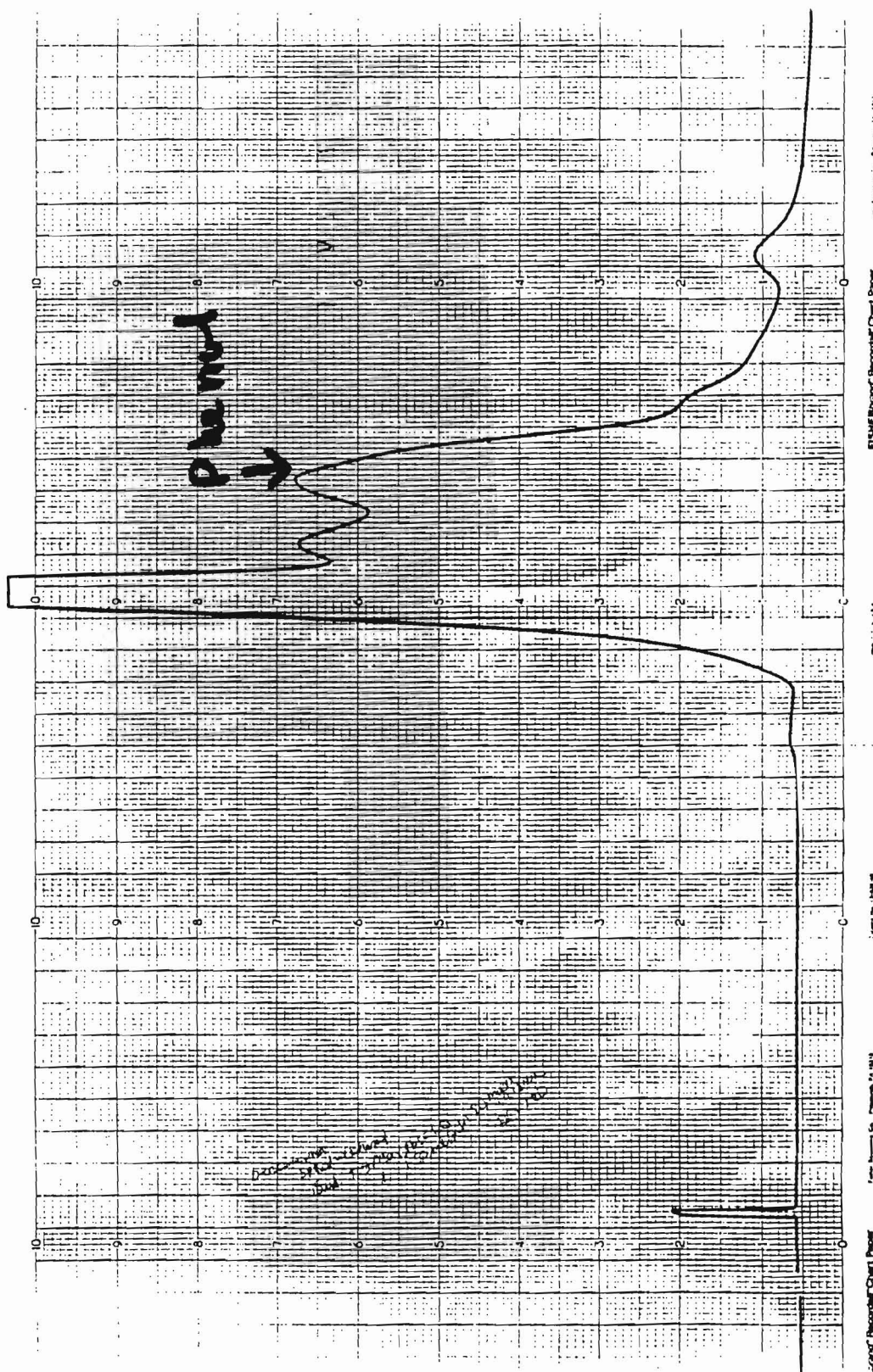
15 μ l sample, Max Abs=1.0, Flow Rate=1.5 ml/min
Eluent: 80/20 MeOH/H₂O with 1% Acetic Acid



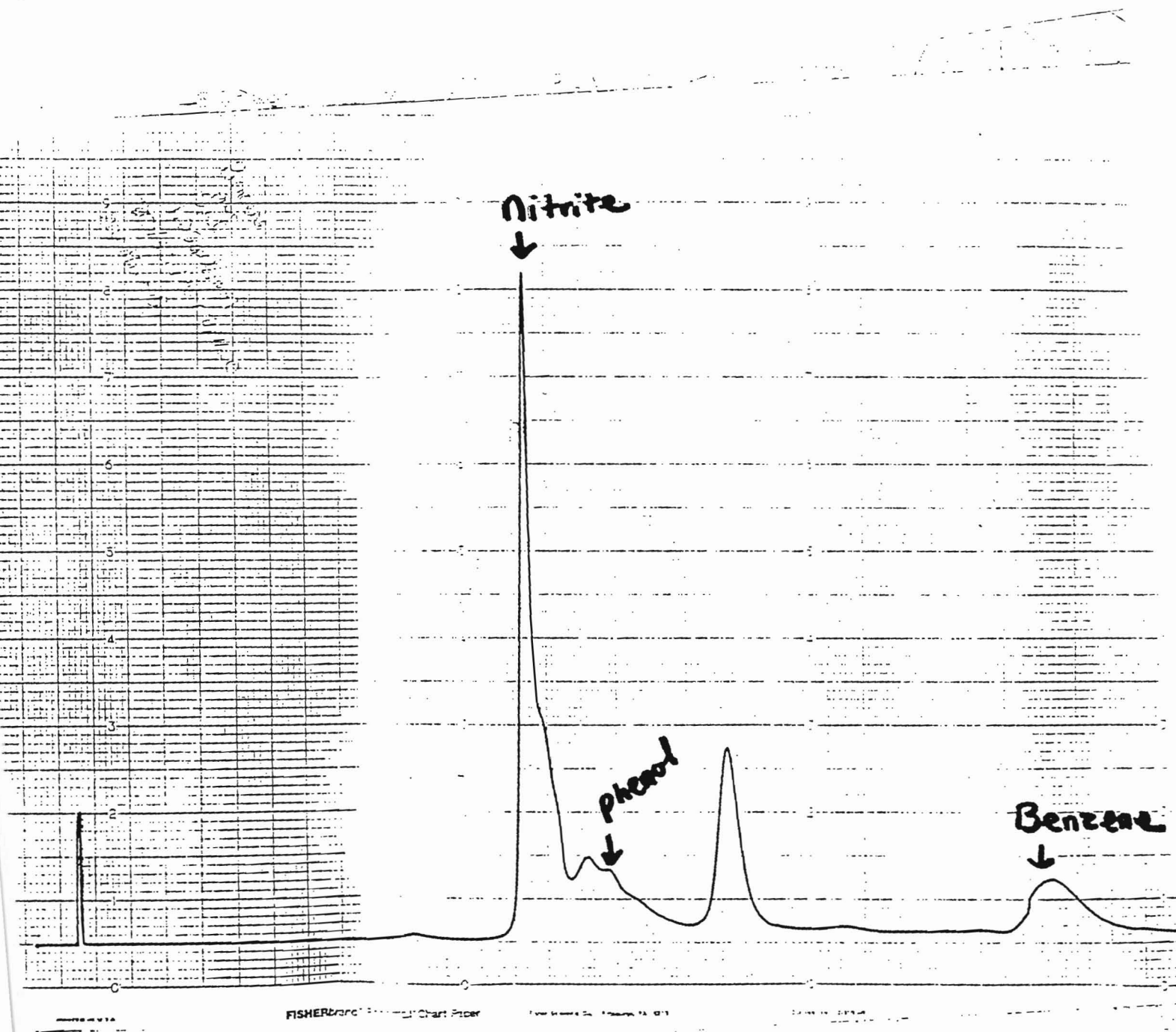
Spectra 11

HPLC Chromatogram of Benzene Photolysate Spiked with Phenol

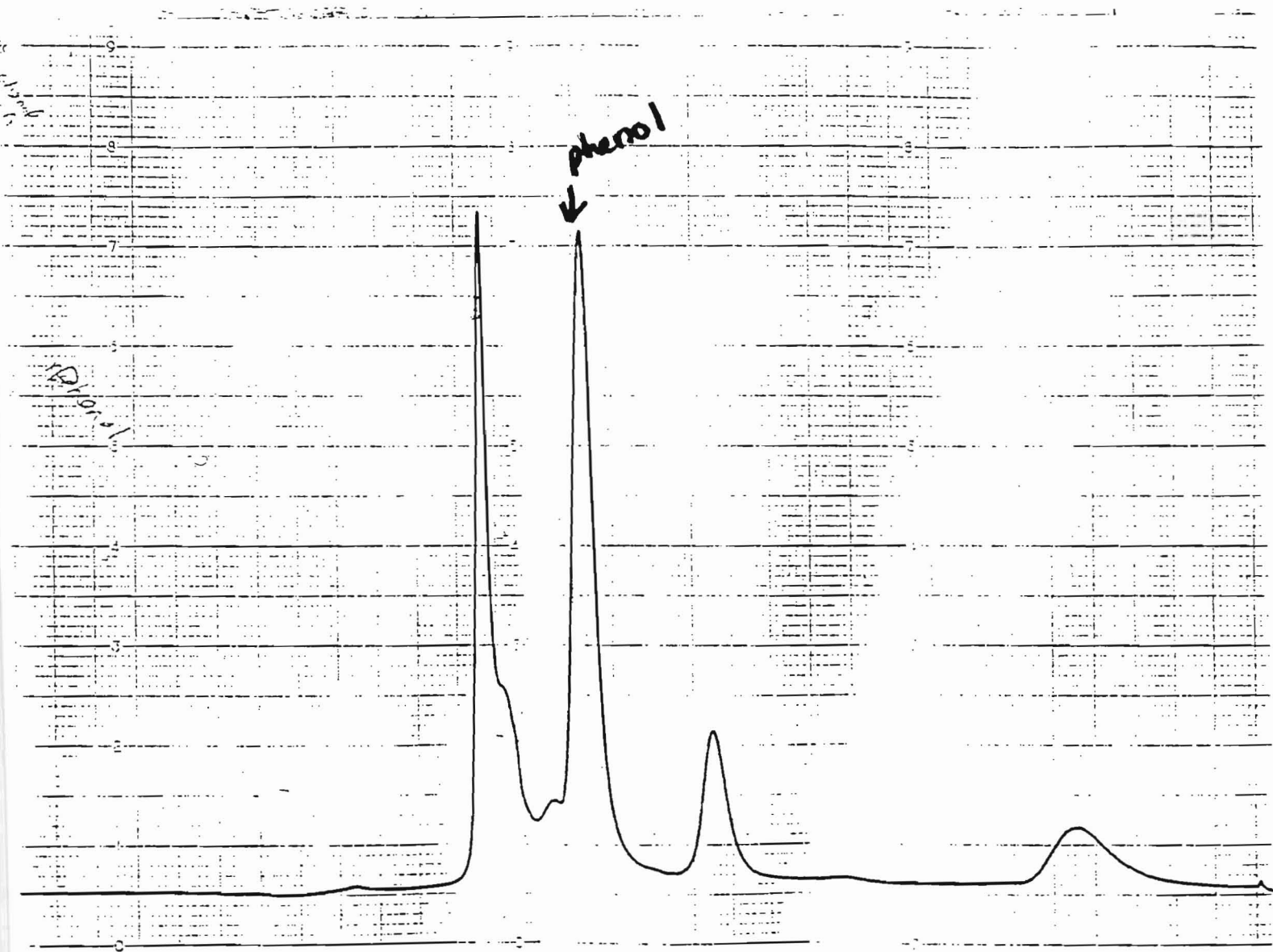
15 μ l sample, Max Abs=1.0, Flow Rate=1.5 ml/min
Eluent: 80/20 MeOH/H₂O with 1% Acetic Acid



Spectra 12
HPLC Chromatogram of Aqueous Benzene Photolysate
15 μ l sample, Max Abs=.5, Flow Rate=1.25 ml/min
Eluent: 70/30 MeOH/H₂O

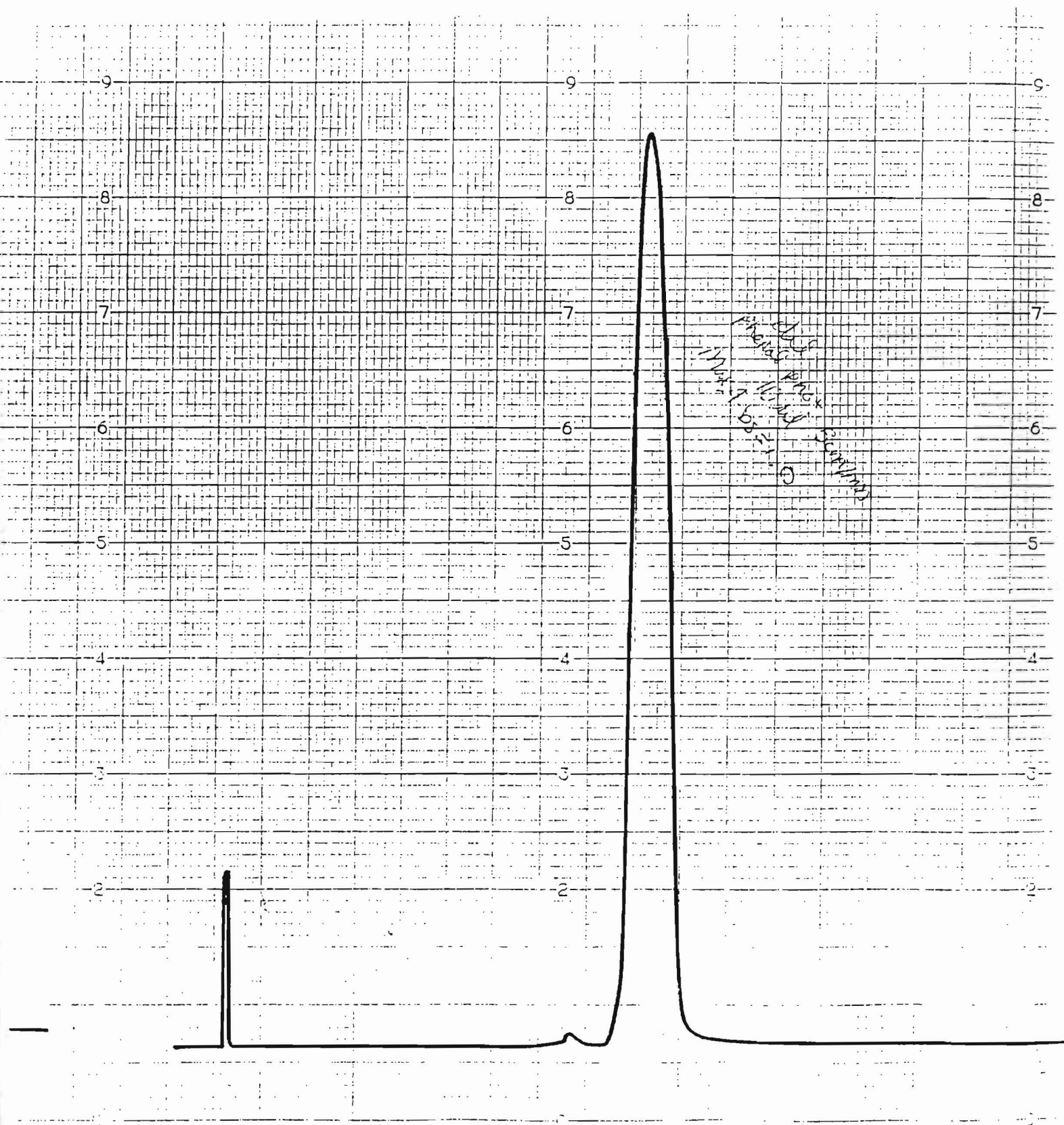


Spectra 13
HPLC Chromatogram of Benzene Photolysate
Spiked with Phenol
15 μ l sample, Max Abs=.5, Flow Rate=1.25 ml/min
Eluent: 70/30 MeOH/H₂O

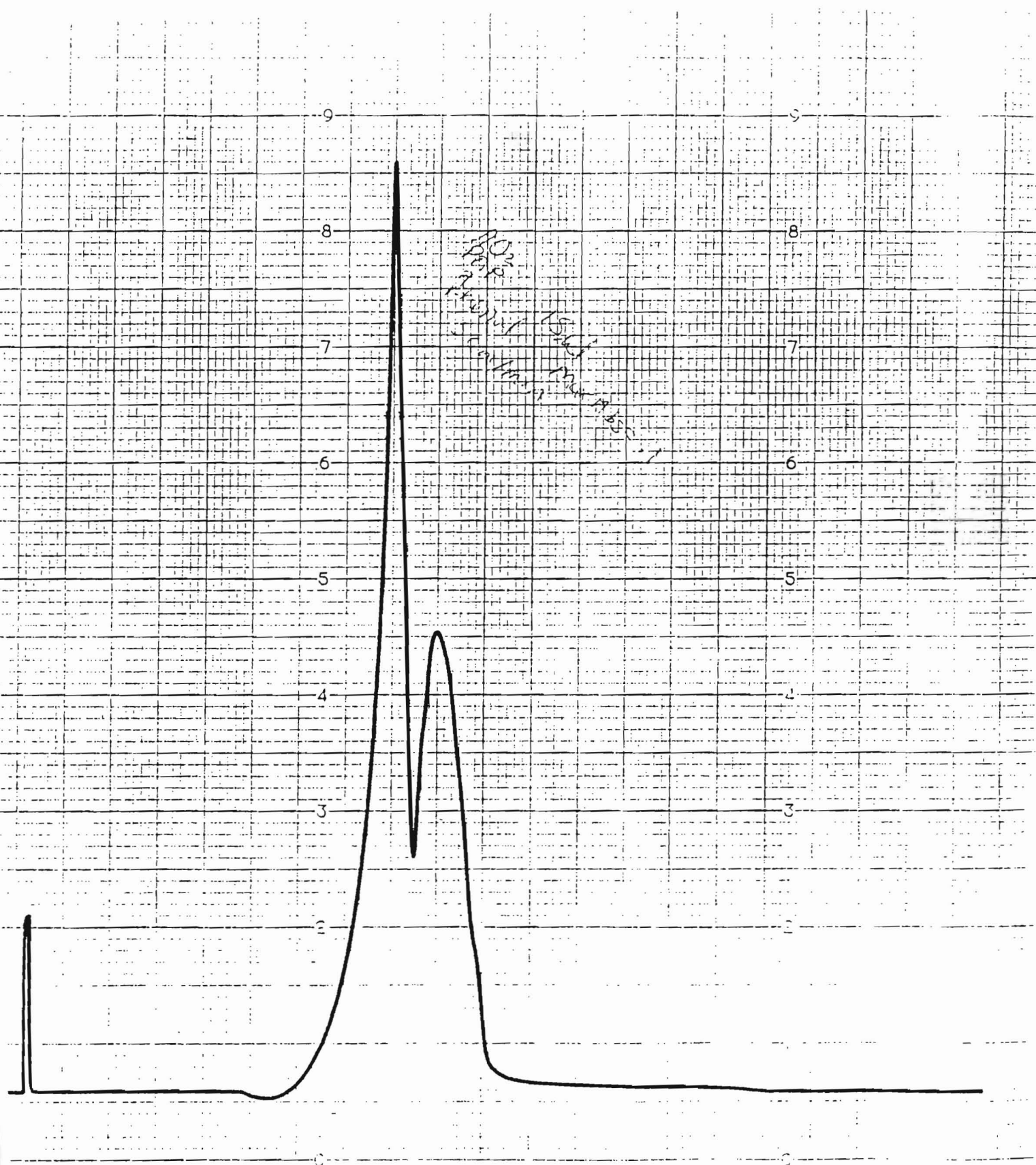


Spectra 14
HPLC Chromatogram of Neutralized Aqueous Phenol
Photolysate

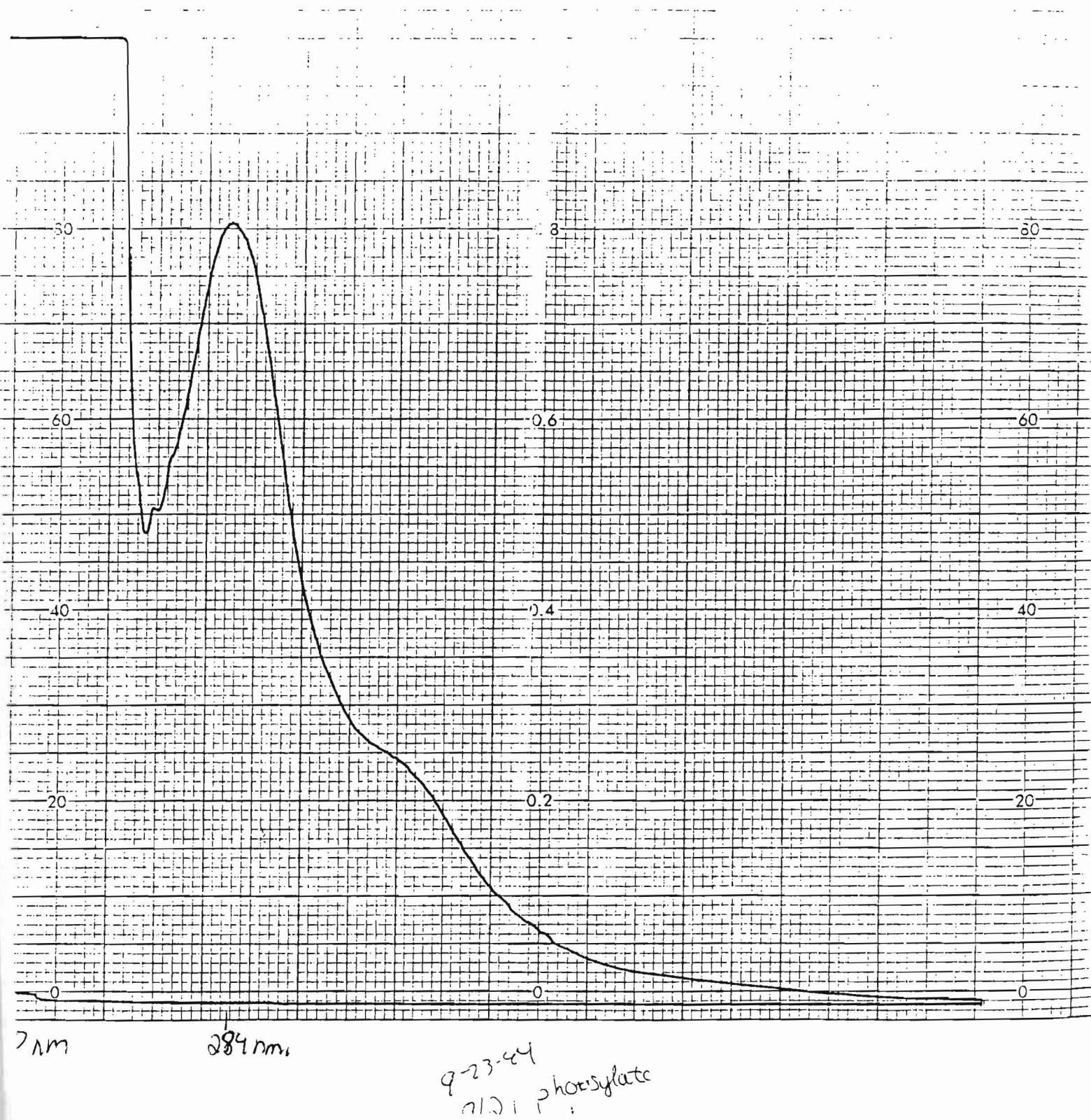
10 μ l sample, Max Abs=1.0, Flow Rate= 2.0 ml/min
Eluent: 100% MeOH



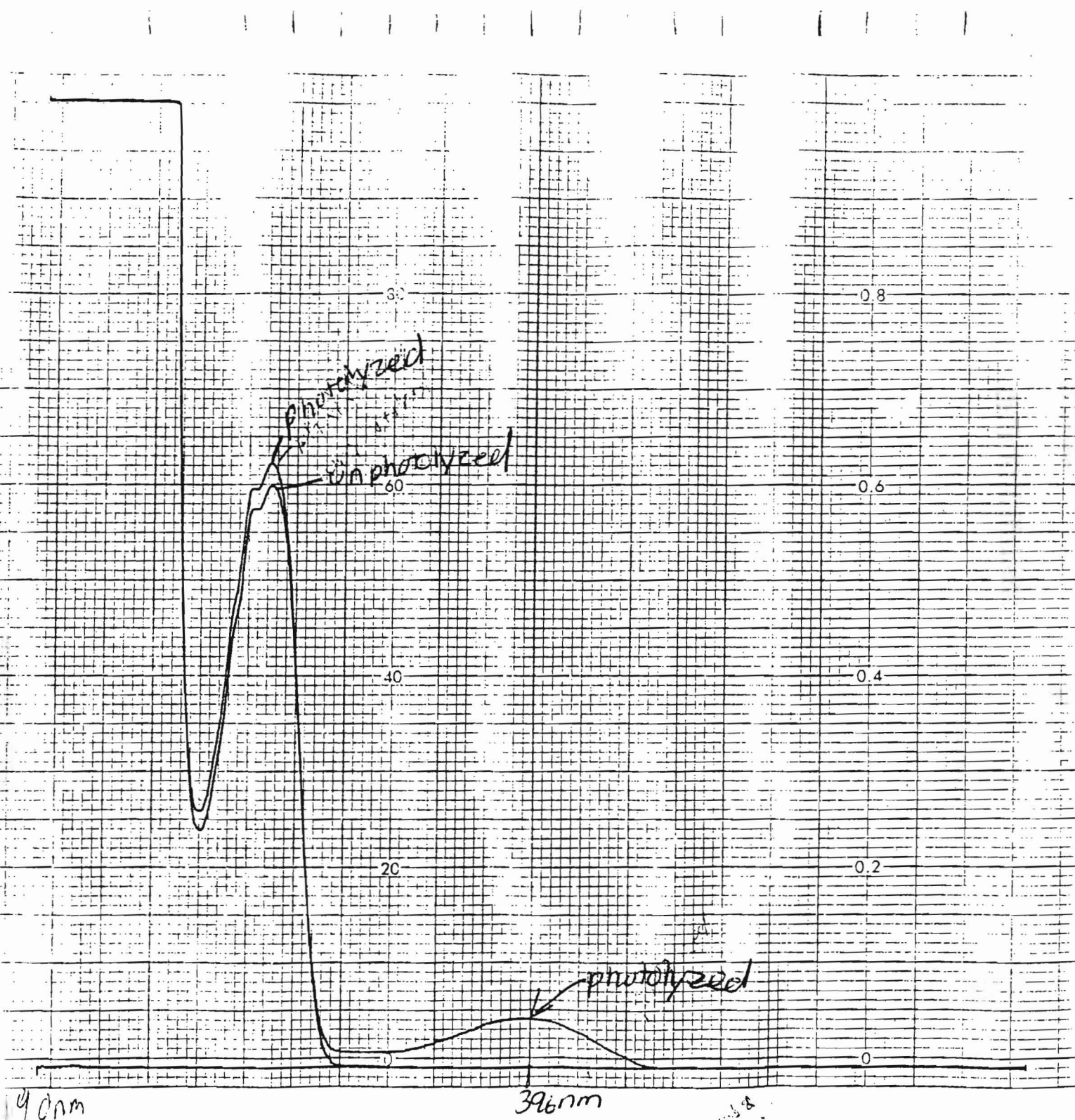
Spectra 15
HPLC Chromatogram of Nitrite, Phenol, and p-Nitrosophenol
15 μ l sample, Max Abs=0.1, Flow Rate= 2.0 ml/min
Eluent: 100% MeOH



Spectra 16
UV-Vis of Aqueous Benzene/Nitrite Photolysate Solution



Spectra 18
UV-Vis of Aqueous Phenol/Nitrite Solution Before and
After Photolysis

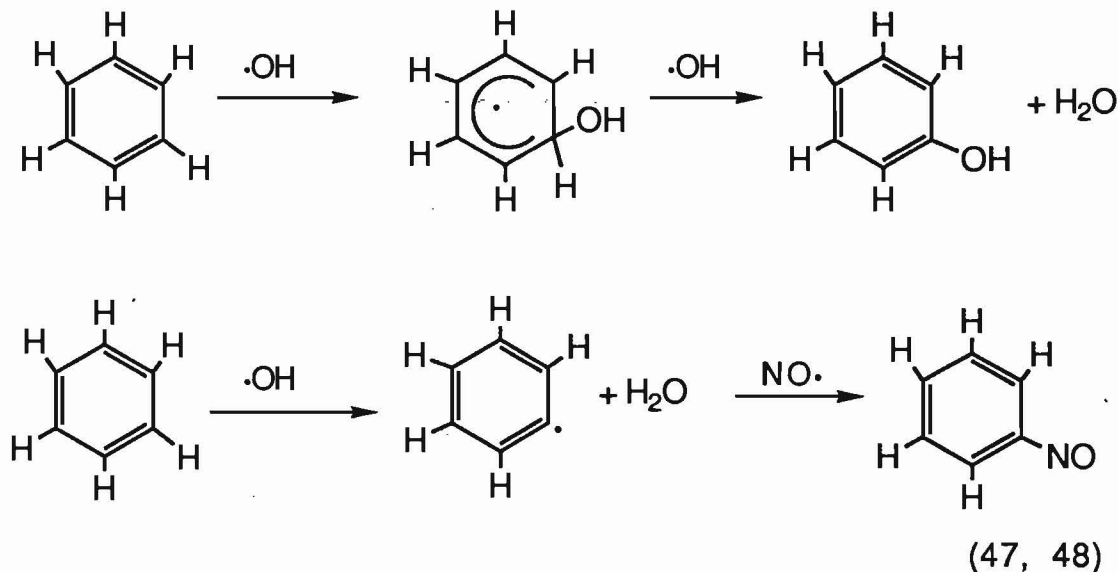


Discussion

Mechanism of addition

The follow mechanism is a hypothesis for what may be occurring photochemically and is based upon Eberhardt's research¹⁹ (equation 42). The $\cdot\text{OH}$ radical attaches to the aromatic ring destroying aromaticity; then a hydrogen is abstracted and full aromaticity returns.

Mechanism of Photochemical Addition

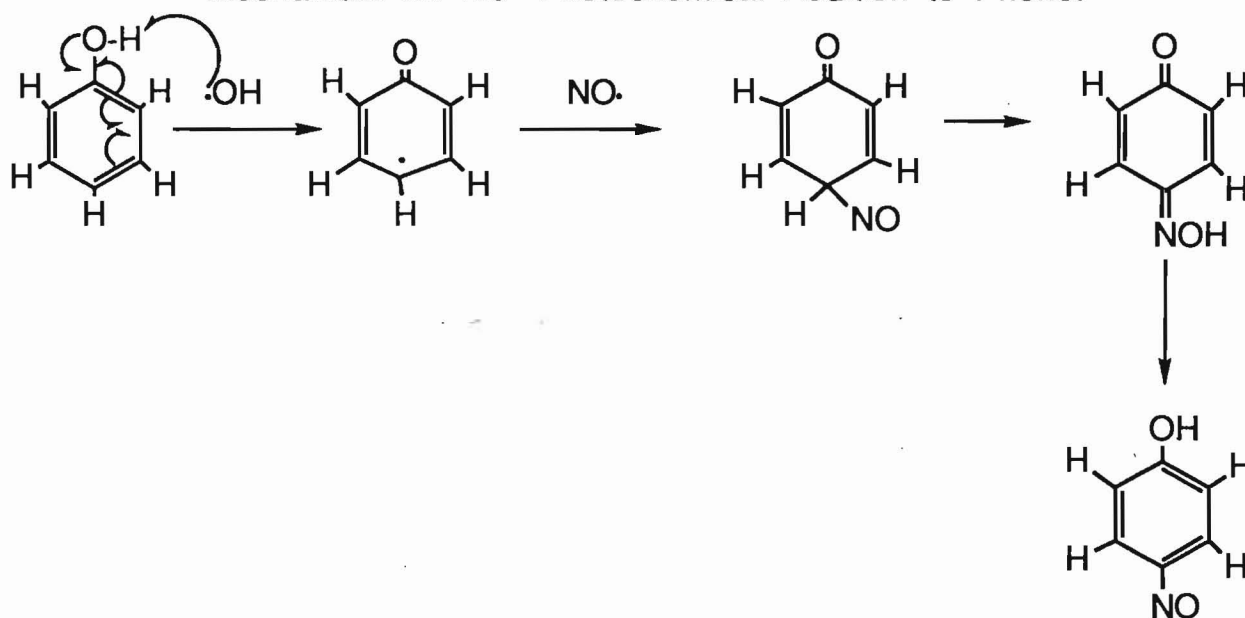


If the hydroxyl radical can add in this manner, then it makes sense that $\text{NO}\cdot$ could also add to the aromatic ring in a similar fashion.

Another reaction scheme to consider is addition of another radical to a ring that has already scavenged one radical species. (Eq. 49) For example, $\text{NO}\cdot$ adding to phenol would occur in either the ortho or para positions since $\cdot\text{OH}$ is an ortho-para director. If the para position dominates (which has been experimentally determined in the dark nitrosation of phenol), then the phenoxyl radical must be

stabilized in the para position before nitrosation occurs. At the ortho position, the oxygen on the nitroso group would be able to hydrogen bond to the hydrogen of the alcohol thus stabilizing this conformation and perhaps causing this form to predominate. This does not occur. Therefore, the position of the radical in the intermediate must be the determining factor of where the nitroso group is located on the ring.

Mechanism for NO \cdot Photochemical Addition to Phenol



(49)

Study of benzene photolysis solution

As noted in the results, the previously clear aqueous benzene-nitrite solution (at pH=12) turned a brown/orange color upon photolysis. Obviously, some sort of photo-initiated chemical change occurred. $\cdot\text{OH}$, $\text{NO}\cdot$ or a combination of radical species may be adding

to the aromatic ring. If both $\text{NO}\cdot$ and $\cdot\text{OH}$ addition are possible, a myriad of compounds can be present including phenol, p-nitrosophenol, nitrosobenzene, catechol, resorcinol, nitrosocatechol, nitrosoresorcinol, and hydroquinone. If oxidation of the hydroxyl substituent occurs, then quinone could also be present. Although acidification during extraction seems to produce no visible change, some sort of suspension or precipitate forms even at a pH of 7 (which has been observed during micropore filtering for HPLC). A product such as phenol and/or p-nitrosophenol will exist in its anionic form at a pH of 12, and as the pH is lowered, the compounds will return to their molecular state making them less soluble in water. (The solubility would have to decrease greatly in order for the compound to precipitate out of solution.) However, this does not explain why the evaporated photolysate extract did not redissolve in methylene chloride very well, since this solvent is somewhat polar yet organic in nature. If the photolysate product is precipitating "out" of water as the pH is decreasing due to a change to its molecular form, methylene chloride would be much more likely to dissolve the organic molecular compound because it is less polar than water. Therefore, acidification must either change one (or more) photolysate product such that this original product is not as soluble in water or form a new compound(s) that is not extremely soluble in either solvent. Another possibility is that one or more of the photolysate products is indeed very soluble in water only in strongly basic conditions and in those conditions will not extract into the methylene chloride. For example, p-nitrosophenol is barely soluble in water at a neutral pH, but at a pH of 12, p-nitrosophenol

neutral forms making them less soluble in water. The suspension or precipitate that "falls out" will not necessarily dissolve in the methylene chloride layer but will sink to the bottom by gravity where it is collected with the extract. Therefore, the precipitate will not redissolve in the methylene chloride since it never was dissolved in methylene chloride in the first place. Oxidation upon exposure to air may be occurring with the evaporated photolysate thus changing its solubility.

The TLC of the extracted benzene photolysate in methylene chloride produces at least 12 individual bands with no separation between them which indicates that more than one product exists. More than likely, different products are present in the benzene photolysate. Column chromatography, under the conditions studied, does not allow for such a fine separation of the photolysate. Unfortunately, not enough of each fraction could be collected from the column to analyze.

Fourier-Transform Infrared Spectroscopy was used in an attempt to identify $\cdot\text{OH}$ and $\text{NO}\cdot$ addition products. Sample sizes of TLC's and of column fractions were often too small and resulted in very noisy spectra. Another problem was that the spectra of the different fractions appeared to be very similar. Infrared spectroscopy was not very useful in identifying NO addition since it absorbs around $1325\text{-}1430\text{ cm}^{-1}$ and OH overlaps that region absorbing at $1315\text{-}1400\text{ cm}^{-1}$.²³ However, the IR did indicate that some hydroxyl addition may be occurring from the small OH peaks in the 3500 cm^{-1} range.

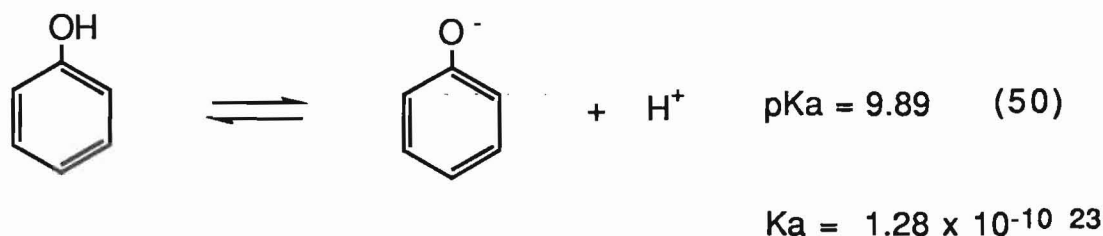
some hydroxyl addition may be occurring from the small OH peaks in the 3500 cm^{-1} range.

Separation of the neutralized, crude benzene photolysate has proven partially successful via HPLC. By spiking the unextracted photolysate with known compounds such as phenol and p-nitrosophenol and by comparing these chromatograms to the pure crude benzene photolysate, specific compounds may be identified if the corresponding HPLC peak height increases upon spiking. Unfortunately, the peaks in the photolysate chromatogram and combinations of closely related aromatic known compounds are not separated very well. The methanol:water ratio is currently being varied in order to optimize separation and improve the chances of a positive identification. Spiking the benzene photolysate with phenol has indeed shown that phenol is present in the original photolysate.

A major factor to consider in HPLC analysis is the neutralization that the crude photolysate must undergo before injection. Precipitation does occur even at a pH of 7 which was observed by comparing the filter used for the crude photolysate at a pH of 12 (no residue was present) to the filter used for the crude photolysate at a pH of 7 (an orange/brown solid is observed). Possible products detected by the HPLC might be formed in the neutralization process instead of the photochemical one. This is a difficult problem to address, but the residue left on the filters will be analyzed in the attempt to identify the product(s) which precipitates upon acidification.

Study of phenol photolysate solution

Phenol, a weak acid, can dissociate into its phenolate anion as seen in equation 50:



At the strongly basic pH of 12, the phenolate ion will predominate being 129 times more prevalent than the neutral molecular form. In a neutral solution (pH=7), the concentration of the molecular form of phenol is 776 times greater than the anion, and at a pH of 2, the ratio of phenol to phenolate is 7.76×10^7 . Since phenolate is a charged species, it is much more soluble in water than phenol, although phenol itself is quite soluble in water (87 g/L)²³. Increasing the pH of the phenol solution allows for more phenol to be dissolved. The increased concentration of scavenger may produce a higher concentration of photochemical products, thus facilitating product identification.

Unfortunately the aqueous phenol-nitrite solution possesses some major drawbacks. Phenol and nitrous acid will react to produce p-nitrosophenol, a possible product in this photolysis. This was discovered in the process of exploring the aqueous phenol-nitrite solution.

The original color of the basic nitrite phenol solution was yellow, and photolysis does indeed result in a color change to a very

dark brown photolysate with a slightly greenish tint. However, a similar color change was observed upon acidification of the unphotolyzed aqueous nitrite phenol solution. It is known that p-nitrosophenol is produced in an acidic environment when phenol and nitrite are present. Obviously, this does not occur to a great extent under basic conditions since no dark color is observed, but perhaps the original yellow color present indicates a small amount of p-nitrosophenol being formed thermally. It has been established that basic phenol and nitrite will undergo a photochemical reaction. Unfortunately, extraction with methylene chloride preceded by acidification cannot be used to analyze the photolysate since unreacted phenol will form p-nitrosophenol upon acidification. Therefore, p-nitrosophenol will be present regardless of whether or not it was produced photochemically. By looking at the differences between the extractions of photolyzed and unphotolyzed phenol solutions perhaps some photolysis product can be determined. The FTIR taken of the two extracts did indeed show differences. The extract of the phenol/nitrite solution before photolysis looked very much like the IR of p-nitrosophenol. However, the photolysate extract appeared different than both PNP and the unphotolyzed extract thus indicating that a photochemical reaction different than a simple formation of p-nitrosophenol is occurring. If the two extractions seem to be identical, this may mean that the same kind of mechanism occurs both photochemically and thermally or acidification may change the photolysis products.

Similar to the benzene photolysate extract, the extracted solid of the phenol photolysate does not readily redissolve in methylene

chloride. Here, it is visibly apparent that some sort of suspension or solid precipitates out of the photolysate upon acidification. Since the phenol photolysate is much more concentrated than its benzene counterpart, more solid could precipitate out of solution making this "fallout" easier to see. The same chemistry is probably at work in both photolysates although the p-nitrosophenol is indeed forming in the phenol photolysate which might account for this precipitate upon acidification. Any phenol produced in the photolysis of the basic benzene-nitrite solution can also react with nitrous acid (upon acidification) to produce p-nitrosophenol which could be precipitating from solution. After all, p-nitrosophenol's solubility greatly decreases when the anion converts back to its molecular form upon acidification.

The TLC of the extracted phenol photolysate eluted with methylene chloride does indeed indicate that some phenol remains after photolysis. Unfortunately p-nitrosophenol does not move in methylene chloride, but will move in more polar solvents such as methanol. Unfortunately, phenol and p-nitrosophenol then have identical R_f values. No eluent that could separate the TLC spots could be found. The photolysate also had a tendency to "streak" up the TLC plate in more polar solvents and would come to rest at the same height as both phenol and p-nitrosophenol.

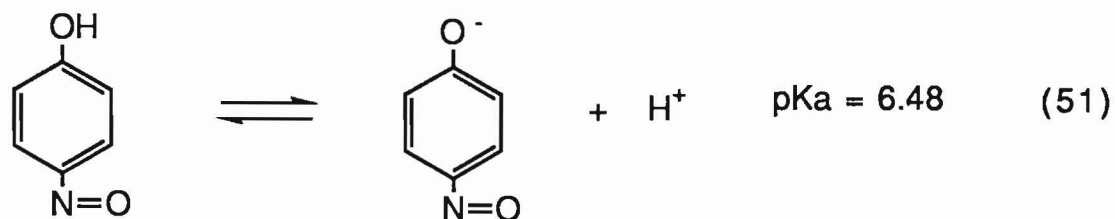
It was thought that perhaps HPLC could help in identifying possible phenol scavenged products by spiking the unextracted photolysate with various knowns. Since phenol was in such a high concentration and since p-nitrosophenol elutes very close to it, the

phenol peak overshadowed any unspiked p-nitrosophenol present thus making it impossible to tell if any of the compound was present.

Possible products

Since $\cdot\text{OH}$ and $\text{NO}\cdot$ addition can occur in a variety of combinations, many different products can form. Some of these include the following: phenol, nitrosobenzene, o-nitrosophenol, p-nitrosophenol, hydroquinone, quinone, catechol, resorcinol, nitrosocatechol, and nitrosoresorcinol.

One possible photolysis product, para-nitrosophenol, exists in equilibrium with its nitrosophenolate anion as shown in equation 51.



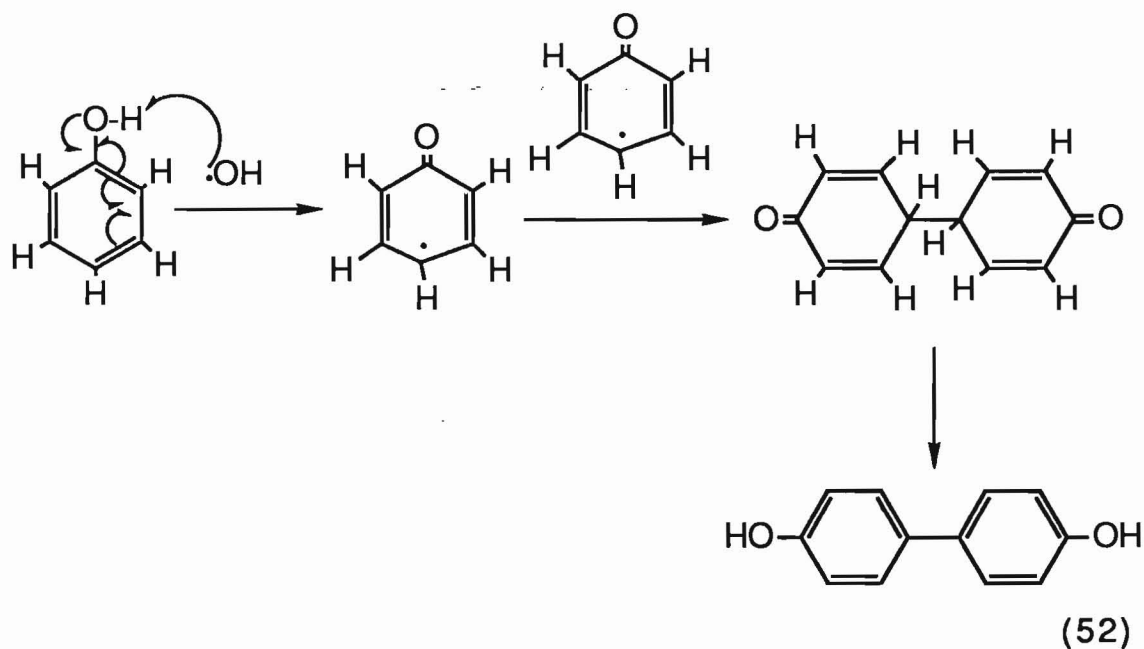
At the pH of photolysis (pH=12), if p-nitrosophenol is present, the p-nitrosophenolate anion exists in 3.31×10^5 times greater concentration than the corresponding phenol. However as the pH decreases, the neutral form will predominate. At a pH of 7, p-nitrosophenol's concentration is only 3.3 times greater than its anion, but at a pH of 2, a large difference exists with the ratio of the molecular to the anion form being 3.0×10^4 . This shift to p-nitrosophenol upon decreasing the pH causes the concentration of the neutral molecular species to increase sufficiently to precipitate out of solution. After all, p-nitrosophenol appears to be only sparingly

soluble in water with a pH of 6 but moderately soluble in strongly basic water forming a dark brown solution. The Dictionary of Organic Compounds states also that p-nitrosophenol is soluble in alkalis giving a brown color which is indeed the color of the photolysate.²⁸ Para-nitrosophenol could very well be forming photochemically and precipitating out of solution upon acidification.

Oligomer formation

A fibrous film-like material formed at the interfaces during extraction of both photolysates which seemed to have affinity for neither water nor methylene chloride. Some consideration has been given to a potential oligomer formation. A series of oligomers of varying chain length might explain the numerous bands with similar spectra found on the TLC of the benzene photolysate extract. If a polymer does indeed form, the aromatic ring must form a radical species. Perhaps this occurs via hydrogen abstraction of phenol (which could be the initial product of benzene photolysis since OH adds so easily to an aromatic ring) to form the phenoxide radical as shown below:

Mechanism of Dimer Formation



The carbon-carbon and carbon-oxygen double bonds will stabilize the radical through resonance, and another radical ring can attach itself to a carbon on the first ring thus undergoing termination. If the ring adds at the ortho position, perhaps additional ring coupling can occur. The radical ring might also be easily scavenged by other aromatic compounds that are not radical species.

Conclusion

The observations and results encountered from the photolysis of a simple aqueous solution containing nitrite and a simple aromatic compound seem to produce more confusion and seem to raise further questions. This broadens the aspect of this research rather than answer the simple questions such of product identity, etc., that could serve as a key to unlock the puzzle of this apparently elusive photochemical mechanism. The possible photochemical products are all quite toxic to the human body causing various problems including cancer and the propagation of free radicals. These photochemical reactions studied in the laboratory could occur on a more dilute scale in the environment which should signal a cause for alarm. For example, nitrite and aromatic compounds originating from air pollution could be "trapped" in water droplets in clouds which could react in sunlight thus forming photochemical smog which covers so many large cities. Lakes, oceans, and streams containing high concentrations of aromatic compounds and nitrites (from fertilizers) might also photochemically produce these harmful compounds, thus damaging the aquatic environment and those who use those resources for drinking and eating needs.

Future Work

Much work lies ahead with this product. The following proposals are just a few aspects of this project that could possibly be explored.

- 1.) Acidification during extraction of the photolysate at colder temperatures (ie. below room temp.) could be attempted in order to slow the phenol nitrosation "dark" chemical reaction. Removing the excess nitrite before extraction by some chemical reaction would also be advantageous. However, finding another method of analysis that does not involve acidification would actually be the best route.
- 2.) The pH of the aqueous photolysate should be studied to determine at exactly what pH the precipitate forms and if precipitation increases or if different products form as the pH decreases.
- 3.) HPLC work should continue in order to achieve further resolution of the photolysate peaks. However, acidification in order to neutralize the photolysate must be taken into account. Switching to a silica column might also improve peak resolution and result in the identification of even more products than what is presently observed.
- 4.) Various solvent mixtures should be used as TLC eluents in order to separate the phenol and p-nitrosophenol R_f values.
- 5.) Using gradient elution with column chromatography might achieve better separation.

6.) A GC-mass spec. of the photolysate extract might help considerably in identifying many of the products that are forming.

7.) Determining the final and initial concentrations of reactants and the concentration of products could be the first step in calculating a photochemical yield.

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