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## Photochemistry of Nitrous Acid and Nitrite Ion

Jane A. Johnson '92  
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PHOTOCHEMISTRY OF NITROUS ACID AND NITRITE ION

Jane A. Johnson

Advisor: Timothy R. Rettich

Chemistry 499 Thesis

Illinois Wesleyan University

May 7, 1992

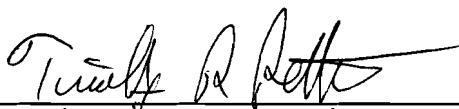
Approval Page

"Photochemistry of Nitrous Acid and Nitrite Ion"

by Jane A. Johnson

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

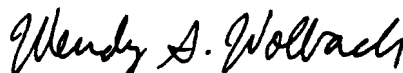
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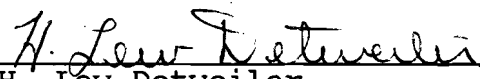
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Illinois Wesleyan University

1992

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## ABSTRACT

A study of the solution phase photochemistry of the nitrous acid/nitrite ion system in both water and non-aqueous solvents has been undertaken. Photolysis at 366nm of the aqueous system is known to form hydroxyl radical and nitric oxide. The relative contributions of the molecular and ionic forms to the photochemical production of radicals is unknown. Scavenging reactions of the hydroxyl radicals in aqueous and nonaqueous solution are used to determine the relative production of  $\text{OH}\bullet$  formed by photolysis of  $\text{HONO}$  and  $\text{NO}_2^-$ .

Molecular nitrous acid is isolated from its conjugate base by extraction into benzene from water. The thermal decomposition of  $\text{HONO}$  in the extraction mixture was measured and it was found to be second order with respect to nitrous acid. The product of the photolysis of this benzene solution, PNP, indicates hydroxyl radical formation.

Nitrite ion dissolves in aprotic solvents, such as DMF and DMSO, without the formation of nitrous acid. Photolysis of these solutions appears to result in the formation of phenol only. The quantum yield for the formation of phenol was determined to be  $1.8 \pm 0.3 \times 10^{-2}$  mol/eins.

## INTRODUCTION AND THEORY

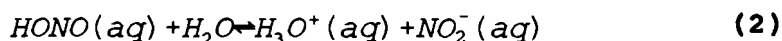
The chemistry of nitrous acid has been of interest in the last decade due to its role in atmospheric pollution. Various nitrogen oxides cause the formation of secondary photooxidants such as ozone, hydroxyl radical and hydrogen peroxide. Because it efficiently absorbs long wavelength ultraviolet light, nitrous acid is an important source of atmospheric hydroxyl radical.<sup>1</sup> Nitrous acid in the gas phase has been determined to buildup during the night, and may be an important source of early morning hydroxyl radical which can initiate photochemical reactions.<sup>2</sup> The gas phase reactions of nitrous acid have been extensively explored, but there have been only a few studies of the chemistry of nitrous acid in water and none in other liquid media.

### Thermal reactions of nitrous acid:

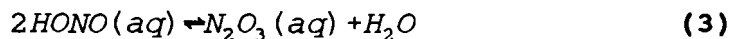
The gas phase reaction of nitrous acid was determined by Cox and Atkins in 1973. Nitrous acid is in equilibrium with nitric oxide and nitrogen dioxide.<sup>3</sup>



In aqueous solutions there are two accepted equilibria: the acid dissociation reaction,

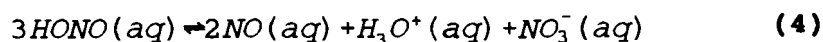


and the dehydration reaction,



Another reaction which has been extensively studied is<sup>4</sup>:

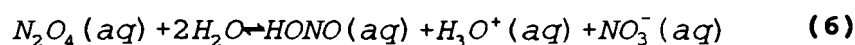
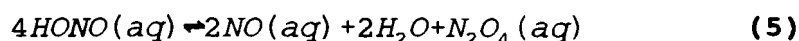




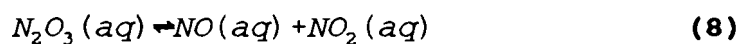
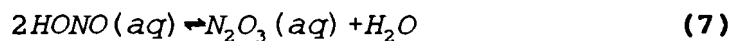
Reactions 2 and 3 are rapidly established equilibria; decomposition by the reaction 4 has a half-life of about 14 hours at 0°C. Consequently the thermal reaction is a significant pathway for the destruction of nitrous acid and must be accounted for in the photochemical reactions.

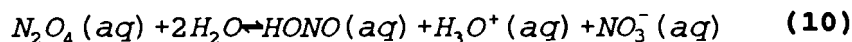
The stoichiometry and kinetic order of reaction 3 with respect to nitrous acid was first determined by Montemartini in 1890.<sup>5</sup> He found first order kinetics at low nitrous acid concentrations and two and one-half order kinetics at higher concentrations. Montemartini's results at low concentrations have been confirmed by later studies.<sup>4,6,7</sup> The higher concentration kinetics however have not been consistently reproduced and orders of 2.5, 3, 3.5 and 4 have been determined.<sup>6,7,8</sup>

In 1928, Abel and Schmid reported two possible mechanisms for the thermal decomposition of nitrous acid in the higher concentration region.<sup>8</sup> These mechanisms are:

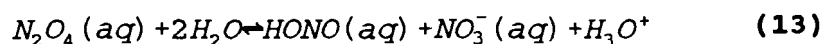
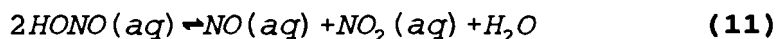


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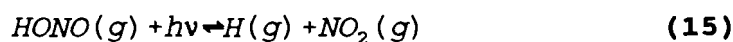
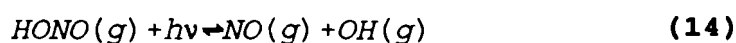
Another possible mechanism was reported by Thie in 1947:<sup>9</sup>



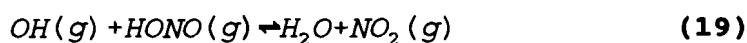
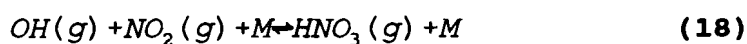
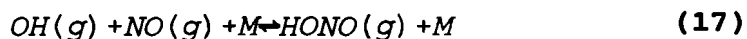
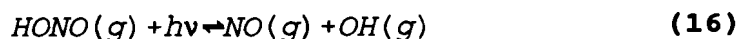
In all three of the mechanisms the final step is the hydrolysis of dinitrogen tetroxide. Later studies of nitrous acid by Usabillaga<sup>6</sup>, Rettich<sup>7</sup>, and Park and Lee<sup>2</sup> do not distinguish among these three mechanisms.

#### **Photochemical reactions of HONO:**

The gas phase photochemical reactions of nitrous acid at 330-380nm were first investigated by Cox and Atkins in 1973.<sup>3</sup> Based on their results they proposed two primary photodissociations:

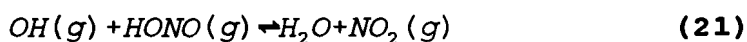
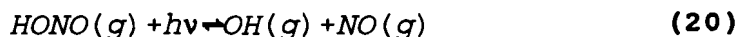


They showed that the total primary quantum yield for these two reactions is near unity. Also they estimated that the quantum yield for reaction 14 is about twice that for reaction 15. Cox<sup>10</sup> suggested a mechanism based on this evidence.



Additional studies by Cox have led to the estimate that reaction 15 contributes less than 10% to the overall reaction and that the primary quantum yield for reaction 14 is  $0.92 \pm 0.16$ .

In another study of the gas phase photolysis, Nash proposed a mechanism based solely upon reaction 14 as the initial step.<sup>11</sup>

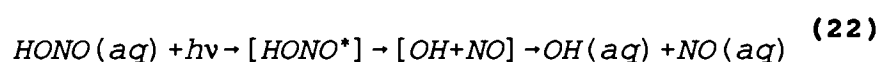


Although other studies have been done on the gas phase photochemistry of nitrous acid, no other mechanisms have been proposed.

The first report of the aqueous photochemistry of nitrous acid was by Murty and Dhar in 1930.<sup>12</sup> They photolyzed solutions at wavelengths above 445nm, and reported quantum yields of up to 15 for the reaction. These wavelengths are in a region where nitrous acid does not appreciably absorb light; nitrous acid absorbs light from about 400-300nm.

It was suggested by Rettich<sup>7</sup> that this decomposition was probably due to a thermal reaction caused by the heating of the solution by the light source. Rettich

conducted an extensive study of the photochemistry of nitrous acid at 1°C and accounted for such factors as ionic strength, pH, nitrite and nitrous acid concentrations, water source, light source, and reaction vessel geometry. He determined that the quantum yield for nitrous acid disappearance increased linearly from 0 at zero concentration to 0.14 at 0.14M nitrous acid. For higher concentrations, the quantum yield remained constant at 0.14. Additionally, he determined the quantum yield of escape from the solvent cage to be 0.095. The reaction for this is



This low value for the primary quantum yield is believed to correspond to the recombination of hydroxyl radical and nitric oxide within the solvent cage.<sup>7</sup>

#### Reactions of Nitrite Ion:

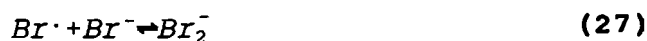
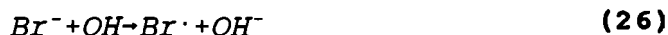
It was originally determined by Holmes in 1926<sup>13</sup> that aqueous nitrite ion undergoes no net photochemical reaction. Treinin and Hayon<sup>14</sup> in 1970 verified this result by irradiating a nitrite solution with light at 228.8nm from a cadmium lamp. The primary process for this reaction was believed to be



which is analogous to the photochemical reaction of organic nitrites. By photolyzing air saturated nitrite solutions in the presence of bromide and carbonate ions, they were able to propose the following mechanism:



The bromide and carbonate ions then reacted with the hydroxyl radical produced as follows:

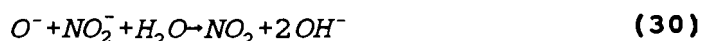


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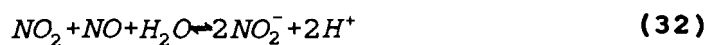


These mechanisms were postulated based on the presence of the transient spectra of  $Br_2^-$  and  $CO_3^{\cdot-}$  radicals.

The  $O^-$  radical and the  $OH$  radical formed in reaction 25 may both subsequently react with additional nitrite present via reactions 29 and 30 or with  $O_2$  present in air saturated solutions to form ozonide (reaction 31).



The lack of net photolysis of nitrite ion was attributed to efficient back reactions.<sup>13</sup> These reactions involve the hydrolysis of several possible nitrogen oxide products. Their overall stoichiometry is



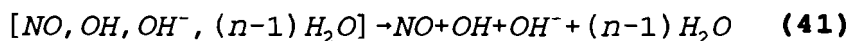
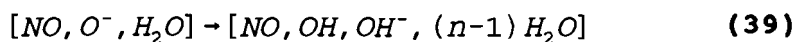
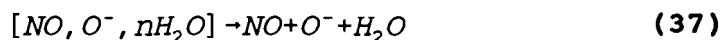
Despite the reported unreactivity of nitrite in aqueous solution, Zafiriou

and McFarland reported in 1981 that nitrite did undergo net reaction in natural (sea) water.<sup>15</sup> The photolysis of nitrite ion by sunlight was reported as:



In a later study, Zafiriou and Bonneau<sup>16</sup> reported the quantum yield of the reaction in terms of the production of hydroxyl radical. They found the quantum yield to be dependent on wavelength (~0.02 at 371.1 and 354.6nm and ~0.06 at 337.1 and 298.5) and on temperature (it increased with increasing temperature). The quantum yield was independent of the pH (in the range 6.5-8.7), trapping agent, pressure of O<sub>2</sub>, and ionic strength.

Zafiriou reported the following mechanism for the net reaction of nitrite:<sup>16</sup>

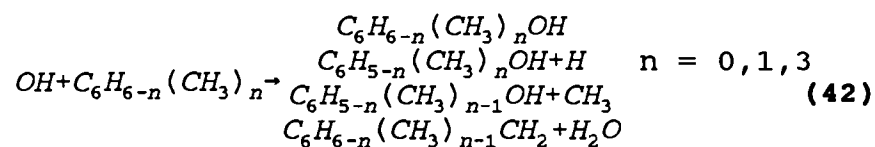


The net loss of nitrite varied in the different waters studied, ranging from 2-27% per day. This variation in quantum yield was attributed to several factors: (1) sensitized photolysis, (2) direct photolysis with a quantum yield sensitive to pH, oxygen concentration, salinity, temperature, and wavelength, (3) regeneration of nitrite by secondary reactions of NO.<sup>16</sup>

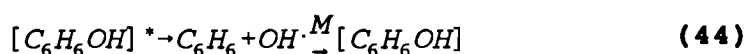
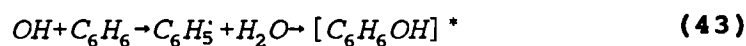
#### **Scavenging of Hydroxyl Radicals:**

Although the presence of nitrous acid can be determined by its UV spectrum, hydroxyl radical, a product of the photolysis of nitrous acid cannot. This is due to two factors: (1) OH is a transient species and is not stable in solution, (2) OH only absorbs in the vacuum UV region, below 200nm.<sup>17</sup> The presence of hydroxyl radical can be determined by its reaction with aromatic or unsaturated organic molecules. The hydroxyl radical attacks the electron rich double bond, taking one electron to bond to the molecule and creating a new radical. When this reaction occurs with an aromatic compound such as benzene, the resultant radical species is more stable than the original hydroxyl radical because of the presence of resonance forms.<sup>18</sup>

The gas phase reactions of hydroxyl radical with benzene and toluene were first investigated by Davis *et al.* in 1975.<sup>19</sup> Davis suggested that the addition of hydroxyl radical was pressure dependent, but no product characterization was done. In 1978, Sloane studied the products of the reaction of hydroxyl radical with 1,3,5-trimethylbenzene, toluene, and benzene.<sup>20</sup> He determined the products of the reaction to be:  
Perry *et al.* investigated the temperature dependence of hydroxyl radical-aromatic

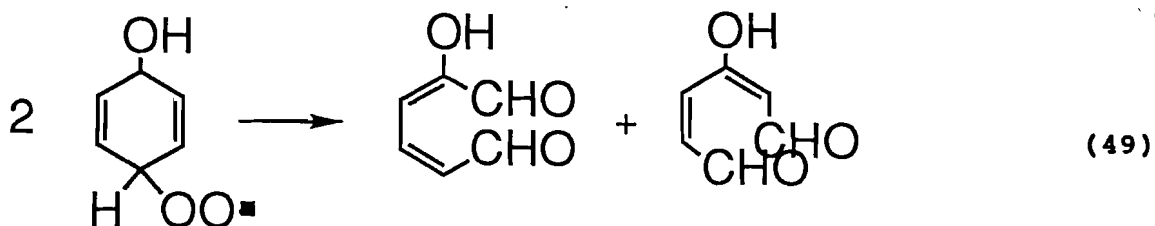
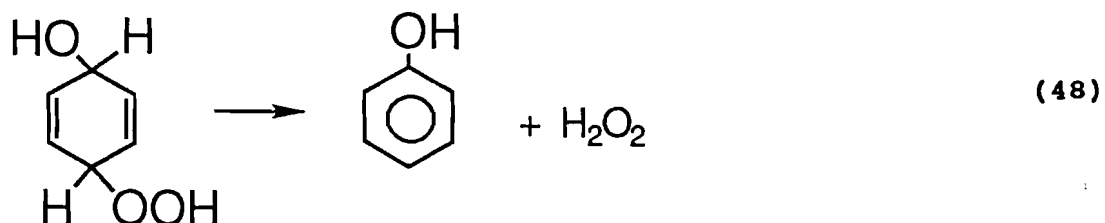
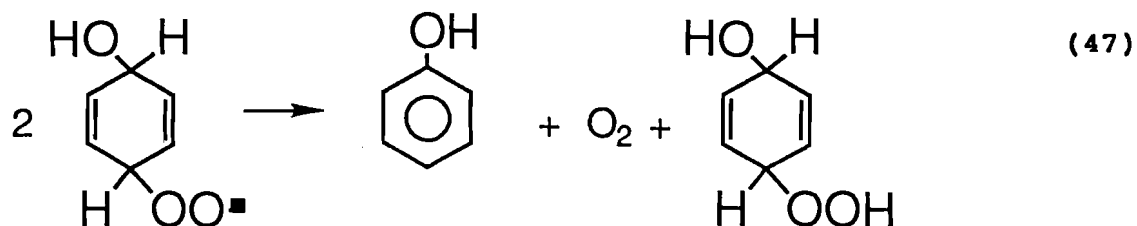
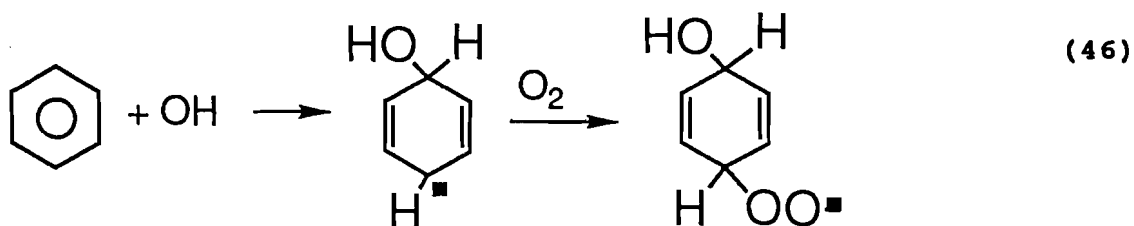


hydrocarbon reactions.<sup>21</sup> From their observations the following reversible mechanism was proposed:<sup>22</sup>

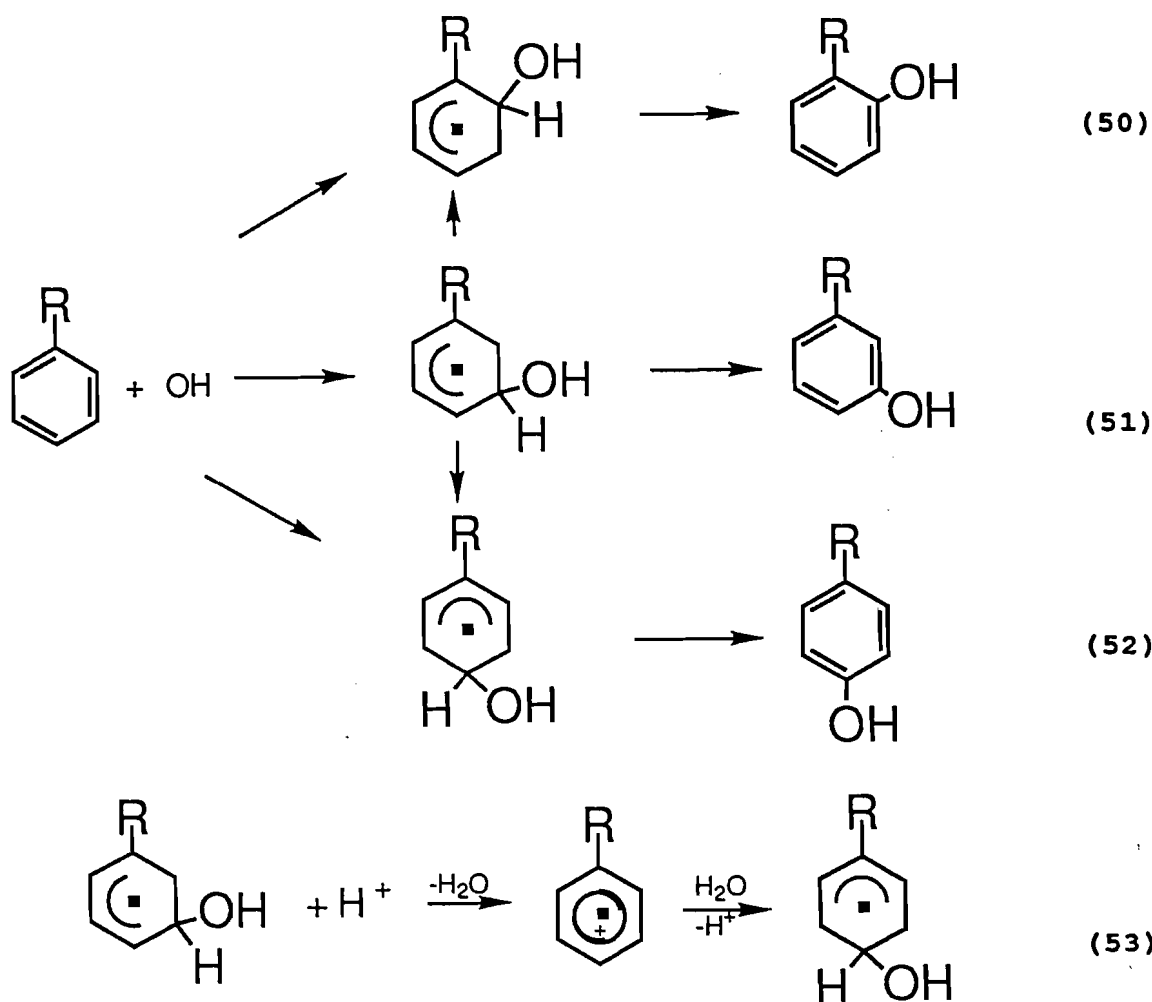


Jacob and coworkers first proposed a mechanism for the reaction of aqueous benzene and hydroxyl radical obtained from hydrogen peroxide solutions.<sup>23</sup> The products of the reaction were phenol,  $\alpha$ - and  $\beta$ -hydroxymuconaldehyde, and hydrogen peroxide.

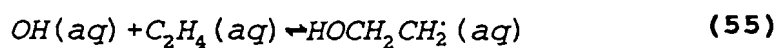
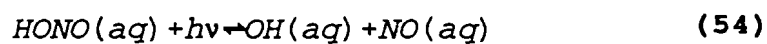


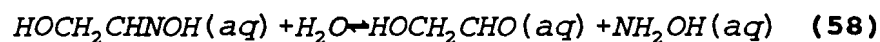
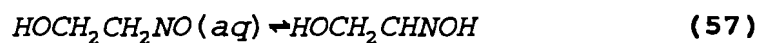


Eberhardt also studied the mechanism of hydroxylation of aromatic compounds. His studies led to a reversible mechanism for the addition of hydroxyl radical to monosubstituted aromatics.<sup>24</sup>



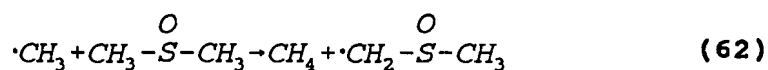
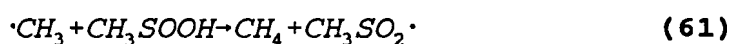
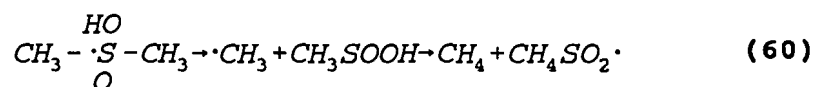
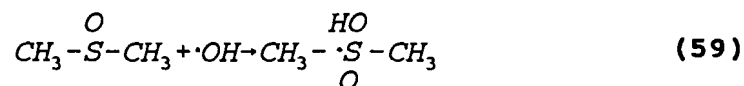
In his study of the photochemistry of aqueous nitrous acid, Rettich<sup>7</sup> used ethylene and benzene to scavenge hydroxyl radicals. The mechanism for the reaction with ethylene is given as:





The product, glycolaldehyde, was found to decrease as the concentration of nitrous acid was increased. This was attributed to the increasing competition with ethylene for the hydroxyl radical formed in the photolysis.<sup>7</sup>

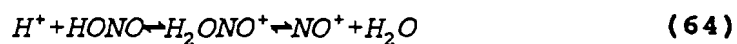
Dimethylsulfoxide, DMSO, has been used as a probe for hydroxyl radicals in biological systems.<sup>25</sup> The reaction of hydroxyl radicals with DMSO to produce methyl radicals was first observed by Norman and co-workers in 1964.<sup>26</sup> The mechanism of the reaction has been studied by ESR and radiolysis. The proposed mechanism is:<sup>25</sup>



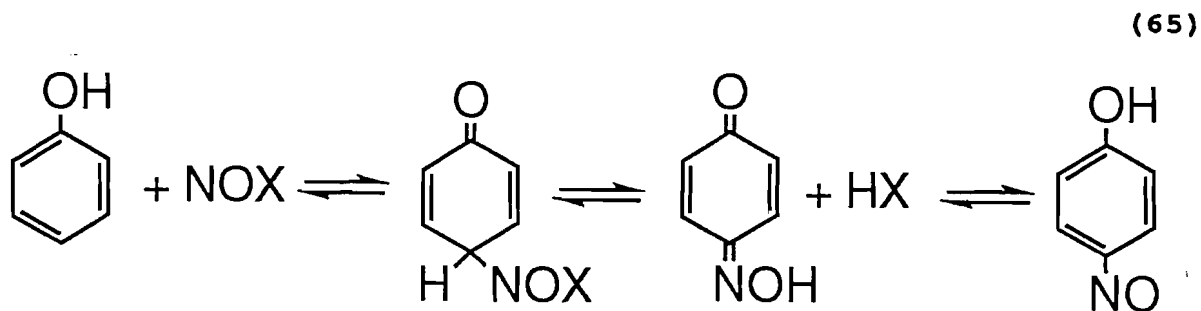
The main product of the reaction is methane gas with a little ethane produced, via reaction 63.

### Thermal nitrosation of phenol:

The kinetics and mechanism of the nitrosation of phenol have been studied by Challis *et al.*<sup>27,28</sup> It is proposed that in aqueous solution nitrous acid is in equilibrium with nitrosonium ion ( $\text{NO}^+$ ):<sup>29</sup>



Both the nitrosonium ion and the hydrated nitrosonium ion can attack the aromatic ring to form p-nitrosophenol (PNP) by electrophilic substitution. The proposed mechanism is:<sup>29</sup>



## EXPERIMENTAL

### Apparatus:

The photochemical reactions were done with a Rayonet photochemical reactor, model #RPR-100. The pH of photolysis solutions was adjusted with 6M NaOH or concentrated HCl. The pH was measured with 0-13 pH paper. Sixteen mercury lamps banded at  $366 \pm 5 \text{ nm}^7$  were used for all reactions. Solutions were cooled to 15-20°C during the reaction by placing a cold finger thermostated to 0°C in the 100ml quartz reaction tube. Photolysis times are listed for individual experiments. Ultraviolet/visible absorbance measurements were taken with a Perkin-Elmer 559 UV-Vis spectrophotometer. The slit width was set to 0.25nm and 1.00cm quartz cells were used.

### Chemicals:

Reagent grade sodium nitrite was obtained from Baker. Nitrous acid was prepared by adding concentrated hydrochloric acid, Fisher reagent grade, to an aqueous solution of sodium nitrite. Benzene, DMF, and toluene, certified grade, were from Fischer Chemical Company. Phenol, 98% reagent grade, DMSO, certified grade, and p-nitrosophenol, 60%, were from Aldrich chemical. Chemicals were used without purification except where noted.

### Photolysis of nitrous acid and nitrite:

A 25.00ml aliquot of 0.2582M  $\text{NaNO}_2$  was combined with 25.00ml of a saturated aqueous benzene solution for both acidic and basic reactions. For the nitrite photolysis, the pH was adjusted to 12 by addition of 0.30ml of 6M NaOH.

The reaction solution was cooled in a 0.0°C antifreeze bath for the acidic reaction. The pH was adjusted to 2 by addition of 0.30ml of concentrated HCl. Aliquots were taken every 15 minutes and diluted 5:10 with water for UV/Vis measurement.

#### **Photolysis of nitrous acid in benzene:**

Solutions of 0.2568M  $\text{NaNO}_2$  and benzene were cooled to 1°C in an antifreeze bath. In a separatory funnel, 25.00ml aliquots of each solution were placed and 1.00ml of concentrated HCl was added. The solutions were mixed and the water layer was removed and neutralized with 5.00ml of 6M NaOH. The benzene layer was placed in a quartz reaction tube with a cold finger set at 1.0°C. Aliquots of the photolysate were taken every 15 minutes and diluted 5:10 with benzene for UV/Vis measurement.

To 5.00ml of the benzene photolysate, 5.00ml of pH adjusted water was added and the two layers were mixed. When the pH of the water was 1, the aqueous layer turned a light yellow and the benzene layer was also a light yellow. Similar results were obtained when the pH of the water was 6.5. When the pH of the water was 12, the aqueous layer quickly turned a dark yellow, without mixing the two layers. All the solutions were analyzed with UV/Vis.

#### **Photolysis of nitrite in DMF:**

To about 40ml of DMF, 0.104g (0.00151mol) of  $\text{NaNO}_2$  and 5.0ml of benzene were added. Approximately 30ml of this solution was transferred to the reaction tube and the cold finger was placed in the tube. The solution was

photolyzed for 30 minutes. After photolysis the solution was a creamy yellow color.

#### **Photolysis of nitrite in DMSO:**

A solution of 0.237g (0.00343mol) of  $\text{NaNO}_2$  and 0.264g (0.00338mol) of benzene in 100.0ml of DMSO was prepared. About 60ml of the solution was transferred to the reaction tube and photolyzed. Every 15 minutes a 2ml aliquot was removed for UV/Vis measurement.

#### **Intensity dependence of nitrite photolysis:**

A single solution for all of the intensity reactions was prepared from 250.0ml of 0.2582M  $\text{NaNO}_2$  and 0.30ml of 6M  $\text{NaOH}$  diluted to 500.0ml with saturated aqueous benzene. Aliquots of 25.0ml were photolyzed for 30 minutes. A 5:10 dilution with water of the photolyzed solution was made for UV/Vis measurement.

#### **Thermal reaction of HONO in benzene:**

Nitrous acid was extracted into benzene by combining 10.00ml of benzene, 10.00ml of 0.2504M  $\text{NaNO}_2$  and 0.30ml of concentrated  $\text{HCl}$  in a separatory funnel. The aqueous layer was removed and neutralized with 2.00ml of 6M  $\text{NaOH}$ . The concentration of the nitrous acid in the benzene layer was monitored periodically for 30 minutes by UV/Vis spectroscopy.

#### **Determination of partition coefficient of HONO:**

Nitrous acid was extracted into benzene as above. The aqueous layer was neutralized to prevent further thermal decomposition. The concentration of

nitrite present in the aqueous layer was determined by UV/Vis and corrected for dilution. It was assumed that the total volume of the aqueous and benzene layers remained constant during the extraction (i.e. the amount of benzene that went into the water was the same as the amount of water that went into the benzene). The amount of nitrous acid in the benzene layer was determined from the disappearance of nitrite from the aqueous layer.

#### **Thermal reaction of nitrite and phenol:**

To about 30ml of water, 1.00g (0.0106mol) of phenol and 0.734g (0.0106mol) of  $\text{NaNO}_2$  were added. The pH of the solution was approximately 6.5. The solution was stirred for about 2hr, at which time it was a dark orange color. Dilution of the solution 1:25 turned it to a light yellow. The color of the solution was also shown to be pH dependent.

When 1.00ml of 6M NaOH was added to the water before the other components, the reaction did not proceed forward noticeably.

#### **Nitrogen and oxygen saturated nitrite reactions:**

A 10.00ml aliquot of 0.2582M aqueous  $\text{NaNO}_2$  (at pH = 12) was placed in a 20ml quartz reaction tube. Oxygen was bubbled through the solution for 3 minutes and the tube was corked. Oxygen was also bubbled through benzene and a 1.00ml aliquot was added to the nitrite solution. The procedure was repeated with nitrogen gas. Both solutions were photolyzed together, without cooling, for 30 minutes. The aqueous layer of the oxygen saturated solution turned light yellow while the aqueous layer of the nitrogen saturated solution remained



colorless.

**Determination of solubility of  $\text{NO}_2(\text{g})$  in benzene:**

Two Erlenmeyer flasks were fitted with rubber stoppers and connected by a length of rubber tubing. Flask 1 was sealed with a one hole stopper with a glass tube in it. Flask 2 had a 2 hole stopper with an inlet tube reaching the bottom of the flask and an outlet tube to the atmosphere. Flask 2 was filled with about 40ml of benzene. Into flask 1 was placed about 40ml of concentrated nitric acid and two 5cm lengths of copper wire. The redox reaction produced  $\text{NO}_2$  gas which was forced into the benzene flask. The benzene turned bright yellow. The yellow color could be bubbled out with oxygen. It also disappeared with time when the flask was left uncovered.

## RESULTS

Table 1: Extinction Coefficients

compound	solvent	$\lambda_{\text{max}}$ , nm	$\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$
HONO	water, pH=2	352	$45 \pm 5$
HONO	benzene,	365	$18.5 \pm 0.6$
$\text{NO}_2^-$	water, pH= 12	352	$22.9 \pm 0.3$
$\text{NO}_2^-$	DMF	362	$28.6 \pm 0.2$
$\text{NO}_2^-$	DMSO	365	$27.8 \pm 0.3$
benzene	water	253	$51.7 \pm 2.5$
benzene	DMSO	268	$8.6 \pm 0.2$
PNP	water, pH=12	290, 390	
PNP	water, pH=7	323	15,600
PNP	water, pH=2	310	
PNP	benzene	290	$494 \pm 36$
phenol	water	260	$940 \pm 180$
phenol	benzene	275	$7.3 \pm 1.7$
phenol	DMSO	280	$2.4 \pm 0.7$

## Actinometry

The incident intensity of the Rayonet was determined by photolysis of a solution of 0.00617M  $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ . The quantum yield of potassium iron oxalate is 1.2. The percent transmittance of the unphotolyzed solution at 366nm was 4%. Table 2: Photolysis of Actinometer

time,s	[Fe2+]	#Fe2+ ions
s	M	atoms/l
3.17	1.006e-04	6.0581e+19
5.75	2.171e-04	1.3074e+20
8.07	3.848e-04	2.3173e+20
10.01	4.953e-04	2.9827e+20
13.28	5.110e-04	3.0772e+20

Table 3: Determination of Incident intensity

#hv abs	mol hv	absorbed intensity	incident intensity
hv/l	mol/l	mol/l*sec	mol/l*sec
5.048e+19	8.39e-05	0.000026	0.000028
1.089e+20	1.81e-04	0.000031	0.000033
1.931e+20	3.21e-04	0.00004	0.000041
2.486e+20	4.13e-04	0.000041	0.000043
2.564e+20	4.26e-04	0.000032	0.000033
avg intensity		0.000034	0.000036
stand dev		0.000006	0.000006

Figure 1

## Aqueous Nitrous Acid

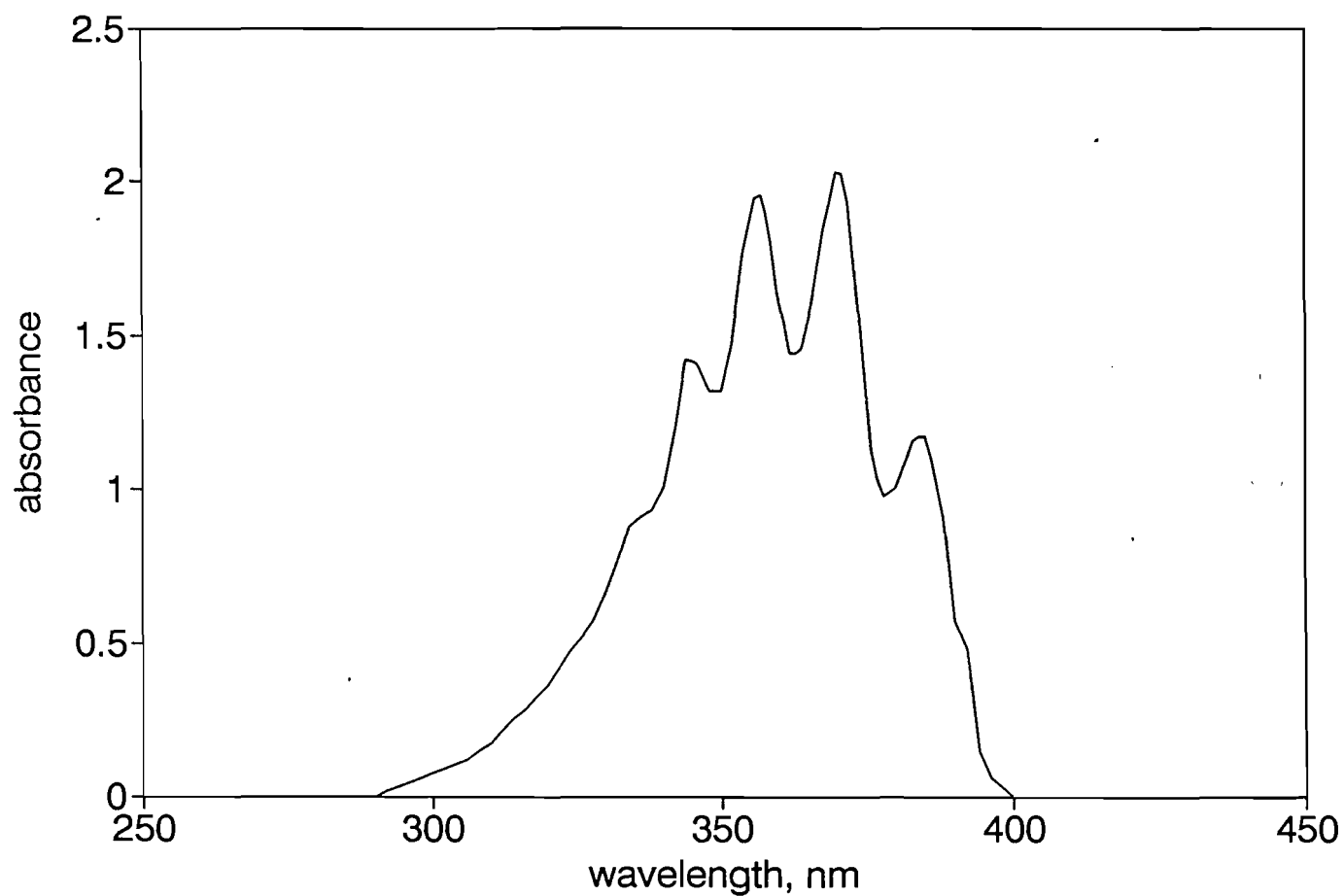
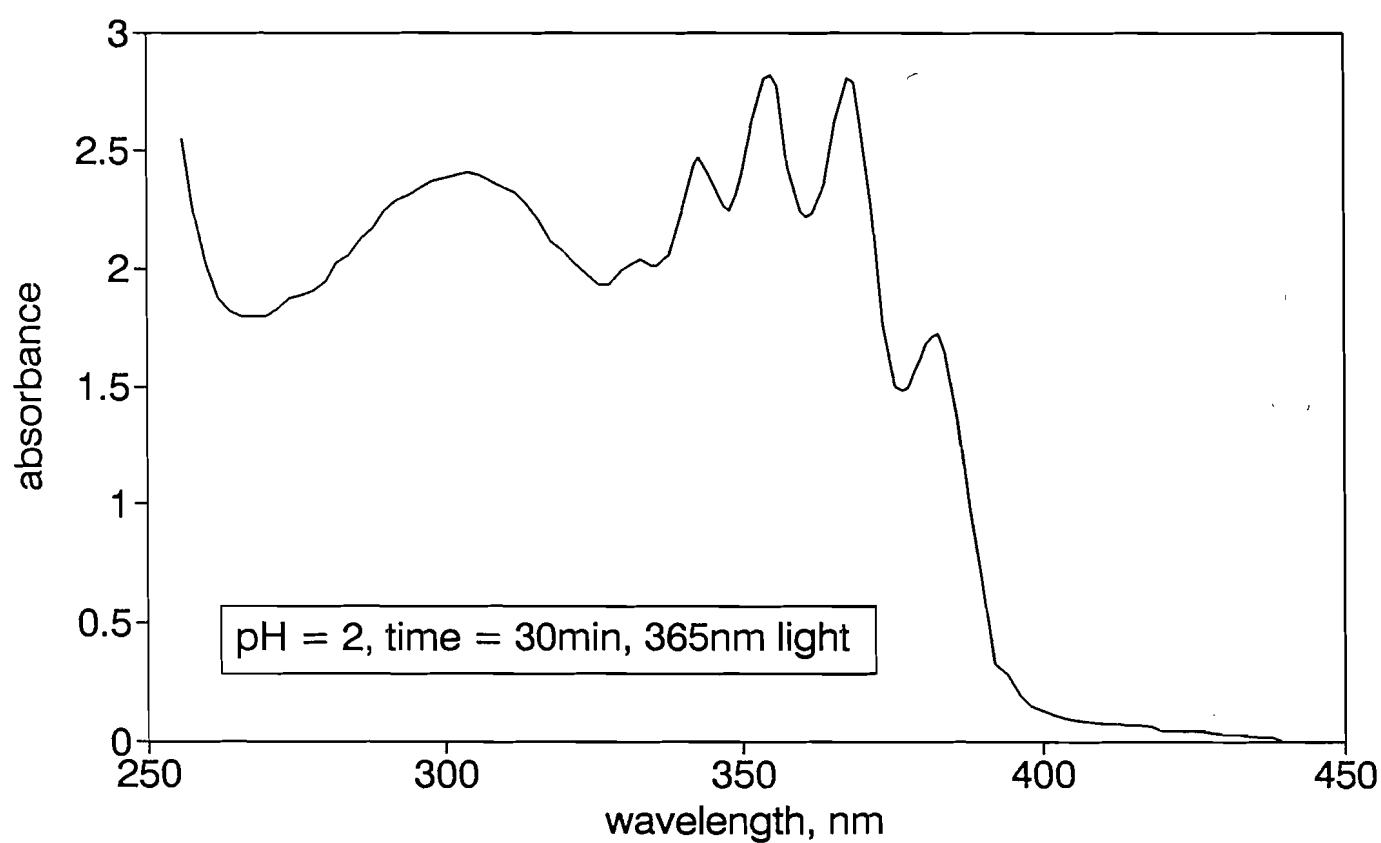


Figure 2

# Photolysis of HONO with benzene scavenger



### Determination of the quantum yield of PNP from photolysis of HONO in water:

The quantum yield for the photochemical decomposition of HONO in water was determined by photolysis of a 0.40M solution of HONO at pH = 2. It was assumed that the increase in absorbance at 300nm was due solely to the formation of PNP,  $\epsilon \approx 10^4 \text{ M}^{-1}\text{cm}^{-1}$ . The thermal decomposition of HONO was not accounted for.

Table 4: Determination of  $\Phi$  for PNP from HONO in Water

time, min	A @370	A @300	conc, $\text{M} \times 10^5$	T@366 $\times 10^6$	I $\times 10^5$ eins/Lsec
0	5.46	0.9	9.00	3.47	3.6
30	5.76	4.98	4.98	1.74	3.6
50	5.82	5.19	5.19	1.51	3.6
70	5.625	5.625	5.63	2.37	3.6
90	5.625	5.55	5.55	2.37	3.6
110	5.25	5.925	5.93	5.62	3.6
130	5.025	6.3	6.30	9.44	3.6
240	4.875	8.25	8.25	1.33	3.6

By regression analysis of the moles of product formed per intensity absorbed per time, the quantum yield is  $7.2 \pm 0.5 \times 10^{-4}$  mol PNP/eins.

Figure 3

## Determination of $\Phi$ (PNP) from photolysis of aqueous HONO

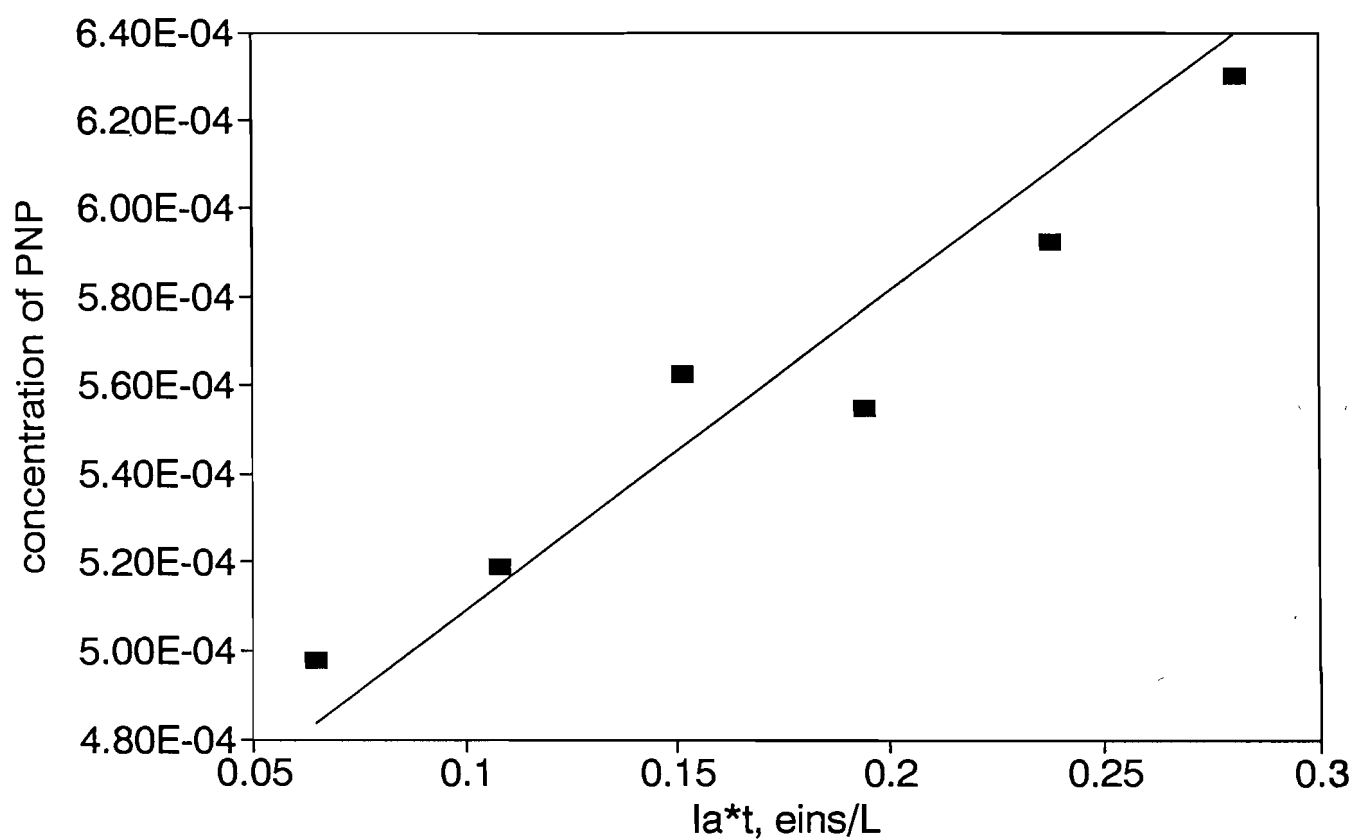


Figure 4

## Aqueous Sodium Nitrite

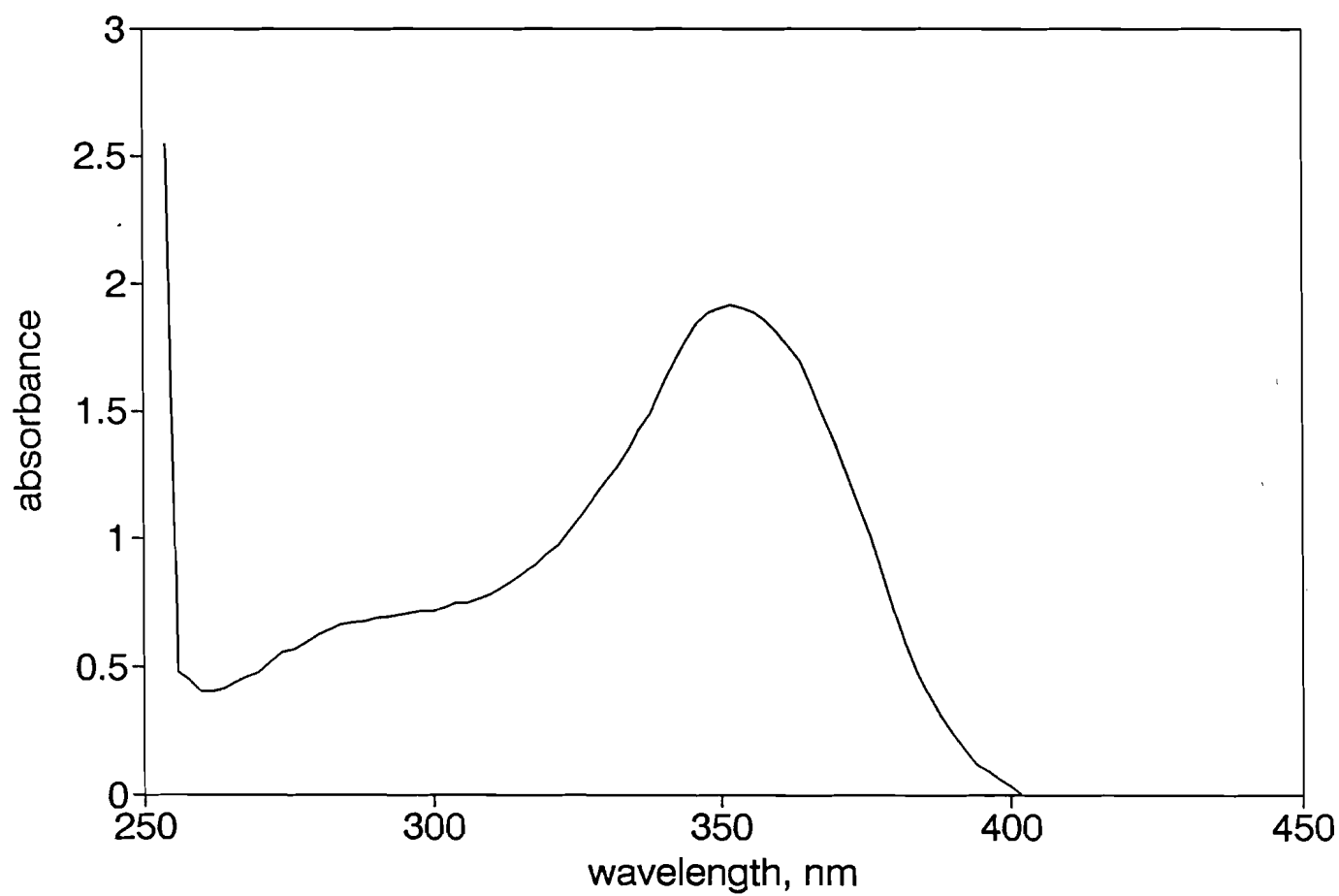
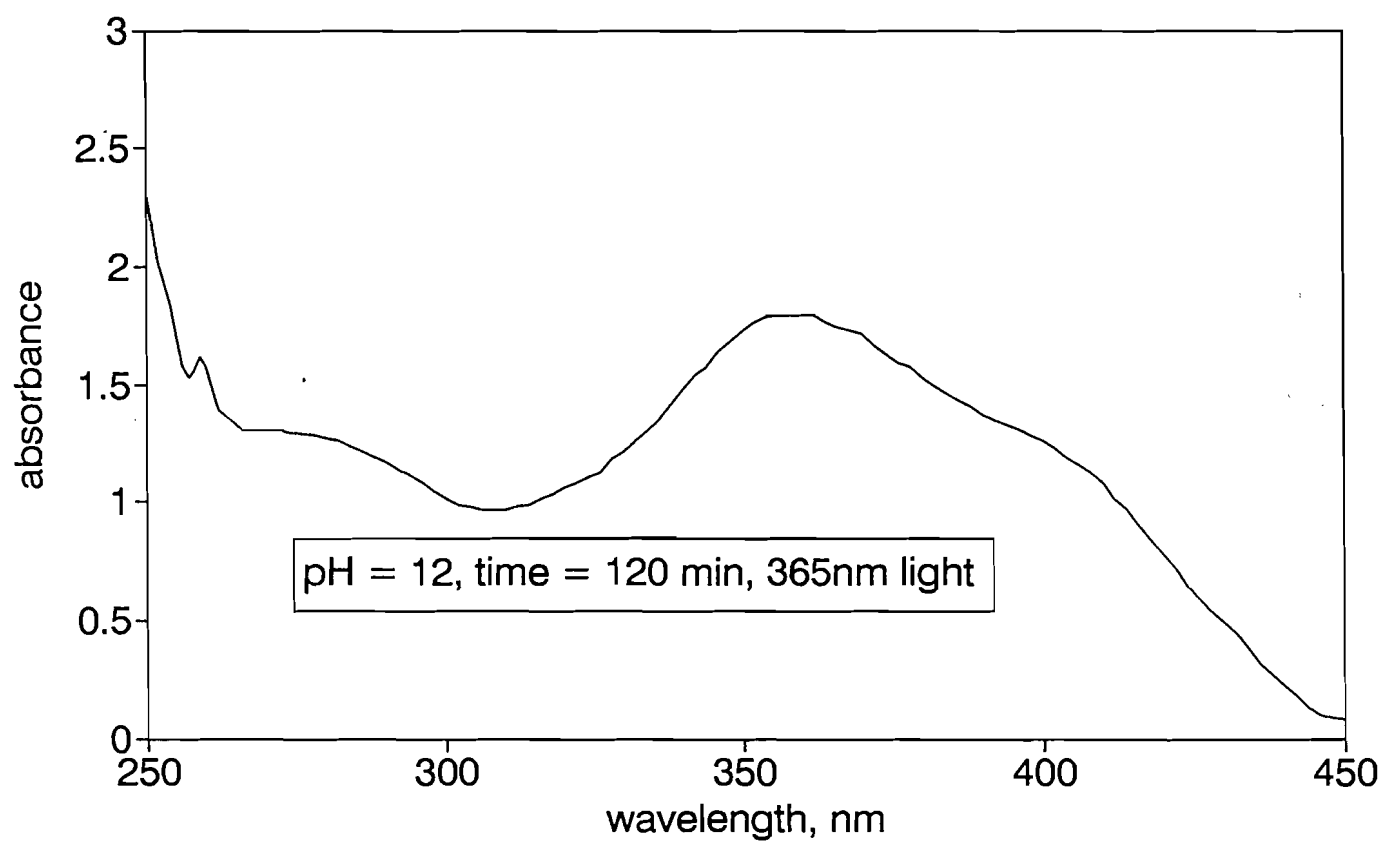




Figure 5

## Photolysis of Aqueous Nitrite with benzene scavenger



### Determination of quantum yield of PNP from photolysis of nitrite in water:

It was assumed that the increase in absorption at 280nm was due solely to the formation of PNP.

Table 5: Photolysis of 0.06M Nitrite with Benzene Scavenger pH = 9

time	A@ 280	A@352
0	0.3	0.705
15	0.48	0.825
40	0.66	0.975
65	0.81	1.125
90	0.93	1.245
120	0.93	1.275

Table 6: Determination of  $\Phi$  of PNP from Photolysis of Aqueous Nitrite

A-A(0)280	conc PNP	T(366)	Ia
	mol/l		ein/L*sec
0.18	0.000018	0.149624	0.000031
0.36	0.000036	0.105925	0.000032
0.51	0.000051	0.074989	0.000033
0.63	0.000063	0.056885	0.000034
0.63	0.000063	0.053088	0.000034

By regression analysis the value of  $\Phi$  of PNP from aqueous nitrite was determined to be  $2.1 \pm 0.4 \times 10^{-4}$  mol PNP/eins.

Figure 6

## Determination of Phi (PNP) from photolysis of 0.06M Aq. Nitrite

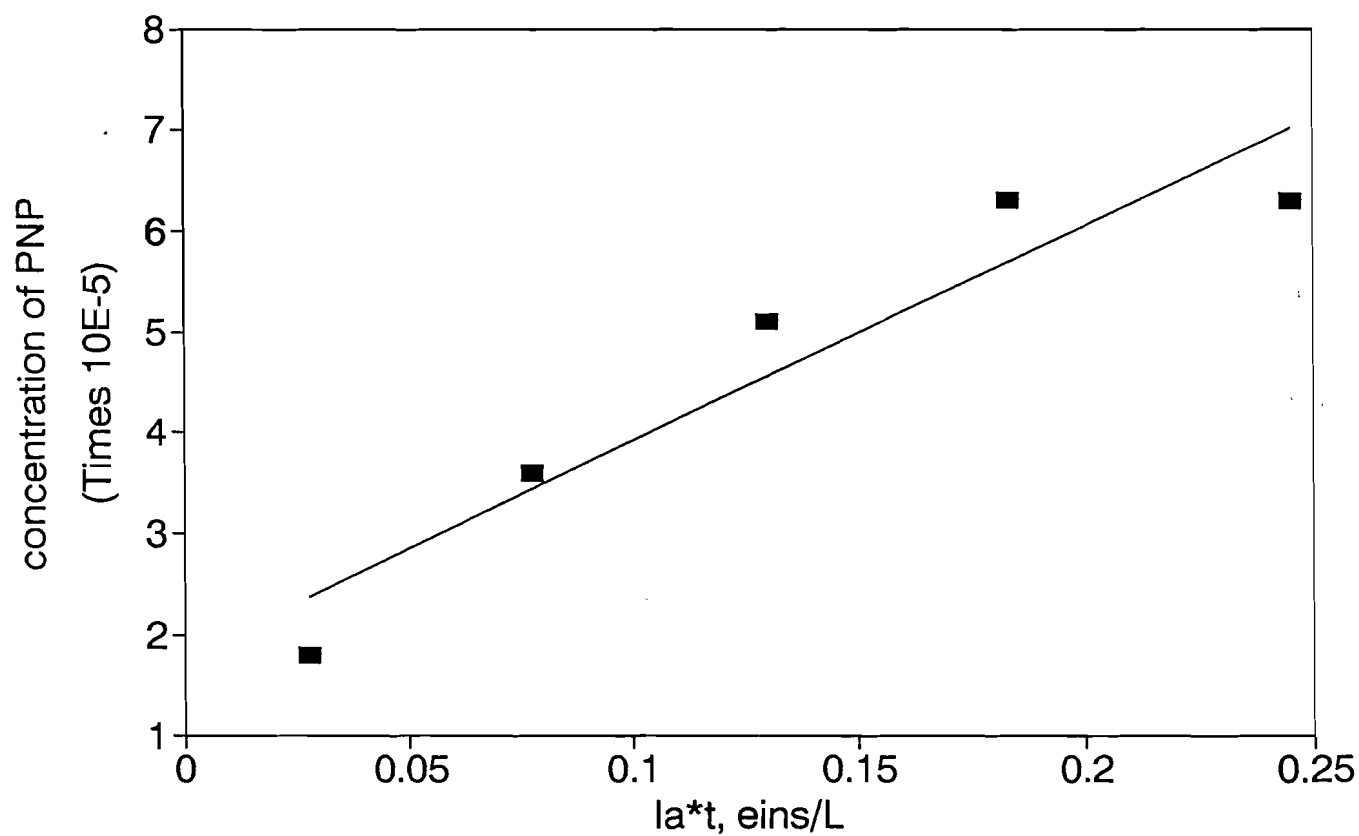


Table 7: Photolysis of 0.15M Aqueous Nitrite  
with Benzene Scavenger, pH = 9

time, min	A@ 280	A@352
0	1.26	3.24
15	1.35	3.36
40	1.53	3.48
65	1.59	3.54
90	1.65	3.57
115	1.71	3.63
145	1.86	3.54

Table 8: Determination of  $\Phi$  of PNP from Photolysis of  
0.15M Aqueous Nitrite

A-A(0)280	conc pnp	T(366)	Ia
	Molarity		eins/Lsec
0.09	0.000009	4.37e-04	0.000036
0.27	0.000027	3.31e-04	0.000036
0.33	0.000033	2.88e-04	0.000036
0.39	0.000039	2.69e-04	0.000036
0.45	0.000045	2.34e-04	0.000036
0.6	0.00006	2.88e-04	0.000036

By regression analysis,  $\Phi$  for the formation of PNP was determined to be  $1.6 \pm 0.2$   
 $\times 10^{-4}$  mol PNP/eins.

Figure 7

## Determination of Phi (PNP) from Photolysis of 0.15M Aq. Nitrite

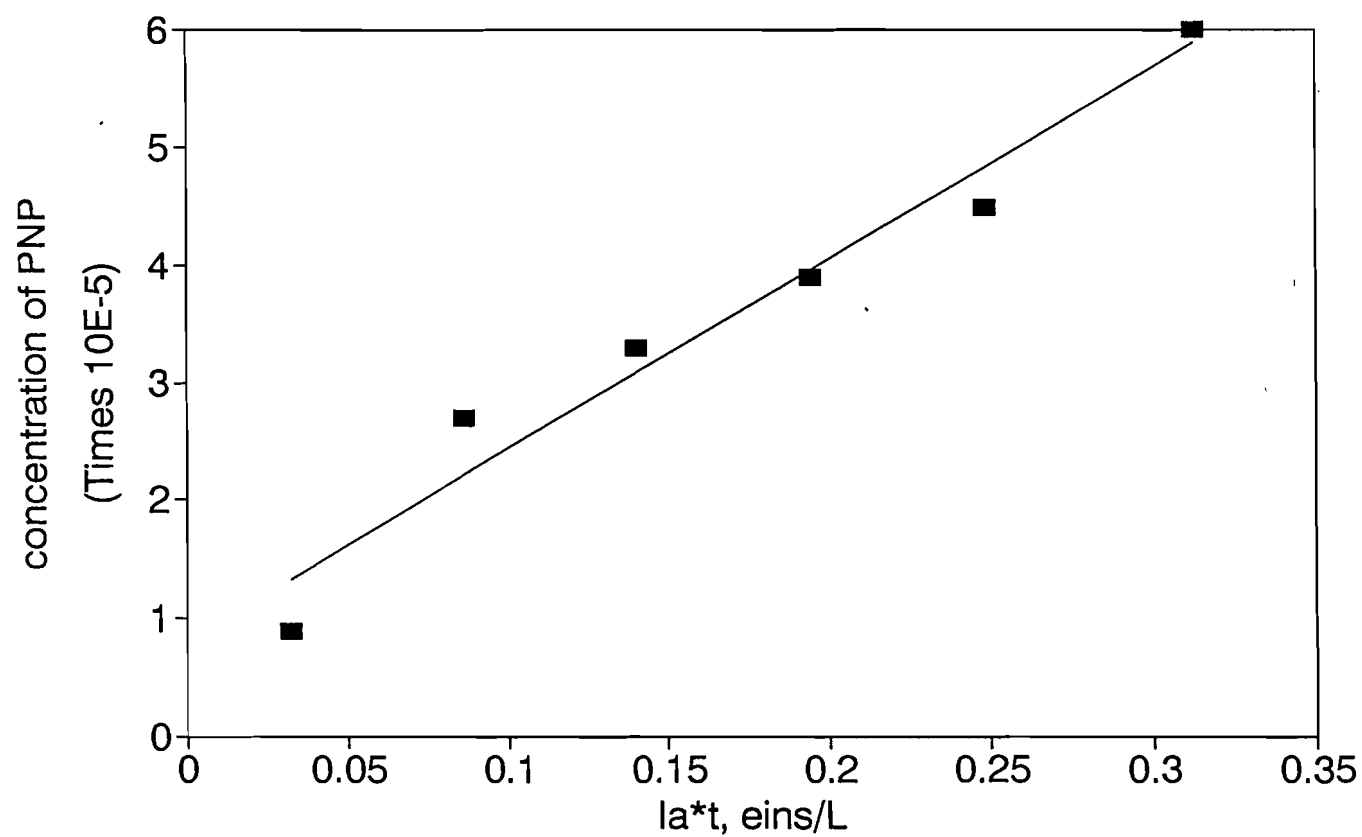


Figure 8

## HONO in benzene before photolysis

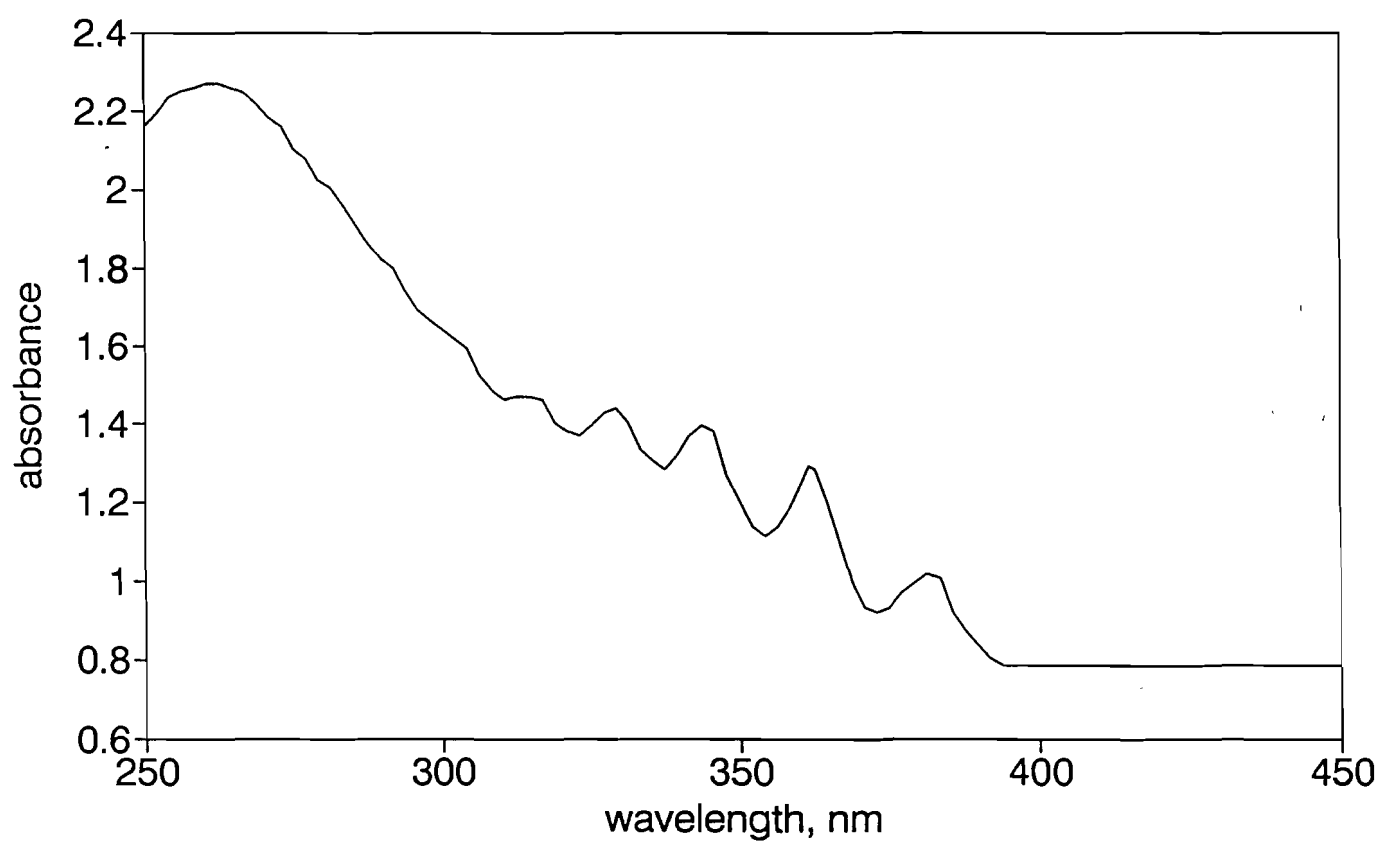


Figure 9

# Photolysis of HONO in benzene

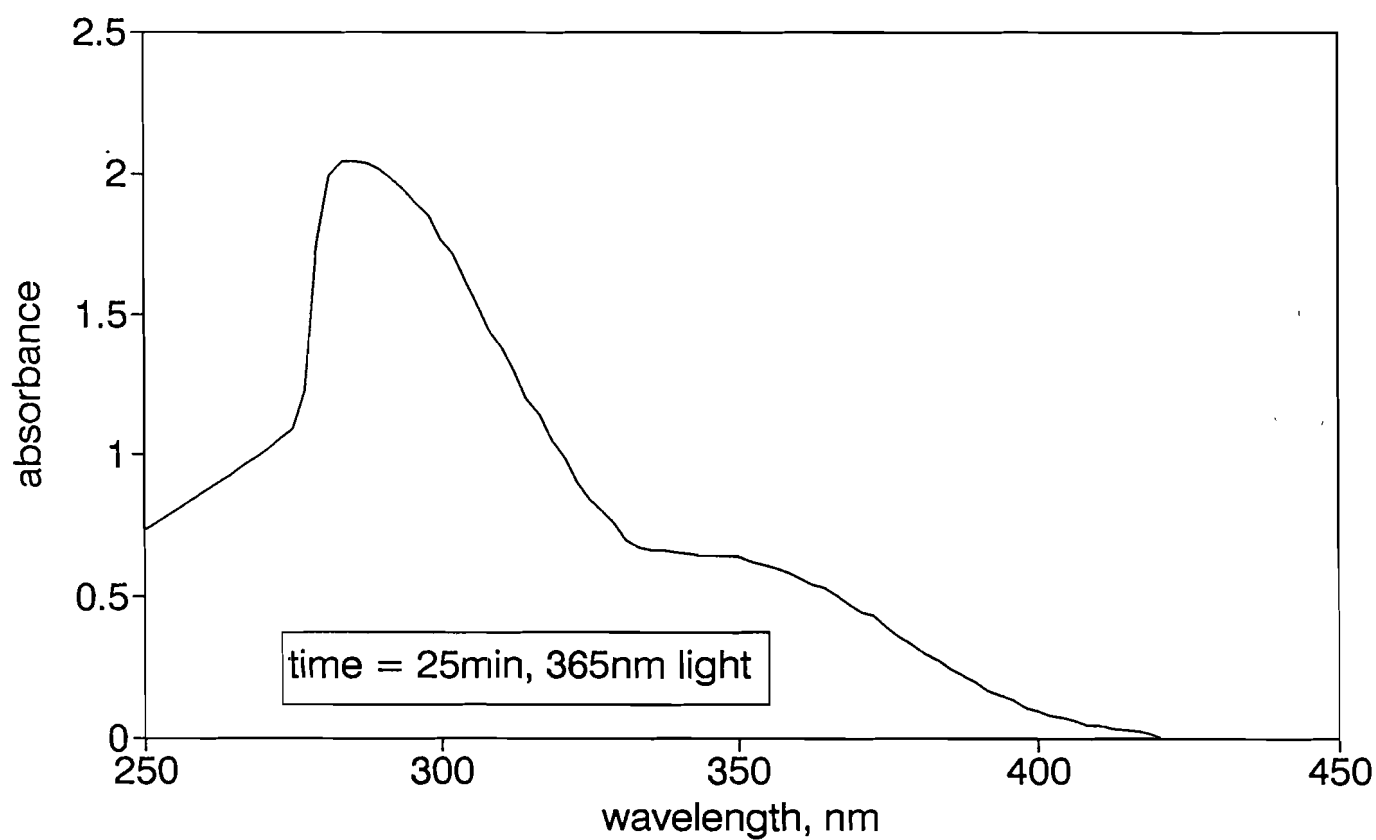
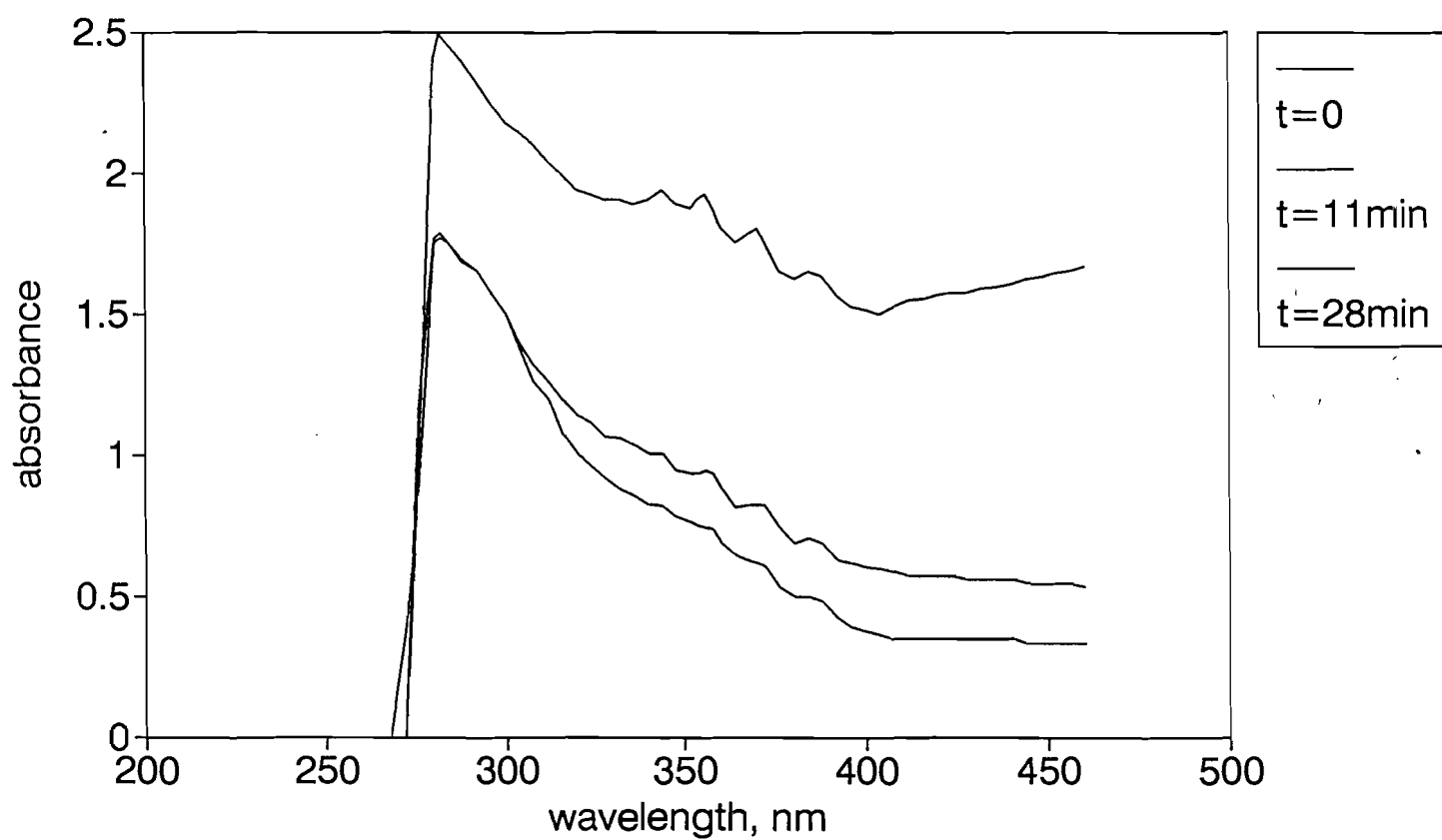


Figure 10

## Thermal Decomposition of HONO in benzene





### Thermal Decomposition of HONO in benzene

The change in concentration of 0.054M molecular nitrous acid in benzene was measured with respect to time. Table 9 gives the absorbencies measured for all of the nitrous acid peaks as well as the NO<sub>2</sub>(g) peak at 282nm. Figure 10 shows the decomposition. To determine an approximate kinetic order with respect to nitrous acid concentration, a plot of 1/[A] at 386nm vs. time was done. These data are given in tables 9 and 10 and figure 11 and 12.

Table 9: Thermal Decomposition of HONO in benzene

time, min	abs 386nm	abs 370nm	abs 356nm	abs 344nm	abs 282nm
0	1.396	1.513	1.632	1.7	2.42
2	1.263	1.372	1.481	1.54	2.14
4	1.048	1.184	1.316	1.39	2.03
6	1.008	1.112	1.223	1.262	1.88
8	0.845	0.981	1.094	1.16	1.84
10	0.791	0.904	1.023	1.08	1.77
15	0.646	0.776	0.908	0.986	1.76
20	0.578	0.712	0.815	0.907	1.77
25	0.486	0.615	0.743	0.838	1.76
30	0.428	0.567	0.699	0.798	1.76

Table 10: Graphing Data for Thermal Decomposition

time	conc	1/conc
0	0.0754	13.3
2	0.0683	14.6
4	0.0545	18.3
6	0.0545	18.3
8	0.0457	21.9
10	0.0428	23.4
15	0.0349	28.6
20	0.0312	32.1
25	0.0263	38.0
30	0.0231	43.3

Figure 11

## Thermal Decomposition of HONO in benzene

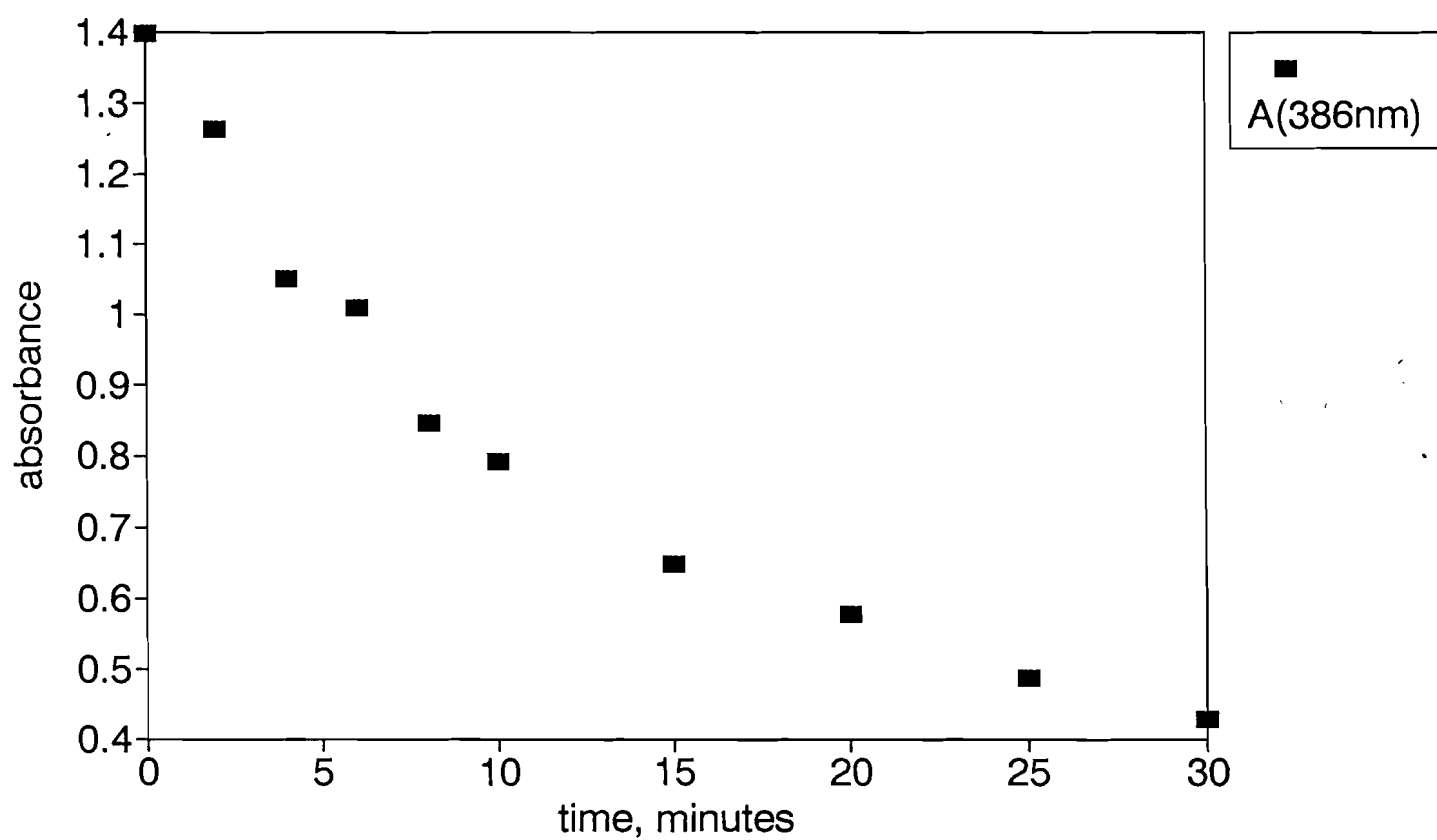


Figure 12

## Second Order Rate Law for Thermal Decomposition of HONO

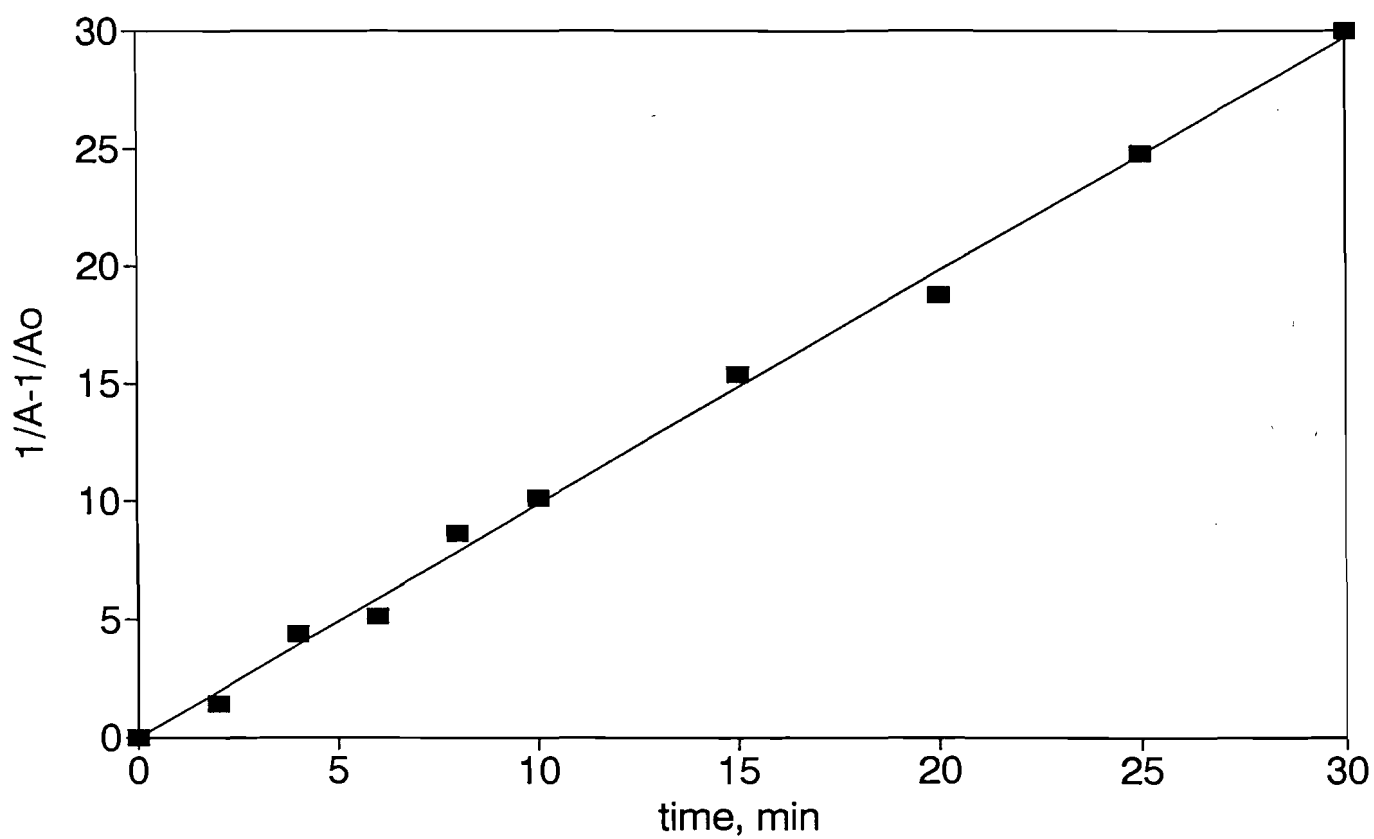


Figure 13

# Nitrite in DMF with benzene scavenger

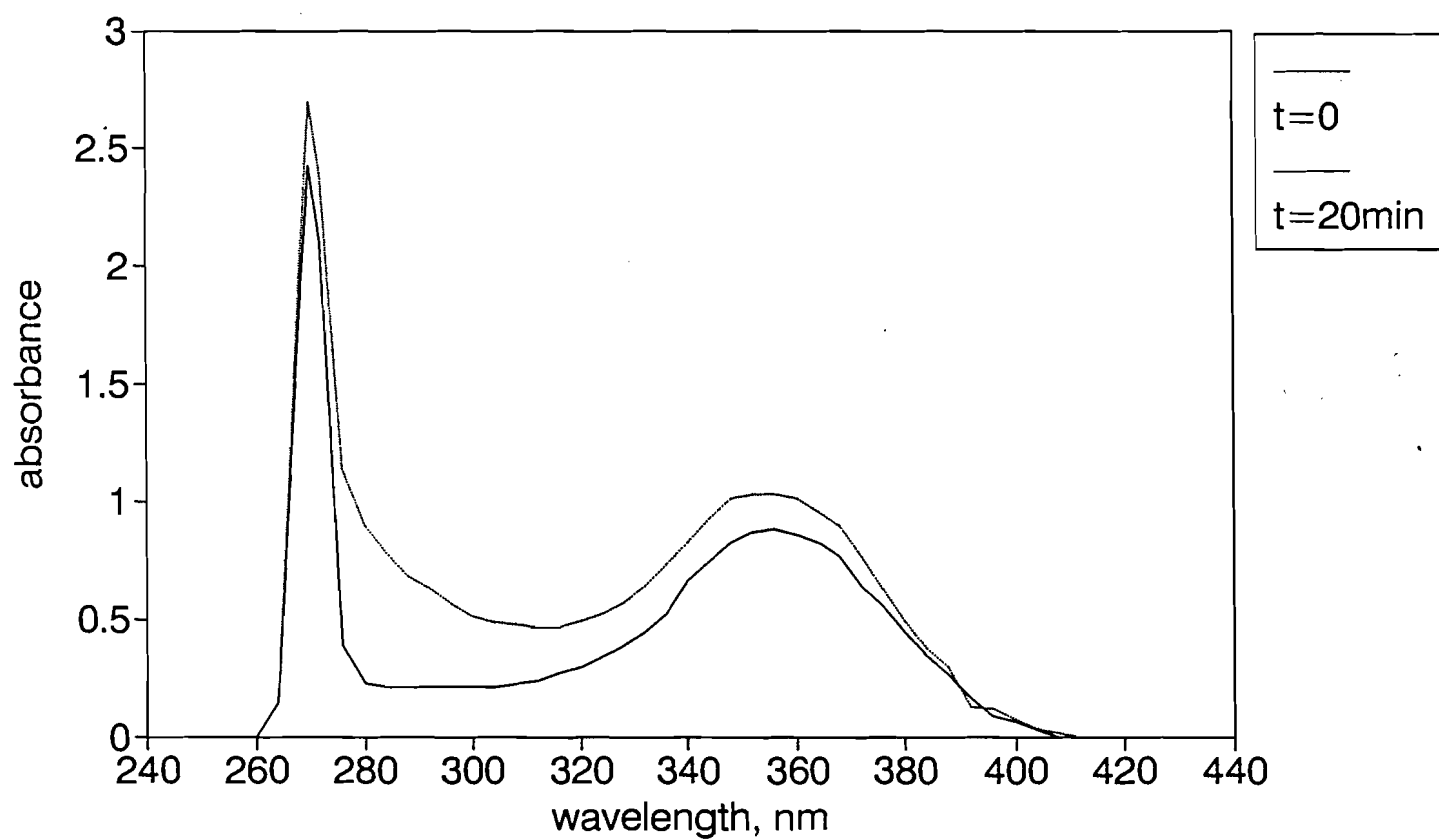
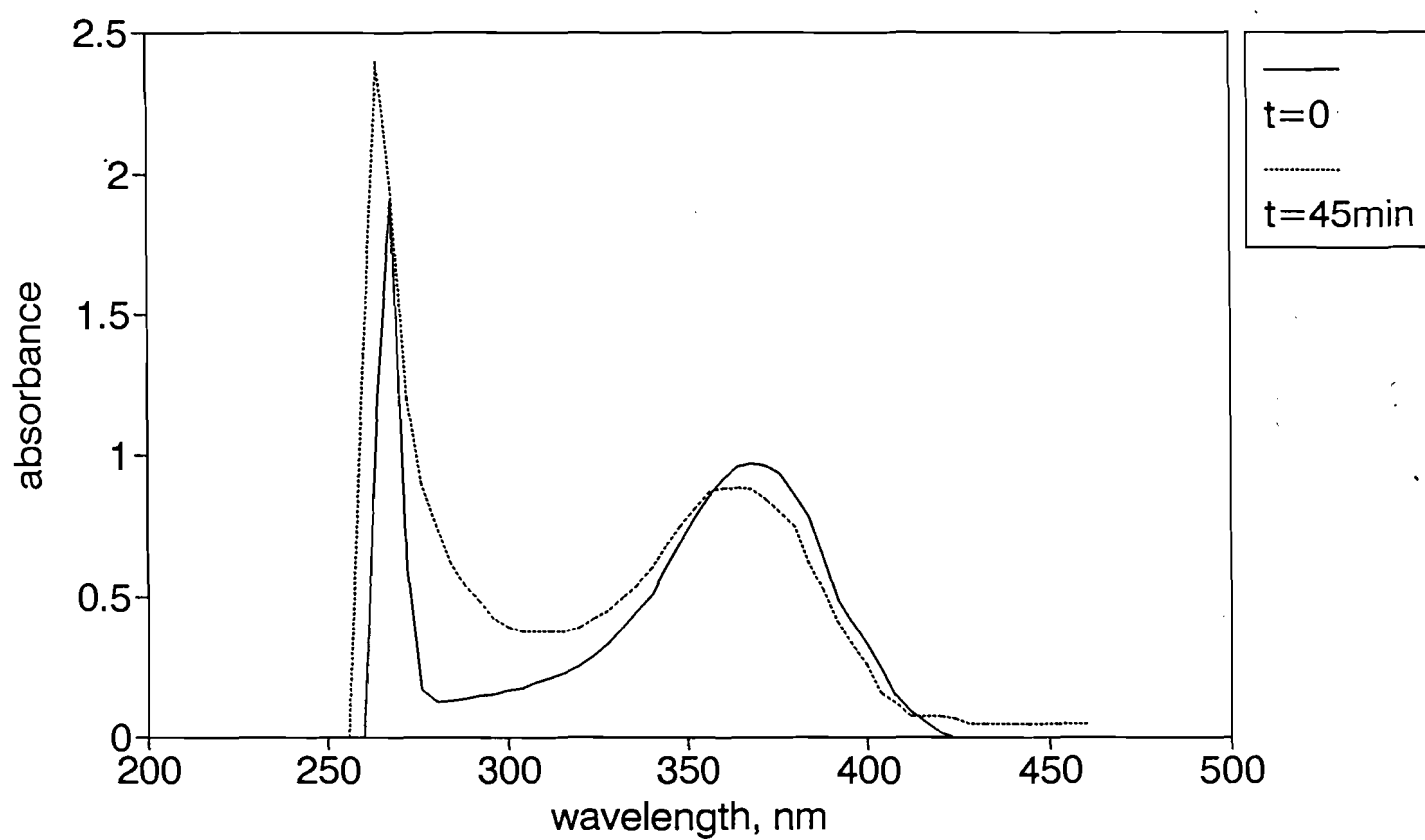


Figure 14

## Nitrite in DMSO with benzene scavenger



### Photochemical Reaction of Nitrite in DMSO:

The photochemical disappearance of nitrite in DMSO was measured by UV/Vis spectroscopy. Since the solution was colorless after photolysis it was assumed that the product of the photochemical reaction was phenol.

Table 11: Photochemical Decomposition of Nitrite in DMSO

time,min	A(263)	A(365)
0	1.94	1.003
15	2.03	1.037
30	2.05	0.996
45	2.1	0.978
60	2.13	0.958
75	2.2	0.961
90	2.23	0.928
105	2.2	0.935
120	2.2	0.923

Table 12: Calculation of  $\Phi$  for  $\text{NO}_2^-$  from  
Photolysis of Nitrite in DMSO

time,sec	conc $\text{NO}_2^-$	Ia
0	0.03608	3.61e-05
900	0.03730	3.73e-05
1800	0.03583	3.59e-05
2700	0.03518	3.52e-05
3600	0.03446	3.45e-05
4500	0.03457	3.46e-05
5400	0.03338	3.34e-05
6300	0.03363	3.37e-05
7200	0.03320	3.32e-05

By regression analysis  $\Phi$  for the destruction of nitrite was determined to be  $1.8 \pm 0.3 \times 10^{-2}$  mol/ein.



Figure 15

## Determination of $\Phi$ (Nitrite) from Photolysis of Nitrite in DMSO

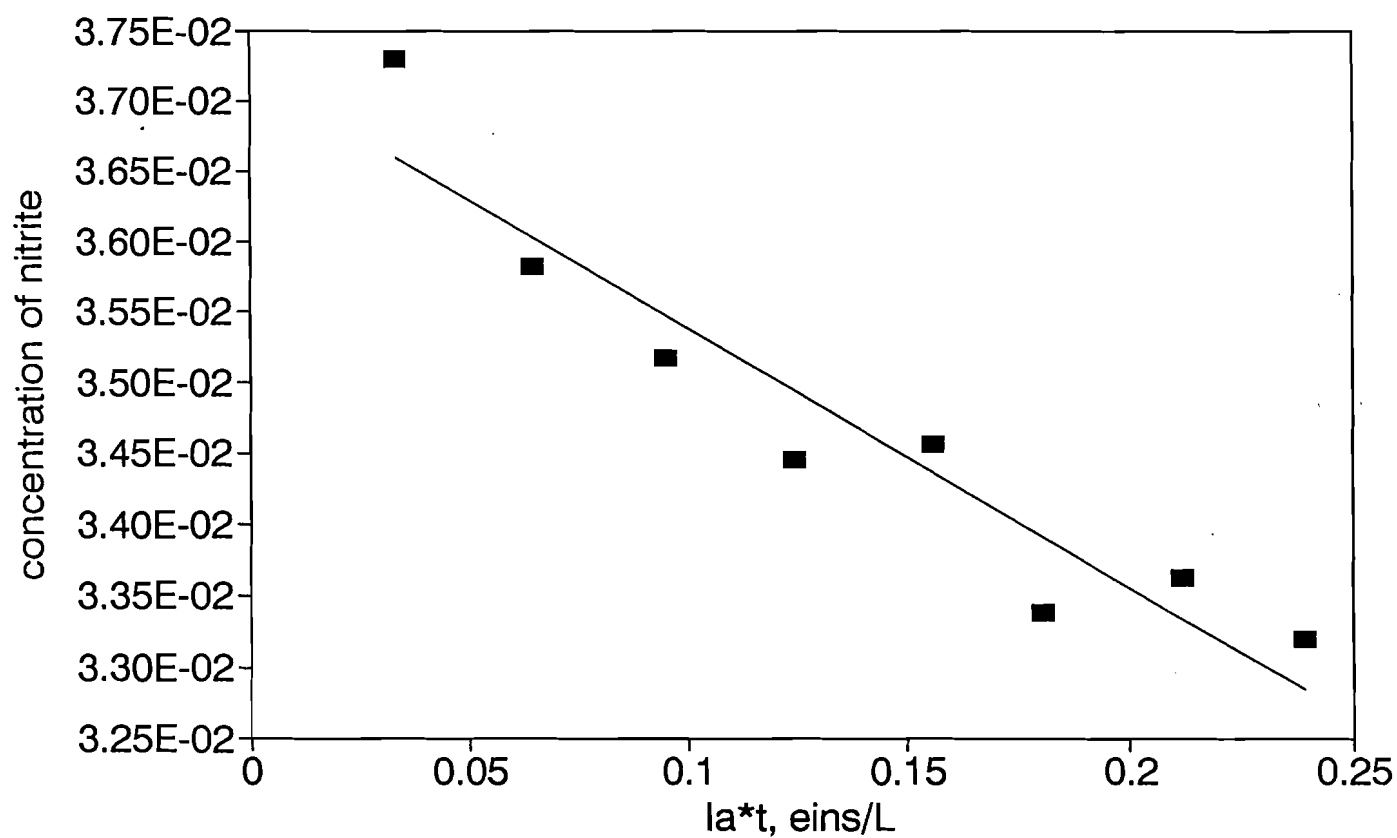
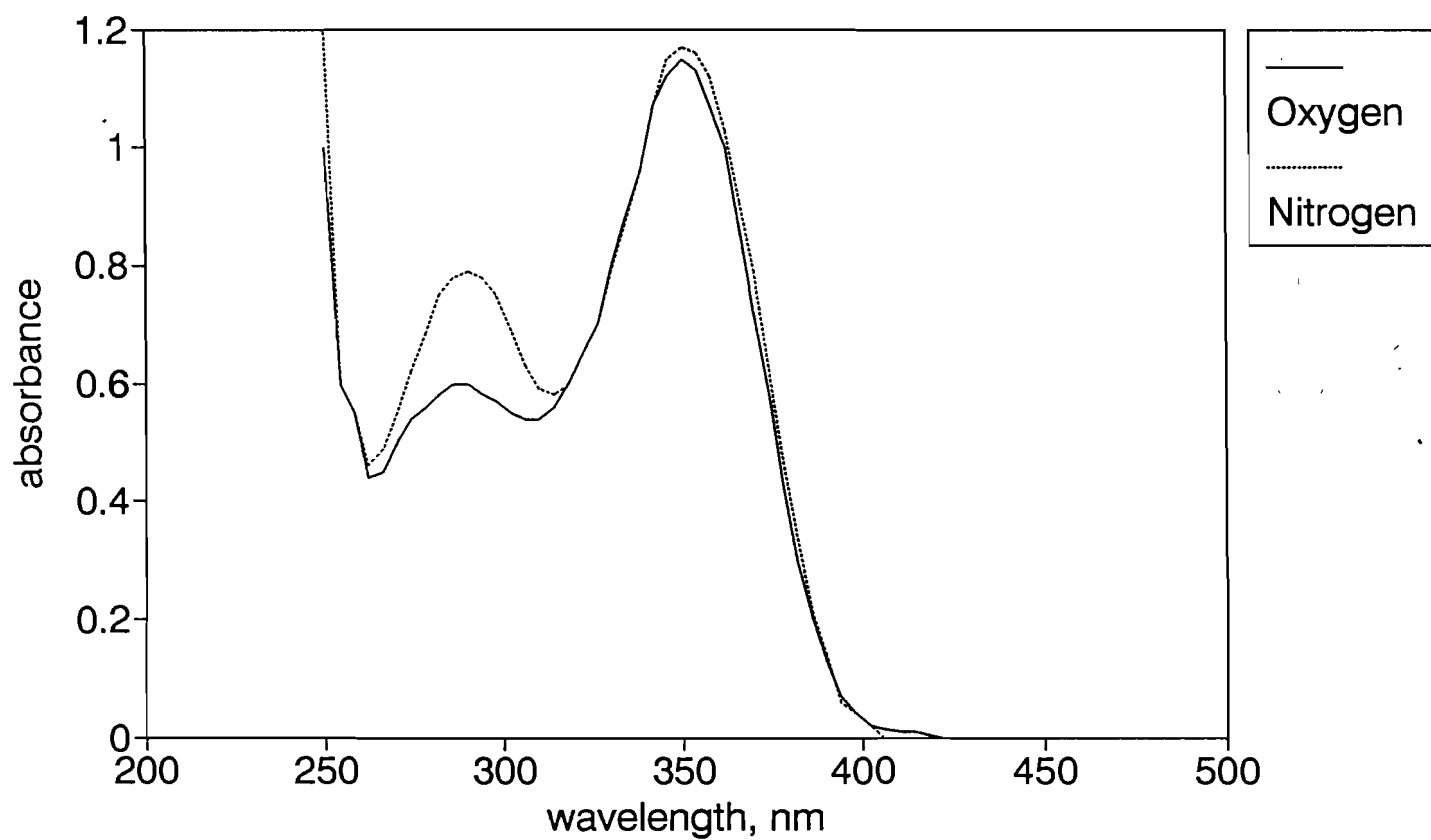


Figure 16

## Oxygen and Nitrogen saturated reactions



### Intensity Study:

The dependence of nitrite photolysis on the intensity of the incident light was determined by photolyzing solutions with a decreasing number of lamps present. The intensity is given as a ratio of the number of lamps present to the total possible present, 16.

Table 13: Intensity Dependence of Nitrite Reaction

I	I <sub>0</sub>	abs(352)	[NO <sub>2</sub> <sup>-</sup> ], M	abs(280)	[PNP], M
1	3.60e-05	3.36	0.147	3.64	3.64e-04
15/16	3.38e-05	3.14	0.137	1.78	1.78e-04
14/16	3.15e-05	2.73	0.119	1.70	1.70e-04
13/16	2.93e-05	2.82	0.123	1.74	1.74e-04
12/16	2.70e-05	2.80	0.122	1.64	1.64e-04
11/16	2.48e-05	2.80	0.122	1.55	1.55e-04
10/16	2.25e-05	3.06	0.134	1.55	1.55e-04
9/16	2.03e-05	3.06	0.134	1.52	1.52e-04
8/16	1.80e-05	3.02	0.132	1.42	1.42e-04

Table 14: Determination of  $\Phi$  for PNP from Photolysis of Aqueous Nitrite at Varying Intensities

T(366)	I <sub>a</sub>	[PNP], M	$\Phi$
0.000437	0.000036	3.64e-04	5.62e-03
0.000724	0.000034	1.78e-04	2.93e-03
0.001862	0.000031	1.70e-04	3.00e-03
0.001514	0.000029	1.74e-04	3.31e-03
0.001585	0.000027	1.64e-04	3.38e-03
0.001585	0.000025	1.55e-04	3.48e-03
0.000871	0.000022	1.55e-04	3.83e-03
0.000871	0.00002	1.52e-04	4.17e-03
0.000955	0.000018	1.42e-04	4.39e-03

Figure 17

# Phenol

in water and benzene

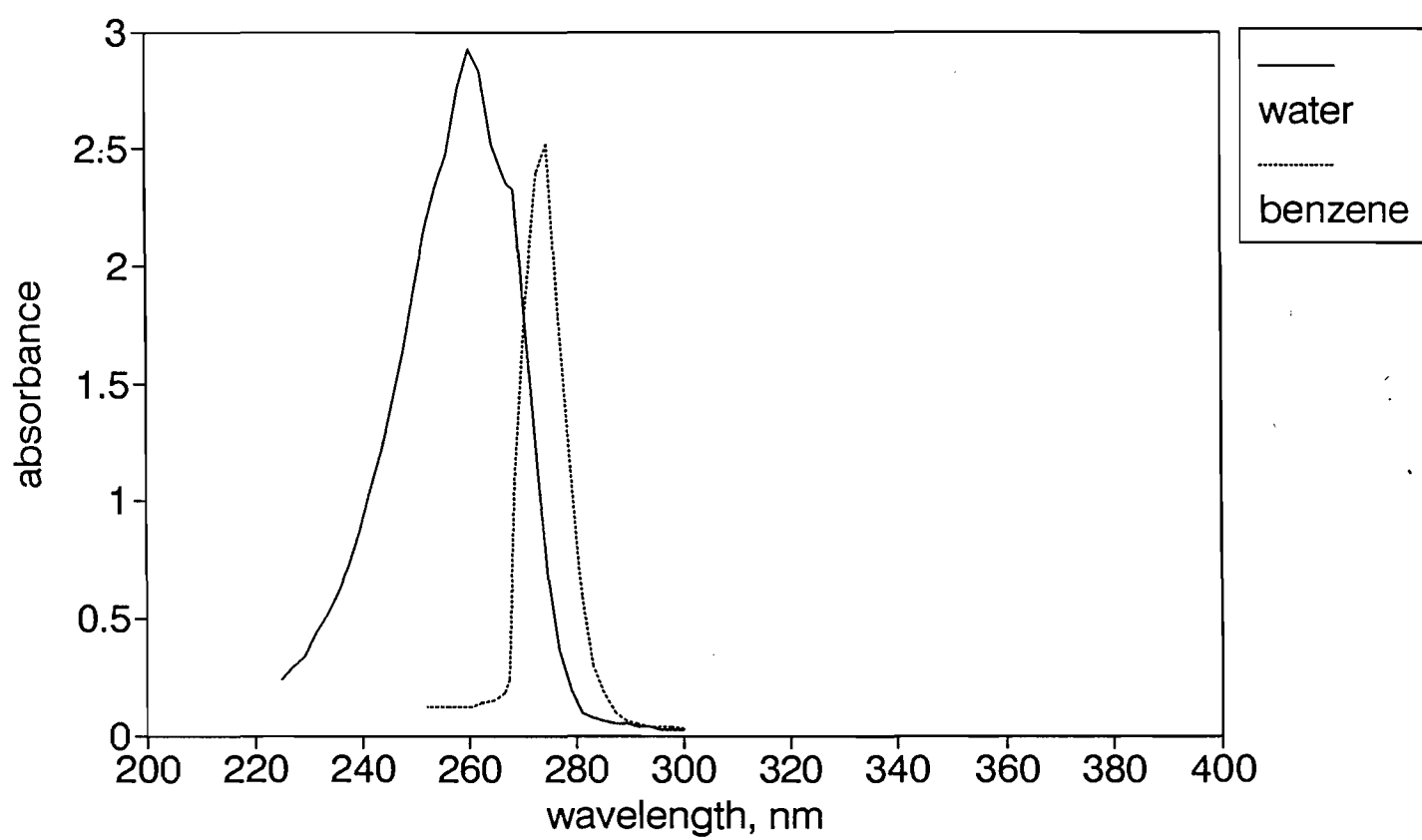


Figure 18

## Phenol in DMSO

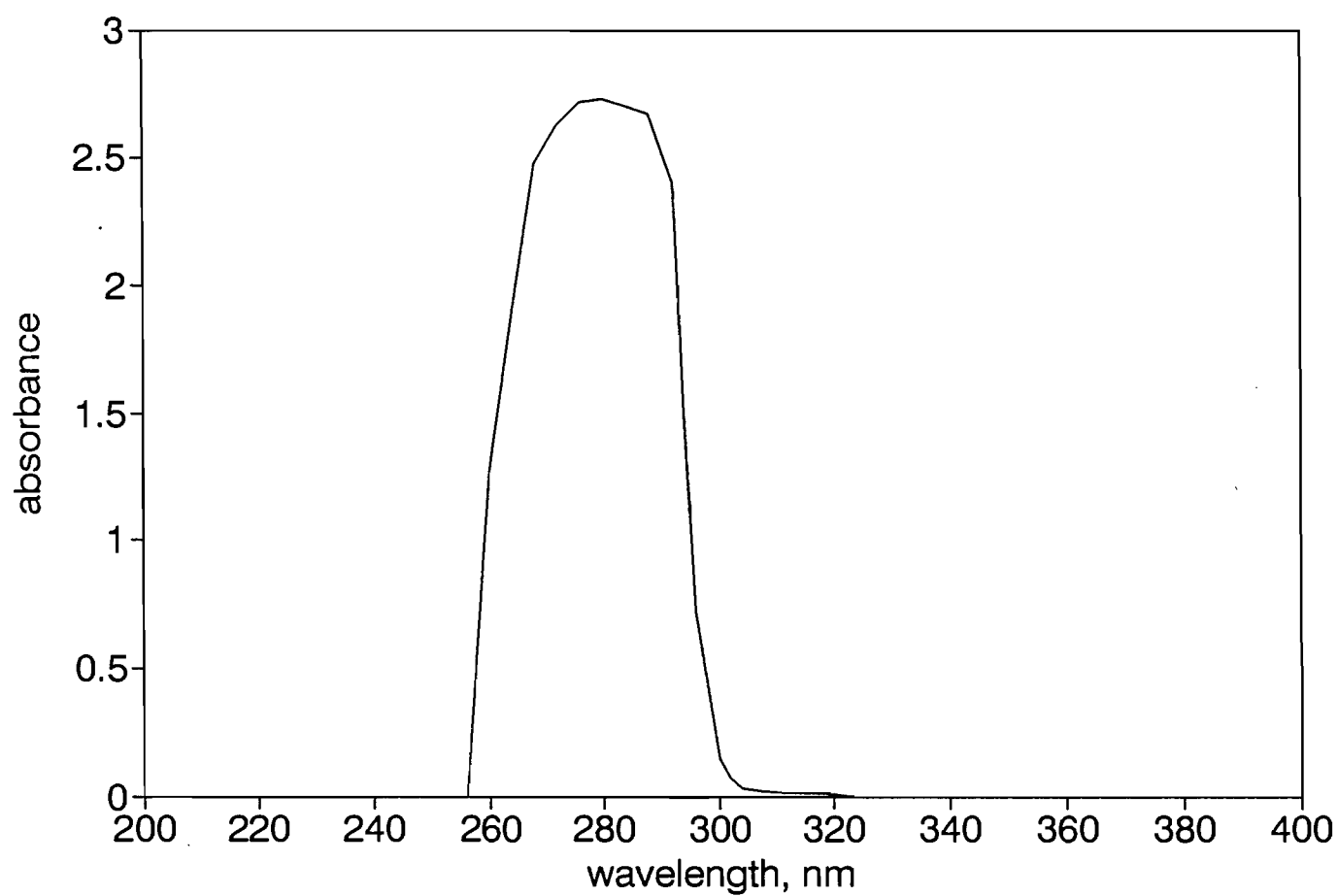


Figure 19

## Aqueous p-Nitrosophenol

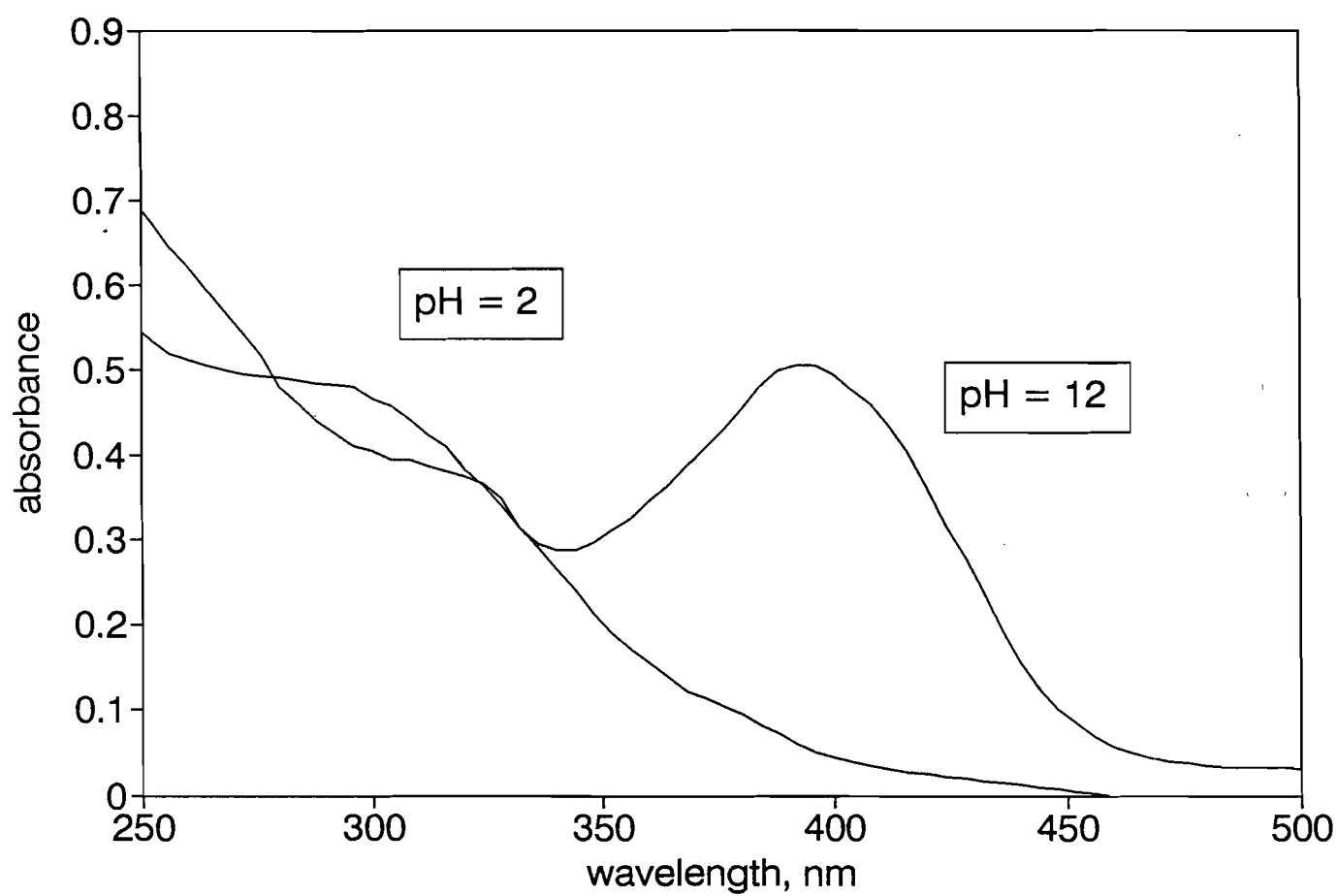


Figure 20

## Thermally made PNP

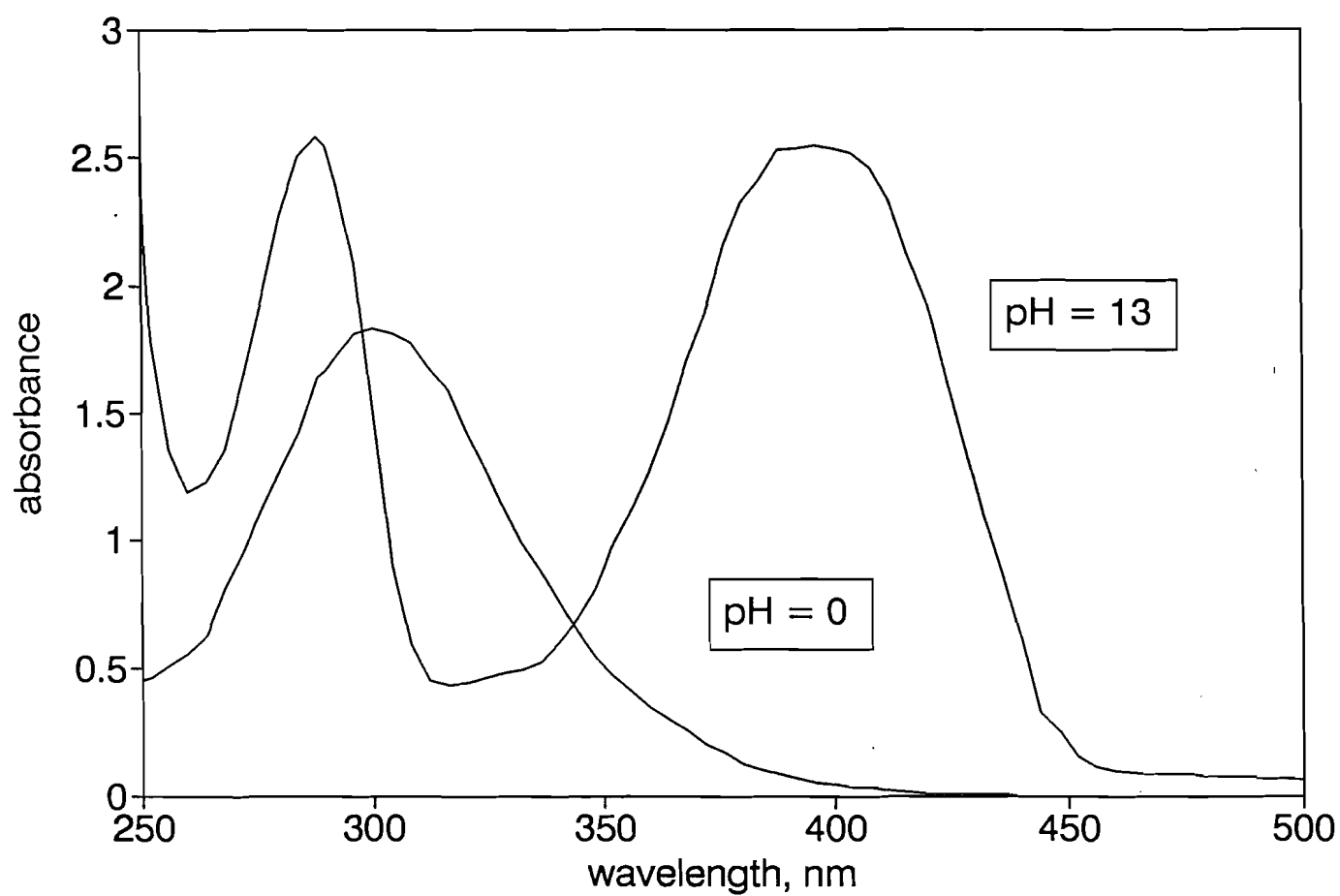


Figure 21

## PNP in benzene

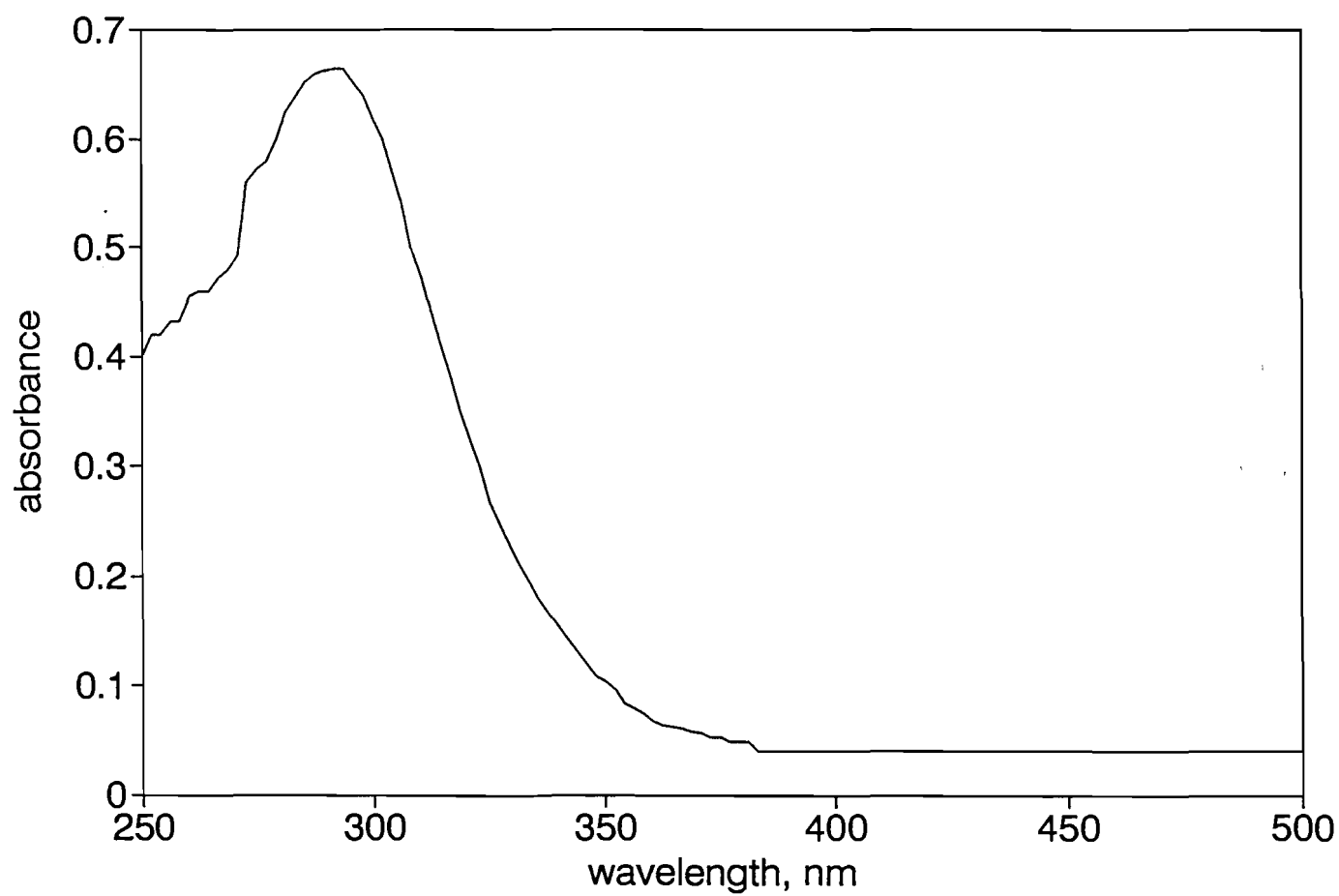
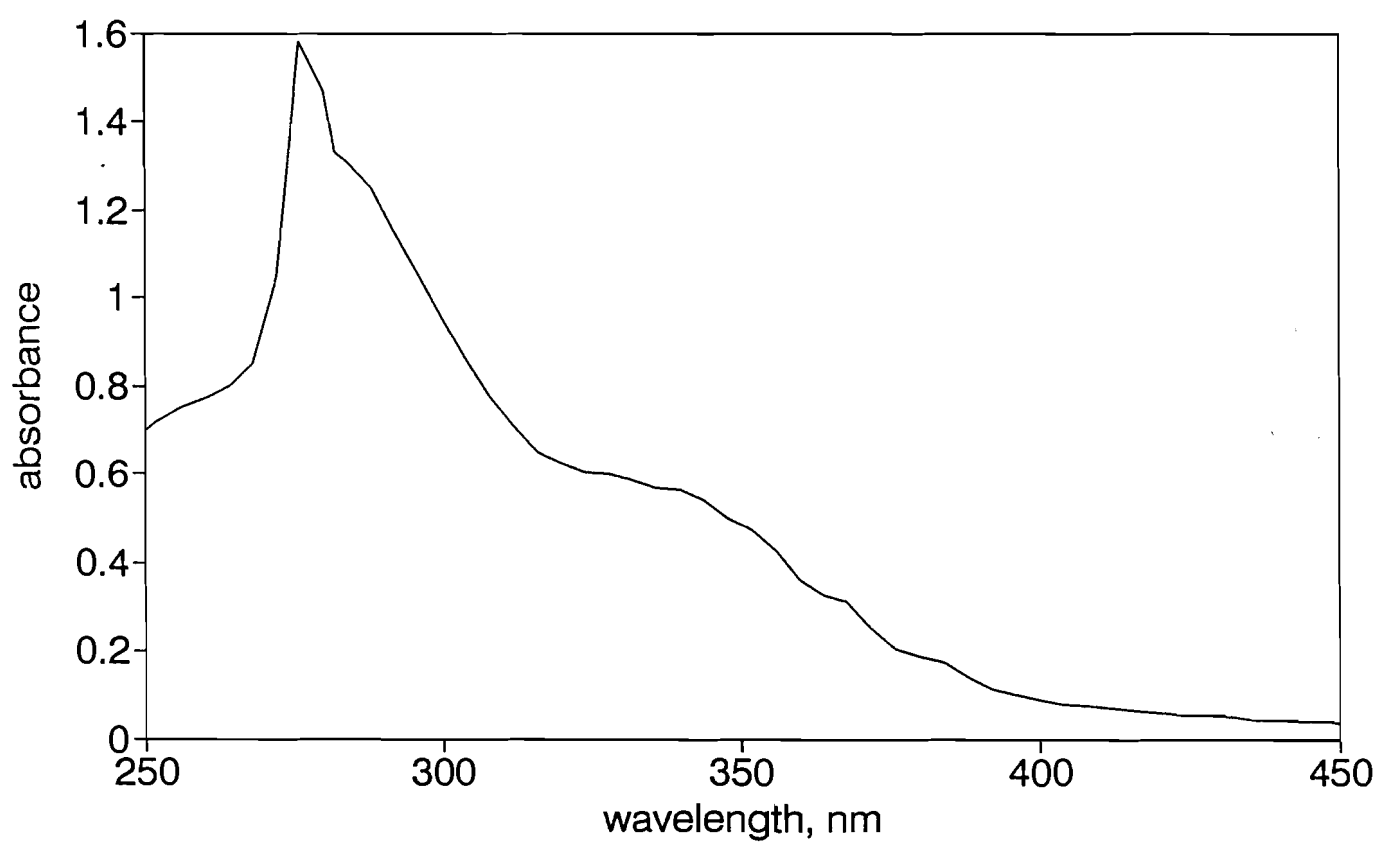




Figure 22

# Nitrogen Dioxide Gas in benzene



## DISCUSSION:

It has been established previously that aqueous nitrous acid undergoes both photochemical and thermal decomposition reactions. The role of nitrite ion however, has not been clearly established, although much of the literature indicates that nitrite does not react photochemically. This research has determined that nitrite ion does undergo a photochemical reaction when irradiated with  $366\pm 5\text{nm}$  light.

The photochemical reaction of nitrous acid is detectable both with and without a scavenger present. Without a hydroxyl radical scavenger added to the solution, nitrous acid is believed to form nitric acid and nitric oxide. When a scavenger is present however, the recombination reactions are inhibited. With benzene scavenger, the product of the nitrous acid photolysis is p-nitrosophenol.

PNP is easily detectable visually because of its characteristic yellow color and its change in color with pH. As the pH of the solution is increased, the yellow color darkens. It was also determined that the color of PNP solutions is dependent on the concentration of PNP. A thermal reaction of phenol with nitrous acid was done at  $\text{pH} = 6.5$ . This pH allows the reaction to go forward because some nitrous acid is present, however it proceeds slowly because of the predominance of the nitrite form. It was determined that the thermal formation of PNP does not occur at a strongly basic pH. By not acidifying the solution, the thermal decomposition of nitrous acid was minimized, allowing a 1:1 reaction ratio as shown in equation 65. After about 15 minutes, the solution was light yellow.

As the reaction time increased, the solution darkened and after about 2 hours the solution was brown. Upon 1:1000 dilution with water however, the solution was again yellow. This change in color may indicate, to a first order approximation, how much PNP is being formed in the photochemical reactions.

Nitrite is thermally stable in solution, even in the presence of hydroxyl scavengers. The photochemical reactivity of nitrite is not understood. Most studies indicate that nitrite does not undergo a net photochemical reaction. This research is able to verify that in the absence of a scavenger, the concentration of nitrite in aqueous solution does not decrease measurably. The absorbance detection limits are about 0.005 units on the Perkin Elmer instrument used for UV/Vis measurements, which corresponds to a  $2 \times 10^{-4} \text{M}$  change in concentration. The average nitrite concentration of aqueous photolysates was  $0.13 \text{M}$ , which indicates only 0.2% of the solution needs to react to be detectable.

In the presence of benzene scavenger however, a photochemical reaction of nitrite was visually detectable. The photolysate solution was light yellow after 15 minutes of irradiation at 366nm. The UV/Vis spectrum taken after 120 minutes of irradiation clearly shows the presence of an additional species (figures 4,5). There is a shoulder on the nitrite peak near 400nm and between 260 and 300 nm there appears to be an increase in absorbance, although a new peak is not distinguishable. At pH=12, at which the reactions were run, the spectrum of PNP has 2 peaks, one at about 395 and the other at 280nm (figure 20). Quantitative analysis of the decrease in concentration of nitrite is not possible with UV/Vis

spectroscopy because the product peaks significantly overlap with the nitrite peak.

There are two possible explanations for the cause of the nitrite reaction. One could be the intensity of the lamps used for photolysis. From actinometry experiments, an approximate intensity of the Rayonet was calculated. The incident intensity, with all 16 lamps present, was calculated to be  $3.6 \pm 0.6 \times 10^{-5}$  eins/L\*sec. This was determined from the number of  $\text{Fe}^{2+}$  ions produced in the photolysis of potassium iron oxalate solution. For every photon absorbed by the actinometer, 1.2 iron (II) ions are produced; the number of iron ions produced per photolysis times gave a minimum number of einsteins of photons absorbed. From the transmittance of the actinometer solution at 366nm, the intensity of incident light can be determined. Previous studies in the literature do not give the intensity of light used, so a direct comparison is not possible. However, previous photolysis work by Exstrom<sup>17</sup> was done with a Blak-Ray B-100A low pressure mercury lamp. Photolysis experiments with nitrous acid generally took about 6 hours. This is about 6 times longer than the current work, indicating his lamp intensity was probably about  $6 \times 10^{-6}$  eins/L\*sec.

Another factor in the detection of the nitrite reaction could be the concentration of the nitrite solution. Exstrom's concentration of nitrite before photolysis was approximately 0.0025M, whereas in this work concentrations of about 0.13M  $\text{NaNO}_2$  were used. The work by Treinin and Hayon<sup>14</sup> was done with  $2.7 \times 10^{-4}$ M nitrite solutions, again significantly lower than this current work. As stated earlier, the detection limits of the UV/Vis spectrophotometer are 0.005

absorbance units or  $2 \times 10^{-4} \text{M}$  nitrite ion. Therefore at the concentrations used by Treinin and Hayon, nearly 2/3 of the nitrite would have to react to be detectable with our instrumentation. The higher concentration of nitrite may also be responsible for the formation of PNP as the final product. Because in aqueous solution there is always both the conjugate acid and base present, an increase in nitrite would mean an increase in nitrous acid as well. The  $\text{pK}_a$  for nitrous acid is 3.4, which means at  $\text{pH}=12$ , in a  $0.13 \text{M}$  nitrite solution there is about  $3 \times 10^{-10} \text{M}$  nitrous acid. This is not a detectable quantity, but it may be enough to form PNP from phenol.

Treinin and Hayon's work was also done without a hydroxyl scavenger present. This research has shown that a hydroxyl scavenger must be present for a decrease in nitrite to be noticeable. Treinin and Hayon also reported a quantum yield of  $\text{NO}_2^-$  depletion to be less than  $10^{-3}$ . With a hydroxyl scavenger present, an estimate of the quantum yield was obtained. It was assumed that, for a given aqueous nitrite reaction, the increase in absorbance was due solely to the formation of p-nitrosophenol. Taking the extinction coefficient as  $10^4 \text{M}^{-1} \text{cm}^{-1}$ , the concentration of PNP formed was determined. The intensity of light absorbed was estimated from the absorbance of the solutions at 352nm. The quantum yield was calculated to be  $(2.1 \pm 0.4) \times 10^{-4}$  mol/eins for  $0.15 \text{M}$  nitrite solution and  $(1.6 \pm 0.2) \times 10^{-4}$  mol/eins for  $0.06 \text{M}$  sodium nitrite. The decrease in the quantum yield with the change in concentration is not significant for these solutions. Further study of the value of the quantum yield with respect to concentration is necessary.

These values for the quantum yield are only one order of magnitude less than Treinin and Hayon's estimate.

A quantum yield much less than 1 indicates that the reaction does not go forward significantly. This is probably because of the efficient back reactions proposed by Holmes<sup>13</sup>. The reason this reaction can be detected is the large absorbance by PNP. Concentrations as low as  $5 \times 10^{-7} \text{M}$  can be detected by UV/Vis spectroscopy. This value for the quantum yield is a lower limit since the formation of phenol, which also absorbs near PNP, would increase the estimate of the moles of products. Phenol has a lower molar absorptivity which means that its concentration would be larger than that of a PNP solution with the same absorbance.

It has been proposed by Jacob and coworkers<sup>22</sup> that oxygen is required in the mechanism of hydroxyl radical scavenging by benzene (see equations 46-49). In their reactions, the hydroxyl radical source was hydrogen peroxide. The need for oxygen in nitrite ion photolysis was evaluated by photolysis of oxygen and nitrogen saturated solutions (figure 16). Qualitatively, the results indicate that oxygen is required. The oxygen saturated solution turned a light yellow upon photolysis, while the nitrogen saturated solution remained colorless. The oxygen solution has a shoulder at about 282nm, which is approximately where PNP absorbs under basic conditions. The nitrogen saturated solution has a very clear peak at 292nm. This could be phenol since it is colorless in aqueous solution and absorbs between 280 and 300nm. If phenol is present, this would contradict the

mechanism of Jacob *et al.*, because very little, if any, oxygen would have been present in the solution. It could also indicate that there is a second mechanism for hydroxyl radical scavenging that is not oxygen dependent.

In aqueous solution there is always both nitrous acid and nitrite ion present due to the acid base equilibrium. In order to separate the relative contributions of each species, nonaqueous solvents were used to isolate the acid and base forms.

Nitrous acid was extracted in benzene from water. Since benzene is a nonpolar solvent, nitrite ion is not soluble in it. Attempts at dissolving sodium nitrite in benzene showed no change in the UV spectrum of the benzene. The partition coefficient for nitrous acid in benzene and water was determined to be  $0.33 \pm 0.03$ , indicating it favors the aqueous phase. Upon extraction of the nitrous acid, the benzene layer turns yellow. This yellow color is due to dissolved  $\text{NO}_2(\text{g})$ , a decomposition product of HONO in aqueous solution. The spectrum of HONO in benzene shows the presence of  $\text{NO}_2(\text{g})$  at 282nm. This was determined by bubbling nitrogen dioxide into benzene. The benzene instantly turned a bright yellow and the solution had to be diluted to be measured spectroscopically. The concentration of nitrogen dioxide is dependent on pressure. When left exposed to the air, the solution slowly lightened in color, whereas a separate aliquot of the same solution did not change significantly when left capped for the same length of time. The spectrum of HONO in benzene has the characteristic "fingers" at approximately the same wavelengths as in aqueous solution. However, the fingers slope upward, probably due to the presence of the

nitrogen dioxide.

By monitoring the concentration of nitrous acid in benzene with respect to time, it was determined that nitrous acid does thermally decompose in benzene. The decrease in absorbance is not due solely to the escape of nitrogen dioxide because the fingers begin to lose resolution with time. For a decomposition reaction of the form



The rate of decomposition is assumed to be of the form

$$R = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n \quad (67)$$

which rearranges to give

$$[A]^{-n} d[A] = -akdt \quad (68)$$

Integration of equation 68 from  $[A_0]$  to  $[A]$  and from 0 to  $t$  gives:

$$[A]^{1-n} - [A_0]^{1-n} = -(1-n)akt \quad (69)$$

Then a linear fit to the data is obtained by plotting

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}} = (n-1)(akt) \quad (70)$$

A plot of the decomposition of HONO data using equation 70 with  $n=2$  gave the best linear fit. The correlation coefficient for the linear regression of the data was 0.996. The slope of the line is equal to  $a \cdot k$ , as shown in equation 70. Assuming  $a=2$ , the value of the rate constant for the reaction at 25°C is  $0.50 \pm 0.02 \text{ M}^{-1} \text{ min}^{-1}$ .



Previous work by Exstrom<sup>17</sup> showed that the thermal decomposition of nitrous acid in water has an order with respect to [HONO] of  $0.5 \pm 0.5$ . This does not overlap with the estimated value of the order in benzene, indicating the mechanism for the decomposition is different. The three proposed mechanisms for the aqueous system (equations 5-13) all include the hydrolysis of dinitrogen tetroxide as the final step. This step is not possible in the benzene system since the amount of water present is very small. It was not determined whether  $\text{NO}_2(\text{g})$  was formed in the decomposition reaction in benzene. The  $\text{NO}_2(\text{g})$  present initially is from the extraction;  $\text{NO}_2(\text{g})$  is formed in the aqueous layer and becomes trapped in the benzene layer before they are separated. One way to determine if  $\text{NO}_2(\text{g})$  is formed from the decomposition of HONO in benzene would be to perform the extraction, bubble out as much  $\text{NO}_2(\text{g})$  as possible and then seal the container to determine if more is formed. The second order decomposition of HONO in benzene may be a result of the dehydration of nitrous acid, equation 3. Of the aqueous thermal reactions of nitrous acid, equations 2-4, this is the only one which is apparently bimolecular and likely to be second order with respect to HONO.

The photolysis of nitrous acid in benzene resulted in a yellow solution. This yellow color did not fade with time, indicating that it was not nitrogen dioxide gas. An extraction with water of the benzene photolysis was done at pH = 1, 7, 12. Both the pH 1 and 7 extractions yielded a visually equal concentration of yellow product in both layers. Mixing the benzene photolysate with an aqueous

solution at pH=12 preferentially extracted the yellow product into the aqueous layer. The extraction noticeably began before all of the water was added to the benzene aliquot. The UV/Vis spectrum of the aqueous layer clearly showed the presence of PNP. Additionally the color and spectrum of the aqueous layer was pH dependent. It was not possible to determine if phenol was also formed in the photolysis. The concentrations of PNP and phenol cannot be mutually determined by UV/Vis spectroscopy because of peak overlap in this region. Phenol, PNP, and  $\text{NO}_2(\text{g})$  all absorb between 280 and 300 nm in benzene. It was also determined qualitatively that the photochemical destruction of HONO does go forward at low temperatures. In several of the early reactions, the benzene, which has a melting point of  $5.5^\circ\text{C}$ , froze to the cold finger. In these "frozen" reactions, the reaction seemed to go forward as well. Attempts were made to photolytically make "yellow snow", by photolyzing nitrous acid in a solid benzene matrix. However, it was difficult to consistently freeze the benzene due to heating from the lamps.

An estimate of the quantum yield of HONO in benzene has not been made at this time. Two factors must be taken into account in determining the quantum yield. One is the destruction of HONO by thermal reactions. To do this the products of the thermal reactions must first be determined. A second factor is the formation of  $\text{NO}_2(\text{g})$ , which is soluble in benzene. Before photolysis, this gas should be bubbled out of the solution so that the initial spectrum does not include its absorbance. Also, since phenol and PNP absorb in the same region (280-300nm), the removal of  $\text{NO}_2(\text{g})$  would allow for better determination of the

amount of products formed.

To isolate nitrite ion from its conjugate acid, sodium nitrite was dissolved in two polar, aprotic solvents, DMF and DMSO. Both solutions were photolyzed in the presence of benzene scavenger. After about 2 hours of photolysis, the DMF solution was a creamy yellow color. The UV/Vis spectrum of the photolyzed solution showed a shoulder off the benzene peak from 280-310nm. The increase in the nitrite peak indicates that products may absorb where the nitrite ion does. Pure DMF does not react photochemically at 366nm;  $\text{NO}_2^-$  may react photochemically in DMF without the scavenger, but the results are uncertain.

In DMSO with benzene scavenger, nitrite also reacts photochemically. The photolyzed solution was clear, but there was a noticeable decrease in nitrite spectroscopically. There was not a separate product peak, however the benzene peak at 263nm increased with photolysis time and broadened. Phenol is colorless in DMSO and has a 40nm wide peak centered at 280nm. Therefore, it seems likely that the product of this photochemical reaction is phenol.

The quantum yield was calculated from the disappearance of nitrite and determined to be  $0.018 \pm 0.003$  mol/eins. This is two orders of magnitude larger than the quantum yield of nitrite ion in water. This is expected because the back reactions that are believed to lessen the quantum yield involve water to reform nitrite. Since there is very little water present, these reactions cannot occur. The most likely mechanism for the reformation of nitrite would be the recombination

of the NO and O<sup>•</sup> radicals. Additionally, the photochemical reaction in DMSO is believed to involve the formation of phenol, not PNP. It is believed that the formation of PNP involves two nitrite or nitrous acid molecules, whereas the formation of phenol may only involve one nitrite ion. It is possible that the aqueous quantum yield may increase when a more exact determination of the products is possible. It is likely that in the aqueous system, phenol is formed before PNP, but because it is masked by PNP in UV/Vis spectroscopy its concentration cannot be determined.

Although DMSO is known to scavenge hydroxyl radicals, no attempts have yet been made to analyze the expected products of such a reaction, methane and ethane.<sup>25</sup> This ability to scavenge hydroxyl radicals may complicate the mechanism of the photochemical decomposition of nitrite. Nitrite forms NO and O<sup>•</sup> (equation 24), which must escape from the solvent cage in order to react with the benzene present. Assuming that nitrite forms hydroxyl radical without the presence of water, the DMSO solvent may react with the hydroxyl radical before it recombines with NO or reacts with benzene. This scavenging by the solvent may significantly increase the overall rate of photochemical reaction by decreasing the amount of back reaction. A similar situation exists with the nitrous acid photolysis in benzene. In this system, the solvent is also the scavenger. Instead of the hydroxyl radical having to escape the solvent cage to react it may simply have to hit the cage.

## FUTURE RESEARCH

This work has raised several questions which have not yet been answered. The main difficulty with the work is the quantitative determination of the products formed. Ultraviolet/visible spectroscopy is not very useful for quantifying these reactions because of the extensive peak overlap between 270 and 300nm. The best method to resolve this problem seems to be chromatographic methods. For the nonaqueous solutions, the solutions can be injected right onto the column. For the aqueous reactions though, it may be necessary to develop an extraction method because basic solutions destroy columns.

Once a method for analyzing the reactions is developed, better values for the quantum yields can be determined. The current values are estimates based on assumptions that either all the product formed is p-nitrosophenol or that the decrease in nitrite is equal to the formation of product. This latter assumption is probably the more accurate of the two.

Chromatographic techniques should also be able to identify the products of the reaction of nitrite in DMF and DMSO. It appears that only phenol is formed in these reactions when benzene is present. This is interesting because in aqueous solution it appears that PNP is the main product of the reaction, suggesting a different mechanism for the two photochemical reactions. Additionally, the mechanism for the formation of hydroxyl radicals from nitrite ion, equations 24-25, shows that water must be present for nitrite ion to form hydroxyl radicals. There is very little water present in the organic solvents used, indicating that there

must be another mechanism for the formation of hydroxyl radicals. From the values of the quantum yields obtained here, this other mechanism is more efficient; any back reactions to form nitrite do not contribute as greatly to the overall reaction.

Additional work is necessary to determine the role dissolved oxygen plays in the reactions. The mechanism for scavenging hydroxyl radicals by benzene indicates oxygen is necessary for the formation of phenol. However, the solution saturated with nitrogen appeared to form a colorless product which could not be identified with current techniques. This may indicate an alternative mechanism in the absence of oxygen. The literature indicates that DMSO is also a hydroxyl scavenger. If chromatographic techniques can be developed to detect the presence of methane in a DMSO solution, then this reaction would be interesting to explore. The quantum yield is expected to be higher since the radicals formed do not have to search for a scavenger because the solvent would be the scavenger. It should also be possible to form nitrous acid in DMSO by combining equal molar amounts of nitrite ion and concentrated sulfuric acid in DMSO. Since sulfuric acid is only 2% water, the acid base equilibrium would be negligible. A direct comparison of the acid and base photochemical reactions, isolated from each other, might then be possible. The reactions in DMF may also be compared similarly.

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