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Photochemical and Thermal Reactions of Nitrous Acid in a Benzene Matrix

Ethan Schrum
Chemistry 499, 1998-99
Senior Research Honors Thesis
Advisor: Dr. Timothy Rettich

Abstract

The photodegradation of nitrous acid in the troposphere is an initiation step in the formation of photochemical smog. NO_x emissions from internal combustion engines react with atmospheric water vapor during sundown hours to form nitrous acid. Daytime sunlight cleaves nitrous acid into OH and NO radicals, which attack hydrocarbons emitted by industry to form the constituents of photochemical smog. In order to increase our understanding of these reactions, we have studied them in the liquid phase. Aqueous nitrous acid was extracted into a liquid benzene matrix to form a clear solution of approximately 0.075 M nitrous acid in benzene, which was irradiated at 366 nm. The photolysis generated a yellow liquid phase and a dark red precipitate. The liquid phase products identified by GC-MS are: *p*-benzoquinone; phenol; nitrobenzene; *o*-, *m*-, and *p*-nitrophenol; 1,3- and 1,4-dinitrobenzene; 2,4-dinitrophenol; biphenyl; and 3- and 4-nitrobiphenyl. Both photochemical and thermal reactions appear to be responsible for the formation of these products. Changes in the product abundances are observed over several hours of irradiation with the sharpest changes occurring in the first hour. Reaction pathways are proposed for all products, and potential mechanisms are discussed. The red precipitate is insoluble in benzene and ether but soluble in water, methanol and acetone. ¹³C-NMR spectroscopy has been inconclusive in identification of the red precipitate.

Introduction

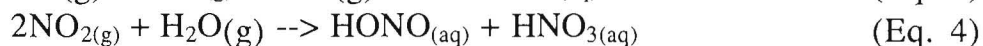
Nitrous acid (HONO) has major environmental importance because of the key role it plays in the chemistry of the troposphere, where the majority of airborne pollutants accumulate. Polluted air masses are characterized by high concentrations of oxidized nitrogen compounds¹, commonly emitted from internal combustion engines. At the high temperatures required by these engines, atmospheric nitrogen and oxygen combine to form nitric oxide (NO).



NO rapidly converts to nitrogen dioxide (NO₂) in the presence of atmospheric oxygen. Collectively, NO and NO₂ are referred to as NO_x.



Park and Lee² propose that NO₂ in turn combines with water vapor to form nitrous acid and nitric acid (HNO₃). The latter falls back to Earth as a major component of acid rain.



Direct formation of nitrous acid is not efficient enough to account for the concentration levels observed in the polluted air of the planetary boundary layer (PBL) of the troposphere³, where it builds up during the night. Ammann et. al. propose that soot-catalyzed production of nitrous acid from NO₂ in the presence of water accounts for the difference¹.



This reaction is presented as a net reaction without explicitly stating the elementary steps, where red_{ads} and ox_{ads} are reduced and oxidized sites, respectively, on the surface of soot particles. The

¹Ammann, M.; Kalberer, M.; Jost, D.T.; Tobler, L.; Rossler, E.; Piguet, D.; Gaggeler, H.W.; Baltensperger, U. *Nature* **1998**, 395, 157.

²Park, J.; Lee, T. *J. Phys Chem* **1988**, 92, 6294.

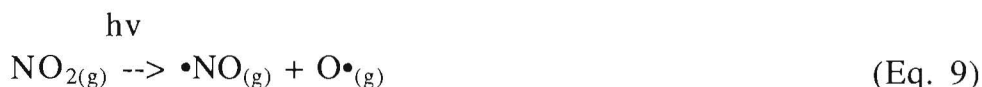
³Lammel, G.; Cape, J.N. *Chem. Soc. Rev.* **1996**, 361.

reducing groups are thought to be C-O and C-H groups in the soot. The results were obtained using NO₂ labeled with ¹³N, and suspended soot particles. The probability of an NO₂ collision with a soot surface was found to be 3.3×10^{-4} , much greater than the probability of 3×10^{-9} observed for other surfaces. The rate of nitrous acid production was found to be steady over a humidity range from 0.5 to 60 %.

When the sun comes up, it photolyzes the nitrous acid, breaking it apart according to the following gas-phase reaction proposed by Cox and Atkins⁴.



When no scavenger is present, hydroxyl ($\bullet\text{OH}$) and nitroxyl ($\bullet\text{NO}$) radicals will recombine to form nitrous acid. However, this scenario is rare. Finlayson-Pitts and Pitts⁵ propose that NO radicals combine with atmospheric oxygen as follows.



Ozone (Eq. 10), while beneficial in the stratosphere because it absorbs ultraviolet radiation, is harmful in the troposphere because it is a strong oxidizer.

The hydroxyl radical is highly reactive and the most aggressive oxidant in the natural environment⁶. Volatile organic compounds and hydrocarbons emitted from factories and other pollution sources combine with hydroxyl radicals to form a variety of harmful secondary products which are major contributors to photochemical smog, a form of air pollution first discovered in Los Angeles in the 1940's. Hydroxyl radicals are difficult to monitor because they are

⁴Cox, R.A.; Atkins, D.H. *U.K. At. Energy Res. Estab. Rep.* **1973**, AER-R7615 as cited in 1.

⁵Finlayson-Pitts, B.J.; Pitts, J.N. *Science* **1997**, 278, 1776 as cited in 10.

⁶Bilski, P.; Chignell, C.F.; Szychinski, J.; Borkowski, A.; Olesky, E.; Reszka, K. *J. Am. Chem. Soc.* **1992**, 114, 549.

unstable in solution and absorb below 200 nm in the UV. Therefore they cannot be monitored with UV-Vis spectroscopy. The only way to track production of the hydroxyl radical is to analyze the products of its reactions with scavengers.

Fisher and Warneck⁷ have shown that hydroxyl radicals in aqueous solution react with benzene scavengers to form phenol. It is postulated that the hydroxyl radical first reacts with benzene to form phenol, which then undergoes a known thermal reaction with additional nitrous acid to form *p*-nitrosophenol.



The hydroxyl radicals were produced by the photolysis of nitrous acid or nitrite. Nitrous acid is produced by the stoichiometric addition of aqueous sulfuric acid to an aqueous sodium nitrite solution, and nitrite ion is produced by the acid-base equilibrium:



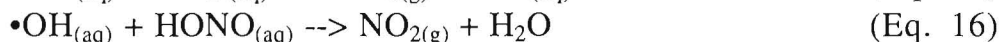
$$K_a = 7.1 \times 10^{-4}, \text{p}K_a = 3.15 \quad (\text{Eq. 14})$$

Fischer and Warneck measured the extinction coefficients for aqueous HNO_2 at 357 and 371 nm as 4.07 and 4.26 $\text{m}^2 \text{mol}^{-1}$, respectively. Those numbers are in approximate agreement with previous work by Alif and Boule⁸, who found the coefficients to be 4.8 and 5.0 $\text{m}^2 \text{mol}^{-1}$ at 358 and 371 nm. The solutions of NO_2^- and 0.0005 M HNO_2 in 0.008 M benzene-saturated water were photolyzed at 274 K at various wavelengths from 280 to 390 nm. They reported a quantum yield (Φ) of 0.35 for $\bullet\text{OH}$ production from nitrous acid at pH 2, about five times greater than $\Phi(\bullet\text{OH})$ from NO_2^- , showing that nitrous acid is a far more efficient source than NO_2^- of $\bullet\text{OH}$ per photon. The quantum yield was constant over the wavelength range. The rate constant for phenol formation was close to the upper limit given by diffusive transport for $\bullet\text{OH}$ and benzene, suggesting that the quantum yield for $\bullet\text{OH}$ should be just slightly higher than that

⁷Fischer, M.; Warneck, P. *J. Phys. Chem.* **1996**, *100*, 18749-18756.

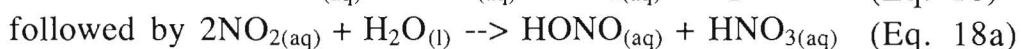
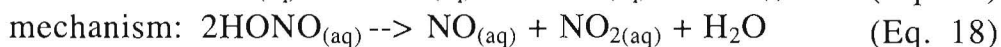
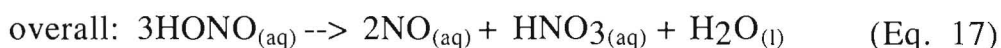
⁸Alif, A.; Boule, P.J. *Photochem. Photobiol.* **1991**, *A59*, 357.

for phenol. The quantum yields are not equal because some of the $\bullet\text{OH}$ reacts with nitrous acid or nitrite before reaching benzene.

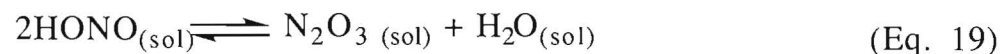


In addition to phenol, the other primary photolysis product was nitrate, detected by anion chromatography. The quantum yield for nitrate was comparable to that for phenol, suggesting that NO radical as a primary product is largely oxidized to nitrate. After one hour the nitrate concentration was about 25% of the original nitrous acid concentration. The ratio of p-nitrosophenol:phenol rose from 0 to 0.055 after one hour, suggesting that p-nitrosophenol is a secondary product.

In addition to its photochemical destruction, nitrous acid thermally decomposes as follows in aqueous solutions, according to Park and Lee²:



Montemartini⁹ found that the decomposition was first order at low concentration, and that the rate was affected by temperature and ionic strength. Nitrous acid is also in equilibrium with its anhydride, N_2O_3 . The anhydride dissociates to NO and NO_2 gases.



Although many studies of the thermal and photochemical reactions of nitrous acid have been done in aqueous solution, there are some limitations to that study. It is difficult to achieve a high concentration of organic scavengers in water. In addition, the nitrite ion, with which nitrous acid is in equilibrium in aqueous solution (Eq. 14)¹⁰, is also photolyzed to hydroxyl radical, obscuring the contribution from nitrous acid alone. To eliminate these problems, we have made solutions of nitrous acid in benzene by mixing benzene

⁹Montemartini, D. *Acc. Lincei. Roma [IV]*, **1890**, 6, 263, as cited in 10.

with the aqueous acid. When the solution separates, some of the molecular nitrous acid should be extracted into the benzene layer, but all of the nitrite ion should stay in the aqueous layer since charged species scarcely exist in benzene. In addition to allowing us to focus on molecular nitrous acid, the use of the benzene matrix gives us a huge concentration of scavengers. No thermal decomposition mechanism of nitrous acid in benzene has been published, but it is likely similar to the mechanism in water.

Villavicencio¹⁰ was the first to study the photolysis of nitrous acid extracted directly into benzene. UV-Vis data showed that nitrous acid was indeed extracted into benzene to an appreciable amount. HPLC analysis indicated that there were possibly 5-6 species in the photolysate; however, none of these could be identified conclusively. We have separated the photolysate into two phases and used GC-MS to identify 12 products in the liquid phase. On the basis of the data from this study, reaction pathways have been proposed for all products and mechanisms for the formation of some of the products have also been proposed. These are displayed in Scheme 1.

Experimental

Procedure

Beakers containing two portions (200 mL each) of distilled water were placed in an ice bath to cool. Into a 1000 mL separatory funnel, 200 mL of benzene (Fisher Scientific, purified grade, MW=78.11 g/mol) was placed. The funnel was placed in an ice/water bath. Into a 600 mL beaker 9.48 g of NaNO₂ (Merck, 97% pure, MW=69.005 g/mol) were weighed and one of the portions of cold water was added. Into a 50 mL beaker 6.72 g of concentrated H₂SO₄ (Fisher Scientific, 18 M) were weighed. The acid was poured into the other 200 mL of water. Some of the diluted acid was poured back into the 50 mL beaker then back to the 200 mL beaker to rinse the remaining acid from the 50 mL beaker. The NaNO₂ and H₂SO₄ solutions were mixed in a 600 mL beaker to produce 0.343 M nitrous acid. Out of this solution, 5 mL was transferred to a 50 mL volumetric flask containing pre-chilled water. The flask was then filled to volume with more water. A UV-Vis spectrum of the resulting solution was recorded to analytically determine the concentration of nitrous acid. The remaining nitrous acid solution was

¹⁰Villavicencio, Ovette. *Photochemical Reactions of Molecular Nitrous Acid in Benzene*. Senior Honors Thesis, Dept. of Chemistry, Illinois Wesleyan University, 1998.

added to the benzene in the separatory funnel and shaken vigorously for approximately 1 minute. The mixture was allowed to separate. The upper (benzene) layer was greenish blue and the lower (aqueous) layer was cloudy. Approximately 300 mL of the aqueous layer was released from the funnel. Of this portion, 5 mL were transferred into a 50 mL volumetric flask containing pre-chilled water. The flask was then filled to volume with more water. A UV-Vis spectrum of the resulting solution was recorded. The remaining mixture in the separatory funnel was then "heart cut." The remaining approximately 100 mL of aqueous layer and about 40 mL of organic layer were collected. The center portion of organic layer, about 130 mL, was then collected. It was analyzed by UV-Vis; the remainder (125 mL) was placed in a quartz tube and irradiated in a Rayonet reactor, model #RPR-100, which used 14 mercury lamps banded at 366 (+/- 1) nm. Before some reactions, dissolved gases were removed by sparging, a process which funnels nitrogen gas through very fine frits at the end of a glass rod. The rod was placed at the bottom of the reaction tube for 5 minutes. During the reaction, the sparger was held just above the reactant mixture to maintain a nitrogen atmosphere. The time of irradiation varied between 5 minutes and 100 hours, during which a precipitate formed. The resulting liquid layer was decanted and the tube thoroughly washed with benzene; the precipitate was then dissolved in either methanol (Fisher Scientific, 99.9%, certified ACS, acetone free, MW=32.04), acetone (Fisher Scientific, histological grade, MW=58.08), or distilled water.

Instrumental

UV-visible spectra were measured on a Varian Cary 1 UV-Vis spectrophotometer using quartz cells of 1.000 cm path length. Fluorescence spectra were measured using a Perkin-Elmer LS 50 Fluorometer, also using quartz cells of 1.000 cm path length. HPLC data were measured on Waters HPLC equipment with M6000A and M45 pumps, a μ -Bondapak C18 column (30 cm long, 10 μ m particles) and a 254 nm UV detector. The eluent was a thrice filtered 80/20 water/methanol solution containing 1.5 g/L potassium hydrogen tartrate, flowing at 2.0 mL/min. The detector setting varied from 0.01 to 2.0; the chart recorder's standard setting was 1 in./min. and 10 mV. All aqueous solutions were syringe filtered with an HA filter and all methanol solutions with an FH filter before injection. All injections were 20 μ L. FTIR data were recorded on a Matteson Genesis Series FTIR. Samples were prepared in KBr pellets or on KBr plates. GC-MS data were collected on an HP 6890 GC-MS with an HP-

5 crosslinked 5% phenyl methyl siloxane column (30 m long, 32 mm i.d., 0.25 μm thick film, phase ratio = 320). Liquid photolysates were injected directly as the benzene solution. The solid photolysate was dissolved in water, acetone or methanol for analysis. All injections were 5 μL ; the syringe was washed with the solvent and the sample twice each and debubbled before each injection. Oven temperatures were varied between 60 and 200 $^{\circ}\text{C}$ and run times ranged from 20 to 60 minutes. The standard run was a 23 minute overall run ramped as follows: 60 $^{\circ}\text{C}$ for 10 minutes; 60-117 $^{\circ}\text{C}$ at 19 $^{\circ}\text{C}/\text{min}$; 117-122 $^{\circ}\text{C}$ at 0.5 $^{\circ}\text{C}/\text{min}$. ^1H and ^{13}C NMR spectra were obtained on a 270 MHz JEOL FT-NMR spectrophotometer, and samples were dissolved in acetone- d_6 .

Results

Characterization of reactants

Colorless aqueous solutions of 0.685 M sodium nitrite and 0.343 M sulfuric acid were mixed to form a colorless, effervescent, 0.343 M solution of HONO. The UV-Vis spectrum of HONO shows a fingerprint pattern consisting of four peaks near 386, 371, 358 and 346 (± 1) nm. The average molar absorptivities of the four peaks over multiple trials were respectively 2.39, 4.35, 4.30, and 3.22 $\text{m}^2\text{mol}^{-1}$. These values compare favorably with the numbers reported by Fischer and Warneck⁷. Small amounts of a brown gas were evolved in the production of nitrous acid. This gas was likely NO_2 from decomposed N_2O_3 , according to Eq. 19-21. When the nitrous acid solution was shaken vigorously with 200 mL cold benzene in a separatory funnel, aqueous and organic layers were formed and larger amounts of brown NO_2 gas were evolved. UV-Vis analysis of the layers showed that each contained nitrous acid (Fig 1). The cloudy, colorless aqueous layer on the bottom, which effervesced and evolved brown gas when released from the funnel, had an average nitrous acid concentration of 0.292 M. The benzene layer on top had a light blue-green color, probably due to the presence N_2O_3 (Eq. 19).

The nitrous acid concentration of the benzene layer was estimated in two ways. In the first method, a theoretical prediction was made based on the amount of nitrous acid lost by the aqueous phase upon extraction. Using this method, the average nitrous acid concentration in benzene was 0.104 M. The second method was direct calculation from UV-Vis data using Beer's law and assuming the same extinction coefficients for HONO as in aqueous solution,

which gave an average concentration of 0.045 M. The data are probably unreliable because the absorption of benzene interferes somewhat with the nitrous acid spectrum. The benzene layer was also analyzed by GC-MS; no peaks other than benzene were seen. No nitrous acid peaks were observed because the detection limit was set at a mass higher than that of nitrous acid.

Characterization of thermolysate

The nitrous acid in benzene solution reacts under various conditions. When the solution stands at room temperature, it becomes colorless because N_2O_3 diffuses out as gas (Eq. 20). GC-MS analysis (Fig. 2) of the solution after two weeks of standing in the quartz tube and two weeks standing in a sealed bottle determined that the product composition in benzene was 51% nitrobenzene, 25% *o*-nitrophenol, 20% 1,3-dinitrobenzene, 2% biphenyl, and 1% 1,4-dinitrobenzene. The red precipitate was not observed. After analysis, this solution was irradiated for 8.45 hours. After 0.83 hour, all of the products increased in overall abundance and 2,4-dinitrophenol appeared in the solution. Notably, nitrobenzene dipped to 36% of the product while *o*-nitrophenol increased to 38% of the product. At the 8.45 hour mark all of the abundances increased several times over their 0.83 hour levels. The percentage of nitrobenzene continued to drop to 17%, the percentage of 2,4-dinitrophenol increased dramatically to 27%, and the percentage of *o*-nitrophenol returned almost to its pre-irradiation level at 27%.

Characterization of photolysate

The nitrous acid in benzene solution was also irradiated immediately after its production, for various lengths of time. The resulting product was a yellow liquid with a red precipitate at the bottom of the tube. GC-MS analysis of the liquid layer identified 12 compounds dissolved in benzene. Figure 3, the GC of the photolysate after 24 hours of irradiation, shows twelve identifiable compounds. The product was 30% *o*-nitrophenol, 18% 2,4-dinitrophenol, 15% nitrobenzene, 10% biphenyl, 10% 1,3-dinitrobenzene, 4% *p*-nitrophenol, 4% *p*-benzoquinone, 4% 1,4-dinitrobenzene, 3% *m*-nitrophenol, 1% phenol, and had traces of 3- and 4-nitrobiphenyl. After 76 more hours of irradiation, there were a few major changes in the composition. Both *m*- and *p*-nitrophenol were no longer present, the amount of 2,4-dinitrophenol decreased by half as its percentage dropped to 11%, and the percentage of *o*-nitrophenol increased to 42%. It is inconsistent that 2,4-dinitrophenol, which other data suggest to be a terminal product, is decomposing. It was

the only compound out of the 12 to increase in total abundance. Some of the compounds may have been thermally or photochemically decomposed to the red precipitate, which is unidentified and difficult to quantify.

A number of experiments were carried out to test the room temperature reactions after irradiation was stopped. These tests were largely inconclusive due to the difficulty in obtaining reproducible GC-MS results from the same sample.

Characterization of Precipitate

The red precipitate is possibly an inorganic salt because it dissolves only in polar solvents (water, methanol, acetone) but not benzene or diethyl ether. ^{13}C NMR data that show no carbon peaks are consistent with an inorganic salt. A ^1H NMR spectrum of crystals dried for several weeks showed two singlets, one at 3.0 and one at 2.1, in a 1:2 ratio. A spectrum of the precipitate extracted directly from the reaction tube with acetone- d_6 had only the peak at 3.0. The peak at 3.0 may be the water peak, which has a standard appearance at 2.7 in acetone- d_6 . HPLC data have shown up to five peaks, but none have been identified. GC-MS analysis has shown peaks, but the only one that has been reproducible has been 2,6-*t*-butyl-*p*-cresol, which is inconsistent with the rest of the data. An IR spectrum of the red precipitate has not been successfully recorded.

Acidity of photolysates and thermolysates

The pH of the thermolysate, even after 30 days of standing, is between 1 and 2. Since nitrous acid is a weak acid in water and even weaker in benzene, it cannot generate this low of a pH, so there must be a stronger acid present. The most likely is nitric acid from the thermal dissociation of nitrous acid (Eq. 17). The UV-Vis spectrum of the thermolysate (Fig. 4) has a peak strongly resembling the peak of nitric acid in benzene at 283 nm. The other peak in the thermolysate spectrum near 350 nm matches closely the absorption peak for *o*-nitrophenol in water. The pH of four photolysates were measured one day after irradiation was stopped. The pH of a solution irradiated for five minutes was 1-2, suggesting that nitric acid was still present. The UV-Vis spectrum was almost identical to that of the 30 day thermolysate (Fig. 4), further confirming the presence of nitric acid. The pH of solutions irradiated for 30, 114, and 220 minutes were all between 5 and 6. These data suggest that the nitric acid supply is significantly diminished between 5 and 30 minutes of photolysis.

Short irradiation time studies

Photolysates were analyzed over a variety of shorter irradiation times. A non-sparged photolysate was analyzed hourly from 40 min. to 6 hours and 40 min. Product abundance is plotted against irradiation time in Figure 5. It shows that *o*-nitrophenol, 1,3-dinitrobenzene and *m*-nitrophenol all increase across the entire range of time. Phenol also increases at the short and long times of irradiation, but is steady from 1.67 to 3.67 hours. Nitrobenzene, biphenyl, *p*-benzoquinone and 1,4-dinitrobenzene increase sharply across the first 1.67 hours, then level off. After 0.67 hours 2,4-dinitrophenol is not present, and just a trace is present after 1.67 hours, but its abundance increases over 20 times by 2.67 hours and approximately linearly after that.

In order to study the critical first two hours of photolysis, where the total product abundance increases sharply, the photolysate of a sparged solution was analyzed about every 25 minutes starting 5 minutes after the lights were turned on. The abundance data from that study is presented in Fig. 6. Biphenyl, *m*-nitrophenol and 1,3-dinitrobenzene increase monotonically, consistent with their behavior from the longer experiment. Nitrobenzene and 1,4-dinitrobenzene increase for the first half hour and *o*-nitrophenol for the first hour, but all three then level off, which is inconsistent with their behavior in the longer, sparged experiment (Fig. 5) when *o*-nitrophenol increased monotonically and nitrobenzene increased until 1.67 hours. However, the leveling off of these three nitrated compounds is simultaneous with the increase of the pH of the photolysate from 2 to 6 and the disappearance of the nitric acid peak from the UV-Vis spectrum, signalling the disappearance of nitric acid, a probable nitrating agent, from the photolysate.

Effects of degassing

Another variable tested was varying the gases dissolved in the benzene solution. Prior to irradiation, a solution of nitrous acid in benzene was sparged five minutes with nitrogen gas, driving other gases out of solution. The solution turned colorless, which signaled the absence of N_2O_3 . During irradiation, the nitrogen sparger was held about 1 inch above the surface of the reaction mixture to create a nitrogen blanket on top of the solution. The sparged and non-sparged solutions were analyzed after similar irradiation times — 1.93 hours and 1.67 hours respectively. The results are shown in Table 1. The total amount of product formed decreased about 30% with sparging.

Among individual products, nitrobenzene and *o*-nitrophenol lost 40% and 58%, respectively, of their mass with sparging.

Photolysis after thermolysis

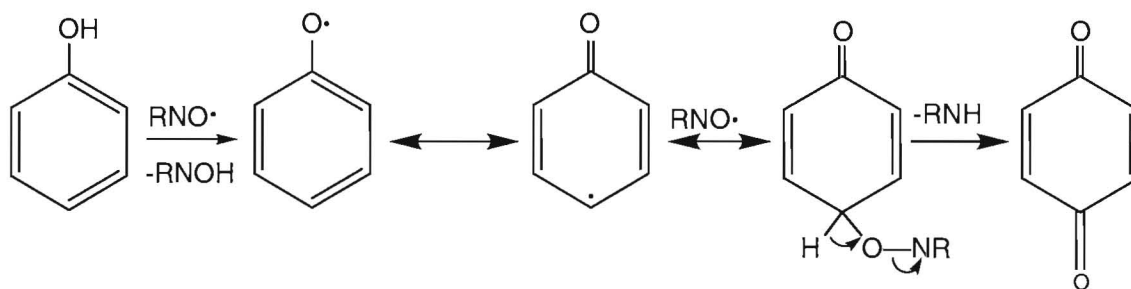
The thermolysate solution that had stood at room temperature for 30 days was irradiated for 8.45 hours. The results are shown in Table 4. The abundances of phenol and *p*-benzoquinone hold steady at zero after 50 minutes of irradiation, but increase after the full irradiation time. The abundance of biphenyl, another proposed product that comes from a hydroxyl radical pathway, increases dramatically after the 8.45 hour period. These data suggest that hydroxyl radical is being generated by the light. It is unlikely that there is any nitrous acid left because of thermal decomposition, so it is likely coming from another source.

Discussion

Products of radical reactions

OH radical attacks benzene to form the hydroxycyclohexadienyl radical¹¹ (Scheme 1). This radical can be converted to phenol, possibly via an unknown mechanism using oxygen gas and producing HO₂ radical⁷, or by abstraction of a hydrogen by another OH radical. The phenol can then be oxidized to *p*-benzoquinone, possibly through a hydroquinone intermediate. The abundances of phenol and *p*-benzoquinone are almost equal in the 2 hour (sparged) irradiation reaction, whereas *p*-benzoquinone was around an order of magnitude more abundant at all times in the 6.67 hour non-sparged irradiation (Fig. 5). These data strongly support the theory that dissolved oxygen is important in the oxidation of phenol to *p*-benzoquinone, since the sparging likely removed quantites of dissolved oxygen from the photolysate. An alternative mechanism for the direct conversion of phenol to *p*-benzoquinone using an NO radical is related by Nonhebel and Walton¹¹:

¹¹ Nonhebel, D.C.; Walton, J.C. *Free-radical Chemistry*. Cambridge: University Press, 1974.



Nitroxide radical abstracts the phenolic proton, creating a phenoxyl radical. That radical is resonance stabilized, which activates the para position for another nitroxide radical to attack. The electrons from the N-O bond transfer to the nitrogen atom, cleaving the N-O bond. The RN⁻ group abstracts H⁺ from the oxidized phenol, leaving *p*-benzoquinone. Although intriguing, this process is not consistent with the data, because no RNH compound is observed, unless it is a very small unidentified peak on the GC. The "R" group would be either an inorganic complex cation or an aromatic group attached to the nitrogen atom that abstracts a proton in the final step.

It appears that *p*-benzoquinone could be a product of a thermal reaction brought about by the heat of the lamps. A nitrous acid in benzene solution was made and left at room temperature for 27 days. It was analyzed by GC-MS and no *p*-benzoquinone was present. The solution was then irradiated. After 0.08 hr. and again after 0.83 hr., no *p*-benzoquinone was present. But after 8.45 hours of irradiation (overnight), *p*-benzoquinone had an abundance of 120 and made up about 2.5% of the total product. In another experiment where the nitrous acid/benzene solution was irradiated immediately after production, the *p*-benzoquinone abundance was 43 after 0.67 hr. By 1.67 hours, the abundance had gone up almost six times, to 240, and varied between that value and 350 for the next 11 hours of irradiation. Thus the bulk of *p*-benzoquinone production occurred between 0.67 and 1.67 hours. The temperature at 0 hours of irradiation is 25°C and the temperature after 6 hours of irradiation is 42°C, so the temperature range between 0.83 and 1.67 hours should be significantly smaller than that. It appears that at some point within that regime, the reaction that produces *p*-benzoquinone acquires sufficient activation energy and proceeds to completion. Alternatively, the activation at a longer reaction time could indicate that significant oxygen has entered the reaction mixture. Since the production of *p*-benzoquinone levels off after less than two hours but the amount of red precipitate produced continues to increase for

many hours, the reaction that produces *p*-benzoquinone is unlikely simultaneously to produce the red precipitate.

Biphenyl and *o*-nitrophenol are present in the 25 °C nonirradiative reaction. If the formation of those compounds requires a hydroxycyclohexadienyl radical (Scheme 1), then nitrous acid in benzene must dissociate thermally at room temperature to hydroxyl radical. This has not been observed in aqueous solution. If such dissociation does occur, it is apparently to a very small extent.

The abundance of biphenyl in the non-irradiative reaction (Table 2) is 11 times smaller than in a similar photoreaction after five minutes of irradiation, 56 times smaller than after 30 minutes of irradiation, and 440 times smaller than after 24 hours of irradiation. The reduction in biphenyl abundance would be expected to be even more drastic than the decline in OH radical production, because 2 hydroxycyclohexadienyl radicals must combine to form one biphenyl (Scheme 1). It could also be possible that an unknown alternative pathway to biphenyl is followed in the absence of light (i.e., when hydroxyl radical is not produced.)

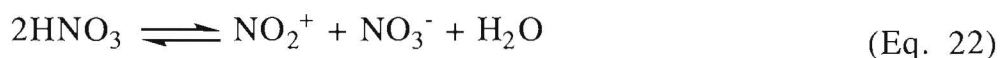
In contrast to biphenyl, *o*-nitrophenol is almost twice as abundant after 30 days of standing at 25 °C than after 5 minutes of irradiation. After 30 minutes of irradiation, though, the irradiated product is almost three times as abundant, and after 24 hours it is 96 times more abundant. These results provide evidence that the nitration of phenol proceeds by both thermal and photochemical pathways. The presence of *o*-nitrophenol in the non-irradiated solution is further evidence that hydroxyl radical is generated thermally to a small extent.

The absence of 2,4-dinitrophenol during the first 1.4 hours of irradiation suggests that it is not a primary photochemical product. The huge jump in abundance between the 1.67 and 2.67 hour marks suggests that the reaction which gives 2,4-dinitrophenol as a product is activated at a certain temperature in that region, if it is continually increasing from the heat of the lamps. The linear increase in abundance for 2,4-dinitrophenol after the 2.67 hour mark suggests that the reaction could be zero order in the reactants, with the rate equalling the rate constant.

Nitration

It is interesting that only nitro-substituted compounds and no nitroso-substituted products were formed. It is possible that the benzene matrix in our study is responsible for prohibiting nitrosation. The accepted mechanism of nitrosation requires protonation of the OH oxygen by H^+ . It is unlikely that H^+ exists in

any sizeable quantity in benzene solution. Thus, the water leaving group and therefore the nitrosonium ion, which benzene attacks in an electrophilic substitution reaction, may not be able to form. Another possible reason for the lack of nitrosated compounds is immediate oxidation to nitro compounds. Since there is a large abundance of nitrated compounds in the photolysates and thermolysates and nitrous acid is the only source of nitrogen in the reaction, it is exceedingly likely that the nitrating process starts with nitrous acid. One scenario, if the nitrosonium ion can be produced in benzene, is a nitrosation of the benzene ring followed by extremely fast oxidation by nitric acid or dissolved O_2 . Nitric acid, which analysis by pH and UV-Vis suggest is almost certainly present, is likely produced by the thermal decomposition of nitrous acid (Eq. 17). It seems unlikely that this nitrosation/oxidation process would be able to nitrate benzene, because an activated ring such as phenol is usually needed to attack the nitrosonium ion¹². Fuson¹¹ states that a dilute solution of nitric acid in water or acetic acid only nitrates phenols if nitrous acid is present, via nitrosation followed by oxidation. Another possibility for nitration is the traditional nitronium ion route. This might occur if sulfuric acid was present due to non-stoichiometric production of nitrous acid that resulted in excess sulfuric acid. There is also a possibility of generating the nitronium ion with nitric acid alone¹³:



Only about 4% of the nitric acid is ionized in this manner, but enough NO_2^+ is formed for nitration. This equilibrium occurs to a small extent even in organic solvents¹³. However, it is uncertain if the nitric acid generated by the decomposition of nitrous acid is concentrated enough to achieve this equilibrium. A solution of 10 drops of concentrated nitric acid in 20 mL of benzene produced nitrobenzene only. Analysis was done by GC-MS 10 minutes after the sample was made. It is interesting to note that no dinitrobenzene was produced, suggesting a different route for its generation. This route could be direct attack of a photogenerated NO radical on the ortho-activated hydroxycyclohexadienyl radical, followed by oxidation by oxygen or nitric acid. It could also involve the NO radical becoming an NO_2 radical which attacks the nitrobenzene ring,

¹² March, Jerry. *Advanced Organic Chemistry, 4th edition*. New York: John Wiley and Sons, 1992.

¹³ Belson; Strachan. *J. Chem. Soc. Perkin Trans. 2* **1989**, 15 as cited in March.

followed by hydrogen abstraction. An NO_2 radical mechanism for the dinitration of olefins¹⁴ is cited in March¹³.

The drastic decline in abundance of the mononitrated products in the sparged photolysate from the higher levels in the non-sparged photolysate (Table 1) suggests that the production of some of the nitrating material, perhaps nitric acid, is influenced by the presence of N_2O_3 . If this is true, however, it is interesting that the amount of the two dinitrobenzenes increases. This observation is consistent, though, with the fact that a stock nitric acid in benzene solution thermally produces only nitrobenzene and not the dinitro compounds.

The ratio of 1,4- to 1,3-dinitrobenzene decreases sharply with increasing irradiation time (Fig 7). Data from both sparged and non-sparged solutions were plotted on the same graph because sparging seemed to have little effect on dinitrobenzene abundance (Table 1a). The changing ratio suggests that the two isomers are formed under different conditions. Table 3 shows that all of the 1,4-dinitrobenzene is formed by the end of the first hour and the abundance is relatively constant afterwards. If we believe that the nitrous acid is consumed by photolysis in the first hour, then the 1,4-dinitrobenzene is completely produced by photoreactions during that hour, since no more is produced afterward. This theory is supported by the absence of 1,4-dinitrobenzene from one room temperature non-irradiative reaction. Small peaks in two other thermolysates are possible artifacts. As irradiation time increases, 1,3-dinitrobenzene continues to increase in abundance. This could be a result of increasing temperature, however, it seems likely that the photolysate would have reached thermal equilibrium by the 7 hour mark. It is more likely that a nitrating agent is being continually liberated or regenerated over time.

In the production of nitrophenols, the reaction almost certainly involves the nitration of phenol rather than the hydroxylation of nitrobenzene. Nonhebel and Walton¹¹ report on work done by Norman^{15,16}, Radda and Jefcoate that showed the activity for nitrobenzene toward radical hydroxylation was over six times smaller than benzene. Their results also showed the product composition of OH radical addition to nitrobenzene was 24% ortho,

¹⁴ Shechter; Gardikes; Pagano. *J. Am. Chem. Soc.* **1959**, *81*, 5420; Shechter; Gardikes; Cantrell; Tiers. *J. Am. Chem. Soc.* **1967**, *89*, 3005.

¹⁵ Jefcoate, C.R.E.; Norman, R.O.C. *J. Chem. Soc. B.* **1968**, 48, as cited in 13.

¹⁶ Norman, R.O.C.; Radda, G.K. *Proc. Chem Soc.* **1932**, 138, as cited in 13.

30% meta, and 46% para. Since our primary product is the ortho isomer, it is unlikely that this mechanism is occurring.

The amounts of 3- and 4-nitrobiphenyl in the photolysate are almost always very close. This observation is inconsistent with theory, because the phenyl group as a benzene substituent is an ortho, para director. 4-nitrobiphenyl is predicted as the primary product, with a second nitration giving mostly 4,4'-dinitrobiphenyl and a smaller amount of 2,4-dinitrobiphenyl¹⁷.

Total Product Abundance

The combined abundance of all the products continually increases over time, although much more quickly initially — the combined abundance tripled between 0.67 and 1.67 hours, but did not quite double over five more hours. This increasing abundance suggests that there is a continual source of nitrating and hydroxylating agents. Nitrous acid is unlikely to be present during lengthier experiments because it is both thermally and photochemically decomposing. It has not been present in any UV-Vis spectrum of a photolysate, but even if it were present it may be obscured by the larger absorbances of the products. It is possible that the radicals are longer lived than the nitrous acid itself. Although the NO radical is quite stable¹⁶, the OH radical is highly reactive. But it is possible that all the OH radicals immediately attack benzene to form hydroxycyclohexadienyl radicals, which might be longer-lived. If phenol is formed only by the conversion of such a hydroxycyclohexadienyl radical, then hydroxycyclohexadienyl radicals must be present even after 6.67 hours because phenol is still increasing in abundance. The trend of increasing overall abundance stops at some longer irradiation time — a 24 hour irradiation showed a total product abundance an order of magnitude higher than the 6.67 hour photolysis, but 42 and 100 hour irradiations showed no change from the 24 hour abundance.

Conclusion

The irradiation of a solution of nitrous acid in benzene produces up to twelve identifiable products dissolved in the benzene: phenol, *p*-benzoquinone, biphenyl, 3- and 4-nitrobiphenyl, nitrobenzene, 1,3- and 1,4-dinitrobenzene, *o*-, *m*-, and *p*-nitrophenol, and 2,4-dinitrophenol. Both thermal and photochemical reactions appear to contribute to the products. In the absence of light, only nitrobenzene, *o*-nitrophenol, 1,3-dinitrobenzene and small amounts

of biphenyl and 1,4-dinitrobenzene form. We have proposed a scheme for the reaction. The first step in the formation of most of the products is attack on a benzene ring by an OH radical to form a hydroxycyclohexadienyl radical. That radical can either have a hydrogen abstracted by another OH radical to form phenol; be oxidized by OH radical followed by O₂ to form *p*-benzoquinone; or combine with another hydroxycyclohexadienyl radical and lose two water molecules to form biphenyl, which can then be nitrated. Phenol can be nitrated to one of three isomers; the ortho isomer can be nitrated again to form 2,4-dinitrophenol. The other first reaction for benzene is with nitric acid, which produces nitrobenzene. Nitrobenzene can then be nitrated to dinitrobenzene by an unknown process possibly involving the NO radical and possibly proceeding differently for the 1,3 and 1,4 isomers. The nitric acid nitrating agent is produced by the thermal decomposition of nitrous acid. The supply of nitric acid is high after 5 minutes of irradiation but diminished greatly after 30 min of irradiation, as evidenced by a change in pH from 2 to 6.

Future Work

Extensive further study needs to be done in order to unravel the mechanisms and confirm the pathways that produce the twelve photolysis products. All of the experiments discussed above need to be run again to make sure that the results are reproducible.

It is crucial to discern which products are being produced by thermal reaction and which are being produced by photolysis. A number of different experiments can be run. One is to keep the photolysate at a cold, constant temperature in order to minimize thermal decomposition of nitrous acid. Our reaction scheme predicts that nitrobenzene and thus the dinitrobenzenes will form minimally under these conditions, because the nitric acid nitrating agent is produced by thermal decomposition of nitrous acid. Another crucial experiment is to monitor the room temperature thermal reaction periodically, starting just after the nitrous acid in benzene solution is made. Thus far we have analyzed this reaction only after weeks of standing, so we know nothing about the short term products. It would also be instructive to monitor this reaction over time via UV-Vis spectroscopy to monitor the rate of thermal decomposition of nitrous acid in benzene, because it has never been published and we do not know how long the nitrous acid stays intact.

We also want to separate the effects of photon absorption from the effects of heat generated by the ultraviolet lamps. One way to do

this would be to simulate the heating ramp created by the lights, which brings the solution to thermal equilibrium at 42 °C. A thermal reaction could be carried out, slowly increasing the temperature from 25 to 42 °C.

We would like to collect more data over a very short time interval just after irradiation begins. Very large jumps in abundance have been recorded in the first 30 minutes of reaction, but with just two data points. It would be quite interesting to analyze the photolysate every minute. We are limited by the GC-MS capability, which allows us to run a sample only every 25 minutes with our current setup. However, if thermal reactions are slow enough, we can take a sample every minute and then hold the sample in an ice bath for later analysis.

We want to study the effects of mass transfer on the composition of the solution. Since we use such a large reaction vessel, different parts of the solution may have a different composition, and we have a bit of evidence to support that. The 1 inch diameter of the reaction tube makes it likely that the solution in the center of the tube does not experience as high of a photon flux, so it would be instructive to use a tube with a much smaller diameter to see if the product composition changes. The distance from top to bottom of the tube is far greater than from side to side; thus there may be even more difference in the composition from top to bottom. Starting with just a very small amount of reactant solution in the bottom of the tube would be a proper test of that possibility. Stirring the normal size reaction mixture would also be a good experiment. In all of these techniques, it would be interesting to see if the precipitate, which normally falls to the bottom of the tube, still appears.

Further investigations of the nitrating mechanism need to be undertaken. The first experiment would be to prepare a reactant solution deliberately stoichiometrically deficient in sulfuric acid, in order to ensure that the solution we have been making does not have excess sulfuric acid due to some experimental error. If we saw a lower concentration of nitrated compounds after using this technique, we could conclude that our previous experimental technique in producing nitrous acid was flawed and try for a new and better synthetic method. If there is no change in products, then varying the overall concentration of nitrous acid while still using stoichiometric amounts of sodium nitrite and sulfuric acid might provide interesting information concerning the amounts of nitrated products formed. Using reduced concentrations of nitrous acid might also be helpful in understanding the radical processes. If the concentration of hydroxyl and nitroxyl radicals was smaller, we

might be able to discern which processes take place via radical reaction. If two reactions compete for the same radical and their rates are a function of the number of radicals absorbed, determining which reaction occurs preferentially will be easier at low radical concentrations.

The use of a sparged reactant solution needs to be studied further. In the previous sparged experiment, a shorter than usual irradiation time was also used, so it was difficult to determine which changes came from sparging alone. Also, it would be beneficial to discern between the effect of removing N_2O_3 and the effect of removing O_2 . Since the blue color of N_2O_3 disappears after just a minute of sparging, the solution could then be quickly reoxidized by bubbling oxygen through before starting irradiation. Additionally, the importance of O_2 in the reactions could be investigated by bubbling it through the photolysate.

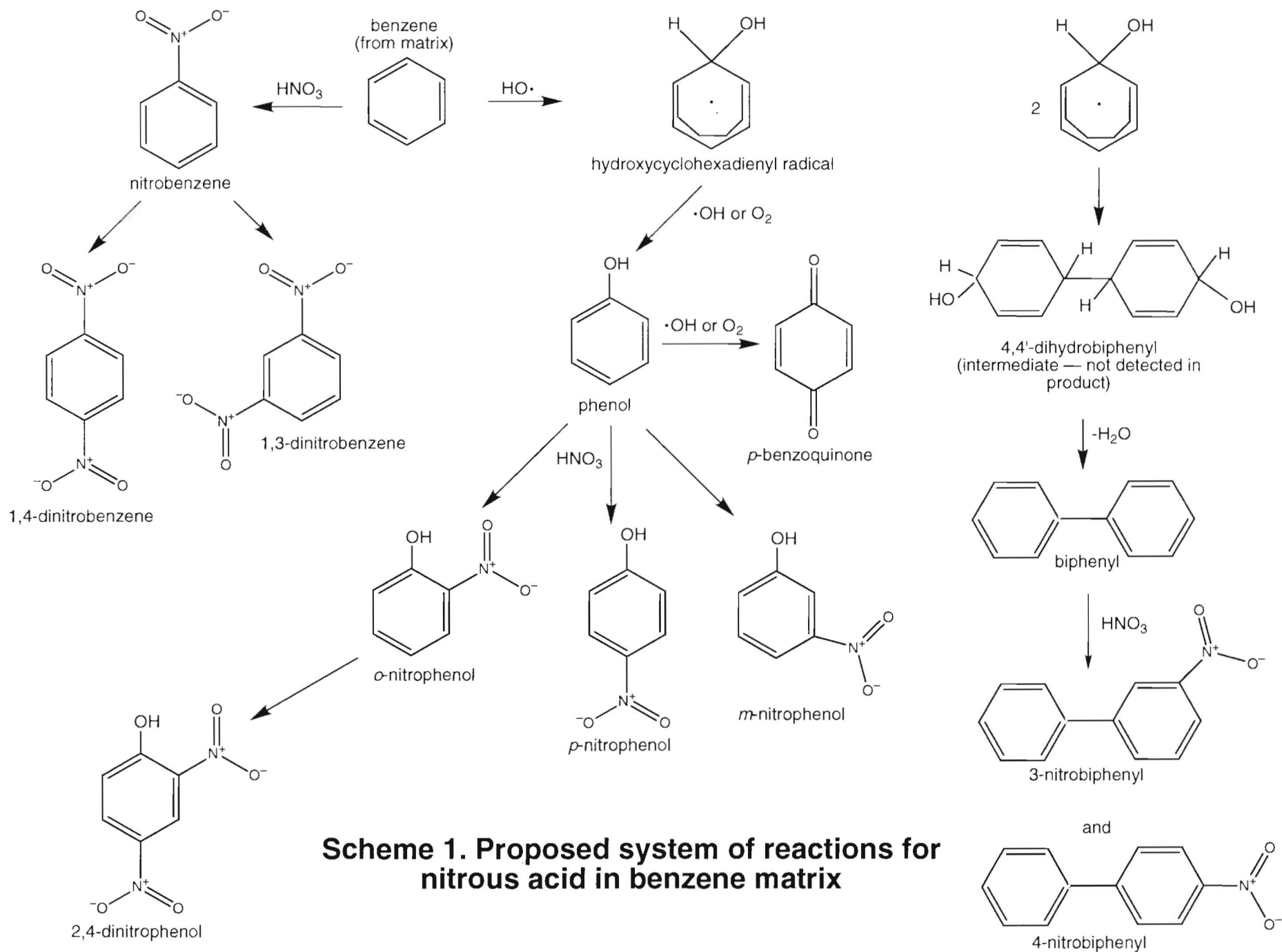
The GC-MS needs to be calibrated for the 12 photolysis products by injecting a benzene solution with known amounts of each compound and correlating the abundance reading on the GC with the concentration of the compound in solution. We could then use mass balance equations for nitrogen and oxygen to see if all of the nitrous acid is being integrated into the products, and if any molecular oxygen is involved.

The red precipitate needs much further investigation. It has been fairly difficult to reisolate the solid after dissolving it in a polar solvent to remove it from the reaction tube. The first priority is to obtain better crystals and obtain a melting point and a good IR spectrum. Confirmation of the previous NMR results by using a larger number of scans would be helpful as well. The flame test should be used to determine the presence or absence of sodium. We would also like to send the precipitate away for elemental analysis.

Optimally, the 12 photolysate products would each be isolated by column chromatography to conclusively prove their existence.

Acknowledgements

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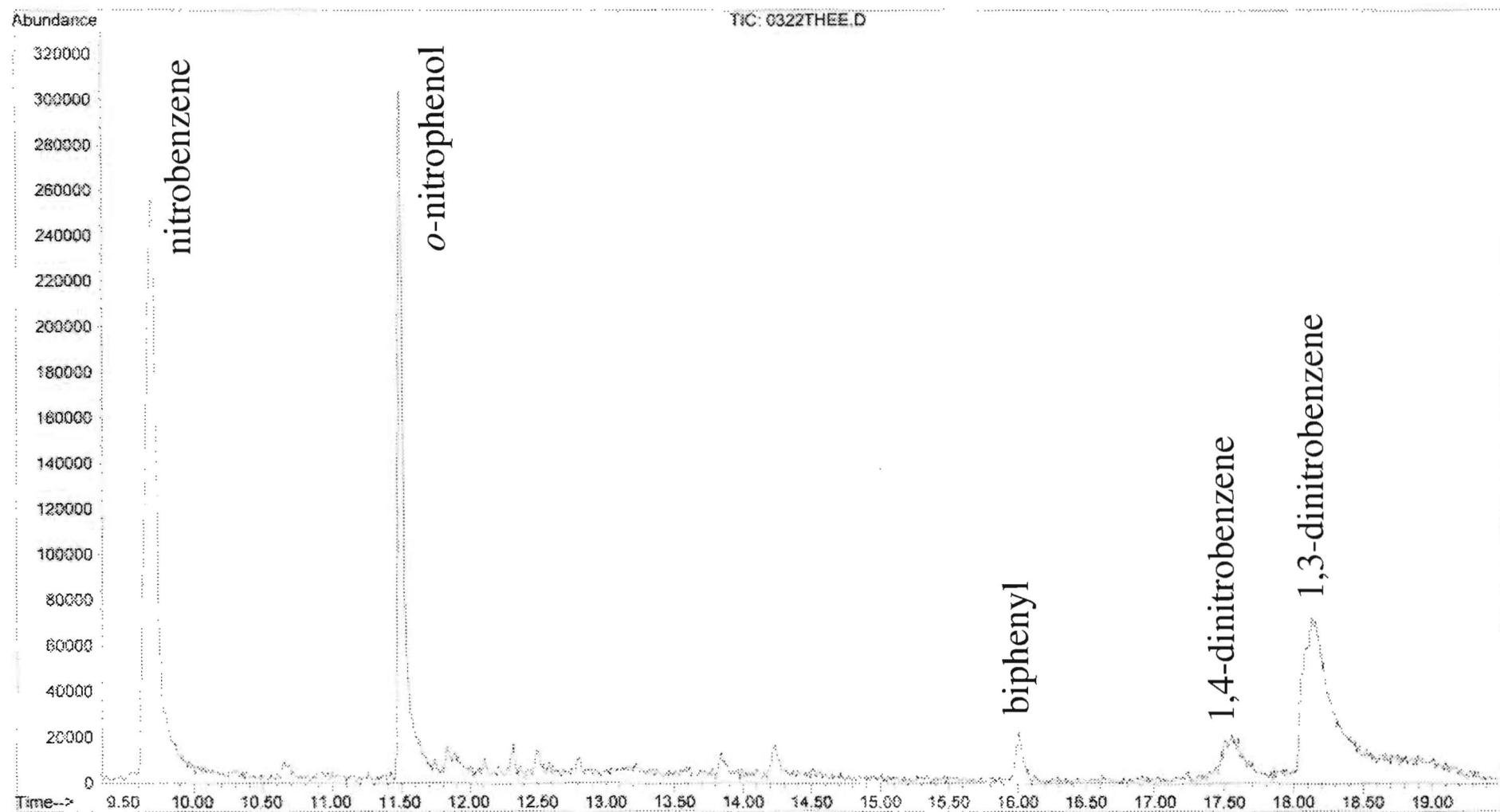


Figure 2. GC of 30 day room temperature thermolysate

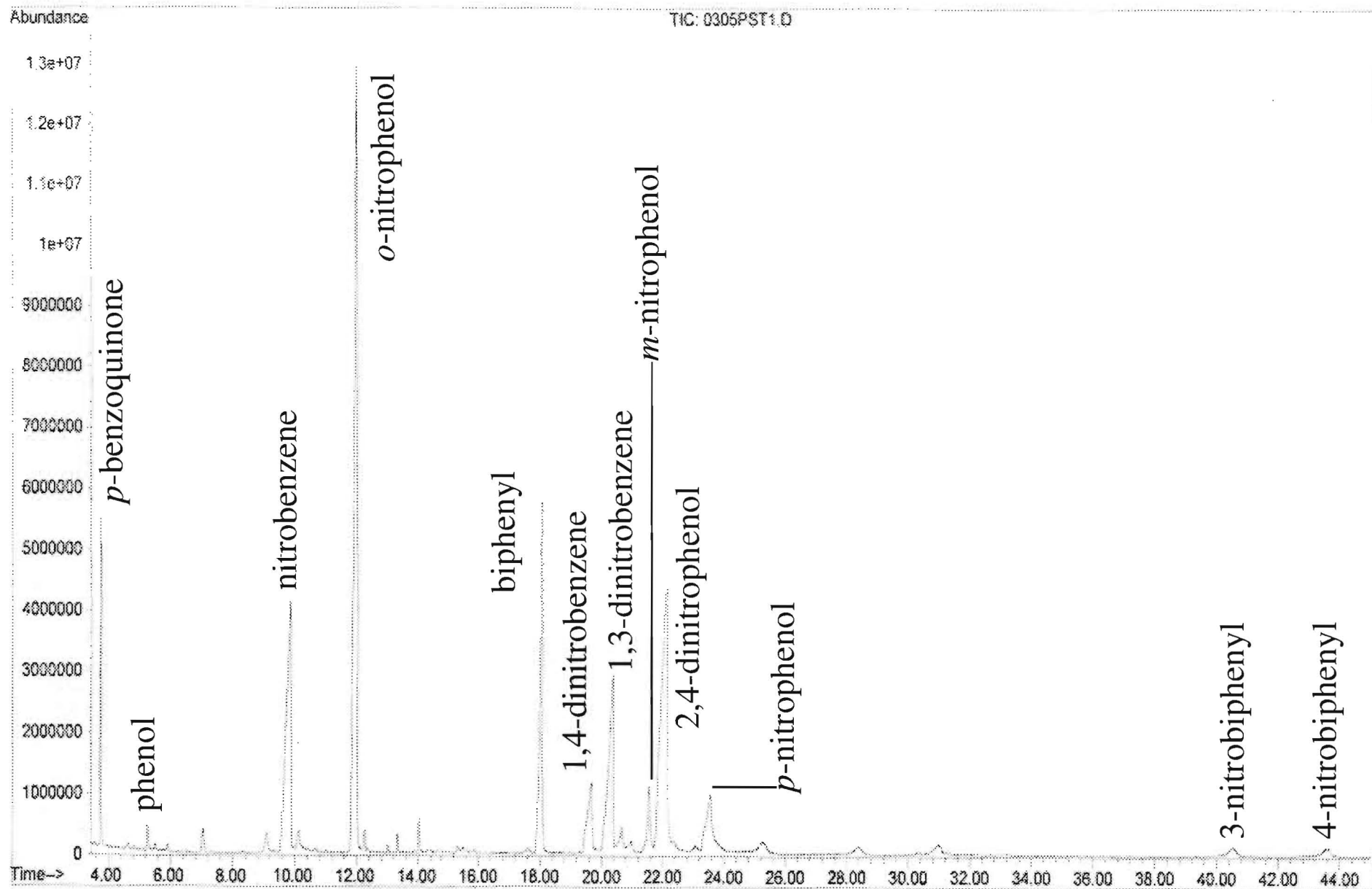


Figure 3. GC of 24 hour photolysate

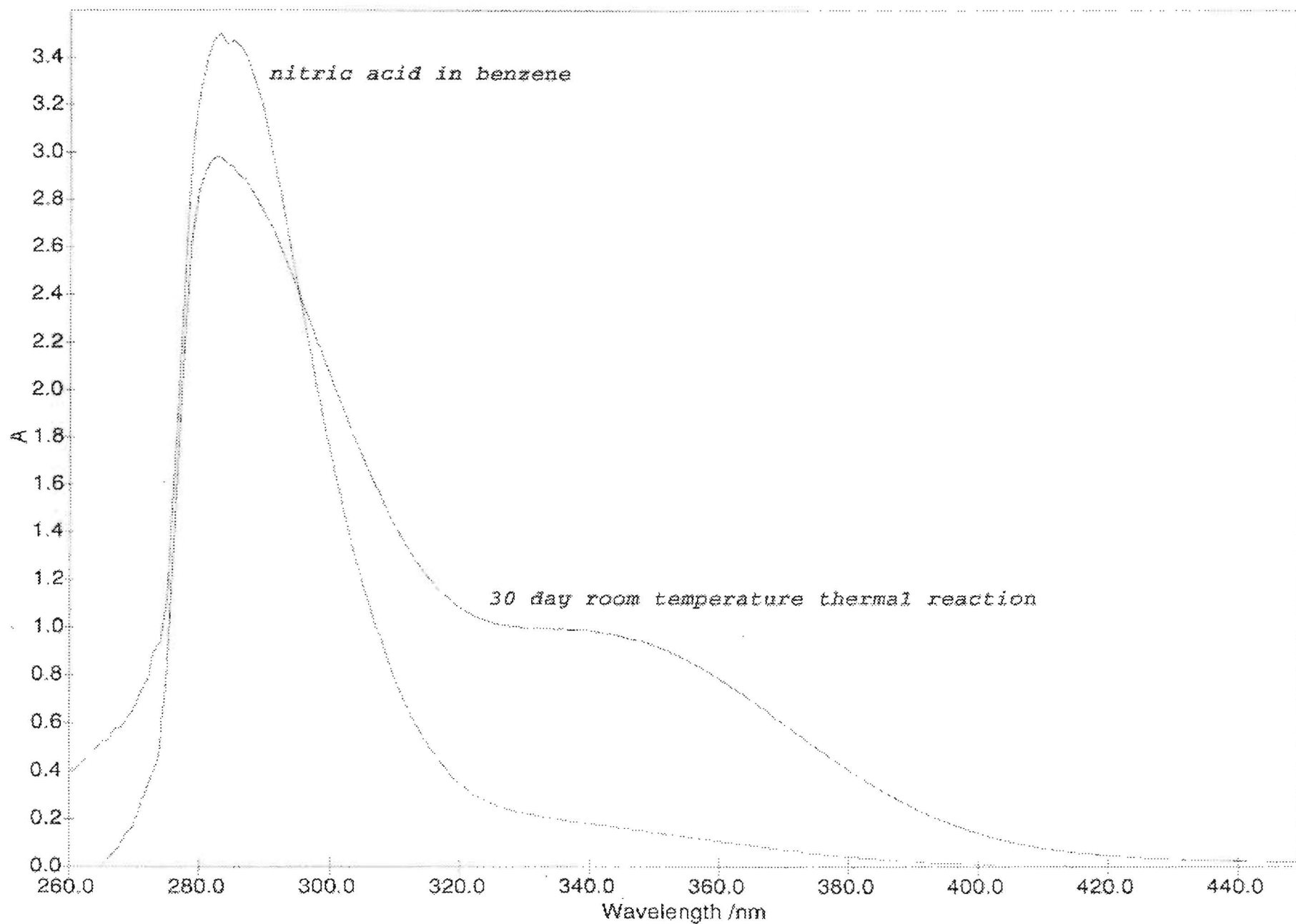


Figure 4. Absorption spectra of nitric acid solution in benzene and 30 day room temperature thermal reaction.

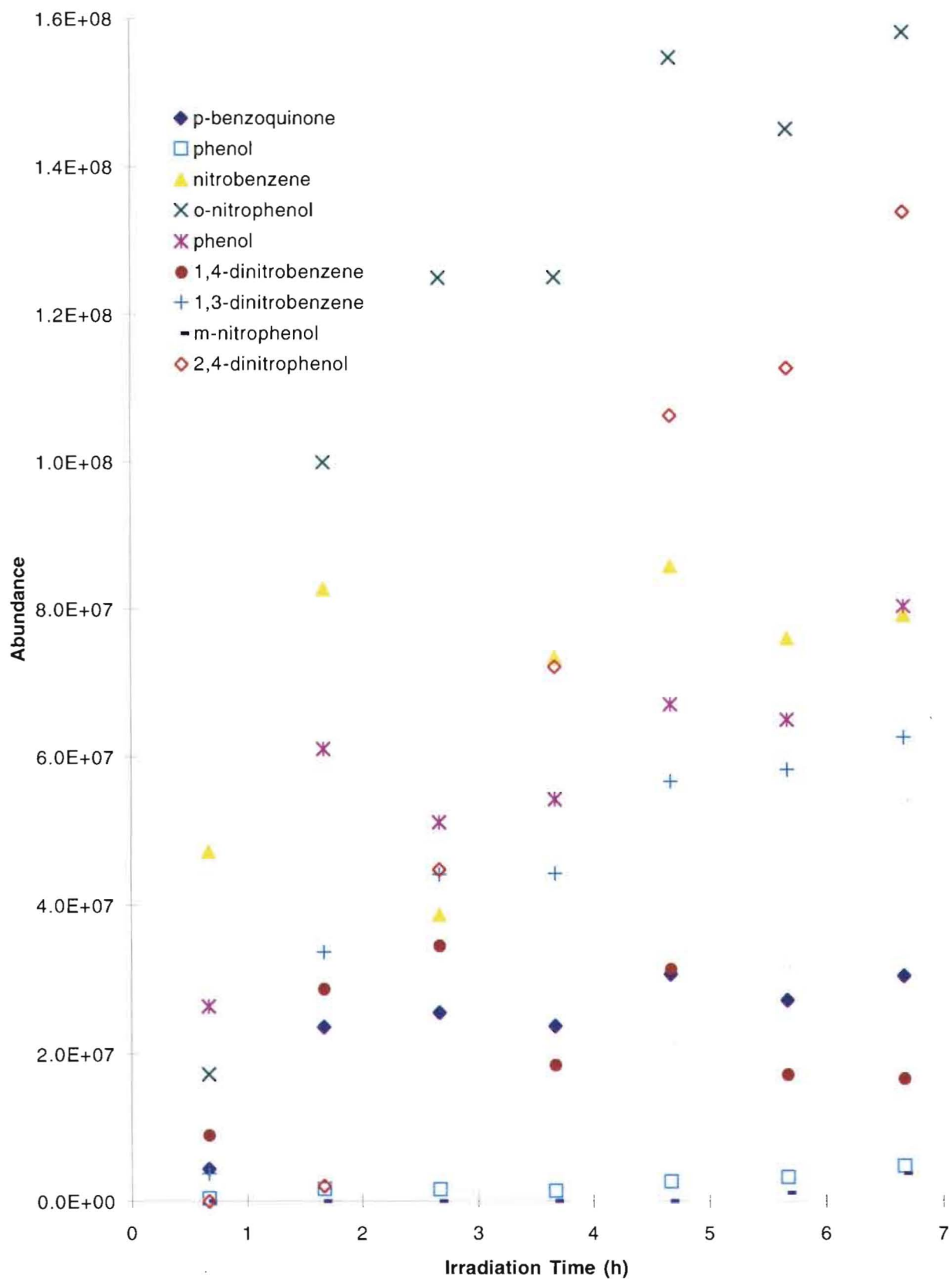


Figure 5. Product abundance vs. time for a 6.67 hour photoreaction

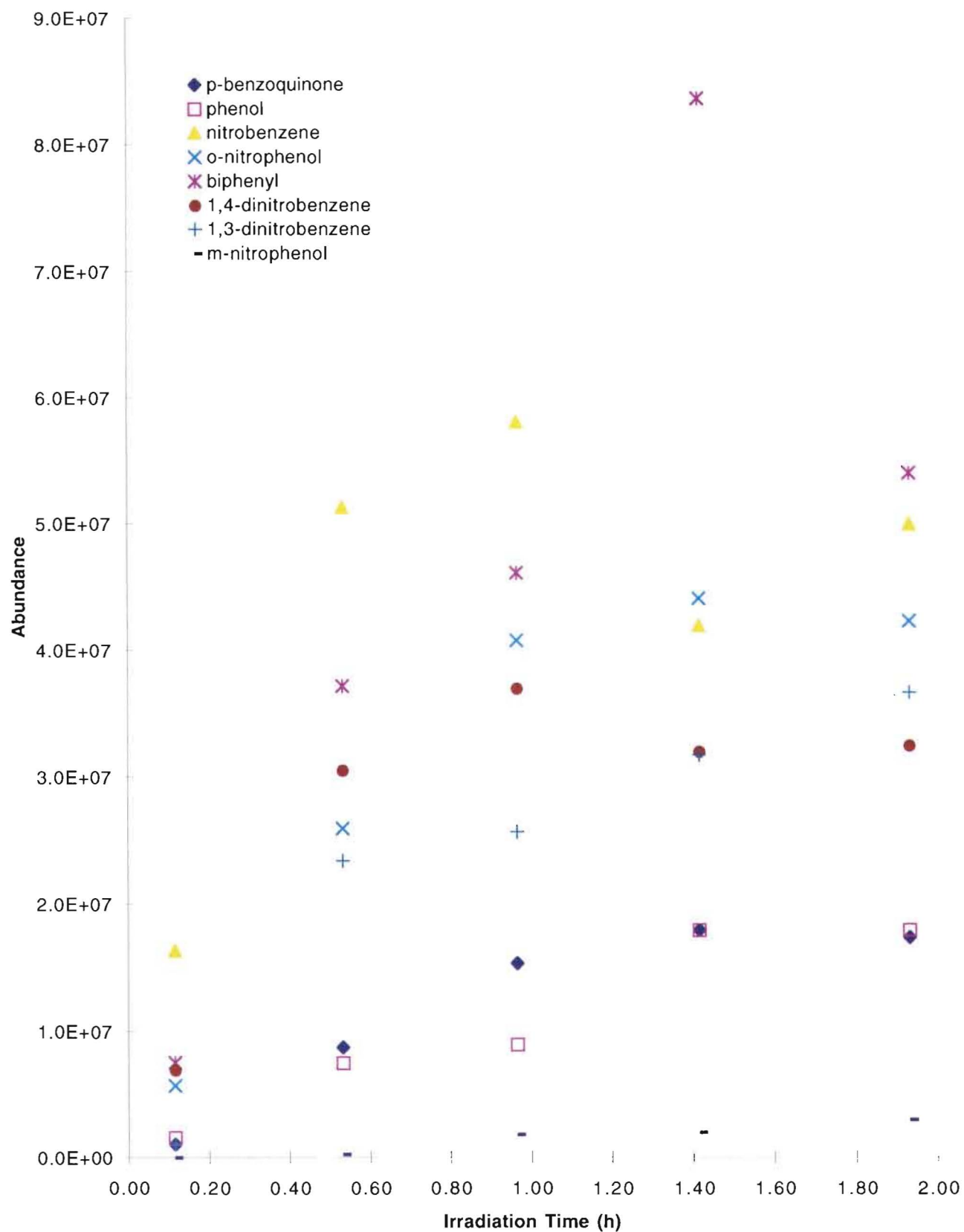


Figure 6. Product abundance vs. time for 2 hour pre-sparged photoreaction

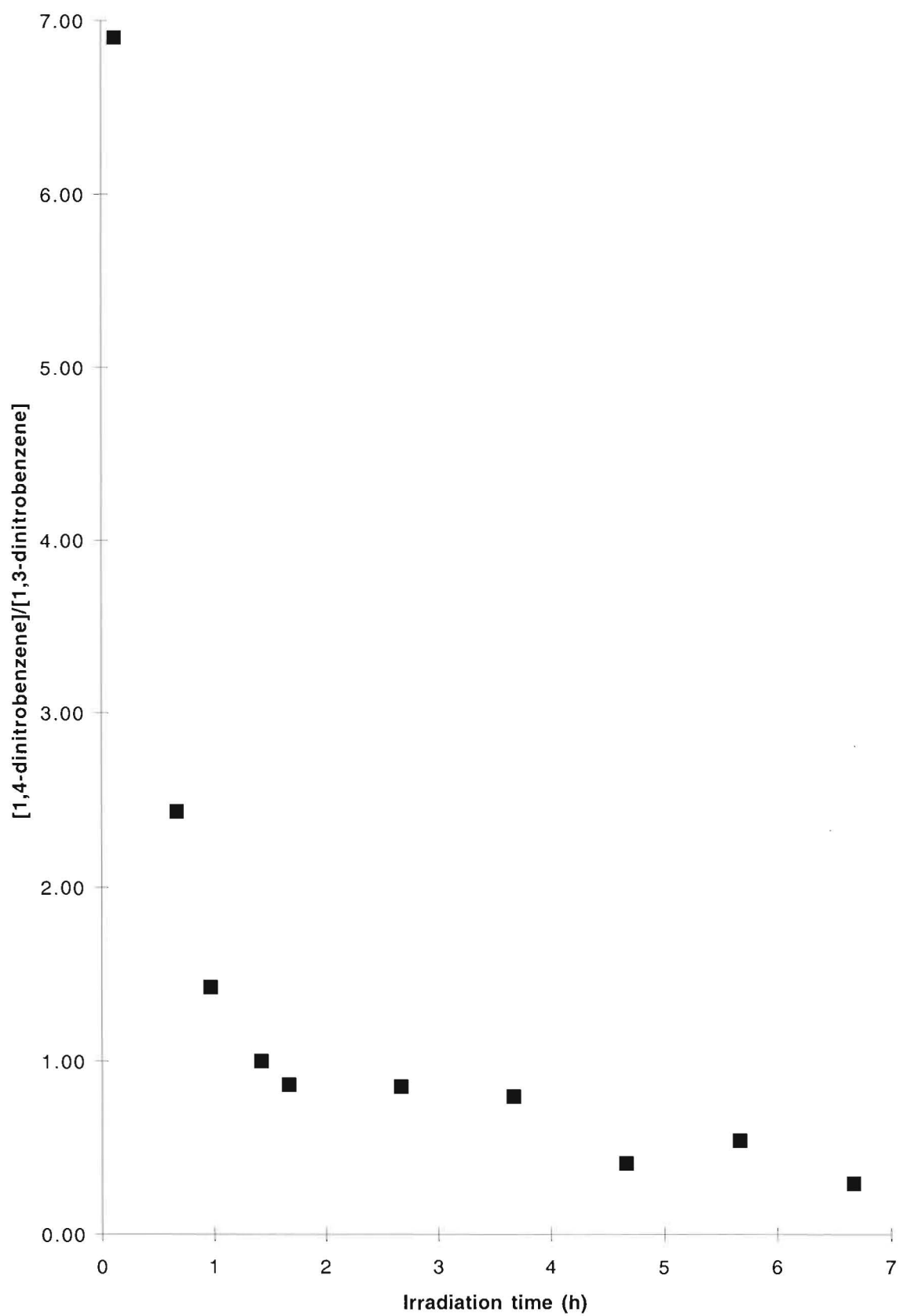


Figure 7. Ratio of 1,4- to 1,3-dinitrobenzene vs. irradiation time

Compound	sparged	non-sparged
<i>p</i> -benzoquinone	170	240
Phenol	180	16
Nitrobenzene	500	830
<i>o</i> -nitrophenol	420	1000
biphenyl	540	610
1,4-dinitrobenzene	320	290
1,3-dinitrobenzene	370	340
<i>m</i> -nitrophenol	30	21
2,4-dinitrophenol	0	0
<i>p</i> -nitrophenol	15	0

Table 1a. Abundance of products in different gaseous atmospheres

Compound	sparged	non-sparged
<i>p</i> -benzoquinone	7	7
Phenol	8	<1
Nitrobenzene	21	25
<i>o</i> -nitrophenol	18	30
biphenyl	23	18
1,4-dinitrobenzene	14	8
1,3-dinitrobenzene	16	10
<i>m</i> -nitrophenol	1	0
2,4-dinitrophenol	0	1
<i>p</i> -nitrophenol	<1	0

Table 1b. Percent composition of product mixture in different gaseous atmospheres

Comparison of thermal and photoreactions

compound	30 day thermal	5 min light		30 min light		24 hour light	
	abundance	abundance	ratio (photo/ther)	abundance	ratio (photo/ther)	abundance	ratio (photo/ther)
nitrobenzene	150	160	1.07	510	3.40	4300	28.67
<i>o</i> -nitrophenol	90	57	0.63	260	2.89	8600	95.56
biphenyl	6.6	75	11.36	370	56.06	2900	439.39
1,4-dinitrobenzene	5.7	69	12.11	31	5.44	1200	210.53
1,3-dinitrobenzene	46	10	0.22	27	0.59	2900	63.04

Table 2. Comparison of thermal vs. photoreactions

irradiation time (h)	1,4-DNB abundance	1,3-DNB abundance	ratio (1,4/1,3)
0.12	69	10	6.90
0.67	90	37	2.43
0.97	370	260	1.42
1.42	320	320	1.00
1.67	320	370	0.86
2.67	290	340	0.85
3.67	350	440	0.80
4.67	180	440	0.41
5.67	310	570	0.54
6.67	170	580	0.29
7.67	170	630	0.27

Table 3. Abundances of dinitrobenzenes after various irradiation times.

Compound	Irradiation Time (hr)		
	0	0.83	8.45
<i>p</i> -benzoquinone	0	0	120
Phenol	0	0	35
Nitrobenzene	200	310	820
<i>o</i> -nitrophenol	98	330	1300
biphenyl	7.6	34	270
1,4-dinitrobenzene	0	48	360
1,3-dinitrobenzene	76	140	600
2,4-dinitrophenol	0	5.2	1300

Table 4a. Abundance of products in photolysate of thermal (30 days at 25 °C) reaction mixture.

Compound	Irradiation Time (hr)		
	0	0.83	8.45
<i>p</i> -benzoquinone	0	0	2
Phenol	0	0	1
Nitrobenzene	51	36	17
<i>o</i> -nitrophenol	25	38	27
biphenyl	2	4	6
1,4-dinitrobenzene	1	5	8
1,3-dinitrobenzene	20	16	13
2,4-dinitrophenol	0	1	27

Table 4b. Percent composition of photolysate of thermal (30 days at 25 °C) reaction mixture.