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Nitrite Photochemistry in 2-Propanol/Water Solution

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Nitrite Photochemistry in 2-Propanol/Water Solution

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Dr. Timothy R. Rettich, Advisor

**Submitted in partial fulfillment of the requirements for
Research Honors**

Department of Chemistry
ILLINOIS WESLEYAN UNIVERSITY

April, 2004

Approval Page

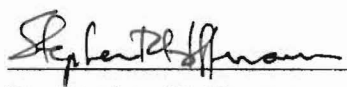
"Nitrite Photochemistry in 2-Propanol/Water Solution

by Joseph B. Binder

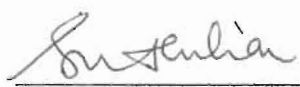
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Abstract

Nitrite ion, a component of nitrogen oxide pollution, is an important source of free radicals in the environment. NO_2^- absorbs ambient ultraviolet light to break into NO and O^- , and in environmental conditions, O^- is converted to hydroxyl radical, OH. Hydroxyl radical reacts with a wide variety of environmental pollutants, including hydrocarbons and nitrogen oxides, so its sources are of interest to environmental chemists. In order to investigate the processes of nitrite photochemistry, nitrite ion was photolyzed at 366 nm in 2-propanol/water solution. This mixed solvent system allows investigation of the effects of varying the solvent cage composition and scavenger concentration on the photolysis process and OH production in particular. A secondary goal was to follow nitrite ion and OH scavenging product concentrations simultaneously. OH radicals were scavenged by 2-propanol to form acetone, which was quantified by derivatization with 2,4-dinitrophenylhydrazine followed by HPLC detection. Acetone yields were compared to nitrite disappearance quantified by ultraviolet spectroscopy for nitrite ion photolyses in 96/4, 98/2, and 100/0 mass/mass 2-propanol/water solutions. Acetone was formed at a higher rate in the 100% 2-propanol solvent, suggesting a shift in mechanism at much lower water concentrations.

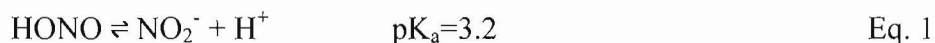
Introduction

Goals. Nitrite ion photolysis in water has been the focus of earlier work, but these studies all use scavenger concentrations much lower than the water concentration and measure either nitrite disappearance or OH scavenging product appearance, not both concurrently.^{1,14,15} Because nitrite is environmentally interesting for its aqueous photochemistry, it is reasonable to study nitrite photolysis mainly in water. Low scavenger concentrations, however, can limit the

observed production of hydroxyl radical. So, increasing scavenger concentrations may better allow the photolysis processes to be observed.

Published studies^{1,14,15} report that the photodecomposition of one nitrite ion produces one hydroxyl radical and that the hydroxyl radical is scavenged to form product(s) in 1:1 stoichiometry. But, with the focus of this project on unusual solvent systems for photolysis, it is conceivable that these expectations may not be followed. To check the expectations, both nitrite and scavenging product concentrations should be monitored and compared. As a result, this project has two main goals: first, to explore photolysis conditions in which the scavenger makes up the bulk of the solvent and, second, to devise means by which both scavenging product and nitrite ion concentrations can be measured.

Background. Nitrous acid and its conjugate base, nitrite ion,



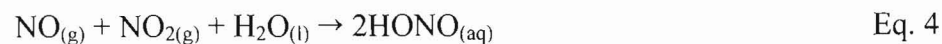
are among the few inorganic photoactive species present in the atmosphere and natural waters.^{1,2} NO_x species are often produced in internal combustion engines³ through the following high temperature reaction:



From nitric oxide, nitrogen dioxide is then rapidly generated:



These compounds are known to react with water to produce nitrous acid:^{4,25}



Nitrous acid and nitrite can absorb ultraviolet sunlight of the shortest wavelength region that is not filtered out by the ozone layer.^{3,4} Upon absorbing this high-energy light, N(III) oxides may break up, forming reactive free radicals, including the hydroxyl radical.³ Because these radicals can react with many different pollutants to modify or destroy them, the photolysis rates of various nitrogen oxides interest environmental chemists.

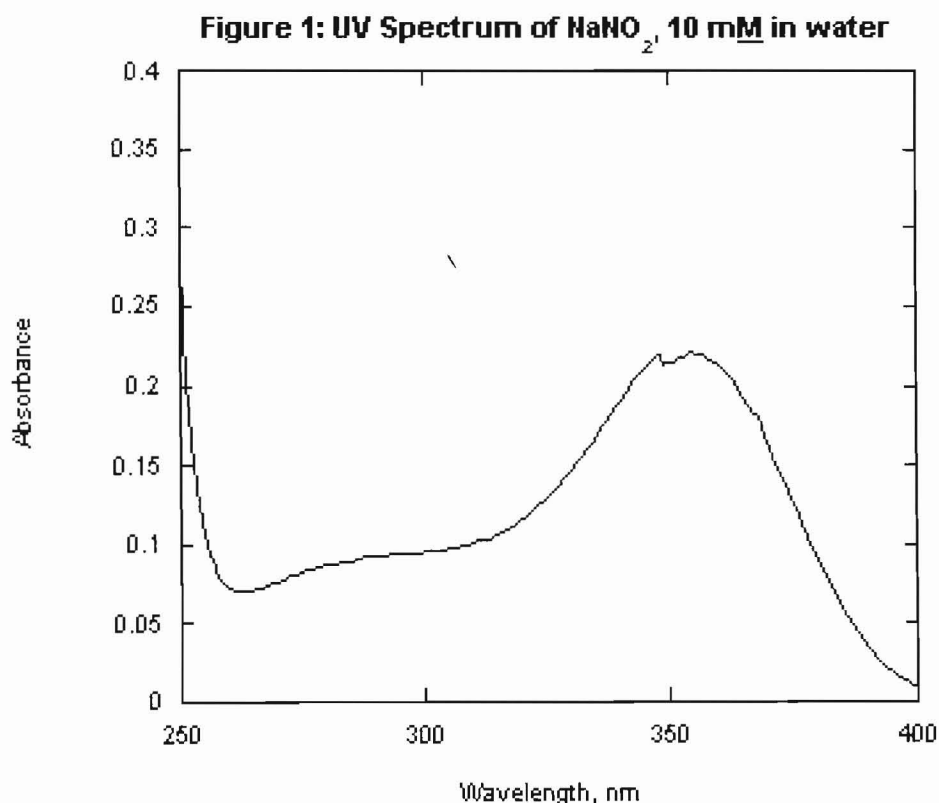
Because it reacts with many trace components of the atmosphere, including organics and NO_x , the hydroxyl radical is a key reactive species of the troposphere, the lowest zone of the atmosphere.⁵ Its concentration averages about 7.5×10^6 molecules/cm³ over land.⁵ OH determines the tropospheric lifetimes of many pollutants, including hydrocarbons and chlorofluorocarbons as well as NO_x . For example, isoprene reacts readily with OH, so this alkene's lifetime is only a few hours, while methane reacts more slowly and has a lifetime of almost ten years, allowing it to rise to the stratosphere, the next higher layer, and disrupt the ozone layer.⁶ Hydroxyl radical also catalyzes the formation of ozone in the troposphere, often through oxidation of organics, leading to the formation of photochemical smog.^{3,6} In this way, OH can be both detrimental and beneficial: it oxidizes pollutants to destroy them, yet the intermediates it generates in the process are pollutants themselves.

The atmospheric nitrous acid concentration typically parallels those of other NO_x pollutants, usually equaling that of nitric acid and about 5-10% of that of NO_2 .⁷ Measurements in Los Angeles, for instance, have revealed HONO at 14 ppb. Typical atmospheric HONO concentrations have been estimated to form hydroxyl radical at rates up to 3×10^7 molecules/cm³/s. (The density of molecules in the atmosphere is on the order of 10^{19} molecules/cm³.)⁷ Nitrous acid concentrations often peak at night and fall during the day as a

result of photolysis in sunlight.⁷ This also explains why nitrous acid contamination is much lower in remote areas where there is not the man-made NO_x pollution to produce it.⁸

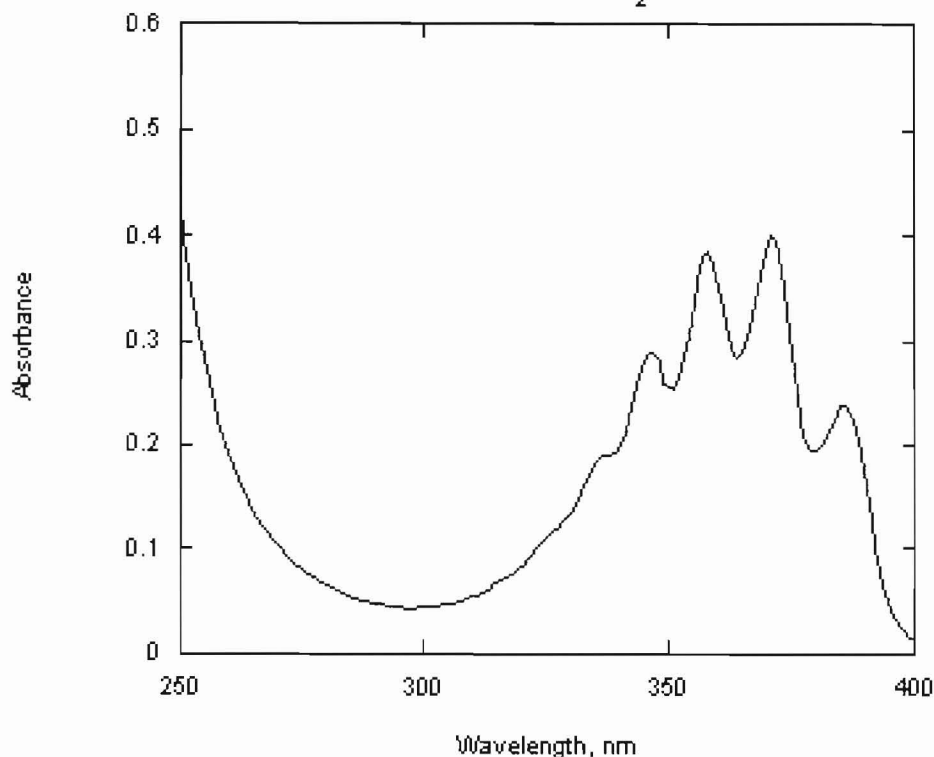
While nitrous acid in gas phase and aerosols is an important atmospheric pollutant, its conjugate base, nitrite, is significant in natural waters.⁹ Zafiriou et al. found nitrite concentrations on the order of 10⁻⁷ M in the central Pacific, decomposing to form hydroxyl radicals at a rate of 4 x 10⁻¹³ M/s.¹⁰ Studies of dew waters in Japan have also uncovered high nitrite concentrations (2.3-17.4 x 10⁻⁶ M) that result in OH radical production.

The absorption spectrum from 300-400 nm of nitrite in water, shown in Figure 1, is a broad peak with a maximum absorptivity of 22.8 L/mol cm at 355 nm and results from an n → π* transition.¹ Nitrite also has a more absorptive π → π* band at shorter wavelengths.¹¹



The spectrum of nitrous acid¹ has a somewhat different shape with five finger-like maxima in a slightly longer wavelength range (Figure 2).

Figure 2: UV Spectrum of HNO_2 , 10 mM in water



When aqueous nitrite absorbs ultraviolet light at its $n \rightarrow \pi^*$ band, it may break into NO and O^- radicals, or form a hydrated electron:¹



The O^- radical is largely protonated at neutral pH, producing hydroxide and hydroxyl radical.¹



Fischer and Warneck investigated the extent of electron production from nitrite at pH 6.1 and found no evidence for its importance.¹ Using nitrous oxide to convert hydrated electrons to hydroxyl radicals,



they found that hydroxyl radical quantum yields were on average 7.6% higher with nitrous oxide addition but this excess was well within the uncertainty of the quantum yield measurement.¹

Thus, Eq. 6 and subsequently Eq. 8 are major expected steps in nitrite photodecomposition.

When no other solutes are present, the radicals react to generate nitrous acid and eventually regenerate nitrite:^{1,12}



Thus, there is predicted to be no net loss of nitrite through photolysis in a system comprised only of nitrite and water. Species with a variety of nitrogen oxidation states are formed during this cycle. Nitrite begins with nitrogen as N(III) and forms N(II) nitric oxide. Combination of hydroxyl radical with nitrite forms N(IV) nitrogen dioxide, which can react with NO to form N(III) dinitrogen trioxide. In the presence of oxygen, N(VI) nitrate may be produced by oxidation of NO_x:¹²



Or, oxygen may oxidize nitric oxide to form NO₂:¹



Also, nitrogen dioxide can combine with water to form nitrous acid and nitric acid:¹



Because the species formed by nitrite and nitrous acid photolysis can be consumed through so many reactions, attempts to measure their rates of production require that the radicals be preferentially reacted with molecules called scavengers to form stable products. Several

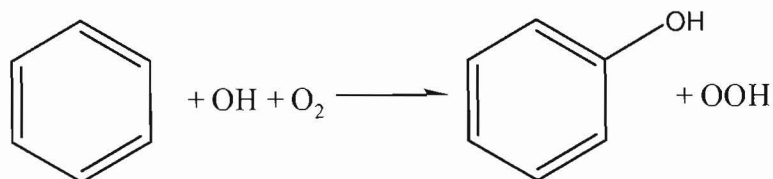
different compounds have been used previously to scavenge hydroxyl radicals, including ethylene,¹³ formate,¹⁴ ethanol,¹⁴ thiocyanate,¹⁵ and benzene.^{1,16}

Rettich used ethylene to scavenge hydroxyl radicals from photolysis of nitrous acid in water, producing about 1 mole of glycoaldehyde and hydroxylamine for every mole of nitrous acid photolyzed.¹³ Alif and Boule scavenged OH from nitrite photolysis with continuous illumination using formate and ethanol, but did not assess the formation of scavenging products. Rather, they simply measured nitrite disappearance.¹⁴ During flash photolysis of nitrite, Zafiriou and Bonneau reacted OH with SCN^- to form $(\text{SCN})_2^-$, which could be detected by ultraviolet-visible (UV-Vis) spectroscopy at its spectral maximum of 475 nm:¹⁵



They found that the hydroxyl radical quantum yield (Φ_{OH}) was independent of pH from 6.5-8.7, $[\text{O}_2]$ from 0-250 μM , and scavenger concentration from 0.03-0.3 M . However, they discovered that Φ_{OH} increased with temperature. Working at 23 °C, they found $\Phi_{\text{OH}}=0.02\pm 50\%$ at 354.6 and 371.3 nm, while at 289.5 and 337.1 nm they obtained $\Phi_{\text{OH}}=0.06\pm 50\%$.¹⁵

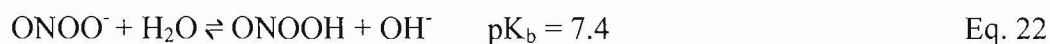
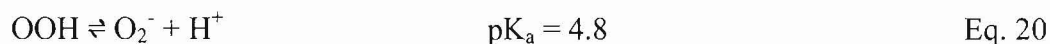
In the most recently published studies, benzene has been used in water to trap hydroxyl radical by reaction to form phenol:^{1,16}



Eq. 19

Using continuous irradiation at 355 nm, temperature of 22 °C, and pH 6.1, Fischer and Warneck found $\Phi_{\text{OH}}=0.025\pm 0.003$, while at 370 nm, they observed $\Phi_{\text{OH}}=0.021+0.003/-0.002$.¹ These more

precise values show good comparison with the data of Zafiriou and Bonneau and have the same general trend of higher quantum yields at shorter wavelengths.¹⁵ Nitrate ion was also observed as a photoproduct, ascribed to decomposition of peroxyxynitrous anion:¹



The above reactions are very fast, so that under the photolysis conditions NO and OOH are converted rapidly to NO_3^- . Fischer and Warneck, however, observed that the nitrate formation rate fell over the course of the photolysis, suggesting that nitrate was consumed in a reaction itself, perhaps



though no precedent for this reaction was reported.¹

Working to simulate the process in natural waters, Arakaki et al. photolyzed nitrite solutions with a broad spectrum source simulating the solar spectrum at the earth's surface.¹⁶ Though they did not report quantum yields, their rates of OH formation measured by benzene scavenging compare favorably with the previous results of Ref. 1 and 15.

The key process in each of these studies, the production of OH from photoexcitation of nitrite, is limited by several factors. The excited species may internally convert its energy into a lower, non-decomposing state, or if it actually dissociates, the radical products may still recombine before they react with any other species.^{1,15} This geminal recombination process results from the structure of the solution itself. The dissolved ions are surrounded by a cage of solvent molecules, and hopping from one cage or cell of solvent to another requires energy to

break the interactions with the cage molecules and insert into another cell.¹⁷ So, the radical fragments produced by photolysis bounce around together inside their shared cage until one obtains the requisite energy and orientation to escape. During this period, they may also collide appropriately to recombine.

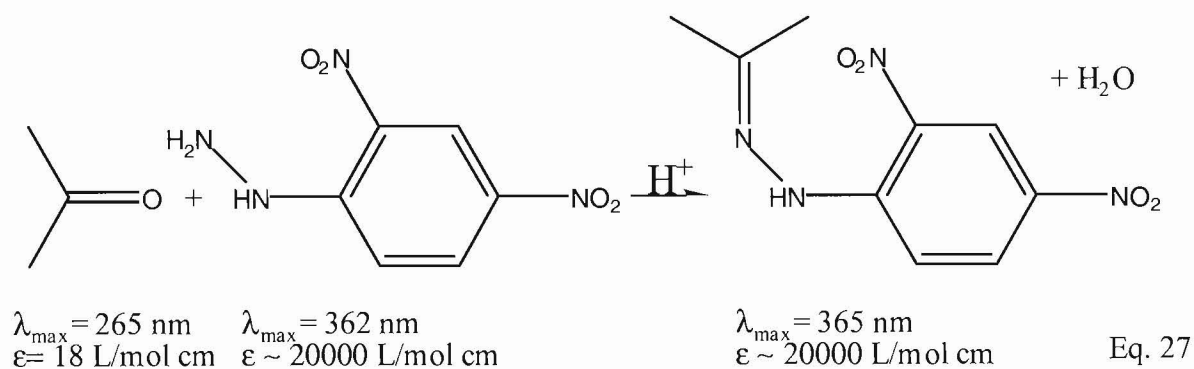
As such, these two processes of internal conversion and geminal recombination may explain some of the wavelength and temperature dependence observed by Zafiriou and Bonneau and Fischer and Warneck. Irradiation at a shorter wavelength gives the excited nitrite more energy, which makes dissociation more likely and likewise gives the fragments more energy to escape their cage. In the same way, increasing the temperature tends to cause the nitrite to begin with more vibrational and kinetic energy, so that it is more likely to fragment when it absorbs light and its photofragments have more kinetic energy to escape the solvent cage more readily.

Given the relation of escape from the solvent cage to the hydroxyl radical quantum yield, it might be interesting to reduce the effect of this factor by increasing scavenger concentration enough that the scavenger forms part of the solvent cage. Most scavengers used previously are incompatible with this approach. Thiocyanate ion is an anionic solute itself, so it cannot solvate the nitrite ion. Benzene (~8 mM)¹ and ethylene (~6 mM)¹³ are not soluble enough in water to allow high scavenger concentrations, while nitrite is not very soluble in benzene alone. However, alcohols provide possible polar alternatives to these other scavengers. One possible alcohol, 2-propanol, was previously used by Warneck and Wurzinger to scavenge hydroxyl radical formed by photolysis of nitrate:¹⁸



Abstraction at the α -position is the most common, accounting for 85.5% of the total hydrogen atom abstraction products. Hydroxyl hydrogen atom abstraction, which produces acetone as well, accounts for 1.2%, while β -abstraction (13.3%), leads to dimerization to 2,5-hexanediol.^{18,19} Similarly, ethanol, which was previously used by Alif and Boule,¹⁴ should have favorable nitrite solubility properties, but its reaction with hydroxyl radical forms acetaldehyde, acetic acid, and 1,4-butanediol.¹⁹ Methanol is also another possible scavenger and is expected to have the best nitrite solubility profile of the three given its dipole moment. Its scavenging products are formaldehyde and formic acid.¹⁹

Of the possible alcohol scavengers, 2-propanol has the most favorable scavenging product detection characteristics. Each of the organic scavenging products of methanol, ethanol, or 2-propanol could be separated by gas chromatography (GC) and quantified by coupled mass spectrometry or flame ionization. The nitrite in the analyte mixture, however, is not volatile enough to pass through the GC column and would lead to salt buildup. In order to perform gas chromatography, the nitrite in the photolysis mixture would have to be decomposed to nitrogen gas and water and its sodium counter ions exchanged for protons. As such, high-performance liquid chromatography (HPLC) offers a more attractive analytical option and suggests the use of 2-propanol. Acetone can be readily detected by UV-Vis spectroscopy after derivatization



with 2,4-dinitrophenylhydrazine (2,4-DNP) and separation by HPLC.^{18,20,21,22} The 2,4 DNP increases the UV absorption of the analyte by a factor of 10^3 while also increasing its retention time on the HPLC column. Detection of formaldehyde and acetaldehyde with the same derivatization has been reported, so these products of methanol and ethanol scavenging could be similarly quantified.²⁰ However, an aldol side reaction during the derivatization is more likely with acetaldehyde than with acetone.²³ Formaldehyde may too easily evaporate from the solution during photolysis, making its measurement difficult. The acetone route is also more well-established for photolyzed nitrogen oxide systems, having been used by Warneck and Wurzinger during photolysis of nitrate.¹⁸

Based on the above qualities, 2-propanol was chosen as a solvent-scavenger for nitrite photolysis in order to investigate the effects of very high scavenger concentration on hydroxyl radical production. Acetone produced by the scavenging reaction was derivatized with 2,4 DNP and detected by visible absorbance after HPLC. Nitrite concentrations during photolysis were monitored by UV-Vis spectroscopy.

Experimental

Instrumental. UV-Vis spectra were acquired with a Varian Cary 1 UV-Vis spectrophotometer with quartz cells of 1.00 cm path length and were referenced to deionized water at room temperature. A spectral bandwidth of 2.0 nm was used. HPLC was performed on a Shimadzu chromatograph equipped with SPD-M10A Diode Array Detector and an Alltech Prevail C18 column (4.6 x 150 mm, 5 μ m, #99208). NMR spectra were acquired using a JEOL Eclipse 270 MHz spectrometer.

Photolysis. For photolysis in 100% 2-propanol (Fisher Scientific, Optima grade, 0.05% H₂O) or reverse osmosis/deionized water, sodium nitrite (Baker and Adamson, reagent grade, 69.00 g/mol) was added to the solvent and stirred to dissolve prior to dilution to volume in volumetric glassware. For photolysis in 2-propanol/water solutions, NaNO₂ was dissolved in a weighed amount of water before dilution to volume. Rough pH measurements with 1 pH unit gradation paper suggested that the solution was approximately pH 6, similar to that reported by Fischer and Warneck.

Photolyses were performed on 50-70 mL of solution in a Rayonet Photochemical Reactor, RPR-100, at approximately 366 nm using Rayonet Photochemical Reactor Lamps, RPR-3500A. The solution was cooled to -2 °C during photoreaction using a cold-finger adapter for the quartz photolysis tube and a Precision Scientific Group R-40 Chiller, 66459. For sampling during photolysis, the lamps were turned off as ~10 mL was poured out of the photolysis tube into a sampling vessel. Parallel to the photolysis, a sample of starting solution was cooled in the chiller well as a thermal reaction control at the same temperature as the photolyzing solution.

Preparation of Acetone-2,4-dinitrophenylhydrazone (Acetone-2,4 DNP). The Procedure of Ref. 23 was followed. Melting point: 124-126 °C (Literature: 126 °C).²³ ¹H NMR (CDCl₃): δ 11.02 (s, 1H), δ 9.12 (d, 1H, *J*=2.47 Hz), δ 8.28 (dd, 1H, *J*=2.72 Hz and *J*=9.65 Hz), δ 7.95 (d, 1H, *J*=9.65 Hz), δ 2.17 (s, 3H), δ 2.08 (s, 3H).

Acetone Assay. The 2,4-DNP derivatization reagent was prepared by dissolving 10.0 mg of Martius yellow dye (Aldrich, naphthol form, 85%, 234.17 g/mol) and 0.29 g of 2,4-dinitrophenylhydrazine (Aldrich, 97%, ~80% dry solids, 198.1 g/mol) in 17 mL of concentrated

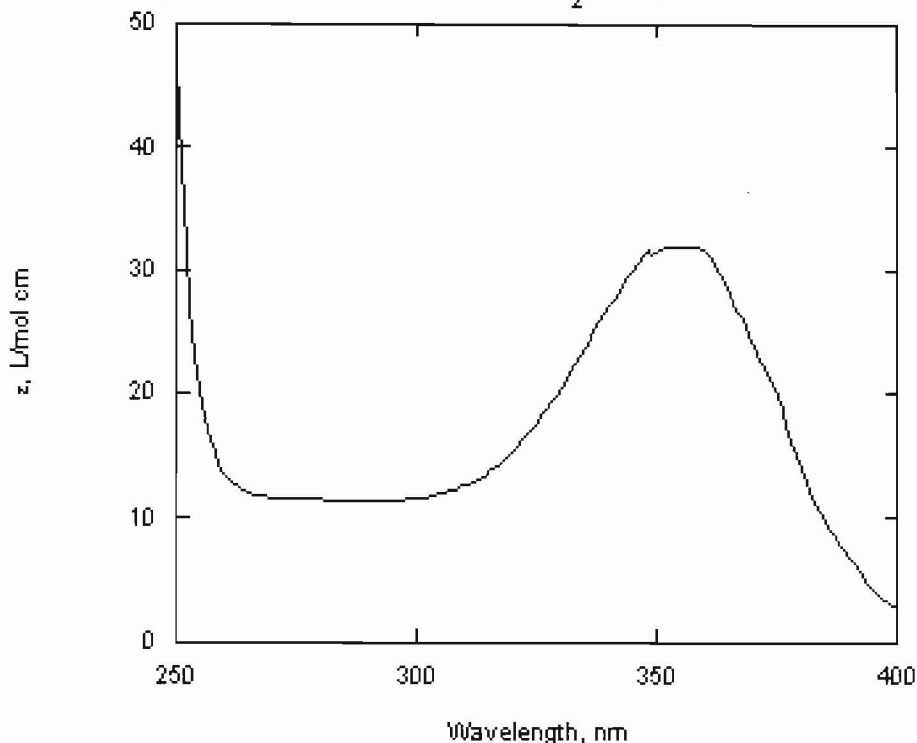
HCl (Fisher, Certified A.C.S. Plus) and 33 mL deionized water. This solution was diluted to 100 mL with absolute ethanol (AAper, USP) to produce a solution ~ 12 mM in 2,4-DNP.

The analyte solution (6 mL) was diluted to 10 mL with the prepared 2,4-DNP reagent and allowed to react at room temperature for at least 15 hours prior to analysis. The hydrazone of acetone (retention time 6.5-8.5 min) was separated from unreacted hydrazine (r.t. 2.3 min) and the Martius yellow internal standard (r.t. 1.5 min) by HPLC (30/70 H₂O/ MeOH, 1.5 mL/min). Components were detected by UV-Vis absorbance over 220-500 nm. Acetone-2,4-DNP was quantified by peak area at its maximum of 365 nm; Martius yellow, at 435 nm.

Results and Discussion

Ultraviolet spectrum of sodium nitrite in 2-propanol/water. In 96/4 2-propanol/water, nitrite absorbs more strongly than in pure water, with an extinction coefficient at 355 nm of 32.3 L/mol cm, compared to the aqueous value of 22.8 L/mol cm.¹ The shape of the band, shown in Figure 3, is similar to that of the aqueous solution (Fig. 1). One consequence of this absorption coefficient is that the lower limit for quantitative spectroscopic detection of nitrite is around 2 mM. Lower concentrations have absorbances less than about 0.06 and in practice led to poor reproducibility. This was reflected in the limit of quantitation of 2 mM determined as the concentration corresponding to ten times the standard deviation of a set of measured absorbances of the solvent.

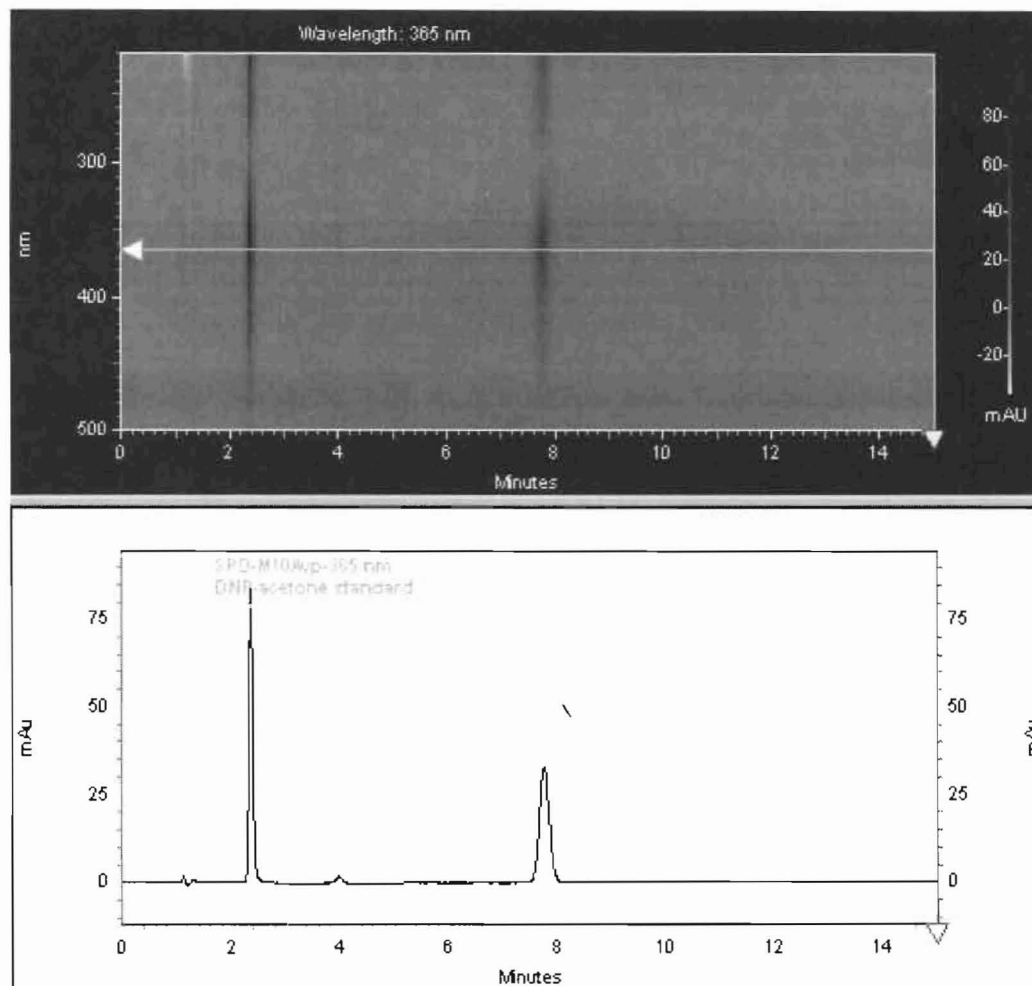
Figure 3: UV Spectrum of NaNO_2 in 2-propanol/water 96/4



Ion selective electrode measurement of nitrite ion. In the interest of lowering the detection limit for nitrite, a nitrite electrode (Thermo Electron 97-46 ionplus) was used to measure sodium nitrite concentrations in both aqueous and 98/2 2-propanol/water solutions. The aqueous solutions produced a linear calibration curve for all NO_2^- concentrations tested (10 μM - 0.1 mM), as did the 2-propanol/water solutions initially. While reproducibility of this technique in water was not established, the manufacturer claims a limit of detection of 0.04 mM NO_2^- . Repeating the calibration procedure twice consecutively in 2-propanol/water solutions resulted in very different potential readings, and storing the electrode in the 2-propanol solution for one day caused the measured potential to fluctuate dramatically. This ruled out potentiometric nitrite measurement in 2-propanol, although the technique remains an attractive alternative to UV-Vis for aqueous work.

Acetone Assay. The acetone-2,4-DNP separates well from 2,4-DNP under the HPLC conditions used and is readily detected by its absorbance at 365 nm, as shown in Figure 4.

Figure 4: Chromatogram of 2,4-DNP and acetone-2,4-DNP, 365 nm



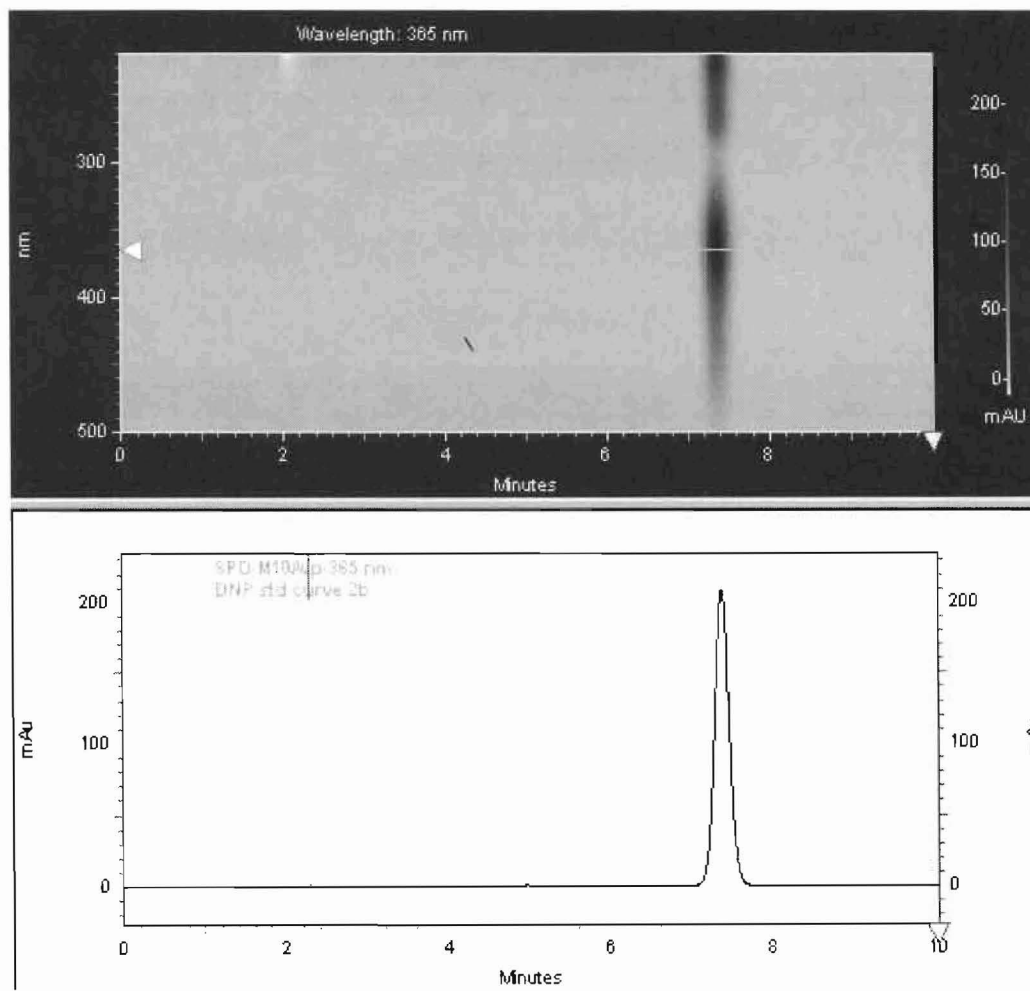
2.2 min: 2,4-DNP

7.8 min: Acetone-2,4-DNP

The first challenge of the project was to adapt the literature procedures for acetone analysis to the needs of the photolyzate samples. The typical macroscale laboratory procedures like that of Ref. 23 involve addition of aqueous acid and 2,4-DNP to the ketone sample and separation of the hydrazone product by precipitation. This sort of method, however, does not

produce a quantitative yield of hydrazone and is not well-suited for low ketone concentrations, so changes had to be made to develop an analytical method. The approach taken by Fung and Guosjean²⁰ and Selim²² was to incorporate an extraction of the less polar hydrazone from the aqueous reaction mixture of 2,4-dinitrophenylhydrazine and acid into an organic phase (hexanes/dichloromethane). This allows the hydrazone to be protected from hydrolysis after it is formed and helps separate it from the hydrazine. This method was attempted with aqueous acetone standards, and did give good separation of the acetone hydrazone from the unreacted hydrazine during extraction (Figure 5).

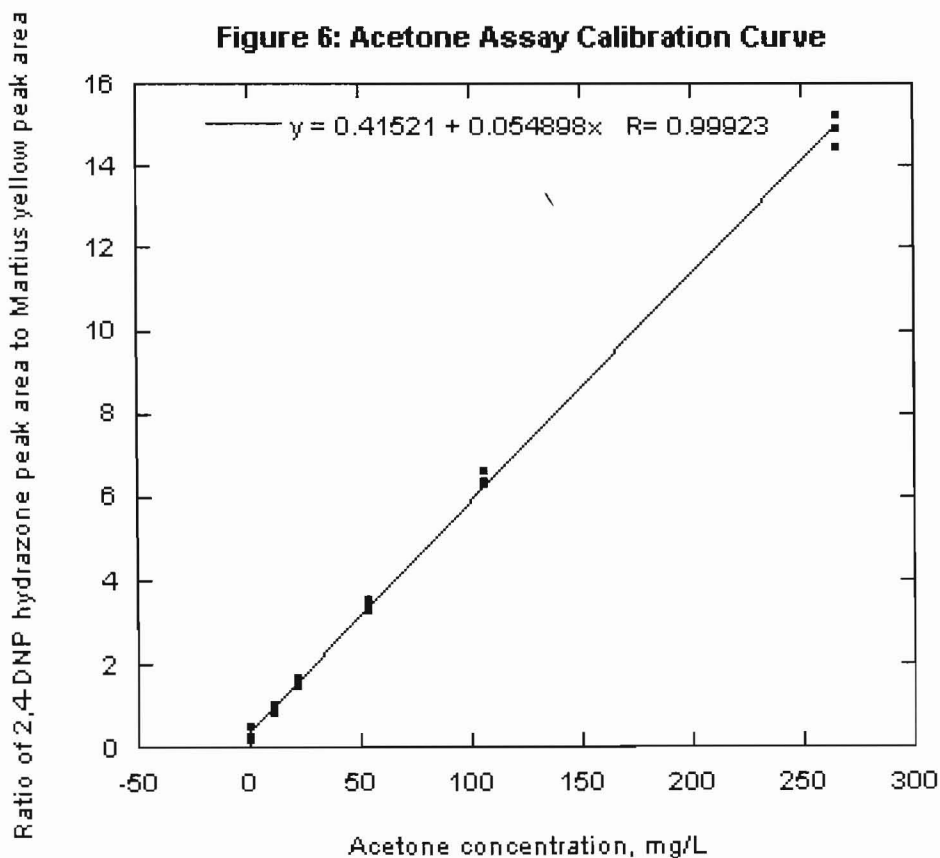
Figure 5: Chromatogram from extraction acetone assay, 365 nm



7.5 min: Acetone-2,4-DNP

Perhaps due to the amount of handling required in the procedure or incomplete conversion and extraction of the hydrazone, the concentrations of acetone-2,4-DNP calculated from the HPLC peak areas were not very reproducible. Also, the relationship between acetone concentration and acetone-2,4-DNP peak area was not linear, possibly because of non-linear partitioning of hydrazone between the aqueous and organic layers in the extraction.

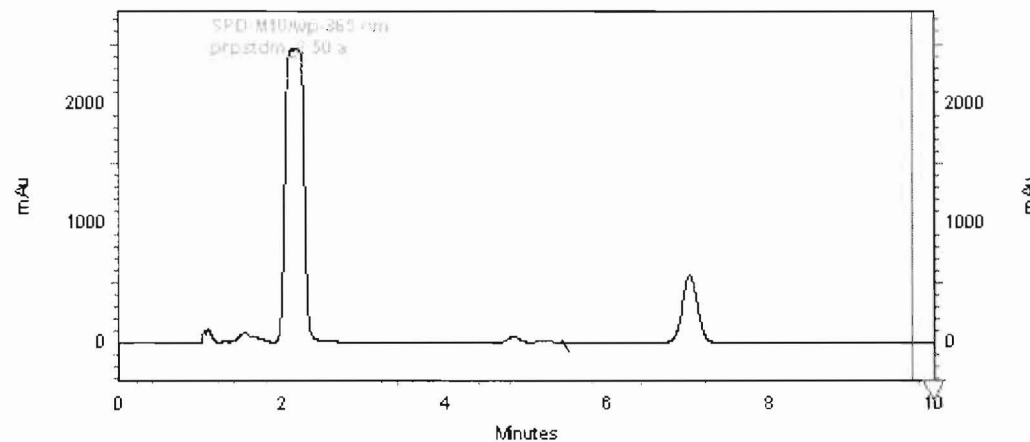
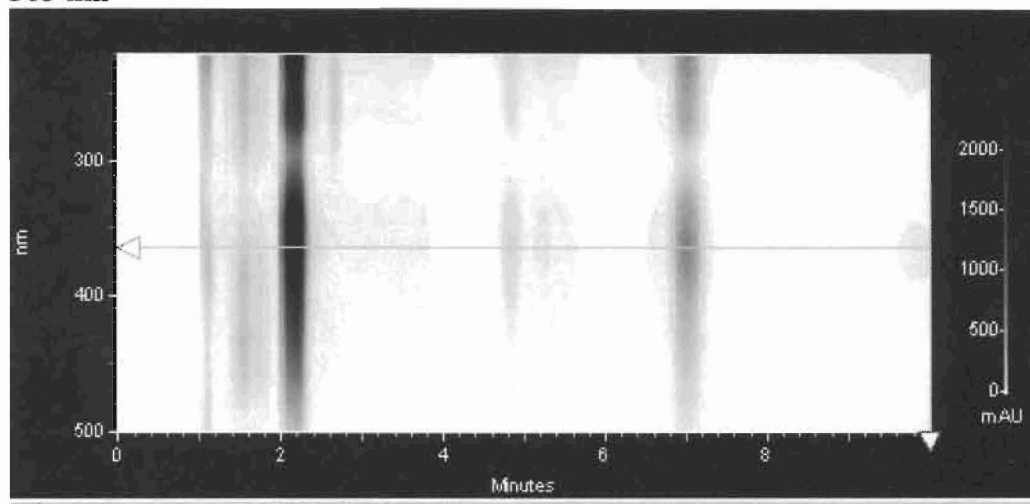
Due to the above difficulties, another approach was devised. A large excess of 2,4-DNP was added to the sample in an attempt to shift the acetone-hydrazone equilibrium to the hydrazone product. This procedure resulted in a linear calibration curve, shown in Figure 6, up to acetone concentrations of about 40% of the 2,4-DNP reagent concentration and more reproducible hydrazone peak areas. The detection limit, around 0.2 mM, was lower than the requirements of the photolyzate samples.



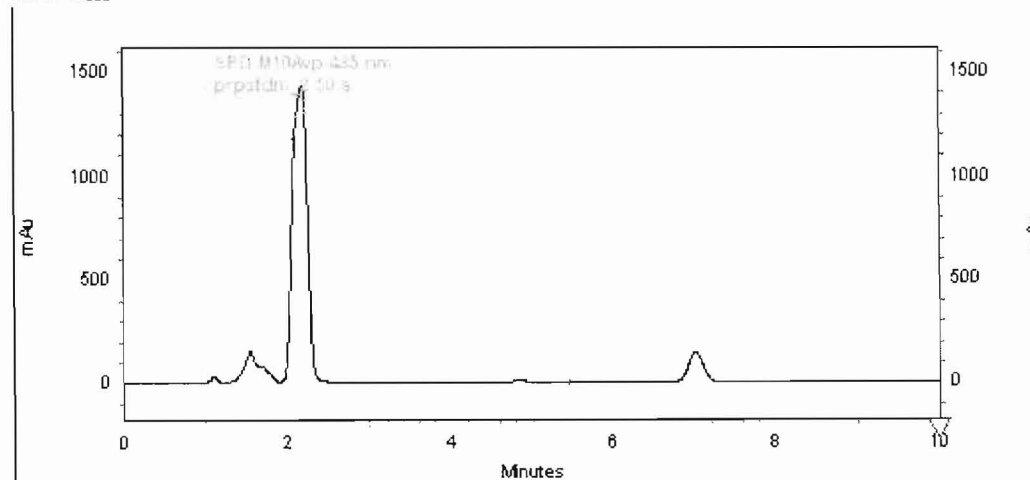
In order to quickly diagnose reproducibility problems, an internal dye standard, Martius yellow, was added to the derivatization reagent, and hydrazone peak areas were normalized to the dye peak area (Figure 7). The normalization process involved dividing the hydrazone peak area by the dye peak area and plotting that quotient against the analyte acetone concentration to obtain a calibration curve.

Figure 7: Chromatogram from acetone assay with hydrazine excess and internal standard

365 nm



435 nm



- 1.5 min: Martius yellow
- 2.2 min: 2,4-DNP hydrazine
- 7.0 min: Acetone-2,4-DNP hydrazone

Photolysis Results. A preliminary study demonstrated that nitrite solutions in water alone showed no measurable change in nitrite concentration after 60 minutes of irradiation at 366 nm.

The first step in photolyzing nitrite in 2-propanol solution was to investigate the solubility of nitrite in the alcohol. Sodium nitrite could be dissolved consistently to about 2.5 mM in 2-propanol. Unfortunately, this concentration was right above the quantitative limit for UV-Vis nitrite detection. In order to work with higher nitrite concentrations, water was added to the 2-propanol to help dissolve the sodium nitrite, so that photolyses were done with both 98/2 (0.9 M H₂O) and 96/4 (1.8 M H₂O) 2-propanol/water with 10 mM NaNO₂.

In the absence of nitrite, acetone did not appear in irradiated 2-propanol, while without irradiation, nitrite did not disappear and acetone did not form. Photolysis of 2-propanol for 1 hour without nitrite yielded no acetone within experimental error. Likewise, within uncertainty, nitrite concentrations did not change during control reactions in identical conditions yet without irradiation. Also, HPLC analyses of these control samples revealed no acetone.

Photolyses of sodium nitrite solutions with varying nitrite and water concentration were performed at 366 nm, -2 °C, and pH 6 with the following results:

Table 1: 100% 2-propanol, 2.12 mM NaNO₂

Time (min)	[NO ₂ ⁻] (mM) ± 0.2	[Acetone] (mM) ± 0.02
0	2.0	0
60	1.3	1.44

Table 2: 100% 2-propanol, 2.45 mM NaNO₂

Time (min)	[NO ₂ ⁻] (mM) ± 0.2	[Acetone] (mM) ± 0.02
0	3.0	0
60	----	1.83
120	1.6	2.84

Table 3: 98/2 2-propanol/water, 10.0 mM NaNO₂

Time (min)	[NO ₂ ⁻] (mM) ± 0.2	[Acetone] (mM) ± 0.02
0	9.1	0
30	10.0	0.35
60	9.8	0.955
120	8.5	1.77

Table 4: 96/4 2-propanol/water, 10.0 mM NaNO₂

Time (min)	[NO ₂ ⁻] (mM) ± 0.2	[Acetone] (mM) ± 0.02
0	9.4	0
30	10.3	0*
60	8.0	1.39
120	12.0*	2.49

*See discussion below.

These data reveal both expected results and surprises.

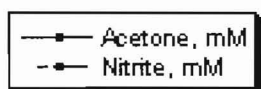
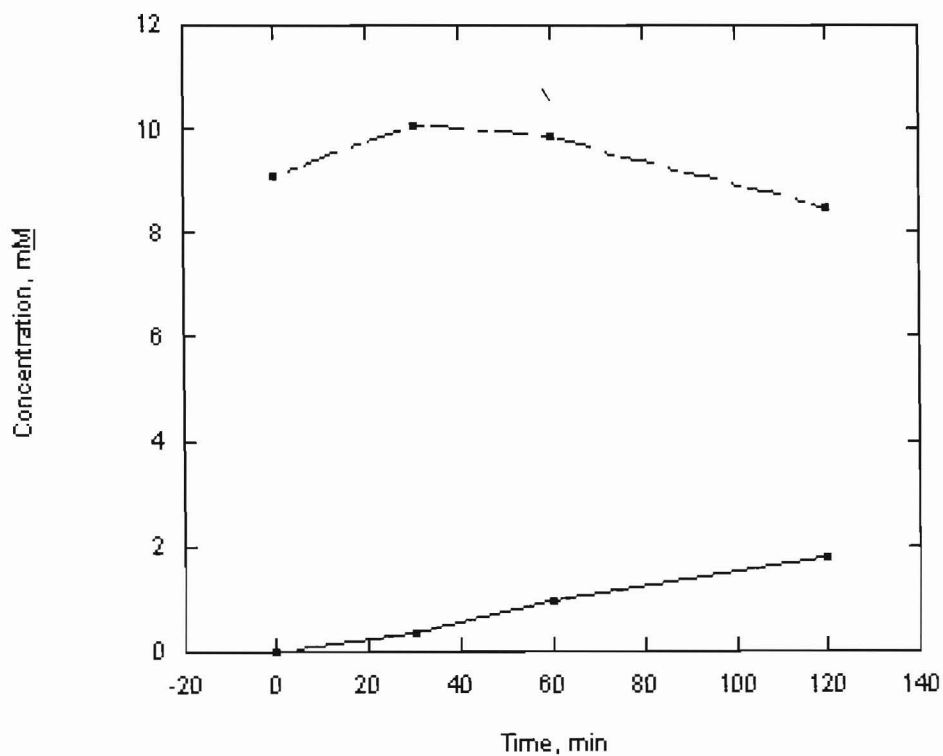
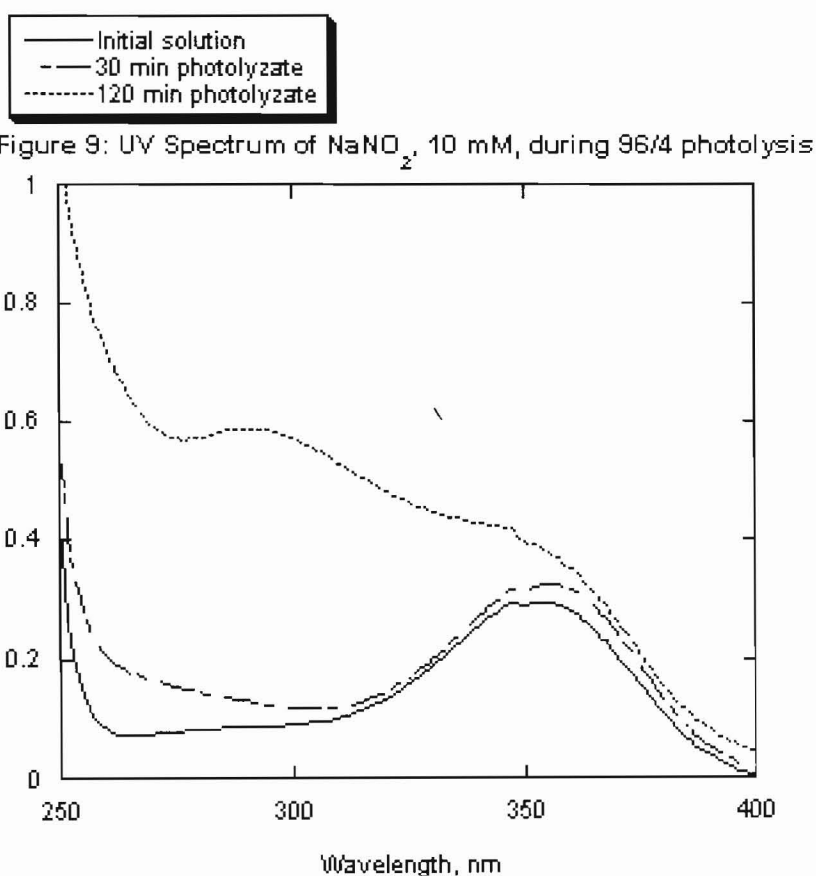


Figure 8: Acetone and Nitrite Data for 98/2 Photolysis



As shown in the plot of acetone concentration in the 98/2 run (Figure 8), the 2-propanol/water solution results show a fairly linear increase in acetone concentration over the course of irradiation, as would be expected, because the flux of photons into the solution remains constant. Assuming that the nitrite concentration is relatively constant, then one can conclude that the absorption of photons is constant, and thus the photodecomposition rate is constant.

On the other hand, the increase in apparent nitrite concentration during photolysis is unexpected. The peak assigned to nitrite also changes shape toward shorter wavelengths (Figure 9), which suggests that another absorptive product is interfering with the nitrite measurement.



One possible interferent is nitrate, a product expected from the reactions of the peroxy radical formed by 2-propanol oxidation (Eq. 19-22). Nitrate has an absorbance maximum at 305 nm, so its peak probably overlaps that of nitrite. However, its extinction coefficient in water at λ_{max} is 7

L/mol cm, less than a third of that of nitrite at 355 nm.¹⁸ Since nitrate would likely be formed at no more than the rate of nitrite disappearance, nitrate cannot alone account for an increase in absorbance at 355 nm. Similarly, acetone absorbs nearby, at 265 nm, but with an extinction coefficient at maximum of 18 L/mol cm it also cannot alone cause the rising absorbance at 355 nm. Possibly some unknown product is formed and causes the interference. Since the absorbance at 355 nm does decrease after initially increasing, this product's rate of formation falls or its rate of destruction increases during the photolysis.

In an attempt to remove this interference, 2 mL samples from the 96/4 run were evaporated to dryness in air and the residues dissolved in 3 mL of water. UV-Vis spectra of the resulting solutions were measured.

Table 5: 96/4 2-propanol/water, 10.0 mM NaNO₂, after drying

Time (min)	[NO ₂ ⁻] (mM) ± 0.2	[NO ₂ ⁻], dried samples (mM) ± 0.2 (calculated concentration prior to dilution by 50%)
0	9.4	7.6
30	10.3	6.6
60	8.0	5.0
120	12.0*	5.8*

*See discussion below.

As shown in Figure 10, the data from the dried samples from 0 to 60 minutes show a more linear decrease in nitrite concentration than do the data from the unmodified samples. This suggests that the evaporation procedure may have removed the interference because the nitrite data from the evaporated samples behave as expected.

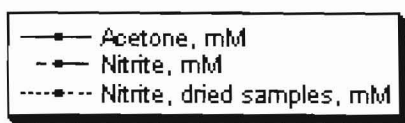
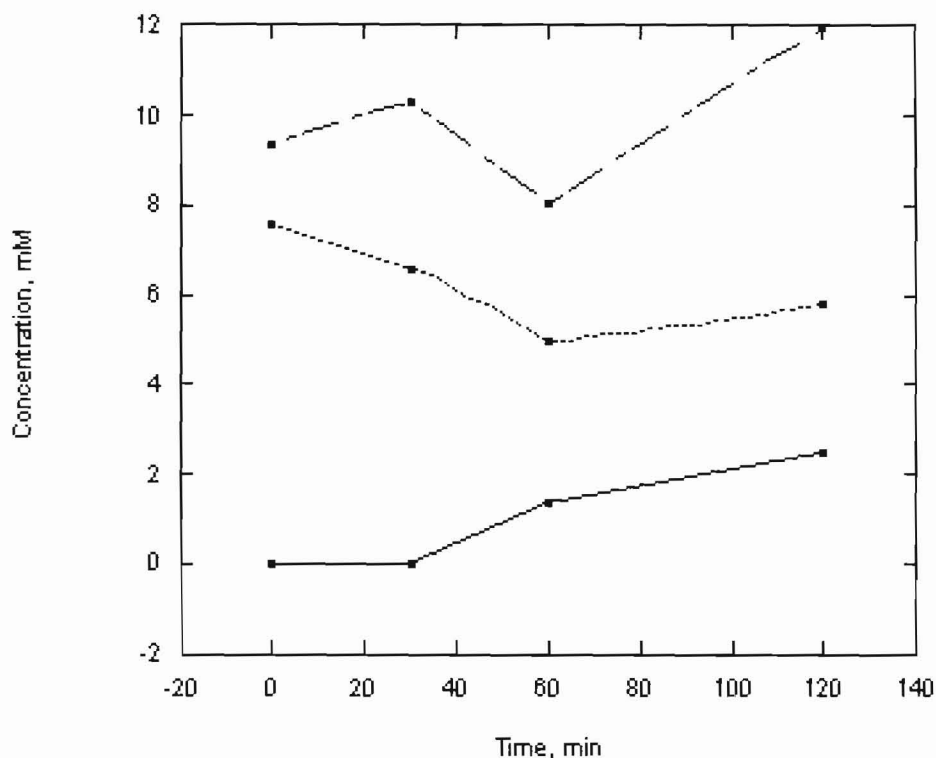
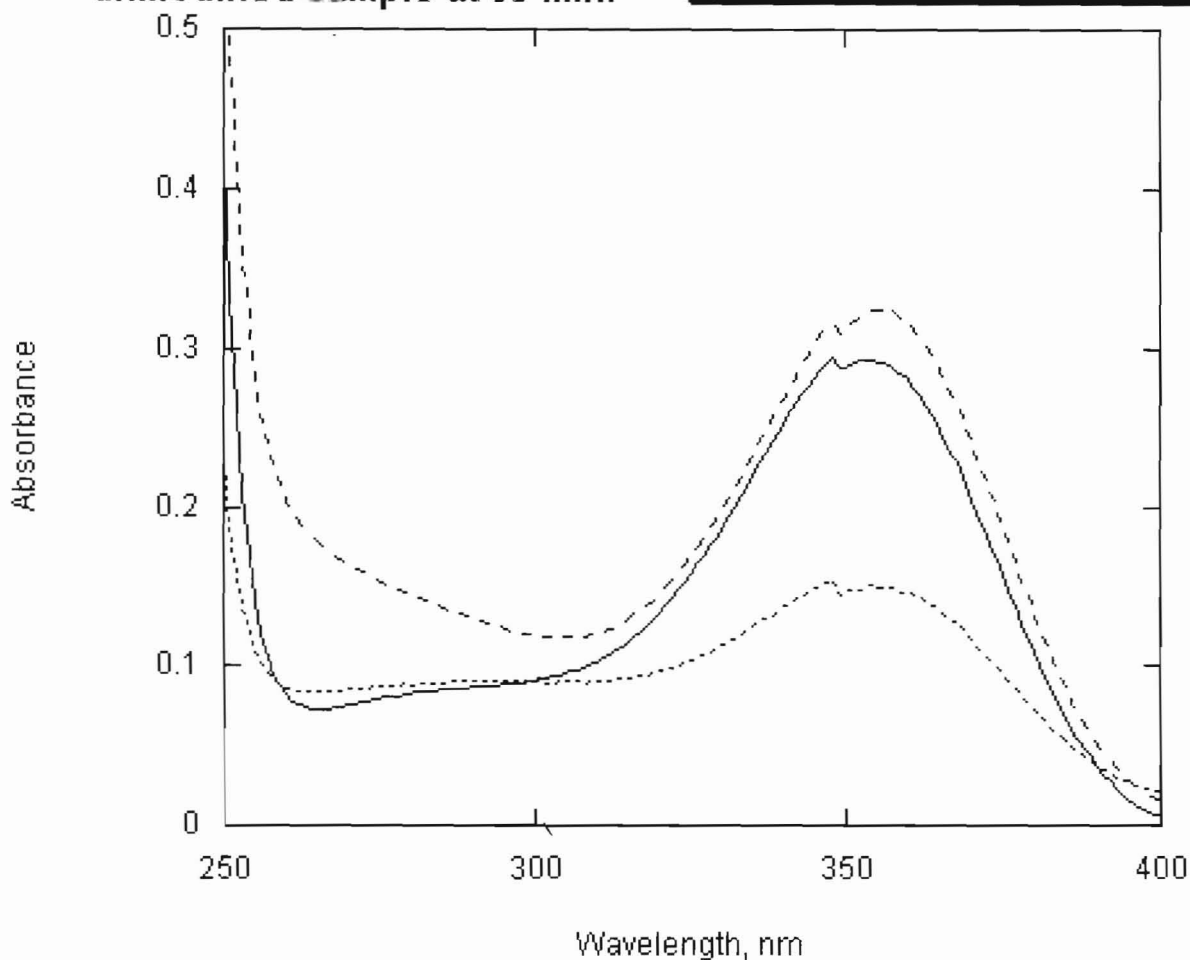


Figure 10: Acetone and Nitrite Data for 96/4 Photolysis



Also, as demonstrated in Figure 11, the UV spectra of the evaporated samples resemble typical nitrite spectra better than the unmodified samples do. However, the 120-minute result (denoted by asterisks in Tables 4 and 5) remains anomalously higher than the others, possibly because of contamination during sampling. The unusual UV spectrum, shown in Figure 9, supports this explanation.

Figure 11: Comparison of UV spectrum of nitrite sample after drying to pre-photolysis nitrite and unmodified sample at 30 min.



With the dried samples' more reasonable measure of nitrite concentration, acetone formation can be compared to nitrite disappearance. No acetone was detected in the 30 minute sample of the 96/4 run (denoted by an asterisk in Table 4), perhaps because of an error in the derivatization procedure. For the 60 minute sample, the mole ratio of acetone formed to nitrite lost is 0.5 ± 0.1 , while a 0.87:1 correspondence would be anticipated from the reactions in the scavenging sequence (Eq. 25, 26). Thus, for the two photolyses with mixed 2-propanol/water solvent and 10 mM nitrite, acetone forms at a rate of 0.01 - 0.02 mM/min , while the best nitrite

data (Table 5) indicate that nitrite disappears at a rate of 0.03 - 0.06 mM/min. More trials need to be run to check whether this result is merely an error or actually describes the system.

The results from the 100% 2-propanol solution photolyses are difficult to interpret, since the nitrite concentration data are suspect. The 2.45 mM nitrite photolysis shows a fairly linear increase in acetone concentration, as expected. The rate of acetone formation from the two trials with ~2 mM nitrite was 0.024 - 0.030 mM/min. Nitrite loss was about 0.01 mM/min. Curiously, the ratio of acetone produced to nitrite lost is 2-3, which, if the nitrite data can be trusted, suggests an acetone formation mechanism in which nitrite is partially regenerated.

Also, the rate of acetone formation is apparently higher for the pure 2-propanol solvent system than for the mixed system. One possible explanation for this result is that altering the ratio of 2-propanol to water by several mass percent modifies the solvent cage enough to make the photodecomposition of nitrite much more efficient. Another possibility is that reducing water content changes the scavenging mechanism to favor formation of acetone. This might be supported by the possibility of nitrite regeneration suggested by the nitrite data. The following mechanism could explain these observations:

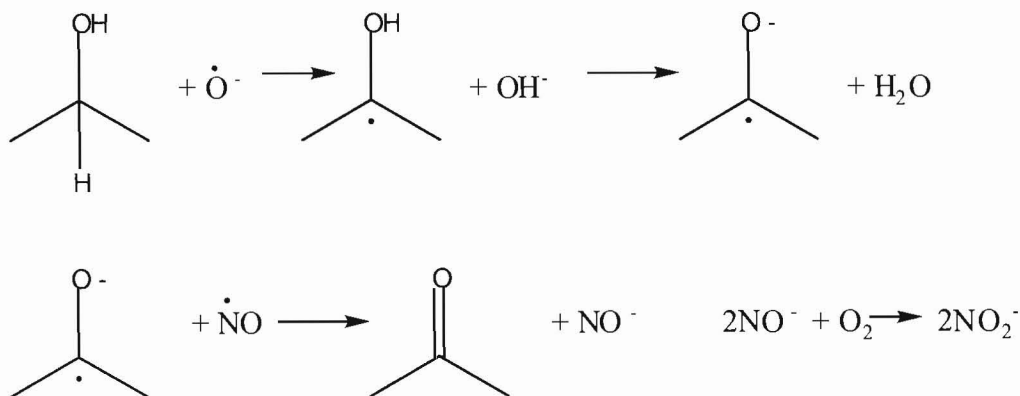


Figure 12: Proposed nitrite regeneration mechanism

Possibly, with much lower water concentrations, the $O^{\cdot-}$ radical abstracts a hydrogen atom from the 2-propanol before being protonated. The 2-propanol α -radical has a pK_a around 10 and may be deprotonated by hydroxide.²⁴ The alkoxide radical produced is a very strong reducing agent, and perhaps could reduce NO to $NO^{\cdot-}$, forming acetone in the process.²⁴ Two $NO^{\cdot-}$ might be oxidized by dissolved oxygen to form nitrite in an analog to Eq. 14. This mechanism, working to some extent in parallel to the expected mechanism, could explain the suggested partial regeneration of nitrite and might lead to faster acetone formation.

Future Work

Many difficulties remain to be overcome in this project. Though a working method for acetone quantification has been developed, nitrite detection by UV-Vis leaves much to be desired. Its limit of quantitation is too high for quantitative work with nitrite concentrations lower than 2 mM and the nitrite absorbance overlaps with those of several possible interfering species. Evaporating the volatile components of the photolyzate to separate them from nitrite may eliminate the interference, but this process may introduce too much uncertainty. Another possibility might be to dilute the 2-propanol solution of nitrite with water in order to use the nitrite electrode for a potentiometric measurement. Even if diluted by a factor of 10, the nitrite levels in the photolyzate would be within the detection range of the electrode. Other possible options are reported in Ref. 18; one is visible spectroscopic detection at 540 nm after Saltzmann diazotization, and the other is ion chromatography coupled to UV detection.

Since it is probably another major photoproduct, nitrate should also be quantified, possibly using ion chromatography as reported by Fischer and Warneck.¹ With the detection procedures established, photolysis conditions could be systematically varied to investigate the

behavior of the system. For instance, the concentration of water could be changed systematically to see what effects it may have on the mechanism. Or temperature could be varied, as in the work of Zafiriou and Bonneau, to see if the temperature dependence of the reactions is different in the 2-propanol solvent-scavenger system. Possibly, because the hydroxyl radical does not have to escape the solvent cage to avoid recombination, the effective activation energy will be lower.

Another direction that might be taken in refining the analytical methods in the project would be to develop a way to look at products by GC or GC-MS. Mass spectral analysis would be helpful in identifying unknown photoproducts, such as the proposed UV interference. Some way to separate the sodium nitrite from the solution could be devised, or nitrite concentrations could be kept low enough to be acceptable for use with the GC. Or, possibly, the advantages of MS could be obtained while avoiding the volatility problems through LC-MS.

Conclusions

In order to examine nitrite photochemistry in 2-propanol scavenger solution, techniques were developed to detect nitrite and the hydroxyl radical scavenging product, acetone. Nitrite was quantified by UV-Vis spectroscopy, while acetone was converted to its 2,4-dinitrophenylhydrazone and measured using UV-Vis detection with HPLC. During photolyses with 10 mM nitrite in 96/4 and 98/2 2-propanol/water, nitrite disappeared at a rate of 0.03 - 0.06 mM/min, while acetone appeared at a rate of 0.01 - 0.02 mM/min. In 100% 2-propanol solvent with $[\text{NO}_2^-] \sim 2 \text{ mM}$, the rate of acetone formation was higher, 0.024 - 0.030 mM/min, possibly indicating a shift in mechanism with much lower water concentration.

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