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SOLUTION (PHOTOOXIDATION STUDIES)(U) OAK RIDGE NATIONAL
LAB TN CHEMISTRY DIV P C HO NOV 84 AMXTH-TE-TR-85001
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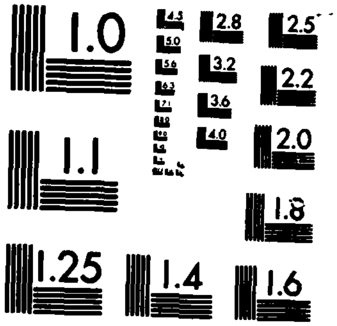

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Degradation Mechanism of 2,4-Dinitrotoluene in Aqueous Solution (Photooxidation Studies)

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Work performed for
U. S. Army Toxic and Hazardous Materials Agency

Interagency Agreement 40-1327-83
Army No. D-3-78-15

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This work was supported by the Toxic and Hazardous Materials Agency of the U. S. Army. The Oak Ridge National Laboratory is operated for the U. S. Department of Energy by Martin Marietta Energy Systems, Inc., under contract number DE-AC05-84OR21400.

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
18 1. REPORT NUMBER AMXTH-TE-TR-85001	2. GOVT ACCESSION NO.
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DEGRADATION MECHANISM OF 2,4-DINITROTOLUENE IN AQUEOUS SOLUTION (PHOTOOXIDATION STUDIES)	5. TYPE OF REPORT & PERIOD COVERED Final Report May, 1983 - November, 1984
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Patience C. Ho	8. CONTRACT OR GRANT NUMBER(s) Interagency Agreement 40-1327-83
9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemistry Division Oak Ridge National Laboratory P. O. Box X, Oak Ridge, Tennessee 37831	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Army U. S. Army Toxic and Hazardous Materials Agency Aberdeen Proving Ground, Maryland 21010	12. REPORT DATE November, 1984
	13. NUMBER OF PAGES 44 + iii
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Unlimited Distribution

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Dinitrotoluene,	Oxidation,
Nitroaromatics,	Detoxification,
Photolysis,	Photooxidation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The synergistic effect of hydrogen peroxide (H_2O_2) and UV radiation from a medium-pressure mercury vapor lamp on the decomposition of 2,4-dinitrotoluene (DNT) in aqueous solution was studied. The most effective conditions for degradation of aqueous DNT solutions were found to consist of a molar ratio of H_2O_2/DNT in the range of 26 to 52 in the presence of unfiltered UV radiation. Under these conditions, the intermediates found after short reaction times (2 to 14 minutes), were 2,4-dinitrobenzyl alcohol, (contd.)

20. ABSTRACT (contd.)

2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid (dominant), 1,3-dinitrobenzene, 3-nitrophenol, 2,4-dinitrophenol, maleic acid derivatives, oxalic acid, glyoxal, and glyoxylic acid. This finding suggests that the degradation pathways of DNT in aqueous solution in the presence of H_2O_2 and UV light are: (1) sidechain oxidation, which converts DNT to 2,4-dinitrobenzoic acid, followed by decarboxylation to form 1,3-dinitrobenzene; (2) hydroxylation, which converts 1,3-dinitrobenzene to mono-, di-, and trihydroxynitrobenzenes; (3) benzene ring cleavage of these hydroxynitrobenzenes, which produces 2- and 4-carbon carboxylic acids and aldehydes; and (4) further photooxidation, which eventually converts the 2- and 4-carbon carboxylic acids and aldehydes to CO_2, H_2O, and HNO_3. Originator supplied Keywords include:

See DD 1473; (Block 19)

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ABSTRACT

The synergistic effect of hydrogen peroxide (H_2O_2) and UV radiation from a medium-pressure mercury vapor lamp on the decomposition of 2,4-dinitrotoluene (DNT) in aqueous solution was studied. The most effective conditions for degradation of aqueous DNT solutions were found to consist of a molar ratio of H_2O_2/DNT in the range of 26 to 52 in the presence of unfiltered UV radiation. Under these conditions, the intermediates found after short reaction times (2 to 14 minutes), were 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid (dominant), 1,3-dinitrobenzene, 3-nitrophenol, 2,4-dinitrophenol, maleic acid derivatives, oxalic acid, glyoxal, and glyoxylic acid. This finding suggests that the degradation pathways of DNT in aqueous solution in the presence of H_2O_2 and UV light are: (1) sidechain oxidation, which converts DNT to 2,4-dinitrobenzoic acid, followed by decarboxylation to form 1,3-dinitrobenzene; (2) hydroxylation, which converts 1,3-dinitrobenzene to mono-, di-, and trihydroxynitrobenzenes; (3) benzene ring cleavage of these hydroxynitrobenzenes, which produces 2- and 4-carbon carboxylic acids and aldehydes; and (4) further photooxidation, which eventually converts the 2- and 4-carbon carboxylic acids and aldehydes to CO_2, H_2O, and HNO_3.

INTRODUCTION

Manufacturing and handling operations in military munitions facilities generate significant volumes of aqueous effluents contaminated with nitrated organics, particularly 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX), and smaller amounts of others, such as 2,4-dinitrotoluene (DNT) which is particularly hazardous to biota. Release of these compounds into the surrounding environment constitutes an environmental hazard.

Among many methods of degradation of explosive nitrobodies, a new and promising approach is the synergistic combination of ultraviolet (UV) irradiation and an oxidizing agent, generally hydrogen peroxide(1-3) or ozone.(4-6) Although this method has clearly been demonstrated to degrade TNT and related materials completely to carbon dioxide, water, and nitric acid, the underlying photochemical and chemical pathways are not understood. Our ultimate goal of this program was to find out the mechanism of the degradation reaction of dinitrotoluene in aqueous solutions by means of UV irradiation with or without the presence of an oxidizing agent, such as hydrogen peroxide.

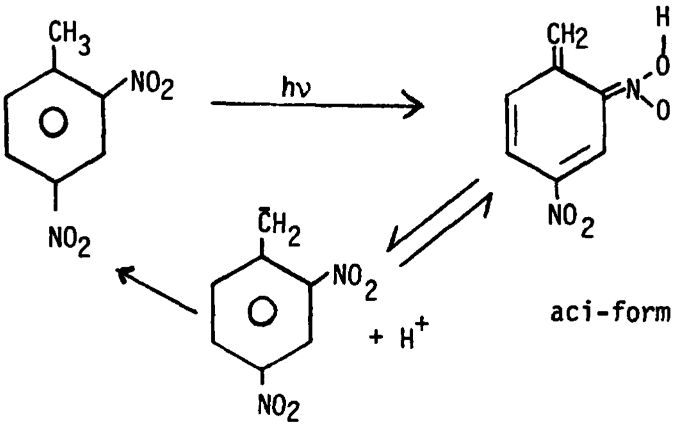
This report presents the results of photooxidation of 2,4-dinitrotoluene and of some of the reaction intermediates, which are produced during the photooxidation of DNT, when exposed in aqueous solution to H_2O_2 and radiation from medium-pressure mercury vapor lamp. A reaction pathway (mechanism) of photooxidation of aqueous DNT solutions is suggested.

BACKGROUND

1. Photolysis

Aromatic nitro compounds absorb intensely in the UV region.(7,8) Specifically, dinitrotoluene in aqueous solution(7) has λ_{max} = 252 nm (ε = ∿15000) with a tail extending to ∿350 nm; this intense band represents the $\pi \rightarrow \pi^*$ transition while the expected weaker $n \rightarrow \pi^*$ band must lie under the tail.

Flash photolysis of 2,4-dinitrotoluene in aqueous solution produces a short-lived colored species, the aci-nitro isomer.(9) The aci-isomer (λ_{max} ∿420 nm) was shown to be in rapid prototropic equilibrium with the DNT anion (λ_{max} ∿500 nm) with an apparent $pK_a \approx$ 1-2. The thermal reversion to DNT took place through a general acid-catalyzed protonation of the anion:



Superimposed on this reversible phenomenon was a slower irreversible development of color. Detailed study of the quantum yields and products from this irreversible photolysis of polynitro aromatics in dilute aqueous solution has been limited mostly to TNT (2,4,6-trinitrotoluene). Ronning and coworkers(10) had reported a quantum yield for disappearance of TNT of 9 × 10^{-3} at 253.7 nm for 5 × 10^{-5} M aqueous air-saturated solutions of TNT. Mabey and coworkers(11) recently reported a quantum yield of 2.7 × 10^{-3} for initial disappearance of TNT as a very dilute solution (10^{-7} M) in air-saturated water at either 313 or 366 nm; however, there was evidence of autocatalytic behavior, and they suggested therefore that disappearance of TNT might be photosensitized by colored products. Similarly low quantum yields ($\sim 10^{-3}$) have been observed for TNT and DNT in hydrocarbon solvents.(8) Thus photolysis by itself is inherently inefficient in destroying polynitro compounds in aqueous solution. For example, Kaplan and coworkers(12) carried out a detailed study of the products from photolysis of saturated aqueous solutions of TNT at 50-60°C by light with wavelength greater than 280 nm (approximate sunlight), and found that TNT could not be degraded by this light; rather more complex mixtures of stable photo products are produced.

Hydrogen peroxide is known to be photosensitive(13) and this property has often been used to induce oxidation of compounds which are not attacked by H_2O_2 in the dark. Light with wavelengths shorter than 400 nm can decompose H_2O_2 to form free hydroxyl radicals. Photodecomposition of H_2O_2 alone is a chain reaction:(13)

$$H_2O_2 \xrightarrow{k_1} 2\cdot OH \qquad (a)$$

$$\cdot OH + H_2O_2 \xrightarrow{k_2} H_2O + HO_2\cdot \qquad (b)$$

$$HO_2\cdot + H_2O_2 \xrightarrow{k_3} H_2O + O_2 + \cdot OH \qquad (c)$$

$$2HO_2\cdot \xrightarrow{k_4} H_2O_2 + O_2 \qquad (d)$$

When the concentration of H_2O_2 is low and substances are present which can trap hydroxyl radicals, then the rate of consumption of H_2O_2 is determined by the primary quantum yield in reaction (a). This process in aqueous solution has been found to be very efficient.(14-18) At 253.7 nm and 27°C, the primary quantum yield was found to be 0.47,(18) while at 313 nm and 25°C, it was 0.3.(16)

2. Oxidation

Oxidation with ozone or hydrogen peroxide (with catalyst) is often considered a potential method to eliminate organic impurities in water. Hydrogen peroxide itself is a much weaker oxidizing agent but the combination of H_2O_2 and a catalyst (such as Fe^{++}, the so-called Fenton's reagent) is an exceedingly active oxidizing reagent. For example, upon oxidation by Fenton's reagent, nitrobenzene in aqueous solution can be converted to a mixture of nitrophenols and polyphenolic derivatives.(19-21) Elimination of the nitro group by hydroxyl radical attack has also been suggested.(22-24)

Ozone in water can be decomposed by hydroxide ions; Hoigne and Bader(25,26) claimed that hydroxyl radicals are the main oxidants formed in decomposition of ozone in water. Reactions of ozone with aromatics show somewhat similar behavior as Fenton's reagent although different mechanisms may be involved. Characteristic reactions on aromatics(21,27-31) are:

a) Substituting an oxygen onto an aromatic ring to form phenols.

b) Cleaving double bonds and electron-rich aromatic rings.

c) Removing substitutents from aromatic rings.

d) Oxidizing alcohols through aldehydes to organic acids.

For example, nitrobenzene can be oxidized by ozone to 2- and 4-carbon carboxylic acids and aldehydes.(21) Further oxidation of aliphatic acids and aldehydes to CO_2 and H_2O with ozone alone apparently is time consuming and difficult.(21,28,30,32)

In summary, it seems that ozone or H_2O_2 with catalyst can oxidize aromatic nitro compounds to some extent but not completely to CO_2.

3. Photooxidation

Leitis(21) has demonstrated that the combination of UV radiation and ozone could degrade nitrobenzene to CO_2, H_2O and HNO_3; i.e., the total organic carbons (TOC) was reduced to zero. Hewes(32) also showed that low molecular weight alcohols, organic acids, amino acids, and polyhydroxyl alcohols were difficult to oxidize with ozone alone but were readily oxidized to CO_2 and H_2O by the UV/O_3 combination.

In a pilot-plant-scale study of UV/O_3 treatment of pink wastewater, containing a mixture of TNT, RDX, and other nitrated materials, Layne and coworkers(6) found that TNT was slowly converted by UV alone and more rapidly by ozone, but in neither case was there a significant decrease in TOC. Only the combination of UV/O_3 rapidly converted TNT and reduced TOC. They suggested that cleavage of the aromatic ring might occur after the methyl group and one nitro group of TNT had been replaced by hydroxyl groups; however, there was no experimental data to support this statement.

The most extensive studies of the UV/H_2O_2 degradation of nitrocompounds have been reported by Andrews and coworkers.(1-3) Bench-scale tests(1) were performed with a UV source with primary output at 253.7 nm; however, the use of a Pyrex Filter limits the wave-length range to $\gtrsim$ 280 nm. For aqueous solutions of TNT (100 ppm), the combination of UV and H_2O_2 was clearly more effective than either agent alone in destroying TNT and reducing TOC. The effect of initial pH was minimal so long as very acidic solutions ($pH < 2$) were avoided. The major final C-containing product was carbon dioxide and the major final N-containing product was nitrate ion. The only intermediate detected in this extensive degradation was 1,3,5-trinitrobenzene (TNB) at rather low levels. Aqueous solutions of DNT were similarly degraded. Pilot-scale data(3) were collected with a commercially available photoreactor containing low-pressure mercury lamps (primary output at 253.7 nm) with quartz rather than Pyrex sleeves. The feed was "pink water." Although the concentrations of both TNT and RDX dropped more rapidly with increasing time of exposure than did TOC, again the only intermediate detected was TNB whose maximum concentration was ∿ 10% of the initial TNT concentration. They suggested the occurrence of the following partial mechanism:

$$H_2O_2 \xrightarrow{UV} 2HO\cdot$$

$$RH + HO\cdot \xrightarrow{UV} R\cdot + H_2O$$

$$H_2O_2 + HO\cdot \xrightarrow{UV} H_2O + HO_2\cdot$$

$$R\cdot + HO_2\cdot \text{ (and/or } HO\cdot) \xrightarrow{UV} \text{eventual oxidation}$$

where R represents organic material. Thus photolytic dissociation of H_2O_2 was proposed as the key step, but it was also implied that the TNT was in an excited state when it reacted with radicals.

Most of the works reviewed above have focused on either nitrobenzene or TNT. However, photooxidation of dinitrotoluene in aqueous solution has received much less attention. Although Andrews et al. briefly note that the

UV/H_2O_2 system is also effective in degrading DNT, no information is given regarding the decomposition products or pathways.

EXPERIMENTAL

Materials

2,4-Dinitrotoluene (Aldrich, 97%) and 1,3-dinitrobenzene (Fluka, puriss > 99%) were purified by liquid chromatography (with a MN-Kieselgel 60 column) to a purity greater than 99.5% (as measured by thin layer chromatography) before using. 2,4-Dinitrobenzoic acid (Fluka, purum > 98%(T)) was recrystallized twice from water. 2,4-Dinitrophenol (Fluka, puriss > 99%) moistened with 20% H_2O was extracted with benzene and dried under N_2 to remove H_2O. 2,4-Dinitrobenzaldehyde (Aldrich, 97%), 3-nitrophenol (Aldrich, 99%), 4-nitrocatechol (Fluka, > 98%(T)), 2-nitroresorcinol (Kodak), 1,3,5-trihydroxy-2-nitrobenzene (Pfaltz and Bauer), phenol (Mallinckrodt, analytical reagent), catechol (Baker), pyrogallol (Mallinckrodt, analytical reagent), maleic acid (Fluke, > 99%(T)), glyoxal (Fluka, pract. ∿ 30% in water) and glyoxylic acid (Fluka, 50% solution in water) were used as received without further purification. Water was deionized and double distilled in glass.

Photolysis Apparatus and Procedures

Mixtures of the organic compounds and H_2O_2 in aqueous solution were irradiated mostly with 200-watt and 450-watt Hanovia medium-pressure mercury vapor lamps fitted with or without filters. The lamp was placed in a cooling chamber section of a quartz immersion wall. Figure 1 shows a detailed arrangement of the apparatus. The medium-pressure mercury vapor lamp has a broad spectrum from the far UV to the infrared region.(33) A low-pressure mercury lamp (GE, G15T8), which is rich in a 253.7 nm line, was also used for comparison. The filters were Pyrex (to block out light < 280 nm) or Vycor (to filter out light < 220 nm) sleeves and a liquid filter of aqueous $CoSO_4$

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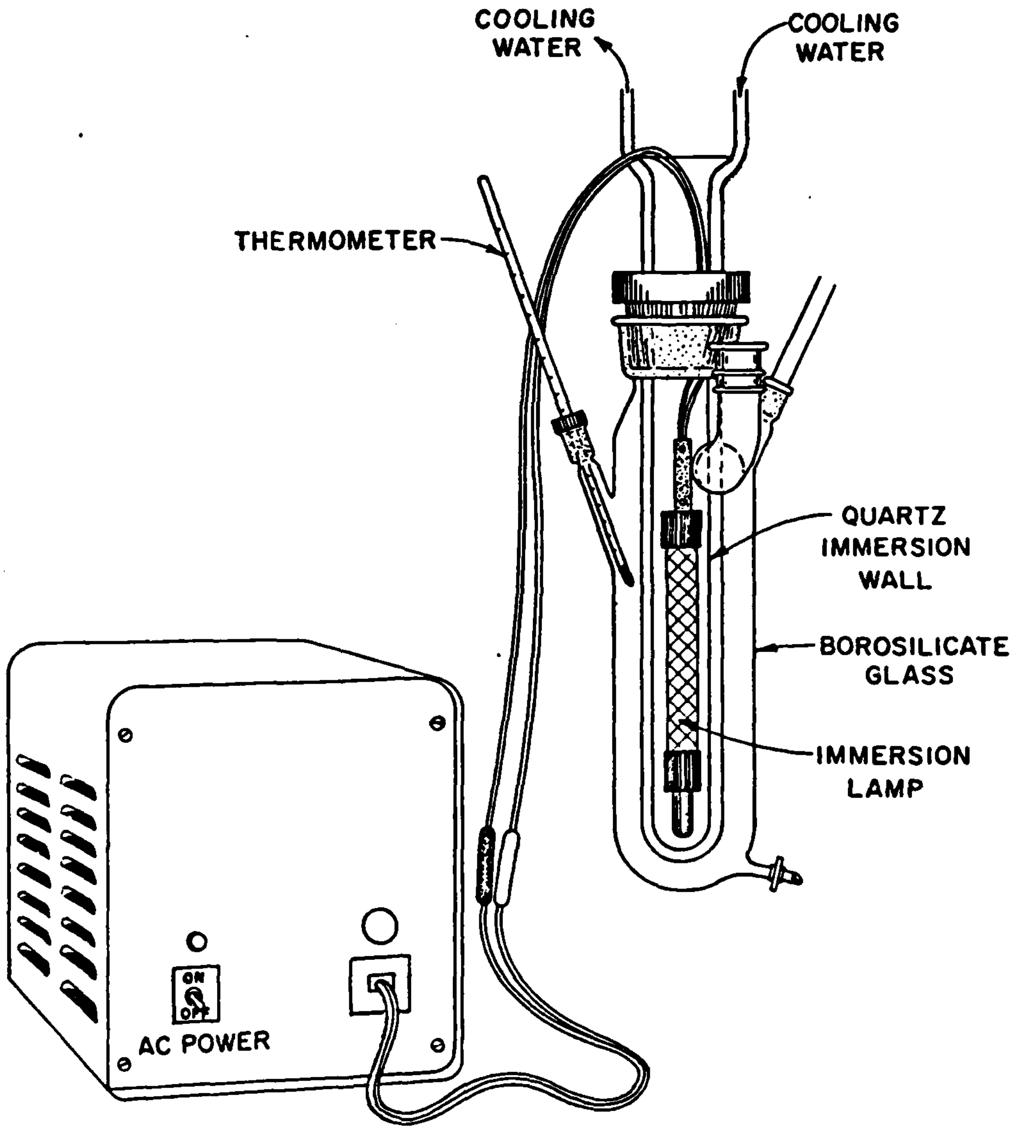


Fig. 1

solution (to isolate the 253.7 nm region from the medium-pressure mercury arc spectrum.)(33) The temperatures of the reaction mixtures in the borosilicate glass reactor were maintained at 27-35°C with circulating cooling water in the cooling chamber. The residence time of the solution in the reactor was monitored by a timer.

The aqueous solutions were prepared with double distilled deionized water with a concentration range of the organics from 200 to 750 ppm, depending on the solubility of the organics. When the solubility of a certain organic compound in water is lower than 200 ppm, the aqueous solution was warmed to about 40°C in order to increase the solubility. Hydrogen peroxide (Mallinckrodt, 30%) was added to the aqueous organic solution right before transferring into the reactor. Samples were collected after the desired time of irradiation. The aqueous reaction mixtures then were extracted twice with ethyl ether before and after the aqueous phase was acidified with concentrated HCl to pH about 1. The ether solutions were dried over Na_2SO_4 before removal of solvent with a rotary evaporator. The residues then were subjected to GC/MS analyses. Confirmation of the structure of intermediates whenever possible was done by comparison with authentic compounds. All authentic compounds (phenols and acids) and the reaction mixtures were silylated with MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide: Pierce) before GC/MS analysis unless noted otherwise.

Analytical Methods

The rates of disappearance of a given organic compound, sucn as DNT, in reaction mixtures were monitored by high performance liquid chromatography (HPLC) equipped with a Varian Vari-Chrom UV-VIS detector. Reverse phase columns of 25 cm long, 10 mm i.d. and 25 cm long, 4.6 mm i.d., packed with Alltech C18, 10_μ, were used for separation and analyses respectively.

Mixtures of glass distilled methyl alcohol (Boldman Chemicals) and deionized double distilled water were used as the mobile phase. The instrument was calibrated with aqueous standard compound solutions. Besides HPLC, reaction intermediates were also characterized after silylation by a Hewlett-Packard HP 5995A gas chromatograph/mass spectrometer (GC/MS) system fitted with a 30-meter Durabond I narrow bond fused silica column (J. W. Scientific). The column temperature was programmed from 50° (3-min hold) to 325°C with an increase of 10°C/min. The injection port temperature was set at 300°C.

Glyoxal and glyoxylic acid were determined by HPLC with a reverse phase C18 column after converting them to 2,4-dinitrophenylhydrazones.(34) A small amount (about 10 to 20 μ moles) of the standard compound or reaction mixture was dissolved in 0.5 ml of methanol and then acidified with 1 drop of concentrated HCl. About 15 to 30 μ moles of 2,4-dinitrophenylhydrazine (Aldrich) was dissolved in 0.5 to 1.0 ml of methanol. The two solutions then were mixed thoroughly and heated at 50°C for 10 minutes. An aliquot of the reaction mixture was injected directly to the reverse phase column for analysis.

Formic acid and CO_2 were not determined in this study.

RESULTS AND DISCUSSION

Photooxidation of aqueous DNT/H_2O_2 mixtures

Saturated aqueous solutions (204.9 ppm) of DNT were first exposed to the 450-watt medium-pressure mercury lamp without the presence of an oxidizing agent. The disappearance of DNT in the aqueous solution was monitored by HPLC with a reverse phase C18 column. The colorless initial aqueous solution turned yellow after about 10 minutes of exposure. The color gradually became darker and the solution became cloudy. After 17 hours of light exposure, the HPLC spectrum (monitored at 254 nm) revealed that many products had been formed during the reaction, while the amount of DNT in the solution had been remarkably reduced (< 0.6 ppm). The pH of the solution dropped from about 7 (aqueous DNT solution) to 4.4 at the end of 17 hours. The disappearance of DNT vs time is given in Table 1.

Table 1 also gives corresponding data on disappearance of DNT vs time in aqueous solutions at various concentrations of H_2O_2. Hydrogen peroxide was added to the aqueous DNT solution prior to light exposure. The molar ratios of H_2O_2/DNT varied from 13 to 104. These aqueous mixtures were exposed to the 450-watt Hg lamp without any filter. Depending on the concentration of H_2O_2, the colorless initial mixtures turned yellow to deep orange between 2 to 10 minutes, then faded gradually as exposure was continued, and finally became colorless (between 60 to 90 minutes). It was interesting to note that the pH values of the reaction mixtures changed with the changing of color. The pH of these initial aqueous mixtures (which ranged from 6.5 to 6.0 depending on the concentrations of H_2O_2) decreased to 2.8 when the orange color appeared and then to 2.4 at the dark orange to brown stage before starting to increase as the color gradually faded away. The pH of the colorless final reaction mixture was about 3.6.

Table 1. Effect of Hydrogen Peroxide Concentration and Time of Exposure on the Extent of Photooxidative Degradation of DNT

Incident Light: 450-watt medium-pressure mercury vapor lamp with no filter.

Time Exposure (min)	Percentage DNT Elimination at Various H_2O_2/DNT Molar Ratios				
	0	13	26	52*	104
10	-	55.0	69.7	76.5	47.2
20	29.9	85.0	94.8	91.0	50.3
30	37.9	-	97.7	97.8	50.3
60	54.6	98.8	99.5	99.4	54.4
90	62.3	-	100	100	-
120	89.0	~100	100	100	66.9
180	-	100	100	-	73.8
240	97.2	-	-	-	82.7
300	-	-	-	-	88.1
360	-	-	-	-	95.9
420	99.0	-	-	-	-
450	-	-	-	-	99.9
480	-	-	-	-	~100
600	99.7	-	-	-	-
1015	< 99.7		-	-	-
-					

*The original concentration of DNT in H_2O was 210 ppm.

It can be seen from Table 1 that the most effective concentration of H_2O_2 is the one with molar ratio of H_2O_2/DNT = 26 to 52. At this molar ratio, the disappearance of DNT in aqueous solution was very fast. It took only about 30 minutes to consume more than 98% of the original 204.9 ppm DNT, and after about 1.5 hours, no organic compounds could be seen in the HPLC and GC/MS spectra of the photooxidized reaction mixture. Therefore, it is clear that there is an optimum concentration of H_2O_2. Excess H_2O_2 in the solution actually retarded the DNT degradation. This finding is in agreement with Andrew's works.(1-3)

Table 2 gives similar results as a function of wavelength of the incident light. Several portions of the aqueous mixture with H_2O_2/DNT = 26 were exposed to the 450-watt Hg lamp equipped with either a Pyrex or a Vycor filter in order to block out or partially block out light in the far UV region; in other words, to reduce the energy of the incident light.

With a Pyrex filter, the colorless aqueous mixture turned to yellow after about 20 minutes. The solution became cloudy at ca. 1 hour. After 14 hours of exposure, it was found that about 92% of the original DNT was eliminated and many other products were produced (according to the HPLC spectrum). With a Vycor filter, which only partially blocked out the far-UV-region light, it was found that the degrading rate of DNT was comparable with the same solution when exposed to the same UV light without filter, except that it took much longer time to completely eliminate the same amount of DNT (intermediates in the UV-Vycor-photooxidized mixtures were not analyzed). Thus it appears the presence of light in the far UV region is a very important factor to degrade DNT in aqueous solution completely. In order to prove further the important roles played by H_2O_2 and light in the far UV region, the same aqueous mixture was also exposed to the 450-watt Hg lamp

Table 2. Effect of Wavelength Range of Incident Light and Time of Exposure on the Extent of Photooxidative Degradation of DNT

Incident Light: 450-watt medium-pressure mercury vapor lamp

Wavelength Range (nm):	200-1400 (No Filter)	$\sim$230-1400 (UV/Vycor filter)	280-1400 (UV/Pyrex filter)	
Type of Solution:	H_2O_2/DNT=26	H_2O_2/DNT=26	Aqu DNT	H_2O_2/DNT=26
Time of Exposure (min)	Percentage DNT Elimination			
10	69.7	43.0	-	7.5
20	94.8	75.0	-	-
30	97.7	84.4	11.1	17.9
60	99.5	97.8	25.4	-
90	100	-	-	-
120	-	99.8	-	-
140	-	$\sim$99.9	34.4	47.3
200	-	-	-	58.7
320	-	-	52.8	-
420	-	$\sim$99.9	-	-
480	-	-	-	84.5
620	-	-	64.5	-
840	-	-	-	92.6
950	-	-	70.2	-

with a Pyrex filter in the absence of H_2O_2. Under these conditions, it was found that the colorless aqueous mixture turned brown in about 20 minutes, and then the solution became muddy with considerable precipitation. After 16 hours, only about 70% of the original DNT has been eliminated and many products other than DNT were detected.

Experiments have also been done by mixing DNT-saturated aqueous solutions with hydrogen peroxide at various molar ratios of H_2O_2 to DNT without UV irradiation. These aqueous mixtures were stirred at room temperature under conventional indoor light for 7 days. The results, given in Table 3, show that oxidation of aqueous DNT solutions with H_2O_2 alone was very slow and elimination of DNT was never complete.

As just mentioned, there was a stage at which the color of the UV-irradiated DNT/H_2O_2 reaction mixture would turn to dark orange before the color began to fade away. This is probably the optimum experimental region ($\sim$ 10 minutes) to search for reaction intermediates. To this end, four partially photooxidized reactions mixtures were studied. In order to obtain larger amounts of intermediates, six liters of saturated aqueous DNT solution were mixed with H_2O_2 at a molar ratio of H_2O_2/DNT = 26 for photooxidation. Two liter aliquots of this aqueous mixture was exposed to the 450-watt Hg lamp for about 2, 5, and 10 minutes, respectively. For comparison, another six liters of the same aqueous DNT solution were mixed with H_2O_2 at a molar ratio of 13 and exposed to a 200-watt Hg lamp for 14 minutes. The pH values of these reaction mixtures generally dropped from ca. 6 to 2.8. According to the HPLC and GC/MS spectra, the intermediates produced from the above four reactions were very similar. A major intermediate, which amounted to more than 90% of the total intermediates detected, and many minor intermediates were found. These aqueous reaction mixtures were first extracted with ethyl

Table 3. Degradation of DNT in Aqueous Solution in the Presence of Various Concentration of H_2O_2 but in the Absence of UV at Room Temperature

H_2O_2/DNT (Molar Ratio)	Percentage DNT Elimination After 7 Days
26.4	25
136	29
280	35.7
571	53.8
889	64.3

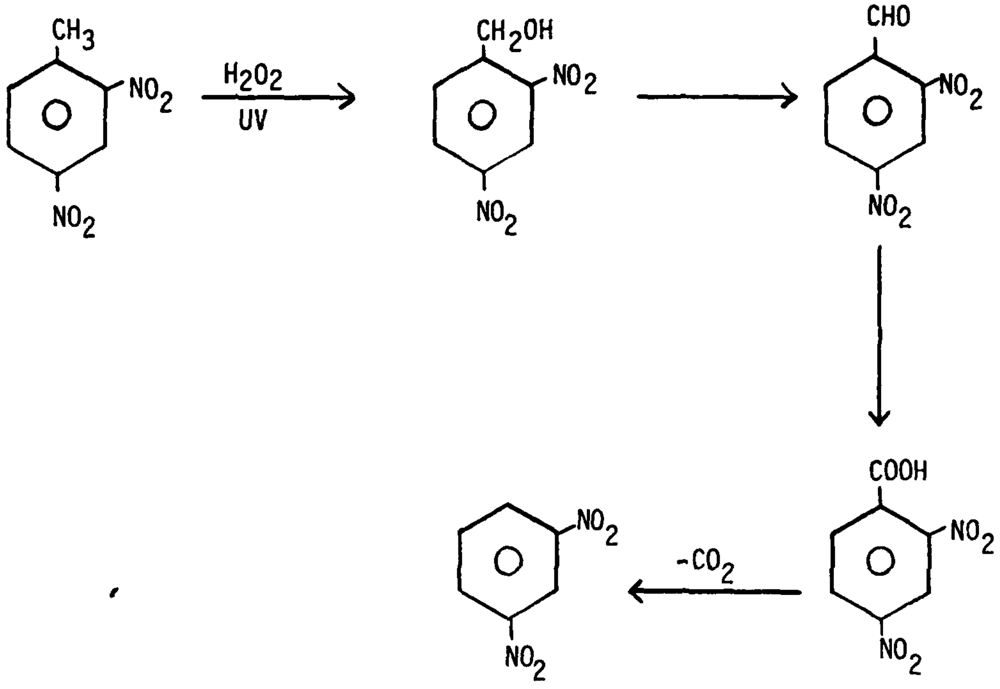
ether (fraction I), then the aqueous phase was acidified with concentrated HCl to pH=1 and extracted again with ethyl ether (fraction II). Solvents were removed from each fraction via rotary evaporation (at 30° to 45°C) under vacuum. The residues were dried under N_2. According to HPLC spectra, most of the unreacted DNT and some less polar intermediates were found in fraction I, small amounts of DNT and polar intermediates were found in fraction II, while almost none of the organics was left in the aqueous phase. The total residues of the 14-minute-exposed reaction mixture, which included fractions I and II and the aqueous phase, corresponded to only about 40% of the starting material (including the unreacted DNT). This reveals that the rate of degradation of DNT is very fast. Sixty percent of the starting material is presumably converted to gases (such as CO_2), very volatile organics, and water. The major intermediate, a polar compound, which could be mostly found in fraction II with a small amount in fraction I, was separated from the other intermediates by preparative HPLC (reverse phase C18 column).

The isolated major intermediate and the residues of fractions I and II from the above four reaction mixtures were silylated with MSTFA (N-methyl-N-trimethylsilyltrifluoroacetamide) and characterized by GC/MS studies. After comparing with the authentic compound, the major intermediate was confirmed as 2,4-dinitrobenzoic acid. Other intermediates found in the mass spectra were divided into three classes: (a) those which could be compared with the available authentic compounds, (b) those which could be compared with the GC/MS spectra of an isomer and (c) those which could be matched with the calculated m/e values of base ion peak, M-15 (molecular ion - ($-CH_3$) ion) ion peak, and molecular ion peak. In class (a) the intermediates found were 2,4-dinitrobenzaldehyde, 1,3-dinitrobenzene, 2,4-dinitrophenol, 3-nitrophenol, maleic acid, and oxalic acid. In class (b) was an intermediate with a mass spectrum (base ion peak m/e = 239; a fragment ion peak m/e = 255) which matched the mass spectrum of silylated 3,4-dinitrobenzyl alcohol (base ion peak m/e = 239; M-15 ion peak m/e = 255) except with a different GC retention time (as usually happens with isomers). This intermediate thus presumably was 2,4-dinitrobenzyl alcohol. In class (c) was 2-hydroxy-maleic acid (2-hydroxy-2-butendioic acid) (mass spectrum: base ion peak at m/e = 147, a typical fragment ion, $(CH_3)_3Si\text{-}O\text{-}\overset{+}{S}i(CH_3)_2$, of dicarboxylic acids, hydroxy acids, and terminal diols;(35,36) and M-15 ion peak at m/e = 333).

2,4-Dinitrohydrazone derivatives of glyoxal and glyoxylic acid were also found in these reaction mixtures.

Aqueous DNT and H_2O_2 mixtures with molar ratios of H_2O_2/DNT = 26 and 13 were also exposed to largely monochromatic light at 253.7 nm, which was produced either from the 450-watt medium-pressure Hg lamp with an aqueous $CoSO_4$ filter solution or from a low-pressure Hg lamp (a germicidal lamp from GE). After 10 to 20 minutes exposure, 2,4-dinitrobenzoic acid was again found as the major intermediate in both cases, and the numbers of other intermediates were markedly reduced and only small amount of maleic and oxalic acid observed.

The large amount of 2,4-dinitrobenzoic acid produced at short times probably indicates that a major part of the degradation in the beginning is sidechain oxidation, that is:



The finding of small amounts of 2,4-dinitrobenzyl alcohol and 2,4-dinitrobenzaldehyde in the reaction mixtures strongly supports the sidechain-oxidizing mechanism. The relatively small amount of dinitrobenzyl aclohol and dinitrobenzaldehyde compared to the large amount of dinitrobenzoic acid indicates that the rate of oxidation of the alcohol and aldehyde derivatives is faster than the rate of decomposition of the dinitrobenzoic acid. A similar oxidative sequence was also observed by Pauch et al. on pyrolysis of TNT in the liquid phase.(37)

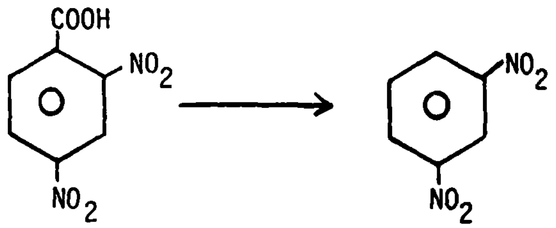
Although this sidechain oxidation of DNT has not been investigated in more detail, it is reasonable to suggest that attack on the methyl group is initiated by hydroxyl radicals formed by photolytic cleavage of H_2O_2.

In order to investigate the reaction pathway subsequent to the formation of 2,4-dinitrobenzoic acid and/or 1,3-dinitrobenzene, photooxidations of several of the identified intermediates were studied next.

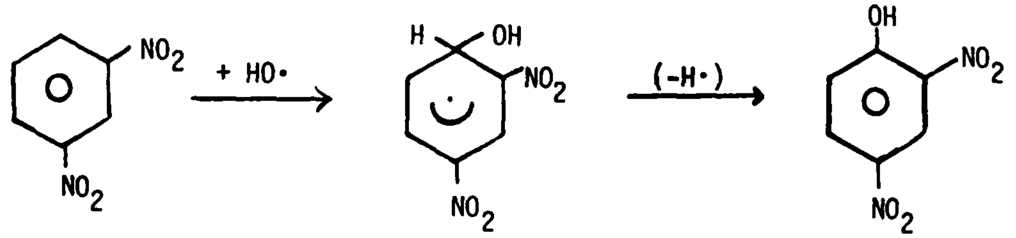
Photooxidation of aqueous 2,4-dinitrobenzoic acid/H_2O_2 mixtures

Aqueous 2,4-dinitrobenzoic acid (DNBA) (545 ppm) solution (250 ml) was mixed with hydrogen peroxide at a molar ratio of H_2O_2/DNBA = 26 and exposed to the 450-watt Hg lamp without filter. The disappearance rate was somehow slower than DNT under the same conditions. This might have been expected because the prominent amount of DNBA which accumulated in the short-time-photooxidized DNT reaction mixture was one evidence of a relatively slow rate of DNBA consumption. Of course, the higher concentration of DNBA in the reaction solution could be another factor to affect the rate.

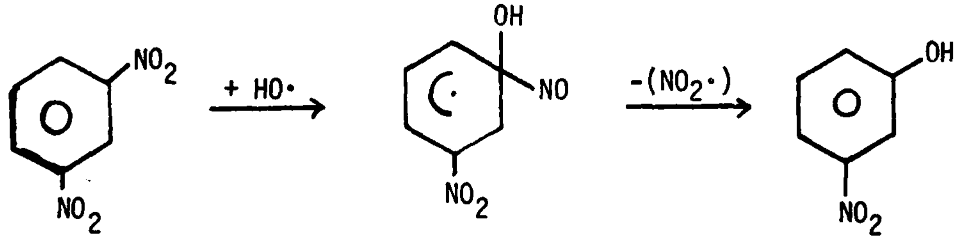
It took about 5.7 hours to completely eliminate the acid in the above aqueous mixture. The pH values of the solution dropped from 2.6 (initial aqueous mixture) to 2.4, then rose back to 2.5 at the end of exposure. According to the HPLC spectra, there was at least one intermediate obtained after 10 minutes and two after 20 minutes. The quantities of these intermediates increased with time of exposure, reached a maximum at about an hour (at this time about 50% of the original acid was eliminated), and then started to decline. Therefore, another 250 ml of the DNBA/H_2O_2 mixture was exposed to the same Hg lamp for 1 hour in order to obtain sufficient amounts of intermediates. By extracting twice with ethyl ether (before and after the aqueous phase was acidified with conc. HCl to pH = 1), two fractions (I and II) were collected. The residues from fractions I and II were silylated with MSTFA and characterized by GC/MS. 1,3-Dinitrobenzene was found definitely to be the major intermediate, and 3-nitrophenol was another intermediate in a significant amount. Both of these intermediates have been proven by comparing the HPLC and GC/MS spectra with those of authentic compounds. Besides these two, other intermediates appeared to be present as well. However, due to the large amount of unreacted DNBA overlapped with other polar intermediates, identification of the others became difficult. Therefore, the residues of fractions I and II were combined and separated by preparative HPLC in order to remove a large portion of the unreacted DNBA. Two more intermediates were discovered in this way. They were 2,4-dinitrophenol and oxalic acid. The presence of 1,3-dinitrobenzene, 3-nitrophenol and 2,4-dinitrophenol not only confirmed reaction (1), but suggested (2) and (3) as well.



(1)



(2)



(3)

Such reactions of hydroxyl radicals have been suggested.(19-24) In reaction (2), addition to an unsubstituted position of the benzene ring gives a hydroxycyclohexadienyl radical(22,23;38-41) which is oxidized further to the phenol derivative. Similar reactions were observed during UV-ozonation of nitrobenzene in aqueous solution which give mixtures of nitrophenols.(21) In reaction (3), addition to an ipso position again achieves ring hydroxylation but now with loss of the nitro substituent. To test this suggestion further, photooxidation of 1,3-dinitrobenzene was studied next.

Photooxidation of aqueous 1,3-dinitrobenzene/H_2O_2 mixtures.

Owing to the low solubility of 1,3-dinitrobenzene (DNB) in water, an aqueous DNB solution (328 ppm) was prepared by dissolving the DNB in water at 40°C and stirring overnight. The aqueous solution then was mixed with H_2O_2 prior to light exposure. The molar ratio of H_2O_2/DNB = 26 and the aqueous mixture was exposed to the 450-watt Hg lamp. The colorless aqueous mixture turned yellow after 10 minutes, this color persisted for about 2 hours before fading away. The pH of the reaction mixture dropped from 5.7 (initial DNB-H_2O_2 mixture) to 2.5 (after two-hour exposure). It was found that about 99% of the original DNB was eliminated after two hours. Samples of the 20-minute and 1.8-hour-exposed reaction mixtures were collected for analysis.

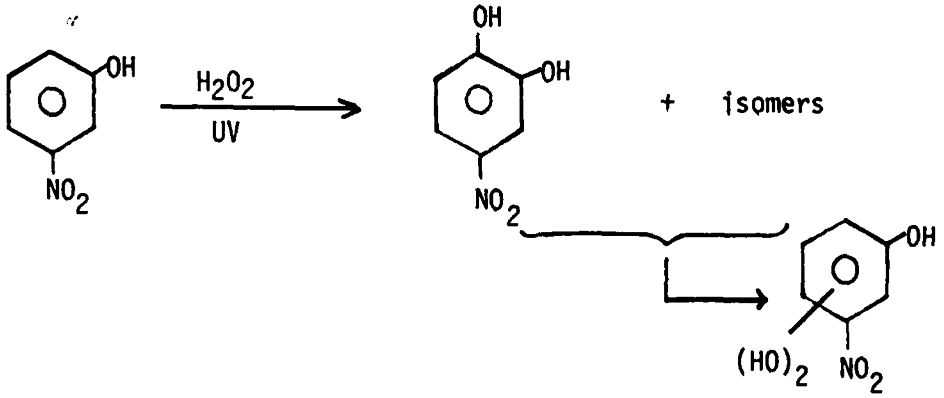
Major intermediates found in the 20-minute-exposed sample (by matching retention times of both HPLC and GC spectra and mass spectra with authentic compounds) were 3-nitrophenol and three isomers of dinitrophenols, the predominate one of which proved to be 2,4-dinitrophenol. The ratio of the total amount of the three dinitrophenols to 3-nitrophenol was about 4 to 1. The 1.8-hour-exposed reaction mixture contained no aromatic compounds. Instead, oxalic acid, mesoxalic acid semialdehyde [$(HO)_2C(COOH)(CHO)$; mass spectrum: base ion peak at m/e = 73, a typical trimethylsilyl ion from silylated carboxylic acids or alcohols,(35,36) and a fragment ion of m/e = 321, which corresponds to the M-15 ion peak], and hydroxy-maleic acid semialdehyde [2(or 3-)-hydroxy-4-oxo-2-butenoic acid; mass spectrum: base ion peak m/e = 73, M-15 ion m/e = 245; the pattern is similar to the spectrum of silylated maleic acid except having longer retention time] were observed. All these intermediates have been reported by other researchers(31,42-44) as reaction intermediates in ozonation of aqueous phenol, trans,trans-muconic acid, and maleic acid solutions. Glyoxal and glyoxylic acid were also found in this 1.8-hour-exposed reaction mixture.

The presence of both 3-nitrophenol and isomers of dinitrophenols in the short-time-exposed reaction mixture once again demonstrated the occurrence of reactions (2) and (3).

Photooxidation of aqueous 3-nitrophenol/H_2O_2 and 2,4-dinitrophenol/H_2O_2 mixtures

Photooxidation of aqueous 3-nitrophenol solution was carried out by mixing the aqueous 3-nitrophenol (497 ppm) with H_2O_2 at a molar ratio of H_2O_2/nitrophenol = 26. The aqueous mixture then was exposed to the 450-watt Hg lamp for total of 5.5 hours. At the end of the run, 3-nitrophenol could not be detected by HPLC and GC/MS spectra. Oxalic acid was the only detectable intermediate left in the reaction mixture. As exposure proceeded, the yellowish initial aqueous mixture changed into brown, gradually faded away, and became colorless after about 1.5 hours. The pH of the solution dropped from 3.6 (initial mixture) to 2.47 (after 1.5 hours). Qualitative analysis of the 15-minute-exposed reaction mixture has been done by HPLC and GC/MS studies. The GC/MS spectrum revealed that very large amounts of dihydroxynitrobenzenes (three isomers) and moderate amounts of trihydroxynitrobenzenes (two isomers) were present. The ratio of the total amount of dihydroxynitrobenzenes to trihydroxynitrobenzenes was about 14 to 1; the ratios of the three dihydroxynitrobenzenes were 1.5 (isomer I) to 1.0 (isomer II) to 1.7 (isomer III). Isomer III was proven to be 4-nitrocatechol by comparing with the authetic compound. In addition to the polyhydroxynitrobenzenes, other intermediates presented were maleic acid and oxalic acid, both in trace quantities.

The presence of large amounts of dihydroxynitrobenzenes and trihydroxynitrobenzenes in the reaction mixture presumably implies that photo-oxidation of aqueous 3-nitrophenol in the presence of H_2O_2 proceeds as shown:



(4)

Similar studies have been done by Leitis(21) on ozonation and UV-ozonation (using a low-pressure mercury lamp with primary output at 254 nm) of nitrobenzene in water. After short reaction times (10 sec.), 2-, 3-, and 4-nitrophenol were obtained as major products. For ozonation and UV-ozonation of 3- and 4-nitrophenol after short times (10 sec.), the first intermediate found was 4-nitrocatechol. Further ozonation and UV-ozonation of 4-nitrocatechol produced a trihydroxynitrobenzene isomer as the only benzene derivatives.

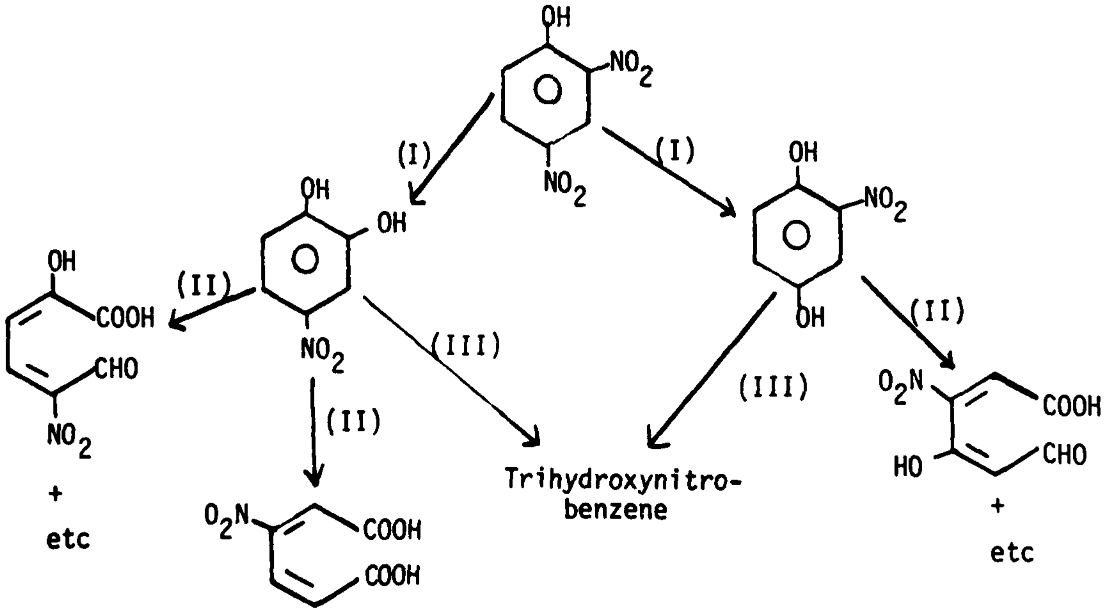
The ozonation of phenol in water has been studied for many years.(28-32) Although, depending on the concentrations of phenol and ozone, the number of intermediates obtained varied, the major conclusions are consistent. The attack of ozone on the aromatic ring leads to either hydroxylation or ring cleavage. Hydroxylation of phenol in aqueous solution gives predominantly catechol and hydroquinone, while ring cleavage gives cis,cis-muconic acid and muconaldehyde (cis,cis-6-oxo-2,4-hexadienoic acid).(31) It seems that ring cleavage might proceed either before or after ring hydroxylation. However, Yamamoto et al.(31) proposed that ozonation of phenol in water is initiated by ring hydroxylation to produce di- and trihydroxybenzene derivatives, followed by aromatic-ring cleavage. Because, on ozonation of hydroquinone in water, the major intermediate observed is a cis,cis-muconic acid derivative (cis,cis-3-hydroxy-2,4-hexadienedioic acid) but not cis,cis-muconic semialdehyde (cis,cis-4-hydroxy-6-oxo-2,4-hexadienoic acid) and the oxidation of aldehydes to carboxylic acids is much slower than ozonolysis of double bonds, the hydroxy-muconic acid must have arisen from 1,2,4-trihydroxybenzene. This also indicates that the hydroxylation may be faster than the cleavage of the aromatic ring.

In order to compare the reaction route of UV/H_2O_2 photooxidation with UV-ozonation, an aqueous phenol/H_2O_2 mixture was photolyzed with the medium-pressure Hg lamp. For better understanding of the reaction mechanism, the reaction rate was slowed down by reducing the amount of oxidizing agent (H_2O_2) and lowering the energy of the incident light (by using the 200-watt Hg lamp with a Vycor filter). The molar ratio of H_2O_2 to phenol was 6.5 and the concentration of the aqueous phenol solution was 640 ppm. The reaction rate was monitored by HPLC with reverse phase C18 column. Several intermediates were produced after 10 minutes of exposure; however, maximum amounts of intermediates were produced after 1.8 hours. Catechol was found as the major intermediate in the 1.8-hour-exposed mixture along with smaller amounts of hydroquinone, pyrogallol, 1,2,4-trihydroxybenzene, maleic acid, and hydroxy-maleic-acid semialdehyde. The results indeed agree with Yamamoto's proposed pathway. It seems that irrespective of the method used (ozonation, UV/O_3 or UV/H_2O_2), the sequence of oxidation of phenol in water is first hydroxylation followed by aromatic-ring cleavage. Photooxidation of aqueous 3-nitrophenol/H_2O_2 mixtures with the medium-pressure Hg lamp should follow the similar route. Leitis(21) has proven that ozonation and UV/ozonation of aqueous 3-nitrophenol solutions also gave ring hydroxylation leading to di- and trihydroxynitrobenzene derivatives before benzene-ring cleavage.

Since 2,4-dinitrophenol was another major intermediate found in the photooxidized aqueous 1,3-dinitrobenzene reaction mixtures, a similar study was also performed with it. An aqueous mixture of 500 ppm 2,4-dinitrophenol and H_2O_2 (the molar ratio H_2O_2/dinitrophenol = 26) was exposed to the 450-watt Hg lamp for a total of 3.4 hours (the time for complete disappearance of dinitrophenol in solution). The initial yellow solution changed into orange after 20 minutes, persisted for about 2 hours, and then suddenly turned back to light yellow before becoming colorless. Correspondingly, the pH of the solution changed from 3.5 (initial H_2O_2/dinitrophenol mixture) to 2.42 and then to 2.47. Samples after 20, 52, and 204 (3.4 hours) minutes of exposure were collected for analyses. The major intermediate found in the 20-minute-exposed sample was, to our surprise, a compound with mass spectra data (base ion peak at m/e = 73 and molecular ion peak (?) at m/e = 331) which could correspond to either hydroxynitromuconic acid semialdehyde (cis,cis-3-nitro-4-hydroxy-6-oxo-2,4-hexadienoic acid) or nitromuconic acid (cis,cis-3-nitro-2,4-hexadienedioic acid). The second major intermediate was 4-nitrocatechol along with trace amounts of a trihydroxynitrobenzene isomer.

In the 52-minute-exposed sample, the amount of nitromuconic acid (or nitrohydroxymuconic aldehyde) was even more dominant. Relatively smaller amounts of 4-nitrocatechol and trace amounts of oxalic acid were also found in this sample. The ratio of the nitro-(or nitrohydroxy-) muconic acid derivative to 4-nitrocatechol in this sample was approximately 5 to 1. The 3.4-hour-exposed reaction mixture contained mainly oxalic acid and trace amounts of nitromaleic acid semialdehyde (cis-2 (or 3)-nitro-4-oxo-2-butenoic acid; mass spectrum: base ion peak m/e = 73, M-15 ion m/e = 202, and molecular ion peak m/e = 217) and mesoxalic acid semialdehyde.

It seems that during photooxidation of aqueous 2,4-dinitrophenol/ H_2O_2 mixtures with the medium-pressure Hg lamp, several competing reactions occurred:



(5)

Since dinitromuconic acid derivatives were not found in any of the above reaction mixtures, the first step of the reaction proceeded as route (I), that is, a nitro group was removed from the benzene ring and replaced with a hydroxyl group. Routes (II) and (III) were similar to the ozonation of catechol or hydroquinone in water.(31) The presence of large amounts of nitro-muconic acid derivatives rather than di- and trihydroxynitrobenzenes in these reaction mixtures presumably implies either that hydroxylation and benzene- ring cleavage both occurred very rapidly in the 2,4-dinitrophenol/H_2O_2 system or benzene-ring cleavage occurred prior to hydroxylation. Note that we suggested above that, for the 3-nitrophenol/H_2O_2 system, hydroxylation proceeds faster than ring cleavage.

Photooxidation of aqueous 4-nitrocatechol/H_2O_2, 2-nitroresorcinol/H_2O_2 and catechol/H_2O_2 mixtures

4-Nitrocatechol and 2-nitroresorcinol are the two commercially available dihydroxynitrobenzenes. Since 4-nitrocatechol was one of the intermediates obtained during photooxidation of both the 3-nitrophenol/H_2O_2 and 2,4-dinitrophenol/H_2O_2 systems, this compound was further photooxidized. In addition, an isomer, 2-nitroresorcinol, was also photooxidized for the sake of comparison of reaction mechanisms, although the possibility to produce the latter was unfavored during photooxidation of either 3-nitrophenol or 2,4-dinitrophenol.

Several experiments have been carried out with various molar ratios of dihydroxynitrobenzene/H_2O_2 and different incident light sources. The results are given in Table 4. The concentrations of 4-nitrocatechol ranged from 611 to 694 ppm, and 2-nitroresorcinol was 632 ppm. The aqueous mixtures were treated as before. In both 4-nitrocatechol/H_2O_2 and 2-nitroresorcinol/H_2O_2 systems the pattern of color changes: yellow → brown → light yellow → colorless were seen and the pH values dropped from ca. 3.2 to 2.5 then back to 2.8 (when the solutions became colorless).

Table 4. Photooxidation Products of Dihydroxynitrobenzenes and Catechol in Aqueous Solution

Organic Compound	H_2O_2/org cpd. (Molar ratio)	UV Source	Time of Exposure (min)	Major Intermediate(s)	Other identifiable intermediates (small to trace amt)
4-Nitrocatechol	26	450-Watt medium pressure	10	Isomers of trihydroxynitrobenzenes	maleic acid, hydroxy-maleic acid semialdehyde,* oxalic acid
	26	"	35	"	maleic acid, hydroxy-maleic acid, oxalic acid
	26	"	84 (1.4h)	"	oxalic acid
	26	"	246 (4.1h)	oxalic acid	Nitro-maleic acid semialdehyde**, hydroxymaleic acid semialdehyde, nitro-maleic acid
	26	200-Watt	134 (2.24h)	oxalic acid	maleic acid, hydroxy-maleic acid semialdehyde, nitro-maleic acid semialdehyde
	6.5	"	132 (2.2 h)	oxalic acid	maleic acid, hydroxy-maleic acid semialdehyde, oxalic acid
	2.0	"	63 (1.05h)	"	maleic acid, hydroxy-maleic acid semialdehyde

Table 4 (contd.)

Organic Compound	H_2O_2/org cpd. (Molar ratio)	UV Source	Time of Exposure (min)	Major Intermediate(s)	Other identifiable intermediates (small to trace amt)
2-Nitroresorcinol	26	450-watt	10	isomers of trihydroxynitrobenzenes	maleic acid
	26	"	96 (1.6 h)	oxalic acid	maleic acid, nitromaleic acid semialdehyde, hydroxymaleic acid semialdehyde
	13	"	10	"	maleic acid
	6.5	"	20	"	maleic acid
Catechol	6.5	200-watt	10	pyrogallol	maleic acid, oxalic acid, 1,2,4-trihydroxybenzene
	6.5	"	108 (1.8 h)	oxalic acid	maleic acid, mesoxalic acid semialdehyde, hydroxymaleic acid semialdehyde, pyrogallol
	6.5	200-watt/ Vycor	20	pyrogallol	1,2,4-trihydroxybenzene
	2	"	72 (1.2 h)	pyrogallol	1,2,4-tridroxybenzene, maleic acid, oxalic acid

*)3-hydroxy-4-oxo-2-butenoic acid or 2-hydroxy-4-oxo-2-butenoic acid.

**)3-nitro-4-oxo-2-butenoic acid or 2-nitro-4-oxo-2-butenoic acid.

Although the results shown in Table 4 were somewhat scattered, it still could be seen that the major intermediate(s) produced were isomers of trihydroxynitrobenzenes or oxalic acid; the ratio was highly dependent on the concentration of hydrogen peroxide, on the intensity of incident light, and on the length of exposure. The reaction patterns of the 4-nitrocatechol/H_2O_2 system and the 2-nitroresorcinol/H_2O_2 system were very similar except there were three isomers of trihydroxynitrobenzenes in the former case, but only one isomer in the latter case obtained after short-time exposure. Other intermediates found in relatively small amounts in these reaction mixtures were maleic acid, nitromaleic acid semialdehyde, hydroxymaleic acid semialdehyde, and oxalic acid.

Thus it appears that photooxidation of aqueous dihydroxynitrobenzene/H_2O_2 mixtures produces trihydroxynitrobenzene, and continuing photooxidation of the trihydroxynitrobenzene eventually leads to benzene-ring cleavage. This has also been demonstrated by Leitis(21) for UV-ozonation of aqueous 4-nitrocatechol solution.

In order to further support the above reaction mechanism, photooxidation of an aqueous catechol/H_2O_2 mixture was studied. To slow down the rate of reaction, the concentration of catechol in water was set high (745 ppm), the ratios of H_2O_2/catechol were low (6.5 and 2.0), and the energy of the incident light was reduced by using the 200-watt medium-pressure Hg lamp equipped with and without a Vycor filter. Dependent on the length of exposure, either pyrogallol or oxalic acid was found as the major intermediate. Other intermediates present were 1,2,4-trihydroxybenzene, maleic acid, mesoxalic acid semialdehyde, and hydroxymaleic acid semialdehyde. The reaction sequence is clearly parallel to photooxidation of aqueous 4-nitrocatechol/H_2O_2 and 2-resorcinol/H_2O_2 mixtures.

Photooxidation of aqueous trihydroxynitrobenzene/H_2O_2 and pyrogallol/H_2O_2 mixtures

A mixture of trihydroxynitrobenzene isomers was isolated from the photooxidized 4-nitrocatechol reaction mixture by preparative HPLC (reverse phase C18 column). The aqueous trihydroxynitrobenzenes (40 ppm) solution was mixed with H_2O_2 at molar ratio of H_2O_2/trihydroxynitrobenzenes (THNB) = 19.5 (the reason for choosing this ratio will be shown later) and exposed to the 450-watt medium-pressure Hg lamp for 20 minutes. The GC/MS spectrum of the 20-minute-exposed reaction mixture revealed that mesoxalic acid semialdehyde and oxalic acid were the two major intermediates. Fairly small amounts of hydroxymaleic acid, hydroxymaleic acid semialdehyde and mesoxalic acid were also observed in the mass spectrum. Glyoxal and glyoxylic acid were also found in this reaction mixture.

To understand the reaction pathway better, in addition to the above experiment, an aqueous solution of 1,3,5-trihydroxy-2-nitrobenzene (the only commercially available isomer) (573 ppm) was mixed with H_2O_2 at molar ratios of H_2O_2/THNB = 26, 19.5, 13, and 6.5 and exposed to the 450-watt Hg lamp for 20 minutes. HPLC spectra showed that the disappearance of the trihydroxynitrobenzene in all four mixtures was fast. The disappearance rate was found proportional to the concentration of H_2O_2 as shown in Table 5. At lower H_2O_2 concentrations, say H_2O_2/THNB = 6.5 and 13, the colorless aqueous mixtures turned to dark brown after 20 minutes of exposure, and some gas bubbles were found in the reaction mixtures. As the molar ratios increased to 19.5 and 26, the aqueous mixtures changed from colorless to light yellow and lots of gas bubbles were obtained. This suggested that a large amount of the starting material was converted to gas, such as CO_2. Table 6 lists all the intermediates, which have been found in these four reaction mixtures by

Table 5. Effect of Hydrogen Peroxide Concentration on the Extent of Photooxidative Degradation of 1,3,5-Trihydroxy-2-nitrobenzene (THNB) Degradation

H_2O_2/THNB (molar ratio)	Time Exposure(min)	Percentage Elimination	Color of Solution
26	20	91.1	light yellow
19.5	"	90.7	"
13	"	77.8	dark brown
6.5	"	53.0	"

Table 6. Photooxidation Products of Trihydroxynitrobenzenes and Pyrogallol in Aqueous Solution

Compound	H_2O_2/cpd (molar/ratio)	Light Source	Time of Exposure (min)	Major Intermediate(s)	Other identifiable Intermediates (small to trace amt)
Mixture of* Trihydroxy-nitro-benzenes	19.5	450-watt medium pressure	20	oxalic acid, mesoxalic acid semialdehyde	mesoxalic acid, hydroxymaleic acid semialdehyde, hydroxymaleic acid
1,3,5-trihydroxy-2-nitrobenzene	26	"	20	oxalic acid	mesoxalic acid semialdehyde, hydroxymaleic acid semialdehyde, maleic acid
	19.5	"	"	"	"
	13	"	"	"	mesoxalic acid semialdehyde, nitro-maleic acid derivatives**
	6.5	"	"	"	"
Pyrogallol	26	"	30	no major intermediate	maleic acid, oxalic acid, mesoxalic acid
	6.5	200 W/Vycor	35	maleic acid	hydroxymaleic acid semialdehyde

*Isolated from photooxidized 4-nitrocatechol reaction mixture.

**$COOHC(NO_2)CHCOOH$ or $CHOC(OH)C(NO_2)COOH$

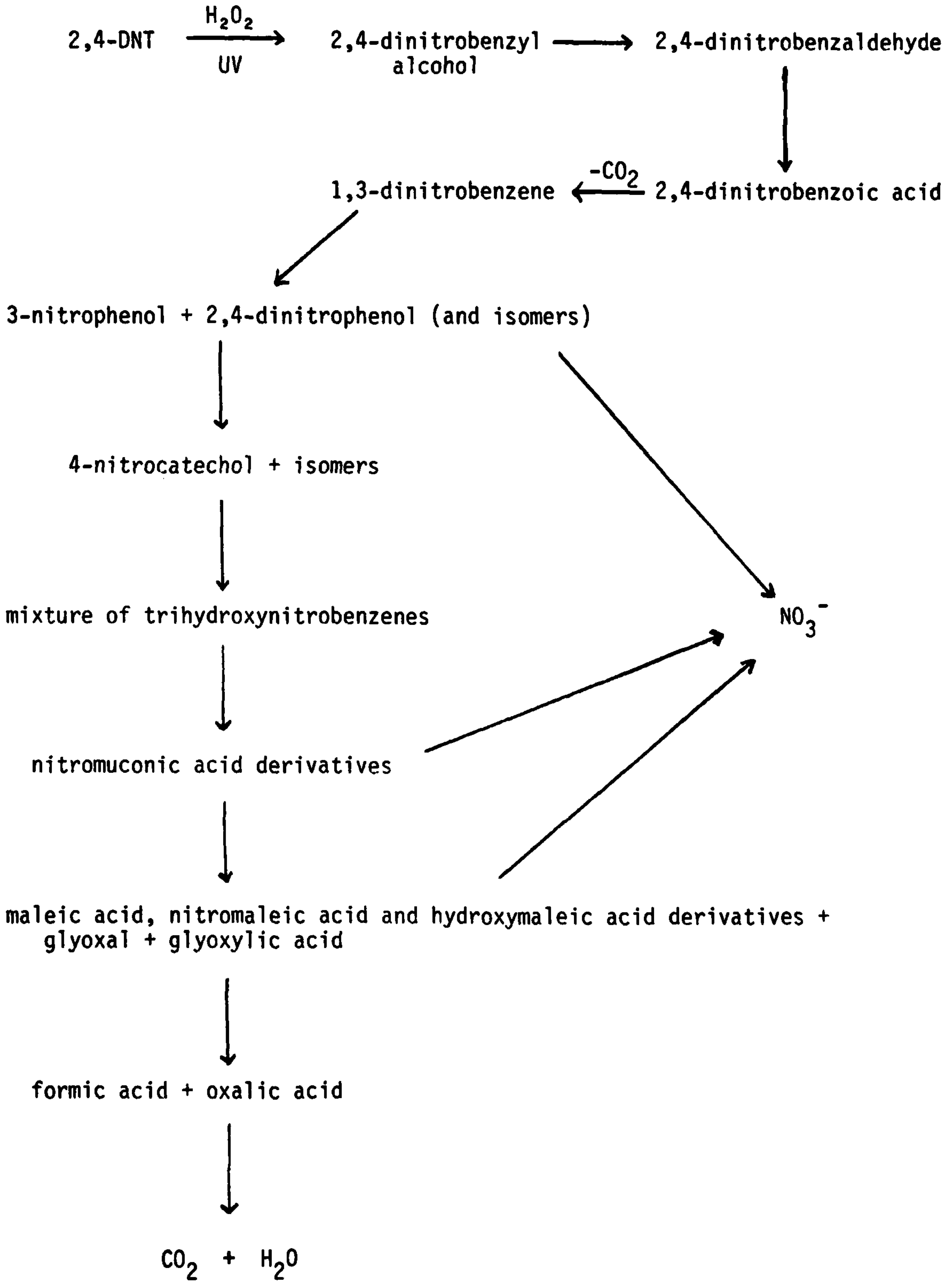
GC/MS. Oxalic acid was found as the major intermediate in all four reaction mixtures. Other intermediates present were mesoxalic acid semialdehyde, maleic acid, nitromaleic and hydroxymaleic acid derivatives. It seems that after the benzene ring cleavage, the degradation of nitromuconic acid derivatives was very fast, because in all cases mentioned above, not a trace of nitromuconic acid derivatives (including acids and aldehydes) was found. They must be very quickly degraded to lower-molecular-weight acids and aldehydes.

An analogous photooxidation of aqueous pyrogallol/H_2O_2 mixtures was also investigated, The molar ratios of H_2O_2/pyrogallol = 13 and 6.5 and these aqueous mixtures were exposed to the 450-watt Hg lamp and 200-watt lamp/Vycor filter respectively for about 30 minutes. The intermediates produced are also given in Table 6. About equal amounts of maleic acid, oxalic acid, mesoxalic acid and hydroxymaleic acid semialdehyde were found in the 450-watt-lamp-exposed sample; in the 200-watt-lamp/Vycor-exposed sample, maleic acid was found as the major intermediate along with trace amounts of hydroxymaleic acid semialdehyde.

Further photooxidation of the low-molecular-weight carboxylic acids, such as maleic acid, oxalic acid, glyoxylic acid, and aldehydes, such as glyoxal, were not performed in this study. For oxidation of maleic acid in water by ozone,(31,43) glyoxylic acid and formic acid were obtained as the reaction products and further oxidation would convert these acids into oxalic acid and CO_2. In addition, from oxidation of oxalic acid and formic acid in water by ozone,(31) CO_2 was obtained as the end product. Similarly, from photooxidation of an aqueous maleic acid solution with UV/ozone,(21) formic acid was found as the major intermediate along with small amounts of glyoxylic acid and oxalic acid. UV-ozonation of aqueous glyoxal produced oxalic acid and CO_2.(21)

The observation of maleic acid and its derivatives, oxalic acid, glyoxal and glyoxylic acid in the 2- to 14-minute-exposed-photooxidized aqueous DNT/H_2O_2 solutions and in 10- or 20-minutes-photooxidized aqueous intermediates (DNT degradation products)/H_2O_2 solutions, presumably suggests that similar degradation sequences of the 2- and 4-carbon carboxylic acids and aldehydes to CO_2 would, also occur when photooxidizing them with UV/H_2O_2.

Based on intermediates identified after each photooxidation of aqueous DNT and its degradation intermediates solutions in this study, one can suggest the following reaction pathway for photooxidation of aqueous DNT solutions with UV/H_2O_2:


2,4-DNT
H_2O_2
UV
2,4-dinitrobenzyl alcohol
2,4-dinitrobenzaldehyde
2,4-dinitrobenzoic acid
$-CO_2$
1,3-dinitrobenzene
3-nitrophenol + 2,4-dinitrophenol (and isomers)
4-nitrocatechol + isomers
mixture of trihydroxynitrobenzenes
NO_3^-
nitromuconic acid derivatives
maleic acid, nitromaleic acid and hydroxymaleic acid derivatives + glyoxal + glyoxylic acid
formic acid + oxalic acid
CO_2 + H_2O

SUMMARY:

1. 2,4-Dinitrotoluene (DNT) in aqueous solution can be efficiently degraded by photooxidation with UV/H_2O_2.
2. The optimal conditions to decompose DNT in aqueous solution with UV/H_2O_2 are a molar ratio of H_2O_2 to DNT ranging from 26 to 52 and the presence of UV radiation of wavelength $<$ 280 nm.
3. Reaction intermediates which have been identified by GC/MS and HPLC are 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid, 1,3-dinitrobenzene, 3-nitrophenol, 2,4-dinitrophenol (and isomers), 4-nitrocatechol (and isomers), isomers of trihydroxynitrobenzenes, maleic acid derivatives, oxalic acid, glyoxal, and glyoxylic acid.
4. Mechanistic conclusions concerning the photooxidation of DNT, inferred from these intermediates include the following:
   a. The initial step of the reaction is photolysis of H_2O_2 in water which produces hydroxyl radicals.
   b. The first attack of hydroxyl radicals is on the methyl group of DNT which induces side-chain oxidation and converts DNT to 2,4-dinitrobenzoic acid and then to 1,3-dinitrobenzene.
   c. After elimination of the methyl group on the benzene ring of DNT, the oxidation further proceeds via hydroxylation of the benzene ring to produce mono-, di-, and trihydroxynitrobenzenes.
   d. Further oxidation of the trihydroxynitrobenzenes leads to benzene-ring cleavage and produces 2- and 4-carbon carboxylic acids and aldehydes.
   e. The 2- and 4-carbon carboxylic acids and aldehydes produced are eventually converted to CO_2 and H_2O.

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