Oxidation of 2,4-Dinitrotoluene Using Fenton’s Reagent: Reaction Mechanisms and Their Practical Applications

NIHAR R. MOHANTY
Environmental Engineer
Department of Environmental Protection, Massachusetts
10 Commerce Way
Woburn, MA 01801

IRVINE W. WEI
Associate Professor
Department of Civil Engineering
Northeastern University
Boston, MA 02115

ABSTRACT

With the strict regulations of present times, chemical oxidation holds tremendous potential for destructive treatment of hazardous wastes which are resistant to biological oxidation. Fenton’s reagent has proved to be an inexpensive and powerful oxidant which has been shown to oxidize a wide variety of organics. In this paper, 2,4 dinitrotoluene (2,4 DNT) was chosen as a model compound following previous work where 2,4 DNT was subjected to oxidation by hydrogen peroxide in the presence of medium power UV source. Various factors that are important to optimize the oxidation of organics were studied. The effect of aeration, step dosing and the role played by the ferric ions on oxidation of 2,4 DNT were verified in this experimental study. The results of our work show that 2,4 DNT can be effectively oxidized in aqueous solutions with Fenton’s reagent. At a H₂O₂:DNT:Fe²⁺ ratio of 20:1:2.5 (molar), 2,4 DNT was completely removed in 5 hours. Finally, the results and the reaction intermediates of the oxidation of 2,4 DNT with Fenton’s reagent vis-a-vis the H₂O₂/UV system are discussed.

INTRODUCTION

Dinitrotoluenes are generated from ammunition factories and other chemical industries. One major use of 2,4 DNT is making 2,4 diaminotoluene for isocyanate production. Dinitrotoluenes are also used for production of dyes, explosives, organic synthesis and as a propellant additive. Over 0.5 billion lb./yr. of 2,4 dinitrotoluene and 2,6 dinitrotoluene were produced in 1982 [11].

Biodegradation, although possible, may require longer time to oxidize 2,4 DNT in aqueous solutions. Use of a strong oxidant may be necessary for treatment of 2,4 DNT in a shorter time. Products resulting from chemical oxidation might be more amenable to biological treatment than the parent compound.

A well documented process for generating oxidants in aqueous solution is Fenton’s reagent, a
combination of H$_2$O$_2$ and a ferrous salt. This mixture (H$_2$O$_2$ + Fe$^{2+}$) forms hydroxyl radicals (’OH) which play the major part in oxidation of organics. Equation 1 depicts the formation of hydroxyl radicals.

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \cdot \text{OH} + \text{OH}^- + \text{Fe}^{3+}$$  \hspace{1cm} (1)

There are numerous other competing reactions which are widely accepted and are given below.

$$\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (2)

HO$_2^-$ is a superoxide radical which is known to have lower oxidation capability compared with ’OH radical.

$$\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$$  \hspace{1cm} (3)

In the presence of UV and H$_2$O$_2$, reactions (13), (14) and (15) have been reported[4].

$$\text{H}_2\text{O}_2 \rightarrow 2 \cdot \text{OH}$$  \hspace{1cm} (13)

$$2 \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$  \hspace{1cm} (14)

$$\text{HO}_2^- + \text{H}_2\text{O} + \text{O}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$$  \hspace{1cm} (15)

If oxidation is not controlled, the H$_2$O$_2$ applied for oxidation of organics could be partly lost. Although this loss can not be eliminated, it may be suppressed to favor the oxidation of organics, thereby economizing the usage of H$_2$O$_2$. The aim of this paper is to identify various conditions that maximize the oxidation process and reduce the contact time using 2,4 DNT as the model compound. TOC measurements seem more suitable for analyzing the oxidation products because TOC measures the ultimate conversion. BOD and COD would not be suitable for evaluating a recalcitrant compound like 2,4 DNT. In this paper, TOC measurements (besides GC and GC/MS studies) were found to be
satisfactory for quantification of the compound under study. Measurement of the toxicity of the reaction product will also be important since the waste has to be treated and returned to nature in an acceptable way. Future studies would incorporate toxicity measurements also.

**MATERIALS & METHODS**

**Peroxide Measurements**

During \( \text{H}_2\text{O}_2 \) measurements, interference of iron was observed. To reduce interference, to a 25mL volume of sample, 2-3 drops of \( \text{NaOH} \) solution were added to raise the pH to about 8. The sample was filtered through a 0.45μ filter to remove the iron precipitates. The filtrate was then analyzed for \( \text{H}_2\text{O}_2 \) by adding a drop of ferroin indicator (to distinguish the end point clearly) and titrating with standard ceric sulfate solution (Fisher standardized, 0.1N). This was found satisfactory for \( \text{H}_2\text{O}_2 \) concentrations in excess of 10 mg/L. Qualitative and quick measurements of \( \text{H}_2\text{O}_2 \) in the range of 0 - 25ppm were made by test strips (EM Science).

**TOC Measurements**

The aqueous samples for measuring TOC were quenched by adding sodium sulfite. Complete removal of peroxide was verified by dipping \( \text{H}_2\text{O}_2 \) test strips. The samples were then acidified with conc. \( \text{H}_2\text{SO}_4 \) to a pH lower than 2 and refrigerated for analysis by a Dohrmann DC80 TOC analyzer.

**GC Measurements**

Organics were measured after removing the residual \( \text{H}_2\text{O}_2 \) in the aqueous phase. The extraction was carried out following EPA method 625 [5]. The samples were poured into a separatory funnel (Pyrex) with a teflon stopcock and 1 mL of 100μg/mL surrogate standard (acenaphthene, Aldrich Chemical Co., 97% pure) was added. The pH was adjusted to higher than 11 with NaOH solution. The sample was serially extracted three times with 60mL methylene chloride (J.T. Baker Inc., HPLC grade, 99.8% by G.C.) and the extract was collected in a flask. The aqueous phase was then adjusted to a pH lower than 2 with \( \text{H}_2\text{SO}_4 \) solution and extracted three times with 60mL methylene chloride as before. The total methylene chloride extract (from alkaline and acidic phases) was kept in a freezer for about an hour to freeze the accumulated water during extraction so that it is easy for the extract to flow through the drying column\(^1\) without clogging. The glass drying column with dimensions 300 mm x 10.5 mm ID x 13 mm OD column was fitted with a coarse frit (Supelco Inc.). The column had 4 inches of granular sodium sulfate (VWR Scientific, purified by following EPA method 625). The dried organic extract (free from moisture) was collected in a K-D apparatus. 1-2 boiling chips (VWR Scientific, purified by following EPA method 625) were added and the apparatus was kept in a water bath at 65 - 70°C until the extract concentrated to about one mL. The K-D apparatus consisted of a macro and a micro concentrator assembly with ground joints including a 310 mm 3 ball Snyder column, a 500 mL flask, a 40mL/10mL receiving vessel and springs to attach evaporative flask to concentrator tube.

From the concentrate, 2μL was injected into the GC for quantitative and qualitative analysis. A standard curve of peak area vs concentration of DNT (these concentrations were in the same range as the expected concentrations of samples) was made and the concentration of acenaphthene and DNT were interpolated from this standard curve. The quality control criteria as specified in method 625 [5] was satisfied to verify the extraction procedure before any samples were analyzed.

The chromatographic instrumentation consisted of a Tracor 560 GC with a flame ionization detector and a 2 meter X 2mm.(ID) glass column packed with 3% SP-2250 on 100/120 SUPELCOPORT (Supelco, Inc.). Helium (62ml/min) was used as the carrier gas. Analytical data were collected by a Linseis L4000 digital recorder (Linseis Inc., Princeton) on an IBM PC using UNISOFT 1.0 data acquisition/evaluation system. To identify reaction products, Finnigan Incos 50 GC/MS system (30m Restek RT\(_x\) capillary column), and Hewlett Packard 5996 with RTE 6 GC/MS system (30m Supelco SPB 5 capillary column) at the Department of Environmental Protection, Lawrence, Massachusetts were used. The oven was programmed to start at 35°C (hold for 2min) then ramp to 300°C at

\(^1\)This tip from Ms. Deborah Theim (Sr. Chemist, EPA Region 1 Lab, Lexington, Mass) worked very well!
10°C/min and the detection used a scan mode in the 34-450 mass/charge range. The identification of unknown compounds were based on comparison of spectra with standard spectra. Retention time of some of the identified compounds (more definitely identified from the GC/MS) were compared with pure standards on the G.C.

Experimental Procedure

The tap water available at faucet was steam distilled in a Corning laboratory still, and deionized in a Millipore Co. Milli - Q 3 filter water purification system deionizer. This was used as a source of reagent water. DNT (Aldrich Chemical Co.) was 97% pure. Aqueous solution of 2.4 DNT was prepared in deionized water. Stock solution of H₂O₂ (3%) was prepared by diluting commercially available 30% H₂O₂ solution (J.T. Baker Inc.). The stock solution was titrated against the commercial ceric sulfate standard solution (Fisher standardized, 0.1N) to calculate its strength before use. Ferrous ion concentration of 10g/L was prepared fresh in deionized water by dissolving FeSO₄. 7H₂O (J.T. Baker Inc.) and acidifying it to pH 3. Sodium sulfite (EM Science, ACS grade) was used for quenching the reaction. The H₂SO₄ and NaOH (in pellets form) were both of ACS grade.

The reactions were carried out in a 2 liter beaker. The ferrous ions were added (in the form of FeSO₄ solution) to the known aqueous solution of 2.4 DNT (usually 0.2mM or 36.4 mg/L) for a fixed Fe²⁺: H₂O₂ molar ratio (usually 0.024) and mixed for a uniform mixture. The pH of the DNT and Fe²⁺ mixture was measured and a pH probe was dipped into the reaction vessel to monitor the pH during the reaction. The temperature of the mixture was also noted. H₂O₂ solution was added for a desired H₂O₂: DNT molar ratio in the beginning of the reaction marking the beginning of the reaction.

If stirring was part of the experiment, the reaction mixture was placed on a magnetic stirring assembly, and a magnetic spinning bar was put into the reaction vessel and stirred. If step dosing (of the catalyst or the oxidant) was part of the experiment, it was added in steps. (Typically 20 steps @ 0.5mL every 9 minutes)

RESULTS & DISCUSSION

Effect of H₂O₂:DNT Ratio on Removal:

To observe the removal pattern of DNT with change in H₂O₂ concentration, experiments were conducted in duplicate by varying the applied H₂O₂:DNT (molar) ratio from 5:1 to 80:1. The ratio of Fe²⁺:H₂O₂ (molar ratio) was 0.024. The initial pH varied from 5 to 4 depending on the initial iron concentration. The pH at the end of the contact period of one hour decreased and ranged from 3.48 (H₂O₂:DNT = 5:1) to 2.4 (H₂O₂:DNT = 80:1). After the contact period, residual H₂O₂ was present in all the experiments except the one with H₂O₂:DNT ratios of 5. The color of the final reaction mixture varied with the quantity of H₂O₂. It was reddish yellow for H₂O₂:DNT ratio of 5 and almost colorless for the ratio 40. It may be possible that some of the by-products have yellow color. At lower H₂O₂, there were higher quantities of reaction by-products explaining the reddish yellow color. It is also possible that at lower H₂O₂ concentrations, lower quantities of OH radicals and subsequently lower quantities of organic radicals are generated. These organic radicals might not be enough to recycle the ferric ions to ferrous form. The presence of ferric hydroxides generate the reddish yellow color observed. Presently, we have no data to support either of the above speculations.

Figure 1 shows the average removal of DNT with variation of H₂O₂:DNT for a contact period of one hour. The chromatograms showed that the concentration of by-products (excluding DNT) also decreased with the increase in H₂O₂ concentration. Since some of the by-products were unknown, the area under the peaks were compared. The consumption of H₂O₂ increased with the amount applied. At higher H₂O₂ concentrations, there would be a greater amount of self decomposition because the "OH generated would react with H₂O₂ and hence reaction 2 would gain prominence. It may be observed from Figure 1 that greater than 99% of the DNT is removed for a H₂O₂:DNT ratio of 20.  

\[ \text{During the early phase of this study, an organic catalase (Ferromax - 1000) was tried to quench the reaction. The chromatograph had many unknown peaks which were from the organic components of the catalase. After this, sodium sulfite was found to be a good alternative because it is inorganic and it removes the remaining H}_2\text{O}_2 \text{ very quickly.} \]
Fe$^{2+}$:H$_2$O$_2$ = 0.024 (molar)
Contact time: 60 min

**Figure 1.** Removal of 2,4-DNT With Change in H$_2$O$_2$: DNT Ratio. Error bars represent 95% confidence intervals based on duplicate experiments.

**RATE OF DNT REMOVAL**

Experiments were run in duplicate to follow the removal of DNT and its intermediate by-products. From Figure 1, a H$_2$O$_2$: DNT ratio of 15:1 was chosen. The average removal of DNT vs time was plotted on log scale in Figure 2. From Figure 2, removal of DNT is seen to follow a pseudo first order reaction with a rate coefficient calculated to be 0.035/min at an applied molar ratio of 15:1:1.8 (H$_2$O$_2$:DNT:Fe$^{2+}$). A discussion about other reaction products will be presented in another section.

**EFFECT OF SEQUENTIAL ADDITION ON OXIDATION**

Sequential addition of catalyst is reported to reduce the requirement of Fe$^{2+}$ for an UV/H$_2$O$_2$ system. [15] It has been reported that step wise addition of H$_2$O$_2$ is more effective than a large initial dose [3].

To study the effect of sequential addition in detail, three experiments were performed by varying the combination of the addition of oxidant/catalyst. The conditions of the three experiments are given in Table I. The TOC, H$_2$O$_2$ and the pH were monitored during the course of the experiment. Figure 3 shows the variation in removal of TOC for each of the three conditions.

**Figure 2.** Removal of DNT with Time
### TABLE I - EXPERIMENTAL CONDITIONS FOR SEQUENTIAL ADDITION

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Initial DNT mM/L</th>
<th>( \text{H}_2\text{O}_2 : \text{DNT:Fe}^{2+} ) (molar)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.42</td>
<td>20:1:2.5</td>
<td>( \text{H}_2\text{O}_2 ) applied in 20 equal steps.</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
<td>20:1:2.5</td>
<td>( \text{Fe}^{2+} ) applied in 20 equal steps.</td>
</tr>
<tr>
<td>3</td>
<td>0.42</td>
<td>20:1:2.5</td>
<td>( \text{H}_2\text{O}_2 ) and ( \text{Fe}^{2+} ) applied initially in a single dose.</td>
</tr>
</tbody>
</table>

There is a competition for \( \cdot \text{OH} \) radicals by \( \text{H}_2\text{O}_2 \), \( \text{Fe}^{2+} \) and the organic substrate as shown in reactions 2, 3 and 4. [13]

![Graph](image)

**Figure 3.** Effect of Step Dosing on Removal of TOC

**Adding \( \text{H}_2\text{O}_2 \) Sequentially**

During the course of reaction, there is an excess of \( \text{Fe}^{2+} \) and hence reactions 1 and 3 dominate. [9] Since substrate:\( \text{H}_2\text{O}_2 \) ratio is high, reaction 2 becomes unimportant and losses of \( \text{H}_2\text{O}_2 \) are minimized. This was observed in experiment 1 (adding \( \text{H}_2\text{O}_2 \) sequentially) where residual \( \text{H}_2\text{O}_2 \) was available for a longer period of time (Figure 3). It was also observed that the reaction mixture became cloudy earlier (compared to experiments 2 & 3) confirming the importance of reaction 3. The residual TOC for the \( \text{H}_2\text{O}_2 \) step dosed experiment was 34% which was low compared to experiments 2 and 3. This corresponds to an efficient generation of \( \cdot \text{OH} \) radicals [9] which is expected because of availability of more than the stoichiometric amount of \( \text{Fe}^{2+} \) during the reaction.

If the organic radicals generated (\( \text{R}' \) from reaction 4) are in higher concentrations, formation of dimers are possible. [14] The most conducive conditions for formation of dimers are:

- Low pH [9]
- Oxygen - free atmosphere [9], [10]
- Higher concentration of organic radicals [14]
To verify the effect of sequential addition of H₂O₂ on generation of byproducts, an experiment was performed with a lower H₂O₂:DNT ratio (H₂O₂: DNT: Fe²⁺ = 10:1:1.25, Initial DNT = 0.28mM/L, Reactor Volume = 500mL) so that the by-products could be traced easily. In this experiment, H₂O₂ was applied continuously by a burette at the rate of 0.028mM/hour. This slow rate of application of H₂O₂ maintained a high substrate:H₂O₂ ratio throughout the experiment, so that effect of reaction 2 as well as chances of dimerization were minimized. The chromatograms of the reaction mixture with sequential addition (Figure 4 (a)) and without sequential addition were compared (not shown). In both of these experiments, same quantity of H₂O₂ & Fe²⁺ were applied. The sequential dosing of H₂O₂ had lower concentration of reaction by-products when compared to the experiment without sequential dosing. These by-products had higher retention times than the parent compound and since these by-products could not be identified, a qualitative comparison was made by comparing the area under the peaks. It is possible that one of these by-products was a dimer.

Adding Fe²⁺ Sequentially

In this case, there is an excess of H₂O₂ available and reactions 1, 2, and 5 gain importance. The H₂O₂ was used up very quickly indicating the importance of reaction 2. The removal of TOC was minimum here indicating losses of H₂O₂, which again shows the importance of reaction 2. During the first 30 minutes, no removal of TOC was observed which was because of lower Fe²⁺ concentration and hence fewer 'OH radicals available for oxidation of organics.

Influence of Aeration

The presence of oxygen is an important factor for oxidation of organics. The dissolved oxygen participates in the reaction only when organic substrate is present. Walling et al. however reported lower yield of products in presence of oxygen. This was explained by reactions 6, 7 and 8:

The rate of reaction 6 is greater than reaction 7 and hence reaction 6 dominates. In presence of higher concentration of Fe³⁺, reaction 8 is favorable resulting in loss of H₂O₂ and terminate the chain reaction. In the presence of higher concentration of Fe²⁺, reaction 9 is favorable which is a chain propagating step.

From the results of Freustein et al. it may be concluded that the rate of degradation and the extent of oxidation dramatically increases in the presence of oxygen. However, there is no major difference in the removal of TOC or COD. They have also reported regeneration of H₂O₂ in the presence of oxygen (reaction 9). Absence of air is also known to produce higher quantities of dimers.

To study the participation of oxygen during the reaction, an experiment was conducted where oxygen was introduced into the reaction mixture by sparging at the rate of 200mL/min. For comparison, another experiment was conducted where nitrogen was sparged at the same rate. H₂O₂ was depleted in the nitrogen purged reaction in 4.25 hours where and was depleted in 6.25 hours for the reaction in presence of oxygen. This indicated that oxygen participated in the reaction and some recycling of H₂O₂ could have taken place in presence of oxygen.

Figure 4 (b) and (c) show the chromatograms of the reaction mixtures purged with nitrogen and oxygen respectively for qualitative comparison of the reaction end products. The residual DNT concentration for the nitrogen sparged reaction was 0.1 mg/L (99.9% removal). For the oxygen sparged reaction no DNT could be traced. The reaction end products for the oxygen sparged case were fewer in number and lower in concentration. This clearly demonstrated the importance of presence of oxygen in reaction mixture. The concentration of an unknown compound (Peak 8, Figure 4) was higher for the nitrogen - purged reaction mixture.

³In this paper, reaction end products are considered as the compounds remaining when all of the H₂O₂ is used up. Intermediate products are considered as the compounds remaining in the reaction mixture while H₂O₂ is still present. Analysis was done after removal of the residual H₂O₂.

⁴The spectrum of this unknown compound was similar to 1,1' Biphenyl, 3,3',4,4'tetramethyl (probability of 11%) and 1,3,5 Trinitro toluene (probability of 50%) according to the library search on the compound. The probabilities being low, no conclusions could be made about the identity of the compound.
Effect of Temperature

The Fenton's reactions have been known to be temperature dependent. To study the effect of temperature, the reaction was run at three different temperatures; 21°C (room temperature), 30°C and 40°C, maintaining all other conditions constant. During the reactions, TOC and H2O2 were monitored periodically. The results are shown in Figure 5. From Figure 5, it was evident that temperature affected the reaction rate considerably.

Hydrogen peroxide was depleted in 5, 4 and 2.5 hours for the reactions at temperatures of 21°C, 30°C and 40°C respectively. The TOC removal was also observed to be greater at higher temperatures. However, there was no major difference in the rate of removal at temperatures of 30°C and 40°C. The generation of OH radicals (reaction 1) is a function of temperature and at high temperatures, the radicals would be generated at a higher rate. In such a case, reaction 12 is expected to dominate and explains the TOC removals at 30°C and 40°C.
Effect of Other Metals

The initial presence of Fe$^{3+}$ or Cu$^{2+}$ enhances the evolution of oxygen in the absence of substrates [1] which is due to reaction 8 (for Fe$^{3+}$). The presence of copper is known to initiate reactions 10 and 11.

\[
H_2O_2 : DNT : Fe^{2+} = 20:1:2.5
\]

Figure 5. Effect of Temperature on Removal of TOC

Copper is also known to accelerate the oxidation of nitrophenols [15]. A smaller dose of Cu$^{2+}$ was observed to be more effective than the presence of Fe$^{3+}$. [13] Since reaction 10 is faster than reaction 8, [9] copper is more effective than Fe$^{3+}$. The initial presence of Fe$^{3+}$ has been known to accelerate the oxidation of chlorophenols. [2] To account for this observation, reaction 7 has been suggested. [2]

To observe the effects of Fe$^{3+}$ and Cu$^{2+}$ in addition to Fe$^{2+}$, three experiments were done. The results are shown in Figure 6. The mixture of Fe$^{2+}$ & Fe$^{3+}$ expedited the oxidation process compared to the presence of Fe$^{2+}$ alone although the total quantity of catalyst was the same. It was also noted that

\[
H_2O_2 : DNT : Fe^{2+} = 20:1:2.5 \text{(Molar)}
\]

\[
H_2O_2 : DNT : Fe^{2+} : Fe^{3+} = 20:1:2:0.5 \text{(Molar)}
\]

\[
H_2O_2 : DNT : Fe^{2+} : Cu^{2+} = 20:1:2:0.5 \text{(Molar)}
\]

Figure 6. Effect of Metals on Removal of TOC
H$_2$O$_2$ was depleted in about 300 minutes in the presence of Fe$^{2+}$ alone, where as in the presence of Fe$^{2+}$ and Fe$^{3+}$ mixture it was depleted in about 180 minutes. This compares well with reported results. [1], [2]

Comparing TOC removal in presence of Fe$^{2+}$ & Fe$^{3+}$ with Fe$^{2+}$ & Cu$^{2+}$, it was observed that initially copper was slow for oxidation of organics but becomes fast later. During the same period, the amount of H$_2$O$_2$ consumed was maximum. It has been reported that ‘Cu$^{2+}$ is a less discriminating radical oxidant than Fe$^{3+}$’ for oxidation of organic radicals.[13] Figure 6 shows that Fe$^{3+}$ was a better catalyst compared to Cu$^{2+}$. This is probably because Fe$^{3+}$ is a more powerful oxidant than Cu$^{2+}$.

COMPARISON WITH UV/H$_2$O$_2$

The UV/H$_2$O$_2$ system is reported to be the most efficient radical producing mechanism. However, the utilization of UV light has been reported to be relatively inefficient due to lower absorption coefficient of H$_2$O$_2$ [4]. The UV/H$_2$O$_2$ combination involves one step initiation and the photolytic dissociation of H$_2$O$_2$ into two ‘•OH radicals as given by equation 13.[4]

Comparing this to the Fenton’s reagent, reaction 1 generates a single ‘•OH radical. The reformation of H$_2$O$_2$ is possible by both the methods. For the UV/H$_2$O$_2$ system, the regeneration of H$_2$O$_2$ is possible by reactions 14 and 15 [4]:

For the UV/H$_2$O$_2$ system, the best removal of 2,4-DNT has been observed in the range of H$_2$O$_2$:DNT (molar) = 26 to 52 [7] which is comparable to Fenton’s reaction. The contact time for the UV/H$_2$O$_2$ system seems to be lower but combining the various techniques described in this paper to reduce time and decrease consumption of H$_2$O$_2$, the reaction time required for Fenton’s reagent may be comparable.

The following pathway was suggested for oxidation of DNT by UV/H$_2$O$_2$ system [7]:

2,4 DNT $\rightarrow$ 2,4 Dinitrobenzyl alcohol $\rightarrow$ 2,4 Dinitrobenzaldehyde $\rightarrow$ 2,4 Dinitrobenzoic acid $\rightarrow$ 1,3 Dinitrobenzene $\rightarrow$ 3 Nitrophenol & 2,4 Dinitrophenol $\rightarrow$ Trihydroxy nitrobenzenes $\rightarrow$ Acids $\rightarrow$ CO$_2$ & H$_2$O.

From this pathway, the first attack of the hydroxyl radicals are on the methyl group (side chain cleavage) followed by decarboxylation. From the GC/MS studies for oxidation by Fenton’s reagent, 1,3 dinitrobenzene and benzoic acid were identified which are similar to the intermediates reported for the UV/H$_2$O$_2$ system. The presence of 1,3 dinitrobenzene suggests that side chain cleavage took place where as the presence of benzoic acid shows the effectiveness of hydroxyl radicals in removal of nitro groups from the benzene ring. The concentration of both these compounds were very low. This may indicate that they are easy to oxidize as compared to other intermediates.

Benzaldehyde and ethylbenzene (or 1,3,5,7 cyclo octatetraene as suggested in the library search) were the two compounds identified during the GC/MS analysis which has not been reported for the UV/H$_2$O$_2$ system. Probably benzoic acid is an oxidation product of benzaldehyde. The presence of ethylbenzene or 1,3,5,7 cyclo octatetraene, however, can not be explained.

Reaction Products

From the chromatograms, it was observed that as DNT was removed, some intermediate compounds were formed which could not be identified. Few of the samples were analyzed by a GC/MS. Table II shows the compounds identified by the GC/MS.

Three unidentified reaction products may be observed from the chromatograms in Figure 3. The spectrum of two unknown products does not match with standard spectra [16], [17], [18] of any pure organic compound. Possibly one of these unknown compounds is a dimer but it could not be verified. The unknown products (Peak 6, Peak 7 and Peak 8, Figure 3) had the following spectrum:

5The retention time matched with pure standards of the compound.
TABLE II - REACTION INTERMEDIATES IDENTIFIED BY GC/MS (FENTON'S OXIDATION)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Identification Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Benzaldehyde</td>
<td>GC/MS, NBS Library</td>
</tr>
<tr>
<td>2. Benzoic Acid</td>
<td>GC/MS, NBS Library</td>
</tr>
<tr>
<td>3. 1,3 Dinitrobenzene</td>
<td>GC/MS and RT on GC^5</td>
</tr>
<tr>
<td>4. Benzene, 1-isocyanato - 3-nitro</td>
<td>GC/MS, NBS Library</td>
</tr>
<tr>
<td>5. m - Nitroaniline</td>
<td>GC/MS, NBS Library</td>
</tr>
</tbody>
</table>

Peak 6 120(100%), 75(90%), 50(76%), 108(63%), 74(50%), 64(41%), 104(35%)

Peak 7 210(100%), 63(30%), 89(21%), 39(20%), 193(10%), 76(10%)

Peak 8 210(100%), 63(29%), 89(22%), 39(19%), 61(12%), 193(10%)

The unknown products were not observed for experiments conducted at H_2O_2:DNT ratios greater than 20 when all of the following conditions were satisfied:

- pH >3
- Air sparging
- Step dosing of H_2O_2
- Temperature >30°C

To observe the effect of all the above mentioned conditions on reaction end products, an experiment was run where H_2O_2 was applied sequentially at a rate of 0.028 mM/hr. The reaction mixture was sparged with air at a rate of 200 mL/min and the temperature was maintained constant at 30°C. The ratio of H_2O_2: DNT: Fe^{2+} for the experiment was 10:1:1.25 (molar). The end products (from this experiment) were compared to those resulting from experiments (a), (b), (c), (d), and (e) as given below:

(a) H_2O_2: DNT: Fe^{2+} =10:1:1.25 (molar), aerated@200mL/min, temp=21°C
(b) H_2O_2: DNT: Fe^{2+} =10:1:1.25 (molar), H_2O_2 step dosed @0.028mM/hr, temp=21°C
(c) H_2O_2: DNT: Fe^{2+} =10:1:1.25 (molar), temp=21°C
(d) H_2O_2: DNT: Fe^{2+} =10:1:1.25 (molar), sparging with oxygen @200mL/min, temp=21°C
(e) H_2O_2: DNT: Fe^{2+} =10:1:1.25 (molar), sparging with nitrogen @200mL/min, temp=21°C

The quantity of end products were lower compared to the end products from experiments (a), (b), (c), (d), and (e). However, this comparison was qualitative on the basis of the area under peaks since the end products could not be identified. The experiments suggested that sequential dosing (with H_2O_2), increased temperature & aeration together reduces the time of contact and increases the degree of oxidation.

The GC/MS analysis done was not sufficient to trace the formation of the intermediates and no definite reaction pathway can be suggested at present. However, when compared with the reaction products reported for the UV/H_2O_2 system [7], only 2 intermediates were found to be similar, 1, 3 dinitrobenzene and benzoic Acid. From this it is not clear whether the degradation completely or partially follows the pattern suggested for the UV/H_2O_2 system.
At higher H$_2$O$_2$:DNT ratios, some residual TOC was found in the reaction mixture. This suggests that some organic compounds could not be extracted by the outlined procedure or the column in the GC/MS was not sensitive to such compounds. Analysis of the reaction mixture using HPLC may provide deeper insight into the pathway of degradation of DNT. From the GC and GC/MS analysis, it was observed that phthalates could not be completely eliminated from the reaction mixture. This could account for residual TOC and usage of H$_2$O$_2$ for their oxidation.

CONCLUSIONS

Fenton’s reagent was capable of oxidizing 2,4 DNT at a molar ratio of 20:1:2.5 (H$_2$O$_2$: DNT: Fe$^{2+}$) at room temperature. However, by increasing the temperature to greater than 30°C, the contact time decreased drastically. The use of Fe$^{3+}$ in conjunction with Fe$^{2+}$ was observed to reduce the contact time also. Application of H$_2$O$_2$ sequentially rather than one single dose was observed to achieve better oxidation. The presence of oxygen in the reaction mixture decreased the concentration of reaction end products. The TOC removal showed that about 30% of the initial TOC could not be removed at a molar ratio of 20:1:2.5 (H$_2$O$_2$: DNT: Fe$^{2+}$).

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of Jerome Keefe of EPA, Oscar Pancorbo and Michael Beberian of DEP, Massachusetts.

REFERENCES


Address Reprint Request To:

Irvine W. Wei
Associate Professor
420SN, Department of Civil Engineering
Northeastern university
Boston, MA 02115