Chapter 4

Photodecomposition of triazine derivatives in aqueous medium using hydrogen peroxide and ferric perchlorate
Abstract

The photodegradations of 2,4,6-trimethoxy-1,3,5-triazine (TMT), 2,4-dioxohexahydro-1,3,5-triazine(DHT), 6-chloro N-ethyl N'-(1-methylethyl)-1,3,5-triazine, 2,4 diamine (atrazine, AT) and cyanuric acid (CA) have been investigated in aqueous medium in the presence of ferric perchlorate as photopromotor using sunlight and UV light. The hydroxyl radical (•OH) generated from the photoreaction of the complex Fe(OH)$^{2+}$, is likely to be the major active reagent. The degradation of these triazines was also studied using photolysis of H$_2$O$_2$ in which •OH is undoubtedly the active species. Comparison of these two methods demonstrates that photolysis in the presence of ferric perchlorate is more effective for the degradation of triazines. It is proposed that in ferric mediated degradation, photoinduced electron transfer in the Fe(III)-T complex formed between Fe(III) and triazines (T) is an additional pathway in the degradation of triazines.
4.1. Introduction and objectives

Triazine derivatives are among the most widely used herbicides and its main mode of action as herbicide is the disruption of the light reaction of photosynthesis.¹ Contamination of ground and surface water by triazines is a serious problem in many parts of the world due to their continual use as herbicides. The maximum permissible concentration of triazines for human consumption is set at 0.1 ppb by the European Economic Community.² However, their concentrations were reported to exceed this value in drinking water and hence their degradation studies in aqueous medium are of vital importance.³ Triazines are stable compounds and are almost inert to direct photodegradation because of their very weak absorption of sunlight. Almost all triazines have their $\lambda_{\text{max}} \leq 250$ nm and are almost inert to direct photodegradation. Therefore, technologies for the destruction or detoxification of triazines are in urgent demand for their removal from water. The conventional methods for the removal of these pollutants from drinking water such as flocculation, filtration, sterilization, reverse osmosis and adsorption on activated carbon are inadequate to degrade the aromatic ring. Decontamination processes using microorganisms like bacteria, is relatively very slow and are therefore almost inefficient in the case of triazines.⁴,⁵ Burkhard and Guth reported that the rate of decomposition of certain triazines could be increased 3-11 times with UV light using acetone as photosensitizer.⁶ Photochemical decomposition studies of certain triazines in both methanol and aqueous solutions have also been reported earlier.⁷,⁸

Advanced Oxidation Processes (AOPs) are found to be more efficient for the degradation of these triazines. AOPs involve the generation of hydroxyl radical (·OH), a powerful oxidizing agent, which reacts with most of
the organic compounds at diffusion-controlled rate. There are several reports on the degradation of triazines using different AOPs such as TiO$_2$/UV$^{9-11}$, H$_2$O$_2$/UV$^{12,13}$, O$_3$/UV$^{14,15}$, Fenton reaction$^{16-18}$, photo-Fenton reaction$^{19,20}$, ultrasound$^{21}$ and radiation chemical technique.$^{22-24}$ In the present work two different AOPs; photolysis of Fe(III)-hydroxy complex and H$_2$O$_2$/UV are used for the degradation of triazine derivatives.

Photolysis of Fe(III)-hydroxy complexes is a known source of *OH.$^{25,26}$ The major photoactive species is the Fe(OH)$^{2+}$ complex predominant in the pH range$^{26}$ 2.5-5. This complex undergo photo initiated electron transfer from OH$^-$ to Fe(III) in the excited state forming *OH and Fe(II). An environmental advantage of this complex is that its CTC band strongly overlaps with the solar UV spectrum (290-400nm) and hence can be easily photolysed using sunlight.$^{26}$ Although this reaction was earlier used for enhancing the efficiency of Fenton reaction,$^{27,28}$ it has been proved later that photolysis of ferric ion salts can be effectively used for the degradation of several organic water contaminants.$^{29-31}$ This reaction has an advantage over Fenton reaction, the reaction between ferrous ion and H$_2$O$_2$ to generate *OH, as it avoids any oxidative interference that could have resulted from H$_2$O$_2$. The quantitative assessment of *OH formed by the photolysis of aqueous ferric perchlorate at acidic pH can be determined using some of its well known reactions with a quantum yield as 0.02.$^{32}$ This system was effectively utilized for the determination of rate constants for the reaction of *OH with several substituted benzenes and biomolecules using deoxy ribose TBA assay.$^{33,34}$

Although there are clear evidences for the formation of *OH as the key intermediate,$^{35-37}$ some reports predict the involvement of another mechanism in the ferric mediated degradation of some organic compounds.$^{38,39}$ This is proposed
to occur as a result of direct electron transfer between Fe(III) and the organic ligand in the excited Fe(III)-organo complex formed between Fe(III) and the organic compound, resulting in the formation of Fe(II) and an organic radical which is further oxidized in the presence of oxygen.\textsuperscript{40} Photo irradiation of acidic and neutral solutions of H\textsubscript{2}O\textsubscript{2} generates \textbullet{}OH as the major reactive species.\textsuperscript{41-43}

In the present work, we have investigated the degradation of a number of triazines by the photolysis of aqueous ferric perchlorate using sunlight and UV-light at low pH and also by H\textsubscript{2}O\textsubscript{2}/UV process. One of the selected triazines CA is of particular importance, as it is reported to be the major end product of degradation of many herbicide-based triazines using different AOPs.\textsuperscript{9,10,44,45} The aromatic ring of CA remains intact as it is resistant towards reaction with \textbullet{}OH and hence its degradation is a major challenge. The results, which we are discussing here, indicate that photolysis of aqueous ferric ion salts is a potential method in the decontamination of organic pollutants which are otherwise not degradable.

4.2. Degradation studies

The degradation studies were carried out mainly using UV photolysis of ferric perchlorate and H\textsubscript{2}O\textsubscript{2} and sunlight photolysis of ferric perchlorate.

4.2.1. Degradations using ferric perchlorate photolysis

The degradations of the selected triazines, TMT, DHT and CA (1 × 10\textsuperscript{-3} mol dm\textsuperscript{-3}) were studied in the presence of aqueous ferric perchlorate (1 × 10\textsuperscript{-2} mol dm\textsuperscript{-3}) at pH 3 using sunlight and UV-light from a medium pressure mercury vapor lamp. Solutions of ferric perchlorate and the selected triazines were kept in the dark for many days and no noticeable change in the concentrations of triazines was observed. The concentrations of triazines at each stage of irradiation were followed by HPLC analysis with spectrophotometric detection. Figure 4.1 shows
the degradation of triazines obtained using sunlight photolysis. It was observed that DHT was completely degraded after 12 min of solar irradiation. CA is usually difficult to degrade using many of the AOPs. However, about 83% of CA was degraded in 15 minutes upon illumination with bright sunlight and remained almost unchanged for longer time of irradiation. In the case of TMT, there was only 30% degradation after 16 min of irradiation and no further change in its concentration was observed after longer exposure to sunlight.

![Figure 4.1](image)

**Figure 4.1.** Sunlight mediated photodegradation of TMT (□), DHT (▲) and CA (●) using ferric perchlorate as photopromoter as obtained from HPLC analyses. The eluents used were 50/50 acetonitrile/water mixture for TMT and triply distilled water for DHT and CA at a flow rate of 1 ml/min and the detection wavelength was 210 nm.

The degradations of triazines were performed using UV-light and the decay profile is shown in figure 4.2. It is seen from the figure that in the case of TMT there was only 20% degradation after 15 minutes and higher time of
irradiation could not induce any further degradation. CA was found to decline to 31% of its initial concentration in 10 minutes and further exposures of UV-light did not induce any degradation. The degradation of DHT using UV photolysis was reported earlier from our laboratory where the compound was completely degraded after 8 min under the same experimental conditions.

![Figure 4.2](image.png)

**Figure 4.2.** UV-light mediated photodegradation of TMT (□) and CA (▲) using ferric perchlorate as photopromoter as obtained from HPLC analyses. The eluents used were 50/50 acetonitrile/water mixture for TMT and triply distilled water for CA at a flow rate of 1 ml/min and the detection wavelength was 210 nm.

Figure 4.3 shows the chromatograms of some of the irradiated samples. The chromatograms obtained for the unirradiated reaction mixture is presented as the inset in each case. Comparison of the chromatograms of the irradiated and unirradiated samples indicates the generation of a number of products during the reaction. But their identity could not be established due to the lack of standards.
Figure 4.3. HPLC Chromatograms of CA and TMT after the photolysis of ferric perchlorate using medium pressure mercury vapor lamp and DHT after the photolysis of ferric perchlorate using bright sunlight. Insets: samples unirradiated. The eluent used for HPLC analyses was triply distilled water for CA and DHT and 50/50 acetonitrile/water mixture for TMT, the detection wavelength was 210nm and the flow rate was 1 ml/min.
The logarithm of the ratio of initial concentration to the concentrations at a given time (t) vs. time is plotted and the pseudo-first order rate constant k is determined from the slope of the plot. The half-lives could then be determined as \( t_{1/2} = \ln(2)/k \). In the case of DHT and TMT, the process is found to be of pseudo-first order as evident from the figures.

![Graph showing pseudo-first order rate plots](image)

**Figure 4.4.** Pseudo-first order rate plots obtained from the ferric perchlorate/sunlight photolysis of the selected triazines. TMT(■), DHT(△) and CA(●). The concentrations were monitored using HPLC with spectrophotometric detection at 210 nm. The eluents used were 50/50 acetonitrile/water mixture for TMT and triply distilled water for DHT and CA at a flow rate of 1 ml/min.

### 4.2.2. Degradations using Hydrogen peroxide photolysis

In order to have more insight into the reaction mechanism occurring in ferric perchlorate photolysis, the degradation of these compounds were studied using \( \text{H}_2\text{O}_2/\text{UV} \) photolysis, where the active agent is undoubtfully the *OH.\[^{42}\] The degradations of the selected triazines were studied using two different initial
concentrations of H\textsubscript{2}O\textsubscript{2}, 10\textsuperscript{-2} and 0.1 mol dm\textsuperscript{-3}. No dark reaction was observed in both cases. The degradation profile of triazines with respect to the time of irradiation is followed by HPLC with spectrophotometric detection. Figure 4.5 shows the degradation of triazines (1 \times 10\textsuperscript{-3} mol dm\textsuperscript{-3}) using 10\textsuperscript{-2} mol dm\textsuperscript{-3} H\textsubscript{2}O\textsubscript{2}. From the figure it is seen that DHT disappeared completely after 60 minutes of irradiation. Only 22\% degradation of TMT was obtained in 15 minutes and no further degradation was observed up to 60 minutes. In the case of CA, there was only 8\% degradation after 60 minutes. The degradation of triazines (1 \times 10\textsuperscript{-3} mol dm\textsuperscript{-3}) using 0.1 mol dm\textsuperscript{-3} of H\textsubscript{2}O\textsubscript{2} is shown in figure 4.6. DHT was degraded completely after 30 minutes of irradiation where as TMT was degraded to 80 \% after 60 minutes which remained almost steady at longer irradiations. In the case of CA there was only 31\% degradation after 120 minutes of photolysis.

**Figure 4.5.** UV mediated hydrogen peroxide (10\textsuperscript{-2} mol dm\textsuperscript{-3}) photolysis of TMT (■), DHT (▲) and CA (○) as obtained from HPLC analyses. The eluents used were 50/50 acetonitrile/water mixture for TMT and triply distilled water for DHT and CA at a flow rate of 1 ml/min and the detection wavelength was 210 nm.
Figure 4.6. UV mediated hydrogen peroxide (0.1 mol dm$^-3$) photolysis of TMT (■), DHT (△) and CA (○) as obtained from HPLC analyses. The eluents used were 50/50 acetonitrile/water mixture for TMT and triply distilled water for DHT and CA at a flow rate of 1 ml/min and the detection wavelength was 210 nm.

Figure 4.7 shows the chromatograms of the photolysis of the selected triazines with H$_2$O$_2$. The chromatograms obtained with unirradiated reaction mixture are also shown in the figure. Comparison of the chromatograms of the irradiated and unirradiated samples indicates the generation of a number of products during the reaction. But their identity could not be established using HPLC due to the lack of standards. One thing that can be predicted from these chromatograms is that the retention times of various product peaks for the same triazine are different in both reactions. This is an indication of different reaction pathways in the two AOPs.
Figure 4.7. HPLC Chromatogram of TMT, CA and DHT after the photolysis of hydrogen peroxide with medium pressure mercury vapor lamp. Inset: Unirradiated samples. The eluent used for HPLC analysis was 50/50 acetonitrile/water mixture for TMT and triply distilled water for DHT and CA at the flow rate of 1 ml/min and the detection wavelength was 210nm.
4.3. Ferric-mediated photodegradations proceed via more than one mechanism

Comparison of these two processes shows that in the case of TMT, ferric perchlorate photolysis using sunlight and UV light is less efficient compared to H₂O₂/UV process, where 0.1 mol dm⁻³ H₂O₂ induced 82% degradation of TMT in 60 minutes (Figure. 4.6.). Since in H₂O₂/UV process, •OH is the active agent formed it is clear that in the case of TMT the major damaging species is the •OH. The •OH can undergo addition reaction or H-atom abstraction with organic compounds resulting in the formation of intermediate radicals that can be further oxidized.⁴⁶ The reaction pathway in the case of TMT can be represented as shown in scheme 4.1.²⁴

![Scheme 4.1](image_url)

The lower degree of degradation of TMT (30%) using ferric perchlorate photolysis can be explained as follows. The rate constant values obtained from pulse radiolysis studies on TMT with OH radicals are reported to be of the order of 10⁹ dm³ mol⁻¹ s⁻¹ and in the reaction of TMT with OH radicals using γ-radiolysis, a complete degradation was obtained after 5 kGy.²⁴
In the present study, it is evident from figures 4.5 and 4.6 that the reaction of TMT with H₂O₂ is in line with the previous report that •OH is the major reactive species. In the case of Fe(III)-mediated photolysis, the lower degree of degradation obtained from HPLC analysis can be due to some back reaction occurring in the presence of Fe(III)/Fe(II) system.

In the case of DHT, both ferric perchlorate photolysis and H₂O₂ photolysis are equally effective for its degradation. Since •OH is the common active species in both systems, the degradation of DHT is mainly by the attack of •OH. Moreover, the rate constant for the reaction of •OH with DHT determined using pulse radiolysis technique is $1.61 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ which clearly supports the active involvement of •OH in the degradation$^{24}$ and is further demonstrated from the complete degradation of DHT observed using gamma radiolysis under N₂O saturation.$^{24}$ However, the much faster degradation in ferric perchlorate mediated photodegradation of DHT indicates that in addition to the reaction of •OH, an electron transfer mechanism is also involved in the degradation.$^{24}$ Therefore the degradation of DHT using ferric perchlorate photolysis can be explained based on the reaction initiated by •OH formed by the photolysis of Fe(OH)$^{2+}$ complex and also the electron transfer mechanism as represented in scheme 4.2.
In order to confirm that there could be two kinds of mechanisms possible in the degradation of DHT we have carried out the UV mediated photolysis of benzene \((1 \times 10^{-3} \text{ mol dm}^{-3})\) in presence of \(\text{H}_2\text{O}_2\) as well as ferric perchlorate and analyzed the product profile using HPLC. In both cases, phenol was a common product, but all the other products were different. Although the other degradation products were not identified, it can be concluded from the retention times of various product peaks obtained in the HPLC analysis that all the products generated in \(\text{H}_2\text{O}_2\) photolysis and ferric perchlorate photolysis were not the same confirming that another reaction mechanism is operating in the latter case. Therefore it can be proposed that in
ferric perchlorate photolysis, in addition to the activity of *OH, the electron transfer mechanism is also likely to occur which of course depends on the nature of the organic compounds studied.

**Figure 4.8.(a).** HPLC chromatogram of benzene in the presence of ferric perchlorate photolysed with UV light. **(b).** HPLC chromatogram of benzene in the presence of H$_2$O$_2$ photolysed with UV light. The eluent used for the analysis was 50/50 acetonitrile/water mixture at a flow rate of 1 ml/min and the detection was at 250nm. The retention times of each component is given on the top of the peaks in minutes.

In the case of CA, photolysis of H$_2$O$_2$ has proved to be inefficient for its degradation where as ferric perchlorate photolysis is very effective for the
degradation of CA (as presented in figures 4.1, 4.2, 4.5 and 4.6). This result shows that \textit{\textsuperscript{1}}OH is not the major damaging species in the case of CA, which is usually resistant to degradation using different AOPs. In order to investigate the involvement of \textit{\textsuperscript{1}}OH in the degradation of CA, gamma radiolysis of millimolar solutions of CA under N\textsubscript{2}O saturation was performed which could induce only 30\% degradation and higher doses had no effect. Therefore in ferric perchlorate photolysis, in addition to the reaction of \textit{\textsuperscript{1}}OH, the electron transfer mechanism plays a major role in the degradation of CA.

In order to have a clear idea about the products of degradation and hence the reaction mechanism involved in the reaction of the selected triazines under the photolysis of ferric perchlorate, we have conducted the LC-MS/MS analysis of samples of AT, DHT and CA irradiated with the UV lamp in the presence of ferric perchlorate. A sample of AT (10\textsuperscript{-4} mol dm\textsuperscript{-3}) along with ferric perchlorate (10\textsuperscript{-2} mol dm\textsuperscript{-3}) was irradiated with UV lamp for 6 minutes and subjected to LC-MS/MS analysis and the products identified are given in table 4.1. Figure 4.9 shows the Q1 MS of the sample of AT.
Figure 4.9. The mass spectrum obtained from the first quadrupole of the mass analyser demonstrating the major components in the reaction mixture of the photolysis of ferric perchlorate in presence of AT using the UV-lamp.

The fragmentation patterns of some of the identified products from the reaction of AT in the photolysis of ferric perchlorate using the UV-lamp is shown in figure 4.10.
Figure 4.10. Fragmentation patterns of some of the identified products obtained from the photolysis of AT in the presence of ferric perchlorate as obtained from LC-MS/MS. 73 is ethylformamide, 100 is 5-amino-1H-1,2,4-triazol-3-ol, 145 is 4-chloro-1,3,5-triazine-2,4-diamine and 188 is 4-chloro-6(isopropylamino)-1,3,5-triazin-2-ol.
Table 4.1. Products of the reaction of AT in the photolysis of aqueous ferric perchlorate using the UV lamp as obtained from LC/MS/MS.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>m/z</th>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>188</td>
<td>4-chloro-6(isopropylamino)-1,3,5-triazin-2-ol</td>
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<tr>
<td>2</td>
<td>174</td>
<td>4-chloro-6(ethylamino)-1,3,5-triazin-2-ol</td>
<td><img src="image2.png" alt="Structure 2" /></td>
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<tr>
<td>3</td>
<td>129</td>
<td>Cyanuric acid</td>
<td><img src="image3.png" alt="Structure 3" /></td>
</tr>
<tr>
<td>4</td>
<td>145</td>
<td>4-chloro-1,3,5-triazine-2,4-diamine</td>
<td><img src="image4.png" alt="Structure 4" /></td>
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<tr>
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<td>---</td>
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<td>------------------------------------------------</td>
<td>------------------------------------------------------------------</td>
</tr>
<tr>
<td>6</td>
<td>139</td>
<td>4-(ethenylamino)-1,3,5-triazin-2-ol</td>
<td><img src="image1.png" alt="Image of 4-(ethenylamino)-1,3,5-triazin-2-ol" /></td>
</tr>
<tr>
<td>7</td>
<td>73</td>
<td>ethylformamide</td>
<td>CH₃CH₂NH CHO</td>
</tr>
<tr>
<td>8</td>
<td>97</td>
<td>1,3,5-triazin-2-ol</td>
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</tr>
<tr>
<td>9</td>
<td>56</td>
<td>Acraldehyde</td>
<td>CH₂=CHCHO</td>
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</table>

A number of studies have been conducted on the degradation of AT using different AOPs.¹⁰,¹²,⁴⁴,⁴⁷,⁴⁸ AT, the most widely used herbicide, is of great environmental concern because of its nonbiodegradable nature. The major products identified from the reaction of AT in various AOPs reported are 4-chloro-6(isopropylamino)-1,3,5-triazin-2-ol, 4-chloro-6(ethylamino)-1,3,5-triazin-2-ol, 4-chloro-1,3,5-triazine-2,4-diamine, 4-amino-6(isopropylamino)-1,3,5-triazin-2-ol, 4-amino-6-chloro1,3,5-triazin-2-ol, and cyanuric acid. The generation of all these products are explained on the basis of the reaction of AT with *OH. In our experiment we have also identified 4-chloro-6(isopropylamino)-1,3,5-triazin-2-ol, 4-chloro-6(ethylamino)-1,3,5-triazin-2-ol, 4-chloro-1,3,5-triazine-2,4-diamine and cyanuric acid which confirms the involvement of *OH in the photolysis of Fe(III). In addition we have identified 5-amino-1H-1,2,4-triazol-3-ol, 1,3,5-triazin-2-ol and 4-(ethenylamino)-1,3,5-triazin-2-ol. The generation of these products can...
possibly be explained on the basis of the reaction of AT with Fe(III) forming a complex which absorbs UV radiation and goes to the excited state. This high energy complex then dissociates into AT⁺(radical cation of AT) and Fe(II). This radical cation can get converted into a radical which can undergo oxidation or reduction as the reaction medium contains both Fe(II) and Fe(III). As there are three nitrogens in the ring of AT, the radical can be localized on any one of the nitrogens. The three nitrogens in the AT ring are having different local environments and hence the radicals localizing on each nitrogen will be different. Therefore the products resulting from each radical will be different depending on the position of the radical. Thus the products with m/z values 138, 100 and 97 are likely due to the eliminations of side chains. We could identify low molecular weight products ethylformamide and prop-2-enal which are generated from the eliminated side chains of AT.

**Figure 4.11.** The mass spectrum obtained from the first quadrupole of the mass analyser demonstrating the major components in the reaction mixture of the photolysis of ferric perchlorate in presence of DHT using the UV-light.
A sample of DHT (10^{-3} \text{ mol dm}^{-3}) along with ferric perchlorate (10^{-2} \text{ mol dm}^{-3}) was irradiated with UV light for 6 minutes and the products were analyzed using LC-MS/MS analysis. The identified products are given in table 4.2. Unlike AT and CA, DHT is non-aromatic and hence the breaking of the ring is more easy. The Q1 MS picture of the sample of DHT in the photolysis of ferric perchlorate is given in figure 4.11.

Figure 4.12 shows the fragmentation patterns of some of the products obtained from the reaction of DHT in the UV photolysis of ferric perchlorate.

**Figure 4.12.** Fragmentation patterns of some of the identified products obtained from the reaction of DHT in the UV photolysis of ferric perchlorate as obtained from LC-MS/MS. 101 is 4-hydroxy-2,4-dihydro-3H-1,2,4-triazol-3-one, 129 is 3-hydroxy-1,3,5-triazine-2,4(1H,3H)-dione.
Table 4.2. Identified products of the reaction of DHT in the photolysis of ferric perchlorate using the UV lamp as obtained from LC/MS/MS.

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<th>Sl. No.</th>
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<th>Name</th>
<th>Structure</th>
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<td>1</td>
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<td>Formylformamide</td>
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<tr>
<td>2</td>
<td>89</td>
<td>Formylcarbamic acid</td>
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<tr>
<td>3</td>
<td>149</td>
<td>{[amino(hydroxy)methyl]carbamoyl} carbamic acid</td>
<td><img src="image3" alt="Structure" /></td>
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<tr>
<td>4</td>
<td>129</td>
<td>3-hydroxy-1,3,5-triazine-2,4(1H,3H)-dione</td>
<td><img src="image4" alt="Structure" /></td>
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<tr>
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<td>4-hydroxy-2,4-dihydro-3H-1,2,4-triazol-3-one</td>
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</tr>
<tr>
<td>6</td>
<td>43</td>
<td>N-methylidenemethanamine</td>
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</table>

As evident from section 4.3 and scheme 4.2, both H$_2$O$_2$/UV photolysis and Fe(III)/UV photolysis are equally effective in the degradation of DHT. The degradation reactions can be demonstrated on the basis of two major reaction mechanisms generally observed in the photolysis of ferric hydroxy complexes. These are direct reaction of $^\bullet$OH and the reaction of a radical cation which is
formed from the dissociation of the excited Fe(III)-organic complex as explained in the case of AT. It is also probable that the intermediate radicals can react with Fe(III) or Fe(II) present in the reaction mixture as these two may act as oxidizing and reducing agents. Due to the nonaromatic nature of DHT the cleavage of the ring is easy resulting in a number of low molecular weight products as evident from the mass spectrum. The mechanisms of the generation of the identified products are given in scheme 4.3.
Scheme 4.3
A number of products have been identified with CA in the photolysis of ferric perchlorate with the UV light and are given in table 4.3. Figure 4.13 demonstrates the product distribution of the reaction of CA in the photolysis of ferric perchlorate using the UV lamp as obtained from the first quadrupole of the LC-MS/MS. The fragmentation patterns of some of the identified products obtained from the LC-MS/MS analysis of the reaction of CA in the photolysis of ferric perchlorate using the UV lamp is given in figure 4.14.

**Figure 4.13.** The mass spectrum obtained from the first quadrupole of the mass analyser demonstrating the major components in the reaction mixture from the photolysis of ferric perchlorate in presence of CA using the UV-light.
Figure 4.14. Fragmentation patterns of some of the products obtained from the photochemical reaction of CA in the presence of ferric perchlorate as obtained from LC-MS/MS. 59 is oxoformamide, 113 is 1,3,5-triazine-2,4-diol, 131 is N,N'-dioxodicarbonimidic diamide and 155 is (hydroxyimino)bis[(hydroxyamino)methanol. 
Table 4.3. Products identified from the reaction of CA in the photolysis of ferric perchlorate using the UV lamp as obtained from LC/MS/MS.

<table>
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<th>m/z</th>
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<td>1</td>
<td>131</td>
<td>N,N'-dioxodicarbonimidic diamide</td>
<td>( \text{N} - \text{C} - \text{N} - \text{C} - \text{N} )</td>
</tr>
<tr>
<td>2</td>
<td>83</td>
<td>( N' )-imidomethyl-( N )-methylideneimidoformamide</td>
<td>( \text{N} \equiv \text{N} )</td>
</tr>
<tr>
<td>3</td>
<td>73</td>
<td>formylformamide</td>
<td>( \text{HC} - \text{N} - \text{CH} )</td>
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<tr>
<td>4</td>
<td>89</td>
<td>formylcarbamic acid</td>
<td>( \text{HO} - \text{C} - \text{N} - \text{CH} )</td>
</tr>
<tr>
<td>5</td>
<td>113</td>
<td>1,3,5-triazine-2,4-diol</td>
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<tr>
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<td>(hydroxyimino)bis[(hydroxyamino)methanol]</td>
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<tr>
<td>7</td>
<td>59</td>
<td>oxoformamide</td>
<td>( \text{O} - \text{H} )</td>
</tr>
<tr>
<td>8</td>
<td>81</td>
<td>1,3,5-triazine</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>226</td>
<td>5aH,10Ah-[1,3,5]triazino[1',2';3,4][1,3]diazeto[1,2'-a][1,3,5]triazino-2,4,7,9-tetrol</td>
<td></td>
</tr>
</tbody>
</table>
Since \'OH has no significant reaction with CA and CA is reported to be the end product of the reaction of AT under different AOPs as reported earlier \textsuperscript{10,12,44,47-50} and from our experiments on CA in the photolysis of H\textsubscript{2}O\textsubscript{2} and \( \gamma \)-radiolysis in oxidizing conditions, the mechanism of generation of the above products can be explained on the basis of Fe(III) forming a complex with CA as explained in section 1.2.4. This complex dissociates generating a Fe(II) along with the radical cation of CA. This can undergo charge neutralization by disproportionation and reaction with other species in the medium. As there are both Fe(II) and Fe(III) in the reaction mixture the resulting species can undergo reduction or oxidation under the conditions of irradiation resulting in ring opened products. Scheme 4.4 demonstrates the generation of the products listed in table 4.3.
Chapter 4

Scheme 4.4
4.4. Conclusion

The behavior of the triazines AT, TMT, DHT and CA in the photolysis of aqueous ferric perchlorate and in the photolysis of hydrogen peroxide using a medium pressure mercury vapor lamp have been followed by HPLC analyses of the samples irradiated for various time intervals. More attention was given on the Fe(III)-mediated photolysis because of its advantage in absorbing the visible light and hence its potential environmental application. The results discussed here demonstrate the usefulness of Fe(III)-mediated photolysis in the degradations of AT, DHT and CA. TMT has very low reactivity in the photolysis of ferric perchlorate. The details about the products generated as a result of Fe(III) mediated photolysis in the case of AT, DHT and CA are investigated for the first time. Analysis of the product profile in the case of AT shows that in many products the chloride is eliminated thereby reducing its toxicity. CA is the main oxidized product of AT which is generally known to be resistant to further oxidation. However, our study clearly demonstrated the oxidation of CA in the photolysis of ferric perchlorate. Furthermore, the product studies presented here give clear evidences that both the formation of ‘OH as the intermediate and the excited state reaction of Fe(III)-organic complex are operative in the photolytic degradation of triazines in the presence of ferric perchlorate.
References


47. E. Pellizzetti, C. Minero, V. Carlin, M. Vincenti, E. Pramauro, Chemosphere, 24(7), 1992, 891.

