# Oxidative Degradation of Triazine Derivatives in Aqueous Medium: A Radiation and Photochemical Study

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Pulse and steady state radiolysis techniques have been used to determine the bimolecular rate constants and to investigate the spectral nature of the intermediates and the degradation induced by hydroxyl radicals ($^{•}$OH) with 1,3,5-triazine (T), 2,4,6-trimethoxy-1,3,5-triazine (TMT), and 2,4-dioxohexahydro-1,3,5-triazine (DHT) in aqueous medium. A competitive kinetic method with KSCN as the $^{•}$OH scavenger was used to determine the rate constants for the reaction of $^{•}$OH with T, TMT, and DHT. The bimolecular rate constants are $3.4 \times 10^9$, $2.06 \times 10^8$, and $1.61 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively, for T, TMT, and DHT at pH ~6. The transient absorption spectra obtained from the reaction of $^{•}$OH with T, TMT, and DHT have single absorption maxima at 320, 300, and 300 nm, respectively, and were found to undergo a second-order decay. The formation of TOH$^{•}$ [C(6)-OH−N(5)-yl radical], TMTOH$^{•}$ [N(5)OH−C(6)-yl radical], and DHT$^{•}$ [C(6)-yl radical] is proposed from the initial attack of $^{•}$OH with T, TMT, and DHT, respectively. A complete degradation of TMT ($10^{-3}$ mol dm$^{-3}$) was obtained after absorbed doses of 5 kGy in N$_2$O-saturated solutions and 16 kGy in aerated solutions. A similar degradation pattern was obtained with DHT in N$_2$O-saturated solutions. Complete degradation was observed with an absorbed dose of 7 kGy. On the basis of the results from both pulse and steady state radiolysis, a possible reaction mechanism involving $^{•}$OH-mediated oxidative degradation is proposed. A complete photodecomposition of DHT was also observed in the presence of ferric perchlorate using ultraviolet light at low pH. Photoinduced electron transfer between Fe(III) and DHT in the Fe(III)−DHT complex and subsequent formation of DHT$^{•}$ are proposed to be the major processes that lead to the complete degradation of DHT at pH 3.

**Keywords:** *Triazine derivatives; oxidative degradation; radiation and photochemical; rate constants; transient absorption spectra; photoinduced electron transfer*

## INTRODUCTION

Triazine derivatives are usually present in the environment in a measurable amount due to their continual use as herbicides (Jung et al., 1980). Degradation studies of triazine derivatives are important not only in the determination of the environmental stability and agricultural use of these compounds but also in their removal from the environment as a water pollutant as well. An understanding of the degradation products and their chemical, toxicological, and pharmacological investigations are also important in the evaluation of the merit of their continued use. Direct photolysis of triazine derivatives is normally difficult due to their weak absorption of light with wavelength >220 nm. It was reported that the rate of decomposition of some triazines has been increased up to 3−11 times using acetone as sensitizer (Burkhard and Guth, 1976; Rejto et al., 1983). Photochemical studies of certain triazine derivatives in both methanol and aqueous solutions and identification of their final products have also been reported (Pape

and Zabik, 1970; Donnare et al., 1996). Furthermore, it is reported that the rate of disappearance of methyl- and halo-substituted *s*-triazine is dependent on the nature of the halogen and alkyl substituents and the solvent employed (Ruzo et al., 1973).

Decomposition of organic pollutants using OH radicals, generally known as advanced oxidation processes (APOs), has gained considerable attention in recent years (Moza et al., 1988; Sundstrom et al., 1989; Bowers et al., 1989; Lipczynska, 1992; Schmelling and Gray, 1995; Wang and Kutal, 1995; Stafford et al., 1996). Radiolysis of water by ionizing radiations, photodecomposition of hydrogen peroxide, photochemical reaction of titanium dioxide in aqueous medium, Fenton reaction, photo-Fenton reaction, and sonochemical reaction in the presence of dissolved gases are the major reactions that lead to the generation of OH radicals in solution state. Unlike the photochemical decomposition studies of triazine derivatives (Burkhard and Guth, 1976; Rejto et al., 1983; Pape and Zabik, 1970; Donnare et al., 1996; Ruzo et al., 1973; Ezio et al., 1990), very little is known about their decomposition due to ionizing radiation, which has enormous potential in the detoxification of organic pollutants (Getoff, 1999). The radiation chemical studies make use of the reaction of both

oxidizing ($^\bullet$OH) and reducing ($e_{aq}^-$) radicals produced by the interaction of ionizing radiations, such as $\gamma$-rays or high-energy electron beam, with water (Spinks and Wood, 1990). Furthermore, the exact bimolecular rate constants of the reaction of OH radicals with triazines are not reported in the literature. In this context, radiation chemical method is an ideal choice for the rate constant measurements for OH radicals as radiolysis of water provides a clean source of OH radicals. Therefore, in the present work, pulse radiolysis was carried out to determine the bimolecular rate constants for the reaction of OH radicals with these systems and to investigate the nature of the intermediates at near neutral pH. $\gamma$-Radiolysis was performed to investigate the oxidative decomposition profile of low concentrations ($10^{-3}$ mol dm$^{-3}$) of 1,3,5-triazine (T), 2,4,6-trimethoxy-1,3,5-triazine (TMT), and 2,4-dioxohexahydro-1,3,5-triazine (DHT) in aqueous medium. Photochemical degradation in the presence of ferric perchlorate was also investigated with DHT at low pH to compare the results obtained with the radiation chemical method.

## EXPERIMENTAL PROCEDURES

Triazine derivatives and KSCN were purchased from Aldrich Chemical Co. and were used without further purification. Ferric perchlorate was synthesized from ferric chloride and sodium carbonate in the presence of 50% perchloric acid. Ferrioxalate solution was prepared before UV irradiation by mixing equal volumes of ferric sulfate (0.012 mol dm$^{-3}$) and potassium oxalate (0.036 mol dm$^{-3}$), which were received from Sigma Chemical Co. All solutions were prepared in water obtained from a Millipore Milli-Q system.

Pulse radiolysis experiments were conducted using a linear accelerator at Bhabha Atomic Research Centre, Mumbai, India. The linear accelerator delivered 7 MeV electron pulses of 50 ns duration. The dose per pulse was determined by KSCN dosimetry by taking a G $\times$ $\epsilon_{500\ nm}$ value of 21520 dm$^3$ mol$^{-1}$ cm$^{-1}$ in aerated aqueous solution and was normally kept at 15 Gy. The transient absorption spectra were recorded by noting the absorbance time profiles at various wavelengths immediately after the solutions had been pulsed. The absorbance of the transients was monitored using a 450 W pulsed xenon arc lamp, a monochromator (Kratus GM-252), and a Hamamatsu R-955 photomultiplier as the detector. The photomultiplier output was digitized with a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis. The rate values are the average of at least three experiments, and the variation was within 15%. The rate constant values were taken from those kinetic analyses for which very good correlation was observed between the experimental and calculated results. The details of the pulse radiolysis setup have been described elsewhere (Guha et al., 1987). $\gamma$-Radiolysis was carried out in a $^{60}$Co $\gamma$-chamber. The dose rate was determined by ceric sulfate dosimetry, and it was found to be ~0.13 kGy/min. Both pulse and steady state radiolysis experiments were carried out at pH ~6.

The photoirradiation of triazine derivatives ($10^{-3}$ mol dm$^{-3}$) in the presence of ferric perchlorate ($10^{-2}$ mol dm$^{-3}$) at pH 3 was carried out using UV light from a Philips fluorescent lamp. The intensity of the light was determined using ferrioxalate actinometry and an absorbed light intensity of $6.0 \times 10^{16}$ einsteins/s/cm$^3$ was calculated. The decrease in concentrations of the triazines and the formation of products (determined from the area of the peak) after radiolysis as well as photolysis were monitored by HPLC (Shimadzu LC-10AS) with UV$-$vis detection (Shimadzu SPD10A). Water was used as the mobile phase at a flow rate of 1 mL/min (25 cm, Nucleosil, 5C-18 column). The identification and quantification of the products were not performed due to the lack of standards. All of the degradation experiments were carried out at least twice, and a very good reproducibility (<10% deviation) was obtained.

## RESULTS AND DISCUSSION

Among the primary radiolytic products of water, hydroxyl radicals ($^\bullet$OH), hydrated electrons ($e_{aq}^-$), and hydrogen atoms (H$^\bullet$) are the major reactive radicals. The primary radicals and molecular products resulting from the radiolysis of water by $\gamma$-radiation or by fast electron between pH 3 and 13 are shown in eq 1 (Spinks and Wood, 1990).

$$H_2O \rightsquigarrow {}^\bullet OH,\ e_{aq}^-,\ H^\bullet,\ H_3O^+,\ H_2O_2,\ H_2 \quad (1)$$

The primary yields of these species in the pH range 3$-$11 are the following: $g(^\bullet OH) = g(e_{aq}^-) = g(H_3O^+) = 0.28$, $g(H^\bullet) = 0.062$, $g(H_2O_2) = 0.072$, and $g(H_2) = 0.047$ $\mu$mol J$^{-1}$ (Spinks and Wood, 1990). Being relatively low in yield, the reaction of H$^\bullet$ in the pH range 3$-$11 is certainly not a major contributing factor in the context of any degradation reaction.

The yield of OH radicals can be doubled by converting $e_{aq}^-$ into $^\bullet$OH using N$_2$O.

$$e_{aq}^- + N_2O \rightarrow {}^\bullet OH + OH^- + N_2 \quad (2)$$
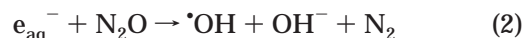
**Pulse Radiolysis.** *Determination of Rate Constants.* The bimolecular rate constants for the reaction of OH radicals with triazines were determined by competition kinetic method using thiocyanate (KSCN). KSCN is a well-known $^\bullet$OH scavenger with a high second-order rate constant ($k = 1.1 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$) (Buxton et al., 1988). The formation of (SCN)$_2^{\bullet-}$ resulting from the reaction of OH radicals with SCN$^-$ can be easily monitored at 500 nm by pulse radiolysis technique. A competition for $^\bullet$OH can be obtained by using appropriate amounts of the triazines. When there are two competing reactions for OH radicals by KSCN and the selected triazines (T) as in reactions 3 and 4, one obtains eq 5.

$$^\bullet OH + SCN^- \underset{-OH^-}{\overset{k_1}{\rightleftharpoons}} SCN^\bullet \xrightarrow{SCN^-} (SCN)_2^{\bullet-} \quad (3)$$

$$^\bullet OH + T \xrightarrow{k_2} \text{products} \quad (4)$$

$$(-d[^\bullet OH]/dt)/(d(SCN)_2^{\bullet-}/dt) = 1 + (k_2[T]/k_1[SCN^-]) \quad (5)$$

Because the absorbance of (SCN)$_2^{\bullet-}$ is a measure of the rate of reaction of OH radicals with SCN$^-$, we can obtain the relation

$$1/A^* = 1/A_0(1 + k_2[T]/k_1[SCN^-]) \quad (6)$$

where $A_0$ is the absorbance that would be obtained in the absence of T and $A^*$ is the absorbance in the presence of T at the end of the reaction. Therefore, a plot of $1/A^*$ versus [T] must give a straight line of slope $k_2/k_1[SCN^-]A_0$ with an intercept on the $Y$-axis of $1/A_0$. The bimolecular rate constant $k_2$ can thus be determined from the slope. On the basis of this model, we have monitored the absorbance of (SCN)$_2^{\bullet-}$ at different concentrations of triazines and obtained straight lines with very good correlation coefficient (cc $\sim$ 0.99). A typical plot obtained in the case of 1,3,5-triazine is shown in Figure 1. The rate constants, thus, obtained for T, TMT, and DHT are $3.4 \times 10^9$, $2.06 \times 10^8$, and $1.61 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The rate constant obtained in the case of TMT is almost an order less in

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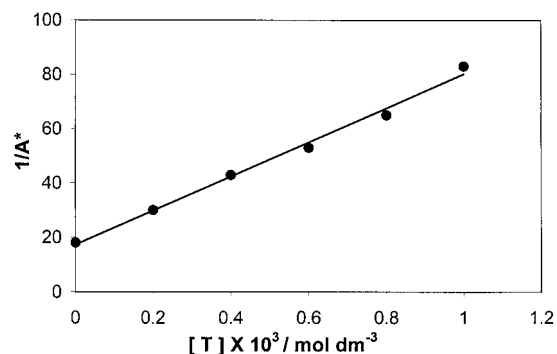
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**Figure 1.** Scavenging of hydroxyl radicals by varying concentrations of T in the presence of KSCN ($1 \times 10^{-4}$ mol dm$^{-3}$). The formation of $(SCN)_2^{\bullet-}$ is monitored at 500 nm as described in the text.
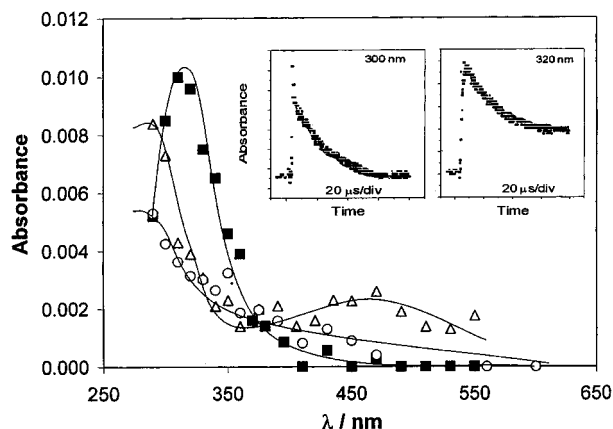


**Figure 2.** Transient absorption spectra recorded in N$_2$O-saturated solutions of DHT ($1 \times 10^{-3}$ mol dm$^{-3}$) ($\triangle$), TMT ($1 \times 10^{-3}$ mol dm$^{-3}$) ($\blacksquare$), and T ($1 \times 10^{-3}$ mol dm$^{-3}$) ($\bigcirc$) at 40 $\mu$s after the pulse. (Inset) Bimolecular decay traces of the intermediates obtained with DHT at 300 nm and with TMT at 320 nm.

magnitude compared to those of T and DHT. This could be due to the presence of three methoxy groups (electron withdrawing in nature) in TMT, which may reduce the electron density in the triazine ring. As the •OH attack is electrophilic in nature, such comparative reduction in the rate constant value is understandable.

*Transient Absorption Spectra.* The optical absorption spectra of the intermediates resulting from the reaction of OH radicals with TMT, DHT, and T were recorded in N$_2$O-saturated solutions containing typically 10$^{-3}$ mol dm$^{-3}$ substrate. The transient absorption spectrum obtained with TMT at pH 6 is shown in Figure 2. The spectrum has an absorption maximum at 320 nm, and it showed a second-order decay ($2k_{320nm} = 3.6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$). A typical second-order decay trace at 320 nm is shown in the inset of Figure 2. The transient absorption spectrum obtained with DHT has an absorption maximum at around 300 nm with a broad absorption between 420 and 500 nm (Figure 2). This also undergoes a second-order decay ($2k_{300\ nm} = 2.5 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) at all wavelengths. The spectrum obtained with T has a $\lambda_{max}$ around 300 nm (Figure 2).

OH radicals can generally undergo addition, H abstraction, and electron transfer reactions. In the case of atrazine, it is reported that it undergoes both H abstraction and electron transfer reactions (Richard et al., 1991). Therefore, such reaction pathways can be considered for TMT also. However, a preferential •OH addition at one of the nitrogen centers leading to the

formation of a radical with structure **1** is proposed, although H abstraction from one of the −OCH$_3$ groups leading to a radical with structure **2** is also probable.
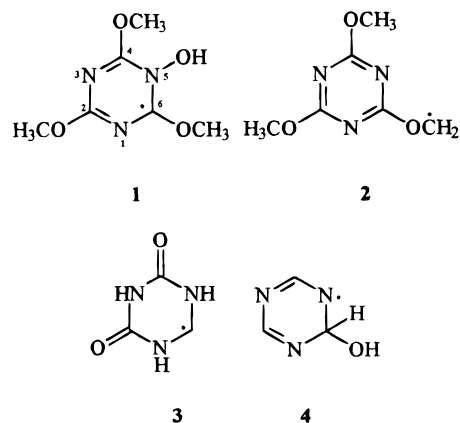


Therefore, the transient absorption spectrum with $\lambda_{max}$ at 320 nm may correspond to the OH adduct of TMT with the unpaired spin density at one of the carbon centers (**1**), but there is no direct evidence for the formation of this radical at this moment. The exact distribution of **1** and **2** is also not known. The intermediate OH adducts can undergo a second-order decay to form some stable products. The OH adducts of pyrimidine derivatives have similar $\lambda_{max}$ values around 320 nm (Hayon and Simic, 1973). Because the structures of pyrimidines are different from that of triazine (only two nitrogens at the aromatic ring), only a reasonable comparison can be made from its transient absorption spectra. In the case of DHT, there is a high chance of H abstraction compared to addition and electron transfer. Therefore, the intermediate spectrum with $\lambda_{max}$ around 300 nm can be assigned to a C(6)-yl radical of DHT, **3**.

In the case of T, the major possibility is expected to be an addition reaction. The addition may occur at a carbon position leading to the formation of an N-centered radical. Therefore, the transient absorption spectrum, characterized by its $\lambda_{max}$ around 300 nm, is attributed to the formation of an OH adduct, **4**. Because all of the carbons in T are in the same environment, additions at C(2), C(4), and C(6) are equally likely. The addition of •OH at the C(8) position of guanine where the adjacent positions are occupied by nitrogen, similar to triazine, is an additional support for this explanation (von Sonntag, 1987).

*γ*-**Radiolysis.** The radiolytic degradation patterns of TMT in N$_2$O-saturated and in aerated conditions are shown in Figure 3. It can be seen that the complete degradation of TMT is obtained after ∼5 kGy in N$_2$O-saturated solutions. However, in aerated solutions, the complete degradation was observed only at 16 kGy. A g(−TMT) value of 0.26 $\mu$mol J$^{-1}$ was calculated from the initial decrease in concentration of TMT in N$_2$O-saturated solutions, whereas only ∼0.15 $\mu$mol J$^{-1}$ was obtained in aerated solution. The comparatively high efficiency of the degradation in N$_2$O-saturated solutions indicates that the major damaging agent is OH radicals (according to eqs 1 and 2). It can be seen from the analysis of the product peaks by HPLC (Figure 4) that only a single product is formed in N$_2$O-saturated solutions, whereas two products are formed in relatively equal yields in aerated solutions. The exact identity of the products could not be determined using HPLC due to the lack of standards. Therefore, the product forma-
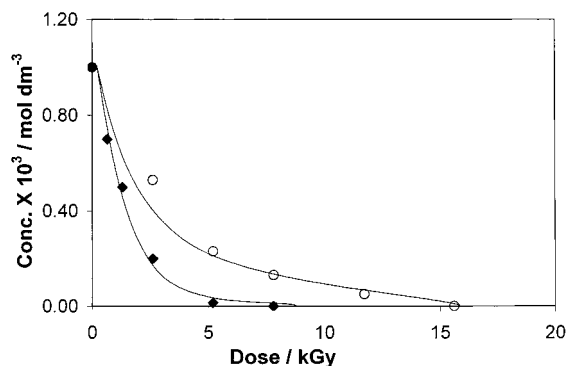
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**Figure 3.** HPLC analysis of the degradation of TMT in $N_2O$-saturated solution (◆) and in aerated solution (○) using $\gamma$-radiolysis. The area of TMT at zero time of irradiation corresponds to a concentration of $10^{-3}$ mol $dm^{-3}$.
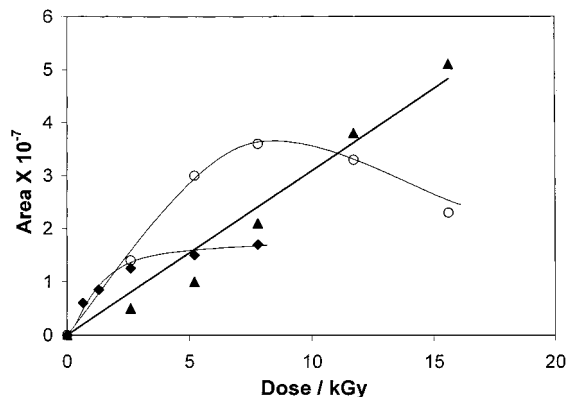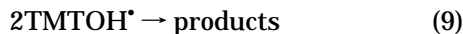
**Figure 4.** HPLC analysis of the degradation products of TMT (measured at the $\lambda_{max}$ of TMT) in $N_2O$-saturated solutions (◆) and in aerated solutions (○ and ▲) using $\gamma$-radiolysis.

tion is monitored only on the basis of the dose-dependent increase in the area of the products as shown in Figure 4.

As mentioned under Transient Absorption Spectra, TMT can preferably undergo OH addition and H abstraction reactions. Because the major damaging agent in $N_2O$-saturated solution is the OH radicals, the degradation reaction can proceed through various reactions of the resulting triazine radicals in solution state. Although the exact nature of the products was not known, a reasonable assumption of the degradation pattern can be represented as shown in reactions 7−10 in $N_2O$-saturated conditions.

$$TMT + {}^{\bullet}OH \rightarrow TMTOH^{\bullet} \quad (7)$$

$$TMT + {}^{\bullet}OH \rightarrow TMT^{\bullet} + H_2O \quad (8)$$

$$2TMTOH^{\bullet} \rightarrow products \quad (9)$$

$$2TMT^{\bullet} \rightarrow products \quad (10)$$

In aerated solutions, both OH radicals and $e_{aq}^-$ have equal contributions (see eq 1) toward TMT degradation. However, a part of $e_{aq}^-$ will be converted into $O_2^{\bullet-}$ (superoxide radicals) by its reaction with $O_2$. Therefore, the degradation of TMT in the presence of $O_2$ is proposed to be a combined effect caused by the reaction of all these three radicals (i.e., ${}^{\bullet}OH$, $e_{aq}^-$, and $O_2^{\bullet-}$). On the other hand, the longer time scale for the complete degradation of TMT compared to that in $N_2O$-saturated conditions clearly indicates the lower efficiency of degradation in aerated conditions. It was not possible
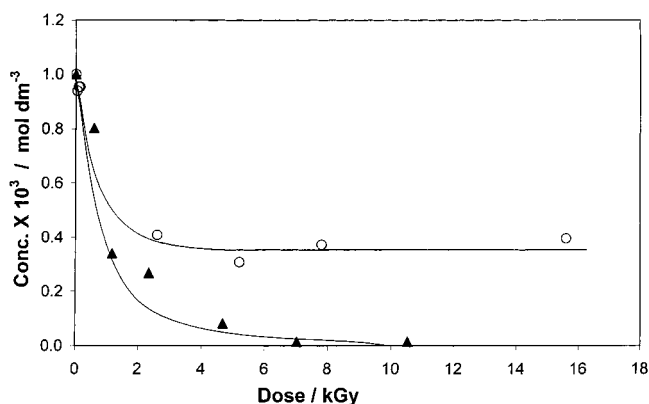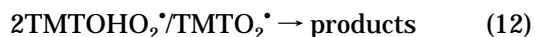
**Figure 5.** HPLC analysis of the degradation of DHT in $N_2O$-saturated solutions (▲) and in aerated solutions (○) using $\gamma$-radiolysis. The area at zero time of irradiation corresponds to $[DHT] = 10^{-3}$ mol $dm^{-3}$.

to calculate the individual contribution of $e_{aq}^-$ and $O_2^{\bullet-}$ toward TMT degradation without the knowledge of the exact rate constant values of $e_{aq}^-$ and $O_2^{\bullet-}$ with TMT, which are not yet reported. A previous study on the photodegradation of atrazine, prometron, and prometrine in the presence of ferric perchlorate reported an effective degradation mechanism in the presence of $O_2$ via formation of peroxyl radicals in aerated conditions (Richard et al., 1991). In the present study a similar possibility for the formation of peroxyl radicals of triazines in aerated conditions is likely. Therefore, in addition to reactions 7−10, a degradation pathway involving the formation of peroxyl radicals is proposed as shown in reactions 11 and 12.

$$TMTOH^{\bullet}/TMT^{\bullet} + O_2 \rightarrow TMTOHO_2^{\bullet}/TMTO_2^{\bullet} \quad (11)$$

$$2TMTOHO_2^{\bullet}/TMTO_2^{\bullet} \rightarrow products \quad (12)$$

The origin of the second product in aerated conditions in addition to the single product formed in $N_2O$-saturated conditions (Figure 4), therefore, must be from one of the reactions initiated by $e_{aq}^-$, $O_2^{\bullet-}$, or peroxyl radicals of TMT.

In the case of DHT, a similar dependence of decay with respect to dose was observed and a complete degradation was obtained at ∼7 kGy in $N_2O$-saturated solution (Figure 5). A g(−DHT) of 0.30 $\mu$mol $J^{-1}$ was calculated from the initial decay of DHT. Because the OH radical reaction may lead to the formation of C(6)-yl radical as described in Transient Absorption Spectra, the major degradation pathway could be from the bimolecular reaction of these radicals in solution state similar to reactions 8 and 10. On the other hand, we could not obtain a similar decay profile for DHT in aerated conditions. The concentration of DHT was found to decrease with dose up to ∼5 kGy, and then it remained almost constant over the region 5−15 kGy (Figure 5). The irradiation experiments with DHT were repeated more than twice and gave similar decay patterns. This result is rather unexpected, and no reasonable explanations could be given for this phenomenon without a detailed product study within the dose range 5−15 kGy.

**Photochemical Degradation.** Photochemical degradation of DHT was investigated in the presence of ferric perchlorate at pH ∼3. It is interesting to note that a complete degradation of DHT is attained within 6 min
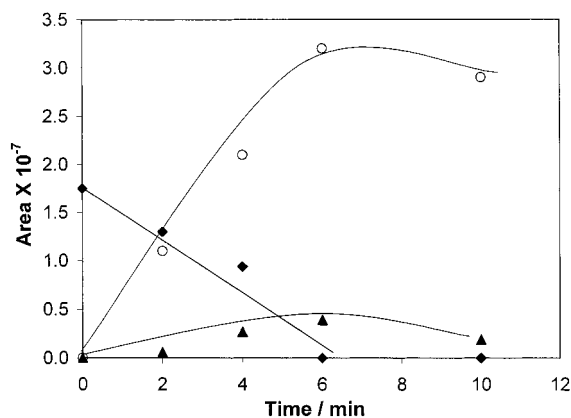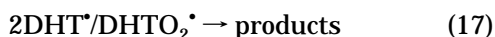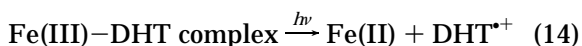
**Figure 6.** HPLC analysis of the photochemical degradation of DHT in the presence of ferric perchlorate at pH 3 (◆) and of the products (measured at the $\lambda_{max}$ of DHT) (▲ and ○). The area at zero time of irradiation corresponds [DHT] = $10^{-3}$ mol $dm^{-3}$.

of UV irradiation. The degradation plot along with the formation of two major products is shown in Figure 6. A solution of ferric perchlorate ($10^{-2}$ mol $dm^{-3}$) and DHT ($10^{-3}$ mol $dm^{-3}$) was also kept in the dark for a prolonged period, and no noticeable change in the DHT concentration was observed.

It has been reported that UV photolysis of aqueous Fe(III) complexes produces OH radicals, for which the main photo-active species is $Fe(OH)^{2+}$ complex, and this occurs mainly at acidic pH (reaction 13) (Richard et al., 1991; Prousck, 1995).

$$Fe(OH)^{2+} \xrightarrow{h\nu} {}^{\bullet}OH + Fe^{2+} \qquad (13)$$
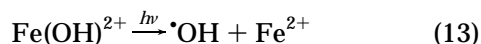
Reaction 13 has been extensively used to investigate the degradation of organic pollutants in aqueous medium (Balzani and Carassite, 1970; Faust and Hoigne, 1990; Richard et al., 1991; Prousck, 1995; Nadtochanko and Kiwi, 1998; Brando et al., 1998). The degradation of organic molecules via an electron transfer mechanism in the excited Fe(III)−organic complex is an alternate mechanism that has been well accepted in recent years (Zuo and Hoigne, 1994). The photo-initiated electron transfer between Fe(III) and organic molecule leads to the formation of an organic radical cation, which in turn undergoes different radical reactions in the presence of $O_2$ in solution state and finally ends up in the degradation of organic molecule. A recent study by Bossmann et al. (1998) also reported the increased quantum yield of the electron transfer in the photoexcited Fe(III)−organic complex compared to the OH radical production in a photochemically enhanced Fenton reaction. In the present case, it is likely that the latter reaction pathway [i.e., electron tranfer in photoexcited Fe(III)−organic complex] is the major process that leads to the DHT degradation. Therefore, the formation of a DHT radical cation ($DHT^{\bullet+}$) from an excited Fe(III)−DHT complex, which initiates the degradation of DHT, is proposed according to reactions 14−17. However, reaction 17 is

$$Fe(III)-DHT \text{ complex} \xrightarrow{h\nu} Fe(II) + DHT^{\bullet+} \quad (14)$$

$$DHT^{\bullet+} \rightarrow DHT^{\bullet} + H^{+} \qquad (15)$$

$$DHT^{\bullet} + O_2 \rightarrow DHTO_2^{\bullet} \qquad (16)$$

$$2DHT^{\bullet}/DHTO_2^{\bullet} \rightarrow \text{products} \qquad (17)$$

only a plausible mechanism because the exact identity of $DHT^{\bullet}$ is still not known. On the other hand, a recent study using laser flash photolysis clearly demonstrated the involvement of OH radical in the oxidation of xylidine from photoexcited ferric chloride and ferric perchlorate at low pH (Nadtochanko and Kiwi, 1998). Therefore, one cannot fully rule out the participation of reaction 13 in the degradation of DHT. Furthermore, the formation of $DHT^{\bullet}$ is very much likely by an H-atom abstraction mechanism by OH radical as mentioned under $\gamma$-Radiolysis. This leads to some "uncertainty" in the exact reaction mechanism by which the species $DHT^{\bullet}$ is formed. On the other hand, it is certain that the degradation is initiated by the formation of a radical, most probably like $DHT^{\bullet}$. On this basis, it can be concluded that photodegradation in the presence of ferric perchlorate is a very efficient method for the complete degradation of DHT.

**Conclusion.** The exact bimolecular rate constants of OH radicals with triazines are required for designing any APOs for their degradation in aqueous medium. The pulse radiolysis technique is one of the few techniques available for such accurate rate constant measurements. The spectral behavior of the intermediate radicals derived from triazine derivatives, which are normally very short-lived, is also presented for the first time. The complete degradation of TMT using $\gamma$-radiolysis highlights the potential application of triazine removal from water using ionizing radiation. Photodecomposition in the presence of ferric perchlorate is an equally efficient method for triazine removal, although the exact reaction mechanism is still not very clear.

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