

Oxidation of substituted triazines by sulfate radical anion ($\text{SO}_4^{\bullet-}$) in aqueous medium: a laser flash photolysis and steady state radiolysis study

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ABSTRACT: Laser flash photolysis has been used to determine the bimolecular rate constants and the spectral nature of the intermediates obtained by the reaction of sulfate radical anion ($\text{SO}_4^{\bullet-}$) with 1,3,5-triazine (T), 2,4,6-trimethoxy-1,3,5-triazine (TMT), 2,4-dioxohexahydro-1,3,5-triazine (DHT), and 6-chloro *N*-ethyl *N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine (atrazine, AT). The rate constants determined were in the range 4.6×10^7 – $3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 6. The transient absorption spectra obtained from the reaction of $\text{SO}_4^{\bullet-}$ with T, TMT, DHT and AT has an absorption maximum in the region 320–350 nm and was found to undergo second-order decay. The intermediate species is assigned to *N*-yl C(OH) radical of T (TOH^\bullet), carbon centered neutral radical of TMT, an OH-adduct of AT and an *N*-centered radical in the case of DHT. The interpretations on the experimental results obtained from TMT are supported by DFT calculation using Gaussian 03. Steady state radiolysis technique has also been used to investigate the degradation of AT induced by $\text{SO}_4^{\bullet-}$. The degradation profile indicated that about 99% of AT has been decomposed after an absorbed gamma-radiation dose of 7.5 kGy. The degradation yield of AT (expressed as $G(\text{-AT})$) was found to be $0.26 \mu\text{mol J}^{-1}$. The degradation reactions initiated by $\text{SO}_4^{\bullet-}$ may thus be employed as a potential alternative for $^\bullet\text{OH}$ -induced degradation of triazines. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: triazine; sulfate radical anion; laser flash photolysis; radiation chemical; DFT calculation; radical cation; pollutant

INTRODUCTION

The production of radical cations in aqueous solution by radiation chemical or photochemical method relies mainly on the use of oxidizing species such as $\text{SO}_4^{\bullet-}$, $\text{Cl}_2^{\bullet-}$, $\text{Br}_2^{\bullet-}$, Ti^{2+} , or photo-excited quinones.^{1–4} Among these, the sulfate radical anion, $\text{SO}_4^{\bullet-}$ ($E^0 = 2.5$ – 3.1 V vs. NHE) is commonly used and it can be generated both radiolytically and photolytically.⁵ It can be produced by the laser flash photolysis of $\text{S}_2\text{O}_8^{2-}$ with laser light of 248 or 266 nm. The reactions of radiolytically produced hydrated electron (e_{aq}^-) and $^\bullet\text{H}$ with $\text{S}_2\text{O}_8^{2-}$ is another method for its production.⁶ It is reported that the reaction of $\text{SO}_4^{\bullet-}$ with several aromatic compounds results in the production of hydroxyl cyclohexadienyl radicals.⁷ But in the case of methoxy derivatives, radical cations of the aromatic compounds have been observed.⁸ It results decarboxylation with

several carboxy derivatives, leading to the production of phenyl radical.⁹ The hydroxyl cyclohexadienyl radical can be formed either by the addition of $\text{SO}_4^{\bullet-}$ to the benzene ring followed by hydrolysis⁷ or by direct electron transfer from the aromatic ring to $\text{SO}_4^{\bullet-}$ followed by hydroxylation with water or OH^- .¹⁰ The radical cations from anisole can be obtained by direct electron transfer or via addition followed by elimination.⁸ Decarboxylation can occur through direct oxidation of the carboxyl group, as is the case with aliphatic carboxylic acids.⁷ The reactions of $\text{SO}_4^{\bullet-}$ is also important in the radical chemistry of nitrogen heterocyclic compounds like purines and pyrimidines. The selectivity of this radical to produce radical cations of purines and pyrimidines has been used to obtain valuable information about the *direct effect* of the ionizing radiation on DNA.⁶ This means, $\text{SO}_4^{\bullet-}$ is very useful to understand the underlying chemistry of the fate of the radical cations of different heterocyclic systems in aqueous medium.

Triazine (a nitrogen heterocyclic compound)-based herbicides are among the most widely used pesticides. Because of the large and prolonged use of these

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herbicides, triazines have been found in ground water as pollutants in many parts of the world. Although the light-induced reactions in wastewater treatment is a promising technique, direct photolysis of triazine derivatives is normally difficult due to their weak absorption of light with wavelength greater than 220 nm.

Oxidative degradation procedures for dissolved or dispersed organic compounds using hydroxyl radicals ($\bullet\text{OH}$) are generally known as Advanced Oxidation Processes (AOPs). *In situ* generation of $\bullet\text{OH}$ by various methods such as photo-fenton reaction,¹¹ photolysis of ozone,¹² photolysis of hydrogen peroxide,¹³ photochemical reactions of titanium dioxide,¹⁴ radiolysis of water,¹⁵ and sonochemical method¹⁶ are the generally used AOPs. A considerable attempt has been made with AOPs based on ozone¹⁷ and hydroxyl radicals^{18–20} to investigate the complete degradation of triazines in the past. A number of reports demonstrated the high reactivity of $\bullet\text{OH}$ with triazines (diffusion controlled) and have shown a degradation pathway in aqueous state.¹⁸

In general, AOPs make use of the high oxidation potential of $\bullet\text{OH}$ ($E^0 = 2.7\text{ V}$). In this context, $\text{SO}_4^{\bullet-}$ is an equally powerful oxidizing radical and was found to react with a wide range of aromatic compounds at diffusion controlled rate.²¹ However, studies on the $\text{SO}_4^{\bullet-}$ reaction pathways are rather limited. In order to look at the possibility of degradation reactions of the heterocyclic ring by $\text{SO}_4^{\bullet-}$, the first step is to understand the fundamental chemistry involved in this radical attack.

In a communication we have shown that cyanuric acid, an end product of the $\bullet\text{OH}$ -induced degradation of atrazine which can not be further degraded by hydroxyl radicals, can be decomposed in aqueous medium using $\text{SO}_4^{\bullet-}$.²² Since this first report on the one electron oxidation of cyanuric acid, two more reports were appeared on the kinetic and energetic of one-electron oxidation of 1,3,5-triazines (Ts).^{23,24} These reports stated that it is possible to oxidize atrazine and few other substituted triazines using $\text{SO}_4^{\bullet-}$. One of these reports demonstrated that $\text{SO}_4^{\bullet-}$ has no measurable reactivity with T.²³ However, a detailed knowledge on the transient intermediates in the electron transfer reaction of $\text{SO}_4^{\bullet-}$ with triazines is still lacking. The present investigation is, therefore, made of the reactions of $\text{SO}_4^{\bullet-}$ with a number of substituted triazines by laser flash photolysis and steady state radiolysis technique. Some of the interpretations of the experimental results are supported by theoretical calculations using Gaussian 03.

EXPERIMENTAL

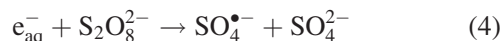
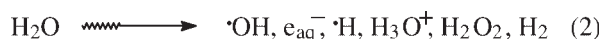
Commercially available high purity chemicals were used without further purification. T (97%), 2,4-dioxohexahydro-1,3,5-triazine (DHT) (95%), 2,4,6-trimethoxy-1,3,5-triazine (TMT) (99%), and 6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazines-2,4-diamine (atrazine, AT)

(98%) were obtained from Aldrich Chem. Co. Potassium peroxydisulphate and 2-methyl propan-2-ol were of analytical grade. In laser flash photolysis experiments, the reaction of $\text{SO}_4^{\bullet-}$ was studied in Ar-saturated aqueous solutions containing $\text{K}_2\text{S}_2\text{O}_8$ ($5 \times 10^{-2}\text{ mol dm}^{-3}$) and triazine ($5 \times 10^{-4}\text{ mol dm}^{-3}$). $\text{SO}_4^{\bullet-}$ is produced in aqueous medium by the photolysis of $\text{S}_2\text{O}_8^{2-}$ at 266 nm using Nd-YAG laser. By using laser flash photolysis, $\text{K}_2\text{S}_2\text{O}_8$ can be selectively photodissociated in the presence of triazines at 266 nm (reaction 1), as the selected triazines have practically no absorption at this wavelength.



Laser flash photolysis experiments were carried out using a SP-Quanta ray GCR-2(10) Nd-YAG laser using the fourth harmonics out put of 266 nm with a pulse width of 5 ns and energy, 50 mJ pulse^{-1} . A DHS-2 dichroic harmonic separator was used to separate the third and second harmonic from the fundamental beam. The monitoring source was a 250 W pulsed xenon lamp. The shutters were opened simultaneously as controlled by a computer. The optical absorption changes were recorded using a Hamamatsu R-777 photo multiplier tube connected with a Hewlett Packard 54201A 100 MHz digital storage oscilloscope. The details of this set-up have been published elsewhere.²⁵

$\text{SO}_4^{\bullet-}$ is also produced by the radiolysis of water containing $\text{K}_2\text{S}_2\text{O}_8$ and 2-methyl propan-2-ol. The relevant reactions are shown below.²⁶



γ -Radiolyses were carried out in a ^{60}Co - γ -chamber. Aqueous solution containing $\text{K}_2\text{S}_2\text{O}_8$ ($5 \times 10^{-2}\text{ mol dm}^{-3}$), atrazine ($1 \times 10^{-5}\text{ mol dm}^{-3}$), and 2-methyl propan-2-ol (0.2 mol dm^{-3}), saturated with high purity nitrogen was used for irradiation. The dose rate was determined using ceric sulfate dosimetry and was about 100 Gy min^{-1} . The concentration of AT after γ -radiolysis was monitored using HPLC (Shimadzu LC10 AS) with UV-VIS detector (Shimadzu SPD 10A). Water was used as the mobile phase at a flow rate of 1 ml min^{-1} (25 cm, Supelcosil C18 column) for the analyses. HPLC analyses in the case of AT were carried out and it was found that this compound did not undergo thermal decay during the experimental time scale. T is not stable for prolonged period in aqueous medium due to hydrolysis; however, it is selected as a

basic structure to understand the reaction mechanism. Therefore, T was added just before the laser flash experiments to avoid hydrolysis to any significant level.

All geometries were optimized at B3LYP/6-311+G** level of theory. Frequency calculations were carried out at the same level of theory to prove that the structures are true minima. NMR values were computed using GIAO method²⁷ at B3LYP/6-311+G** level. All calculations were done using Gaussian suite of programs.²⁸

RESULTS AND DISCUSSION

Kinetics

The second order rate constants for the reaction of $\text{SO}_4^{\bullet-}$ with triazines were determined at pH 5. In the absence of any substrate, $\text{SO}_4^{\bullet-}$ undergoes a bimolecular decay. A typical decay trace of $\text{SO}_4^{\bullet-}$ obtained at 460 nm is shown in Fig. 1. In the presence of triazine, the decay of $\text{SO}_4^{\bullet-}$ was highly enhanced and was dependent on the concentration of the triazines (Fig. 1). Therefore, the pseudo first-order rate (k_{obs}) is monitored as a function of varying concentrations of triazine. The plots of k_{obs} versus concentrations of triazines gave straight line graphs, with intercept at zero (a typical plot obtained in the reaction of T is shown in Fig. 1), with very good correlation coefficients (≥ 0.98). From the slope of these straight line graphs, the second-order rate constants were determined. These rate constants were in the range $1.9\text{--}300 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 1). These are lower by two orders of magnitude compared to the reactions of $\bullet\text{OH}$ with similar triazines¹⁸ except in the case of AT. Although these two radicals have comparable oxidation potentials, the magnitudes of rate constants are widely

Table 1. Second order rate constant (k_2) obtained for the reactions of $\text{SO}_4^{\bullet-}$ with triazine derivatives at pH 5

Compound	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1,3,5-Triazine (T)	8.1×10^7
2,4,6-Trimethoxy-1,3,5-triazine (TMT)	5.1×10^7
2,4-Dioxohexahydro-1,3,5-triazine (DHT)	4.6×10^7
6-Chloro- <i>N</i> -ethyl <i>N'</i> -(1-methylethyl)-1,3,5-triazine 2,4-diamine (AT)	3×10^9

different. This difference can be attributed to the difference in the mode of reactions. $\bullet\text{OH}$ generally adds to the double bonds, whereas $\text{SO}_4^{\bullet-}$ undergoes an electron transfer reaction (inner sphere or outer sphere) with aromatic ring. Furthermore, the relatively high rate constant obtained in the case of the reaction of $\text{SO}_4^{\bullet-}$ with AT is attributed to the presence of electron-donating groups attached to the triazine ring and the electrophilic nature of the $\text{SO}_4^{\bullet-}$. In an earlier report, it was shown that the $\text{SO}_4^{\bullet-}$ has no measurable reactivity with T, though it has a high reactivity with AT ($1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).²³ But our experiments clearly demonstrate that $\text{SO}_4^{\bullet-}$ has reasonable reactivity with T which can be monitored in the microsecond time scale. In the present work, a slightly higher rate constant is obtained ($3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) compared to the reported rate constant²³ and this value was found to be highly reproducible.

Absorption spectra of the transients

The transient absorption spectra were obtained from the photolysis of Ar-saturated solutions containing $\text{K}_2\text{S}_2\text{O}_8$

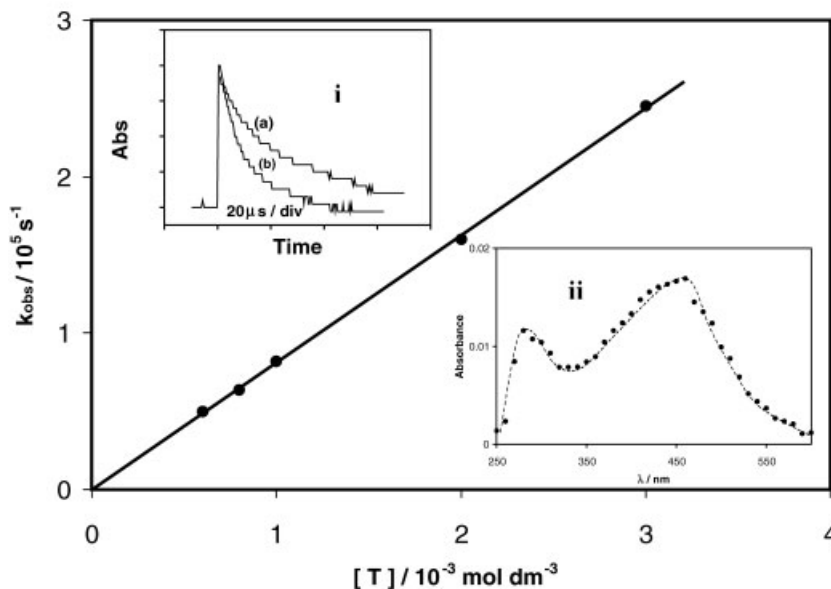


Figure 1. The pseudo first-order decay of $\text{SO}_4^{\bullet-}$ (k_{obs}) versus concentration plot obtained with 1,3,5-triazine (T). **Inset:** (i) Decay traces of $\text{SO}_4^{\bullet-}$ in the absence (a) and in the presence of T ($5 \times 10^{-4} \text{ mol dm}^{-3}$) (b). (ii) Absorption spectrum of $\text{SO}_4^{\bullet-}$ obtained by the laser flash photolysis of peroxydisulphate ($5 \times 10^{-2} \text{ mol dm}^{-3}$) at $1 \mu\text{s}$

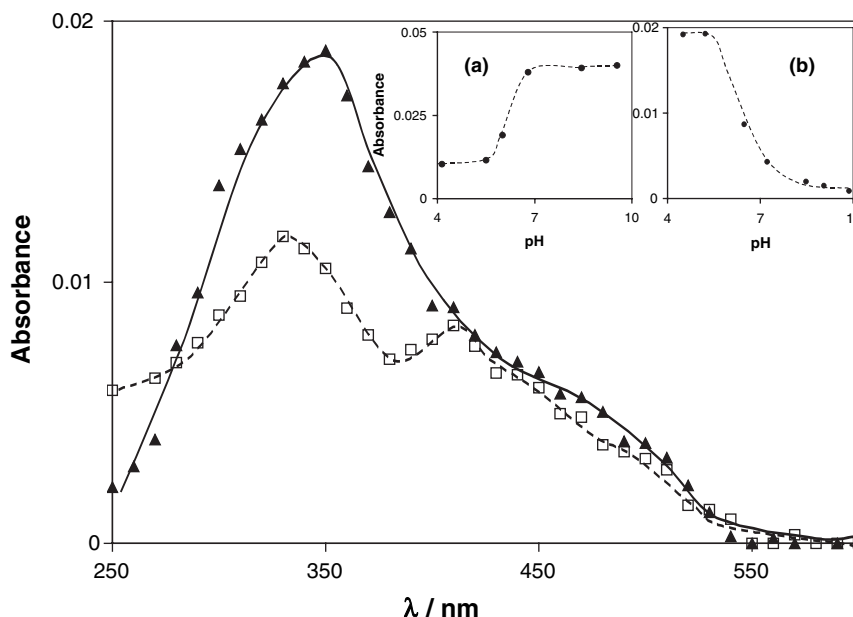


Figure 2. Transient absorption spectra obtained by the laser flash photolysis of Ar saturated solution of peroxydisulphate ($5 \times 10^{-2} \text{ mol dm}^{-3}$) containing 1,3,5-triazine ($5 \times 10^{-4} \text{ mol dm}^{-3}$) (\diamond) and 2,4-dioxohexahydro-1,3,5-triazine ($5 \times 10^{-4} \text{ mol dm}^{-3}$) (\blacktriangle) at $10 \mu\text{s}$. **Inset:** pH versus absorbance of (a) 1,3,5-triazine at 330 nm and (b) 2,4-dioxohexahydro-1,3,5-triazine at 350 nm

by monitoring the absorbance *versus* time profile in the range 250–600 nm (Fig. 1). $\text{SO}_4^{\bullet-}$ has a well-defined absorption spectrum with a λ_{max} at 450 nm ($\epsilon_{450 \text{ nm}} = 1100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and a small shoulder around 290 nm.²⁹ The absorption spectra of the intermediates resulting from the reactions of $\text{SO}_4^{\bullet-}$ radical with T, and DHT are shown in Fig. 2. Figure 3 shows the transient absorption spectra obtained in the reaction of $\text{SO}_4^{\bullet-}$ with TMT and 6-chloro-*N*-ethyl-*N'*-(1-methylether)-1,3,5-triazine-2, 4-diamine (atrazine, AT). The initial spectrum recorded $1 \mu\text{s}$ after the laser flash in the case of all the triazines has similar features of the absorption spectrum of $\text{SO}_4^{\bullet-}$. However, the spectrum recorded $10 \mu\text{s}$ after the laser flash showed different absorption maxima. In the

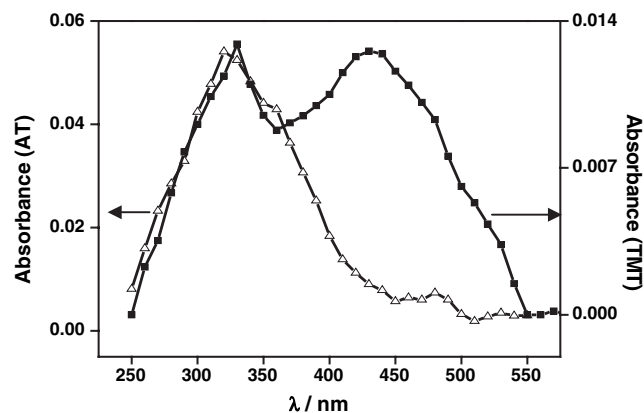


Figure 3. Transient absorption spectra obtained by the laser flash photolysis of Ar saturated solution of peroxydisulphate ($5 \times 10^{-2} \text{ mol dm}^{-3}$) containing 2,4,6-trimethoxy-1,3,5-triazine ($5 \times 10^{-4} \text{ mol dm}^{-3}$) (\blacksquare) and 6-chloro *N*-ethyl *N'*-(1-methylethyl)-1,3,5-triazine 2,4-diamine ($5 \times 10^{-4} \text{ mol dm}^{-3}$) (\triangle) at $10 \mu\text{s}$

case of T, the spectrum recorded $10 \mu\text{s}$ after the laser flash showed a λ_{max} at 330 nm (Fig. 2) and for AT the absorption maximum is obtained at 320 nm (Fig. 3). However, in the reaction of TMT with $\text{SO}_4^{\bullet-}$, the transient spectrum obtained at $10 \mu\text{s}$ after the flash is characterized with an absorption maximum at 330 and 430 nm. But for DHT, the absorption maximum is observed at 350 nm (Fig. 2). The spectra recorded at higher time scales (30 and $60 \mu\text{s}$) for all these triazines showed only second-order decay. When the absorbance is plotted against pH, in the case of T, a typical pKa curve with an inflection point at 6.8 is obtained (Fig. 2). Similarly for DHT also, a pKa curve is obtained with inflection point at 6.8.

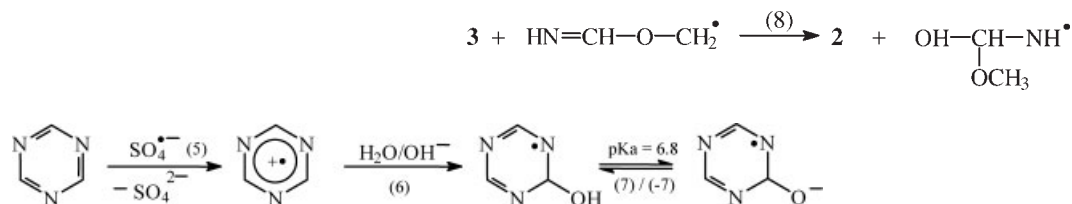
In general, $\text{SO}_4^{\bullet-}$ reacts with several aromatic compounds by an addition-elimination reaction resulting a radical cation.^{30,31} The stability of this radical cation depends on the nature of the substituents and their position in the aromatic ring. The unstable radical cation may deprotonate to form a neutral radical or it may further react by the addition of OH^- leading to the formation of an OH-adduct. It is reported that in the case of pyrimidines, an adduct is formed initially by the reaction of $\text{SO}_4^{\bullet-}$.³² This adduct may be either long lived or it dissociates rapidly to give a radical cation and SO_4^{2-} . Hydroxyl adduct might also be formed from this radical cation by addition of OH^- . The radical cation and the adduct can be distinguished by their difference in the reaction with oxygen. The radical cations, in general, have very little or slow reactivity with oxygen,³³ but the adduct can easily react with oxygen.³⁴

In the reaction of T with $\text{SO}_4^{\bullet-}$, the major possibility is expected to be an addition-elimination reaction. It is, therefore, assumed that a radical cation is formed initially.

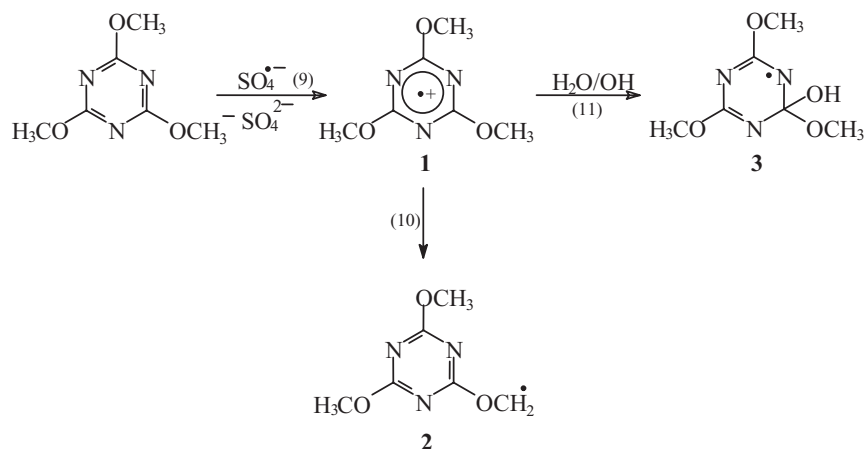
This radical cation is not likely to be stable as the triazine ring itself is electron deficient. The radical cations from pyrimidines, which are slightly more electron rich compared to triazines were reported as very unstable and cannot be detected in the microsecond time scale.³⁵ The immediate reaction of the radical cation is, thus, likely with OH^- so that an OH adduct of T can be formed. Because of the symmetrical structure of T, the OH adduct may be in any one of the three carbon atoms. Therefore, the probable species would be an OH-adduct (*N*-ylC(OH) radical). This assignment is further supported by a very clear acid base equilibrium of the intermediate. An absorbance *versus* pH plot measured at 10 μs after the pulse at 330 nm (see inset Fig. 2) gave an inflection point at pH 6.8. Since the intermediate of T has pKa value about 6.8, it is proposed that at higher pH, the OH adduct undergoes a deprotonation reaction and exists in its anionic form. The proposed mechanism of the reaction of $\text{SO}_4^{\bullet-}$ with T is shown in Scheme 1.

As in the case of T, $\text{SO}_4^{\bullet-}$ can undergo an electron transfer reaction with TMT leading to the formation of a radical cation, **1** in the initial stage. Since the $-\text{OCH}_3$ group has inductive effect (+I effect), it may tend to stabilize the radical cation of TMT as in the case of anisole.⁸ Triazine itself is an electron-deficient molecule and hence, the stabilization of its radical cation due to the $-\text{OCH}_3$ groups may not be efficient. It can undergo deprotonation or an addition of OH^- . The deprotonation may lead to a neutral radical **2**. However, this deprotonation, if possible, could be from one of the $-\text{OCH}_3$ groups. The other possibility is the formation of

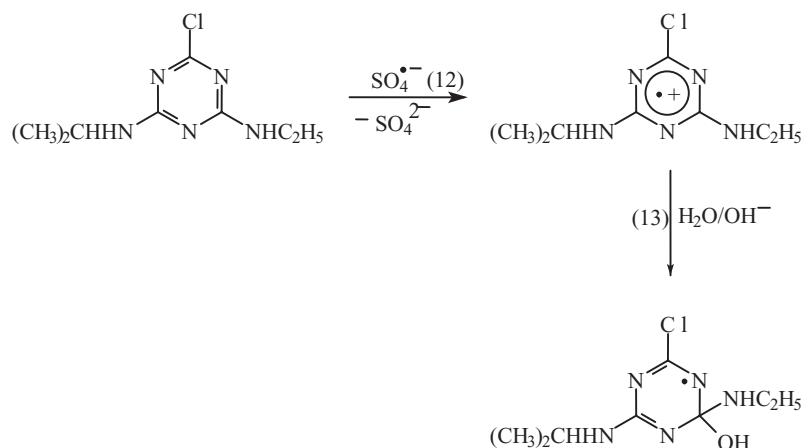
OH-adduct as shown in Scheme 2 which results a neutral radical of the type **3**. The spectral features from the reaction of $\bullet\text{OH}$ with TMT¹⁸ are widely different from that obtained from the reaction of $\text{SO}_4^{\bullet-}$ with TMT (Fig. 3). The OH adduct spectrum is characterized by its absorption maximum at 320 nm¹⁸, whereas the transient spectrum from the present reaction has two distinct maxima at 330 and 430 nm. Therefore, the OH adduct of TMT does not contribute to the present transient absorption spectrum. In order to clearly distinguish these three possibilities (existence of the radical cation of TMT (**1**), deprotonation from $-\text{OCH}_3$ group (**2**), and the formation of OH-adduct (**3**)), we have performed theoretical calculations using Gaussian 03. All geometries were optimized at B3LYP/6-311+G** level of theory.³⁶ Frequency calculations of important systems concluded that structures **1**, **2**, and **3** do not have any imaginary frequencies. We have computed the Nuclear Independent Chemical Shift (NICS)³⁷ values at the center of the radical cations of TMT at B3LYP/6-311+G** level of theory using GIAO method. The NICS value for structure **1** (radical cation) is computed to be 1.67, shows that structure **1** is not an aromatic system. Therefore, structure **1** should have a tendency to get converted into either **2** or **3** because both are aromatic and thereby, more stable. The NICS value of structure **2** and **3** at the center is -4.7 and -3.5 , respectively. Comparison of these values with those of benzene³⁷ indicates that structure **2** and **3** are aromatic. Comparison of the stability of the two radicals **2** and **3** using isodesmic reactions³⁸ (Eqn 8) indicate that system **2** is stabilized over **3** by 17.01 kcal mol⁻¹.



Scheme 1. Proposed mechanism of the reaction $\text{SO}_4^{\bullet-}$ with 1,3,5-Triazine



Scheme 2. Proposed reaction mechanism of $\text{SO}_4^{\bullet-}$ with 2,4,6-trimethoxy-1,3,5-triazine



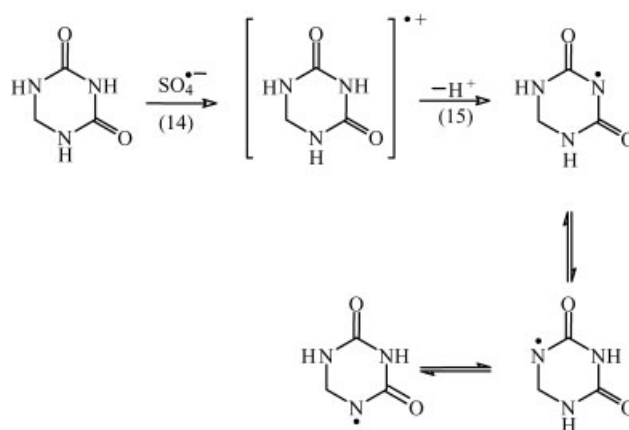
Scheme 3. Proposed reaction mechanism of $\text{SO}_4^{\bullet-}$ with 6-chloro *N*-ethyl *N'*-(1-methylethyl)-1,3,5-triazine-, 2,4 diamine

These values indicate that structure **2** is more aromatic than **3**, thereby structure **2** is more stable. Generally, $\bullet\text{OH}$ adds to the double bond of aromatic compounds giving rise to OH-adducts. However, it undergoes both addition and H-abstraction with atrazine.¹⁹ The absorption maxima at 440 nm of the transient spectrum reported with AT¹⁹ was largely assigned to the carbon centered radical in the side chain. It is further reported that the OH adducts of *S*-triazines absorb more towards lower wavelengths (300–350 nm).^{18,19} This means both our experimental findings on the transient absorption spectrum and the conclusion on the stability of radical **2** from theoretical calculations match very well. It is, therefore, proposed that the major transient intermediate from TMT on its reaction with $\text{SO}_4^{\bullet-}$ is a carbon centered radical **2** as shown in Scheme 2.

In the reaction of AT with $\text{SO}_4^{\bullet-}$, it is expected to undergo an addition-elimination reaction resulting in the formation of radical cation in the initial stage (reaction 12). Subsequently, an addition of OH^- may occur at the carbon center leading to the formation of a nitrogen-centered radical. The reaction of $\bullet\text{OH}$ with AT is once again useful in the present case. In the reaction of $\bullet\text{OH}$ with atrazine, an intermediate is obtained with a strong absorption maximum at 440 nm.¹⁹ The absorption of OH-adduct radicals contributes nearly 45% and may be hidden due to the absorption of a carbon centered radical which is formed from the H-abstraction of the ethyl side chain by $\bullet\text{OH}$ or strongly red shifted due the substituent effects.¹⁹ This means that the observed transient absorption spectrum is not fully due to the OH adduct of atrazine, but largely due to a carbon centered radical. On the other hand, the OH-adducts of triazines generally have absorption maximum between 300 and 350 nm.¹⁸ In the present case, the formation of a carbon centered radical (in the ethyl side chain) can be fully ruled out since this is possible only when $\bullet\text{OH}$ is involved in the reaction. Therefore, the only probability is the formation of an OH-adduct (*N*-centered radical). When the reactive

species is $\bullet\text{OH}$,¹⁹ the major contributor to the transient spectrum is the carbon centered radical (at the side chain). But the absorption spectrum in the present case has λ_{max} at 320 nm which can be well interpreted to the existence of an OH adduct of AT. The corresponding OH adduct is thus assigned to a nitrogen centered radical as shown in Scheme 3.

In the case of DHT, the most probable species is proposed as an *N*-centered radical of the type shown in reaction 15 which can be formed by the deprotonation of the radical cation. However, the deprotonation can be from one of the protons attached to nitrogen and therefore, it would lead to the existence of three nitrogen centered radical tautomers as shown in Scheme 4. A report on the deprotonation of the radical cations of uracil and its derivatives, which results a neutral radical³⁹ supports this assignment. It is, therefore, proposed that the transient absorption spectra, obtained with DHT has an absorption maxima around 350 nm, is due to the formation of an *N*-centered radical, which has three tautomeric structures as shown in Scheme 4. Furthermore, the plot of absorbance *versus* pH (Fig. 2) of the



Scheme 4. Proposed reaction mechanism of $\text{SO}_4^{\bullet-}$ with 2,4-dioxohexahydro-1,3,5-triazine

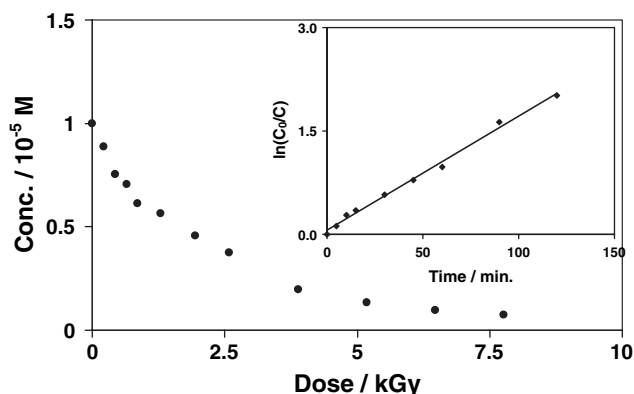


Figure 4. The degradation profile of 6-chloro *N*-ethyl *N'*-(1-methylethyl)-1,3,5-triazine 2,4-diamine induced by $\text{SO}_4^{\bullet-}$ (●) measured by HPLC after γ -radiolysis. **Inset:** First-order nature of the decay profile induced by $\text{SO}_4^{\bullet-}$. C_0 is the initial concentration of AT and C is that at time t . (Dose rate of the gamma source was 100 Gy min^{-1})

N-centered radical at 350 nm shows an inflection point around pH 6.8.

Steady-state radiolysis

In addition to the understanding of the basic chemistry involved in the reaction of $\text{SO}_4^{\bullet-}$ with triazines, the viability of such reactions in the degradation of triazine is also of interest. Being known as an important water pollutant, the degradation of AT was monitored using γ -irradiation (at different doses) in an Ar-saturated solution containing triazine, 2-methyl propan-2-ol and $\text{S}_2\text{O}_8^{2-}$ where $\text{SO}_4^{\bullet-}$ is the major reactive radical (reactions 2–4). The degradation profile is shown in Fig. 4. As can be seen from the Fig. 4 that 99% of the AT has disappeared after an absorbed dose of 7.5 kGy. When the concentration is plotted in a logarithmic scale, a clear first order nature of degradation is observed with a rate constant of 0.016 min^{-1} . The degradation yield, expressed as $G(-\text{AT})$ which is the number of molecules destroyed per 100 eV absorption of radiation energy, was calculated from the slope of initial decay of AT. This is about $0.26 \mu \text{ mol J}^{-1}$. This value is nearly quantitative (a G -value equal to the yield of $\text{SO}_4^{\bullet-}$ ($0.28 \mu \text{ mol J}^{-1}$) is expected as the quantitative yield), and therefore, it is clear from the figure that $\text{SO}_4^{\bullet-}$ does initiate degradation of AT. The degradation of AT is expected to follow via the hydroxyl radical adduct since the radical cation of AT gives rise to the OH-adduct as discussed in the previous section. The degradation is likely initiated by the bimolecular reaction of these radicals. On the other hand, the final product of this reaction was not analyzed as it is beyond the scope of this work at the moment. The purpose was only a demonstration of the degradation of AT induced by $\text{SO}_4^{\bullet-}$.

CONCLUSION

Laser flash photolysis technique has been used for the elucidation of the reaction mechanism of $\text{SO}_4^{\bullet-}$ with triazine derivatives in aqueous medium. The spectral details of the short-lived intermediate radical derived from the reaction of $\text{SO}_4^{\bullet-}$ with triazine derivatives have been presented for the first time. The intermediate spectrum obtained in the case of T is in contradiction with the earlier report that $\text{SO}_4^{\bullet-}$ has no measurable reactivity with T.^{2,3} The higher reactivity of $\text{SO}_4^{\bullet-}$ with AT compared to other selected triazines is a demonstration of the potential use of this radical for the degradation of triazine-based herbicides in aqueous medium. The degradation of AT is a clear demonstration of the potential use of $\text{SO}_4^{\bullet-}$ in the degradation of triazine-based herbicides though a variety of practical difficulties need to be resolved before it finds its utility.

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REFERENCES

- Jovanovic SV, Simic MG. *J. Phys. Chem.* 1986; **90**: 974–978.
- Fisher GJ, Smith EJJ. *Photochem. Photobiol.* 1983; **37**: 32–37.
- Candeias LP, Steenken S. *J. Am. Chem. Soc.* 1989; **111**: 1094–1099.
- Novais HM, Steenken S. *J. Phys. Chem.* 1987; **91**: 426–433.
- Eberson L. *Adv. Phys. Org. Chem.* 1982; **18**: 79–185.
- Steenken S. *Chem. Rev.* 1989; **89**: 503–520.
- Norman ROC, Storey PM, West PR. *J. Chem. Soc. B.* 1970; 1087–1095.
- O'Neill P, Steenken S, Schulte-Frohlinde D. *J. Phys. Chem.* 1975; **79**: 2773–2779.
- Gillbert BC, Larkin JP, Norman ROC. *J. Chem. Soc. Perkin Trans 2.* 1972; 1272–1279.
- Snook EM, Hamilton GA. *J. Am. Chem. Soc.* 1974; **96**: 860–869.
- Pignatello JJ. *Environ. Sci. Technol.* 1992; **26**: 944–951.
- Peyton GR, Huang RY, Burleson JL, Glaze WH. *Environ. Sci. Technol.* 1982; **16**: 448–453.
- Legrini O, Oliveros E, Braun AM. *Chem. Rev.* 1993; **93**: 671–698.
- D'Oliveria JC, Al-Sayyed G, Pichat P. *Environ. Sci. Technol.* 1990; **24**: 990–996.
- Getoff N. *Radiat. Phys. Chem.* 1999; **54**: 377–384.
- Hua I, Hoffmann MR. *Environ. Sci. Technol.* 1997; **31**: 2237–2243.
- Prados M, Paillard H, Roche P. *Ozone Sci. Eng.* 1995; **17**: 183–194.
- Joseph JM, Jacob TA, Manoj VM, Aravindakumar CT, Mohan H, Mittal JP. *J. Agric. Food Chem.* 2000; **48**: 3704–3709.
- Tauber A, von Sonntag C. *Acta hydrochim. Hydrobiol.* 2000; **28**: 15–23.
- Donnare L, Arnaud R, Lemaire J, Deflandre A, Richard H. *J. Photochem. Photobiol. A Chem.* 1996; **96**: 71–78.
- Buxton GV, Greenstock CL, Helman WP, Ross AB. *J. Phys. Chem. Ref. Data* 17. 1988; 513–886.

22. Manoj P, Varghese R, Manoj VM, Aravindakumar CT. *Chem. Lett.* 2002; **1**: 74–75.
23. Azenha MEDG, Burrows HD, Canle ML, Coimbra R, Fernandez MI, Garcia MV, Rodrigues AE, Santaballa JA, Steenken S. *Chem. Commun.* 2003; 112–113.
24. Canle LM, Fernández MI, Santaballa JA. *J. Phys. Org. Chem.* 2004; **18**: 148–155.
25. Venkatachalapathy B, Ramamurthy P. *Phys. Chem. Chem. Phys.* 1999; **1**: 2223–2230.
26. von Sonntag C. *The Chemical Basis of Radiation Biology*. 1987.
27. Wolinski K, Hilton KJF, Pulay P. *J. Am. Chem. Soc.* 1990; **112**: 8251–8260.
28. Frisch MJ, *et al.*, *Gaussian 03, version 6.0*. Gaussian, Inc.: Pittsburgh PA, 2003.
29. Hayon E, Treinin A, Wilf J. *J. Am. Chem. Soc.* 1972; **94**: 47–57.
30. Merga G, Rao BSM, Mohan H, Mittal JP. *J. Phys. Chem.* 1994; **90**: 9158–9164.
31. Merga G, Aravindakumar CT, Rao BSM, Mohan H, Mittal JP. *J. Chem. Soc. Faraday Trans.* 1994; **90**: 597–604.
32. Willson RL. *Int. J. Radiat. Biol.* 1970; **17**: 349–358.
33. Sehested K, Holcman J. *J. Phys. Chem.* 1978; **82**: 651–653.
34. Davies MJ, Gilbert BC. *J. Chem. Soc. Perkin Trans 2.* 1984; 1809–1815.
35. Schuchmann H-P, Deeble DJ, Olbrich G, von Sonntag C. *Int. J. Radiat. Biol.* 1987; **51**: 441–453.
36. (a) Becke AD, *J. Chem. Phys.* 1993; **98**: 5648–5652. (b) Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988; **37**: 785–789.
37. Scheleyer PvR, Maerker C, Dransfeld A, Jiao H, Hommes NJRVE. *J. Am. Chem. Soc.* 1996; **118**: 6317–6318.
38. Hehre WJ, Radon L, Schleyer PvR, Pople JA. *Ab Initio Molecular Orbital Theory*. John Wiley and Sons: New York, 1986.
39. Bothe E, Deeble DJ, Lemaire DGE, Rashid R, Schuchmann MN, Schuchmann HP, Schulte-Frohlinde D, Steenken S, von Sonntag C. *Radiat. Phys. Chem.* 1990; **36**: 149–154.