

Reactions of Hydrated Electrons with Triazine Derivatives in Aqueous Medium

RANI VARGHESE,[†] HARI MOHAN,[‡] P. MANOJ,[†] V. M. MANOJ,[†]
 USHA K. ARAVIND,[†] K. VANDANA,[†] AND C. T. ARAVINDAKUMAR*^{*,†}

School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, India, and Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

A study is made of the kinetics and mechanism of the reaction of radiolytically produced hydrated electron (e^-_{aq}) with some triazine derivatives [1,3,5-triazine (T), 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)] in aqueous medium using pulse and steady-state radiolysis techniques. The second-order rate constants were determined from the pseudo first-order decay of e^-_{aq} in the presence of triazines at 720 nm, and the values obtained with T, TMT, AT, and CA are in the order of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and that of DHT was $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 6. The transient absorption spectra from the reaction of e^-_{aq} with T and TMT are characterized by their λ_{max} at 310 nm, and those of DHT and CA are around 280 and 290 nm, respectively. However, a very weak and featureless absorption spectrum is obtained from AT. On the basis of the spectral evidence and on the quantitative electron transfer from the transient intermediates to the oxidant, methyl viologen (MV^{2+}), the intermediate radicals are assigned to N-protonated electron adducts (with the unpaired spin density at carbon) of triazines. The degradation profiles, monitored as the disappearance of parent triazine concentrations as a function of dose, obtained with AT, TMT, CA, and DHT, highlight the potential use of e^-_{aq} in the degradation of triazines.

KEYWORDS: Pulse radiolysis; steady-state radiolysis; second-order rate constants; electron adducts; degradation

INTRODUCTION

Triazine derivatives are among the most widely used herbicides, and its main mode of action as a 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; 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. 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 are relatively very

slow and therefore are 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 a photosensitizer (6). Photochemical decomposition studies of certain triazines in both methanol and aqueous solutions have also been reported earlier (7, 8). Electrochemical reduction of triazine pesticides including propazine and prometryne at mercury electrode has been recently reported (9–11). Advanced oxidation processes (AOPs), which make use of the reaction of a highly oxidizing radical, the hydroxyl radical ($\cdot\text{OH}$), are becoming increasingly popular for an effective degradation of organic pollutants, and these include the degradation by $\text{H}_2\text{O}_2/\text{UV}$ (12, 13), O_3/UV (14), ultrasound (15), Fenton reaction (16–19), and radiation chemical techniques (20–22).

Among the various AOPs, the radiation chemical method can be considered as a potential technique in understanding the fundamental reactions that lead to aromatic degradation, as it allows us to create a selective oxidizing or reducing environment in the solution state (23, 24). The oxidizing condition is attributed to the reaction of $\cdot\text{OH}$ and the reducing condition to the hydrated electron (e^-_{aq}) [and hydrogen atom ($\text{H}\cdot$)] generated

* To whom correspondence should be addressed. Fax: +91-481-2731009. E-mail: CT-Aravindakumar@rocketmail.com.

[†] Mahatma Gandhi University.

[‡] Bhabha Atomic Research Centre.

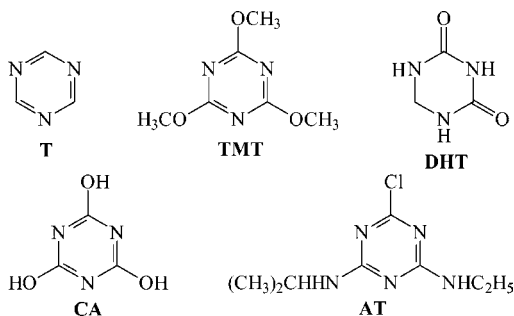
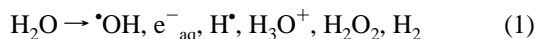


Figure 1. Structural formulas of the selected triazines.

by the radiolysis of water by γ -rays or high-energy electrons (24).



Most of the degradation studies of triazines reported so far are based on AOPs that make use of the oxidizing property of hydroxyl radicals. e_{aq}^- is one of the most powerful reducing agents with a reduction potential of 2.86 V. The rate constants for the reaction of OH radicals as well as e_{aq}^- with a variety of nitrogen-containing heterocycles have been reported as diffusion controlled (25). However, only few studies have concentrated on the degradation of organic water pollutants in aqueous solutions under reductive conditions (26–28). Therefore, the objective of this study is to investigate the mechanistic aspects of the reaction of e_{aq}^- with triazines and to explore the possibility of its application in the degradation of triazines on a laboratory scale. We have used a reductive environment using the highly reducing radical, e_{aq}^- , produced by the radiolysis of water and investigated the reaction kinetics, the properties of the short-lived electron adducts, and the degradation reactions of triazine and some of its substituted derivatives in aqueous medium at near neutral pH. Both pulse and steady-state radiolyses have been carried out. The selected triazines are 1,3,5-triazine (T), 2,4,6-trimethoxy-1,3,5-triazine (TMT), 2,4-dioxo-hexahydro-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), and the structures of these compounds are shown in **Figure 1**. Although T is not stable for prolonged periods in aqueous medium due to hydrolysis (29), it is selected as a basic structure to understand the reaction mechanism. The oxidant, methyl viologen (MV^{2+}), has been used to demonstrate the reducing nature of the electron adducts. To our knowledge, this is the first report on the degradation of triazine derivatives using a reducing radical or a radical other than hydroxyl radical.

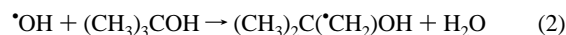
MATERIALS AND METHODS

The triazine and its derivatives [T (97%), TMT (95%), DHT (99%), AT (98%), and CA (97%)] were purchased from Aldrich Chemical Co. (United States) and were used without further purification. The initial concentration of triazines was kept at 10^{-3} mol dm^{-3} (i.e., T = 81.08 mg/L; TMT = 171.16 mg/L, DHT = 115.09 mg/L, AT = 215.6 mg/L, and CA 129.06 mg/L). All of the solutions were prepared in either triply distilled water or water purified by Millipore Milli-Q system. T was added just before the pulse irradiation as it can undergo hydrolysis in aqueous medium (29). However, in the case of steady-state radiolysis experiments, the time required to irradiate and finally to analyze the sample by HPLC was close to about 2 h; a significant decay of T had been observed (see Steady-State Radiolysis).

A linear accelerator that delivered 7 MeV electron pulses of 50 ns duration was used to carry out pulse radiolysis experiments (30). The dose per pulse was determined using KSCN dosimetry taking a $G_{\epsilon_{500}}$ nm value of 2.15×10^{-4} m 2 J $^{-1}$ in aerated aqueous solution (31, 32)

and was kept at 14 Gy. A low dose per pulse (6 Gy) was used to study the electron-transfer reaction from the electron adducts to MV^{2+} . This oxidant was well-suited for the study of electron-transfer reactions because of its good selectivity, its low tendency to react by addition, and inherent high detection sensitivity due to the large extinction coefficient at 605 nm of its semireduced form [$\epsilon(\text{MV}^{\cdot+})_{605\text{nm}} = 12800$ dm 3 mol $^{-1}$ cm $^{-1}$] (33). The concentrations of triazines and MV^{2+} were kept in such a way that most of the e_{aq}^- ($\geq 90\%$) reacts with triazines. The transient absorption spectra were recorded by monitoring the absorbance–time profiles at various wavelengths. The absorbance of the transients was monitored using a 450 W pulsed xenon arc lamp monochromator (Kratos GM-252) on the exit of which a Hamamatsu R-955 photomultiplier was fixed, which was used as a detector. The photomultiplier signal was then fed to a 100 MHz storage oscilloscope and was transferred to a computer for kinetic analysis.

γ -Radiolysis was carried out in a ^{60}Co - γ -chamber. The dose rate was determined using ceric sulfate dosimetry (24). The degradation of the parent triazines and the generation of products (determined from the area of product peaks) after γ -radiolysis were monitored using HPLC (Shimadzu LC10 AS) with a UV–vis detector (SPD 10A) at a wavelength 210 nm. A methanol/water mixture (10/90) was used as the mobile phase in a 25 cm, Supelcosil 5C-18 column at a flow rate of 1 mL/min. The retention times for the parent triazines were as follows: T, 3.01 min; TMT, 7.43 min; DHT, 3.55 min; AT, 5 min; and CA, 4.40 min. All of the experiments and analyses were performed at least twice and obtained a very good reproducibility. In the radiolysis of water, a totally reducing condition can be achieved by the addition of *t*-butyl alcohol (0.3 mol dm^{-3}), a scavenger of OH radicals, and purging with argon or nitrogen to eliminate O_2 , which can convert e_{aq}^- into superoxide radical (34) (reactions 2 and 3).



Alternatively, an oxidizing condition can be achieved by saturating the solutions with NO_2 , which converts e_{aq}^- into OH radicals.



The radiolytic yields are expressed in terms of G values, which can be defined as the number of molecules formed or destroyed per 100 eV absorption of radiation energy, and in SI units, these yields were $G(\cdot\text{OH}) \approx G(e_{\text{aq}}^-) \approx G(\text{H}_3\text{O}^+) = 0.28$ $\mu\text{mol J}^{-1}$, $G(\text{H}^{\cdot}) = 0.062$ $\mu\text{mol J}^{-1}$, $G(\text{H}_2\text{O}_2) = 0.072$ $\mu\text{mol J}^{-1}$, and $G(\text{H}_2) = 0.047$ $\mu\text{mol J}^{-1}$.

RESULTS AND DISCUSSION

Pulse Radiolysis. The hydrated electron has a well-defined absorption spectrum with a maximum around 720 nm (24). The second-order rate constants for the reaction of e_{aq}^- with triazines at pH 6 were determined from the decay of e_{aq}^- at 720 nm at different concentrations of triazines, along with its own decay in the absence of triazines. The decay of e_{aq}^- was best fitted for a first-order kinetics, and this decay has shown a concentration dependence. Therefore, the pseudo first-order rate constants (k_{obs}) vs concentration plots were found to be linear with very good correlation coefficients (≥ 0.98 , and the maximum deviation observed in the linear regression plots was within 10%). A typical k_{obs} vs concentration plot obtained in the case of T is shown in **Figure 2**. The decay traces obtained in the presence as well as in the absence of T are also shown in **Figure 2**. The k_{obs} vs concentration plots obtained with all of the triazines have intercepts in the Y-axis (for a typical plot, see **Figure 2**) that corresponds to the self-decay of e_{aq}^- , most likely due to its reaction with trace amount of impurities. Such intercepts in the case of the reactions of e_{aq}^- have been reported in a number of earlier studies (35, 36). The second-order rate constants obtained

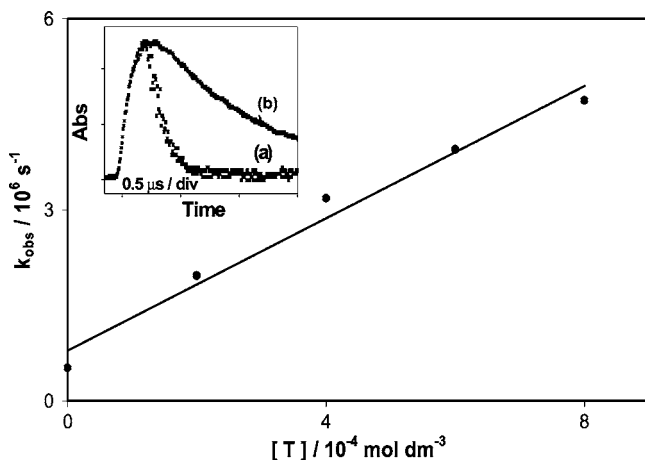


Figure 2. Plot of pseudo first-order rate constant obtained for the decay of e^-_{aq} at 720 nm (k_{obs}) vs concentration of T. Inset: The decay traces of e^-_{aq} at 720 nm (a) in the presence of T ($2 \times 10^{-4} \text{ mol dm}^{-3}$) and (b) in the absence of T.

Table 1. Kinetic and Spectral Parameters Obtained from the Reaction of e^-_{aq} with Triazines at pH 6 Using Pulse Radiolysis

triazines	k_2^a ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	λ_{max} (nm)	ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$G(\text{MV}^{2+})$ ($\mu\text{mol J}^{-1}$)	k^b ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
T	5.2×10^9	310	1099	0.28	4.3×10^9
TMT	3.75×10^9	310	1714	0.27	2.8×10^9
DHT	1.07×10^8	280	1861	0.28	2.3×10^9
AT	4.8×10^9	360	-	-	-
CA	1.4×10^9	290	1109	0.27	2.1×10^9

^a Second-order rate constant for the reaction of e^-_{aq} with triazines. ^b Second-order rate constant for the reaction of protonated electron adducts of triazines with MV^{2+} (these are calculated from the absorption build-up of MV^{2+} at 605 nm).

for T, TMT, AT, and CA are in the order of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and for DHT, it is $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 1).

As can be seen from Table 1, the second-order rate constants obtained with T, TMT, AT, and CA are diffusion-controlled because of the high electron affinity of the triazine ring. However, a slight reduction in the rate constant values was observed on going from T to CA, which can be attributed to the increased electron density in TMT and CA due to the presence of $-\text{OCH}_3$ and $-\text{OH}$ groups leading to the electrostatic effect. The second-order rate constant obtained for DHT was by an order lower in magnitude as compared to the other three compounds, likely due to the nonaromatic nature of DHT.

The optical absorption spectra of the intermediates resulting from the reaction of e^-_{aq} with T, TMT, DHT, AT, and CA were recorded at pH 6. Among these triazine, the transient absorption spectrum obtained for AT was very weak and featureless. All other triazines resulted in well-defined transient absorption spectra on reaction with e^-_{aq} . The time-resolved spectra obtained with these compounds were found to undergo a second-order decay ($2k \sim 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The transient spectra measured at $3 \mu\text{s}$ after the pulse are given in Figure 3. In the case of T and TMT, the absorption spectra are characterized by their λ_{max} at 310 nm. The absorption spectrum obtained with CA has a λ_{max} close to 290 nm and that with DHT to 280 nm along with a shoulder around 360 nm. The absorption traces below 280 nm were not recorded due to poor S/N ratio. The spectral parameters are summarized in Table 1.

In order to understand the nature of the electron adducts, we have investigated the electron-transfer reaction of the electron adducts with the oxidant, MV^{2+} . The formation of methyl

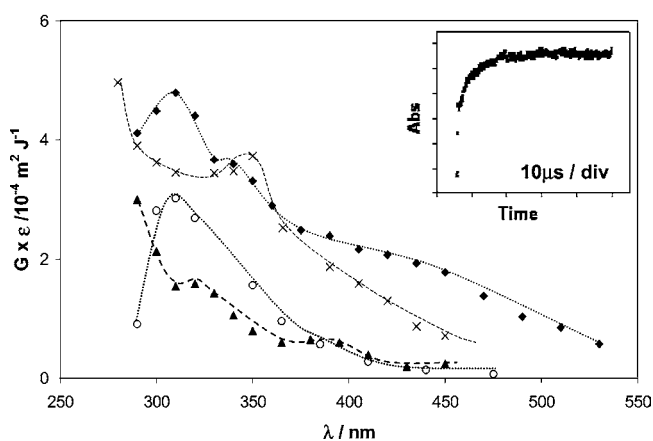
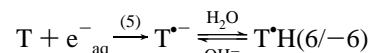


Figure 3. Transient absorption spectra recorded at pH 6 in argon-saturated millimolar solutions of T (O), TMT (◆), DHT (x), and CA (▲) containing *t*-butyl alcohol (0.3 mol dm^{-3}) at $3 \mu\text{s}$ after the pulse (dose/pulse = 14 Gy). Inset: Absorption build-up of MV^{2+} resulted from the electron-transfer reaction of the intermediate obtained from TMT to MV^{2+} (dose/pulse = 6 Gy).

viologen radical cation ($\text{MV}^{\bullet+}$) was monitored at 605 nm. A well-defined build-up of $\text{MV}^{\bullet+}$ is observed with all of the triazines. A typical trace showing the build-up of absorption due to $\text{MV}^{\bullet+}$ is given in Figure 3. The $G(\text{MV}^{\bullet+})$ and the second-order rate constants (approximate) for the electron-transfer reactions of the electron adducts to MV^{2+} are compiled in Table 1. The G values were calculated by taking a typical ϵ value of $\text{MV}^{\bullet+}$ as $12800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 605 nm (33).

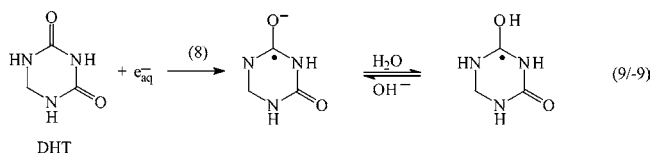
In general, e^-_{aq} undergoes addition at the highly electron affinic nitrogen in the heterocyclic ring as observed in the case of purines and pyrimidines (37, 38). The resulting radical anion, being highly proton affinic, can get protonated by water. The protonation and deprotonation reactions at a heteroatom are faster than at carbon (36, 37). We propose a similar electron addition at nitrogen centers of triazine ring with all of the selected triazines. Because all three nitrogens in T are identical, an electron adduct with the negative charge at one of the nitrogens is proposed.



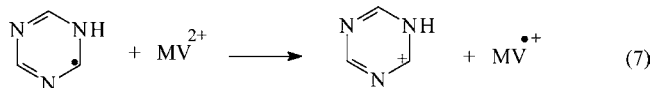
The electron adducts of triazines are expected to be stronger bases and hence can be rapidly protonated by water (reaction 6). The protonation of $\text{T}^{\bullet-}$ is therefore likely to be very fast as observed with purine electron adducts (35–37) where the rate of protonation at the heteroatom is of the order of 10^8 s^{-1} . Therefore, it is logical to assume that the triazine electron adduct gets protonated at nearly equal (or higher) rate due to the presence of three equivalent nitrogens in the triazine ring. It follows that the transient intermediate characterized by its absorption spectrum with λ_{max} at 310 nm must be a protonated electron adduct of T as the protonation could be complete much before the detection time of the initial spectrum (i.e., $3 \mu\text{s}$ after the pulse).

The results obtained with MV^{2+} further support the structural assignment of the protonated electron adducts. The observed G value for $\text{MV}^{\bullet+}$ at pH 6 was $0.28 \mu\text{mol J}^{-1}$. This follows that there is a quantitative electron transfer from the protonated electron adduct (where its G value is expected as $0.28 \mu\text{mol J}^{-1}$) to MV^{2+} . This is understandable from the proposed structure of the protonated electron adduct of T as shown in reaction 7 in which the unpaired spin density is at one of the

Scheme 1



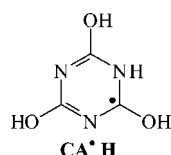
carbon atoms in the triazine ring (C-yl radicals). Such carbon-centered radicals are known to be able to transfer one electron to reducing agents such as MV^{2+} and pNAP (*para*-nitroacetophenone) (35, 39).



TMT, being a highly symmetric heterocycle similar to T, a very similar electron adduct, followed by its protonation by water, is proposed. Once the radical anion is formed, its protonation would be faster than in the case with T due to the presence of three $-\text{OCH}_3$ groups that make the radical anion more basic. Therefore, the spectra characterized by its λ_{max} at 310 nm are attributed to the N-protonated electron adduct of TMT (carbon centered radical). The well-defined build-up of MV^{2+} and the quantitative $G(MV^{2+})$ value (i.e., $0.27 \mu\text{mol J}^{-1}$) are clearly in line with the proposed protonated electron adduct of TMT with the unpaired electron density at carbon.

On the basis of the well-established properties of the electron adducts of uracil (39, 40), it is proposed that the e_{aq}^- can efficiently add to one of the $>\text{C}=\text{O}$ groups in the case of DHT (Scheme 1). As both $>\text{C}=\text{O}$ groups are in the same environment, the resulting electron adducts could have the same absorption spectra. As this radical anion is highly proton affinic, its fast protonation can be justified at pH 6 similar to uracil radical anion (39, 40) where oxygen protonation occurs very fast with a $\text{p}K$ value of 7.3. The oxygen-protonated carbon-centered radical situated in the middle of two $-\text{NH}$ s in the case of uracil has an absorption spectrum with a maximum around 290 nm (40). The situation is very similar with DHT where the protonated electron adducts (reactions 8 and 9) have $>\text{C}^{\cdot}-\text{OH}$ between two $-\text{NH}$ s. The absorption spectra with maximum around 280 nm are, therefore, attributed to the protonated electron adduct of DHT.

It is clear from **Table 1** that the electrostatic effect due to the increased electron density in the triazine ring in the case of CA decreases the rate constant value on going from T to CA. Therefore, the rate of protonation of the electron adduct of CA, undoubtedly, will be higher as compared to T due to the increased basicity of the electron adduct. The protonated electron adduct has a $>\text{C}^{\cdot}-\text{OH}$ radical site similar to the protonated electron adduct of DHT, which is essentially responsible for the absorption spectrum. A λ_{max} at shorter wavelengths is, therefore, anticipated, similar to the case with DHT (the structure $\text{CA}^{\cdot}\text{H}$ is given below).



On the basis of this understanding, the spectrum characterized by its λ_{max} around 290 nm is attributed to the N-protonated electron adduct with the unpaired spin density at carbon. The

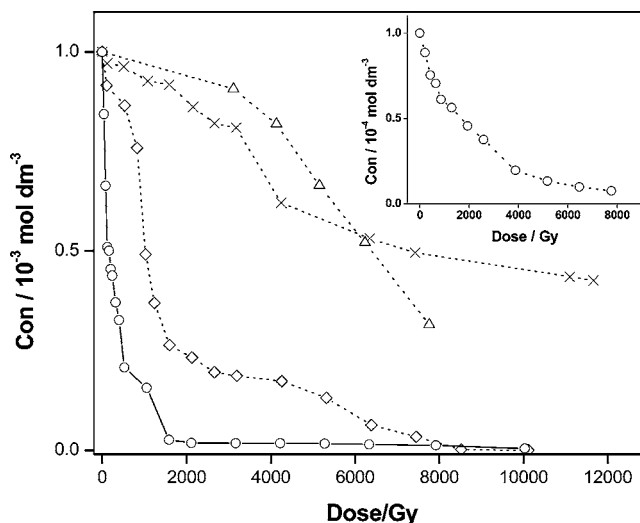


Figure 4. Degradation profiles (HPLC analyses) of T (○), TMT (◇), DHT (×), and CA (△) from the reaction of e_{aq}^- using γ -radiolysis. Inset: degradation profile of AT (The degradation of T is a combined effect of both radiolysis and its hydrolysis; see the text).

reducing nature of this radical [$G(MV^{2+}) = 0.27 \mu\text{mol J}^{-1}$; see **Table 1**] can be understood as in the previous cases.

Steady-State Radiolysis. In order to look at the reaction of e_{aq}^- in an environmental perspective, the degradations of T, TMT, AT, CA, and DHT at pH 6 have been investigated by monitoring their decrease in concentration at different times of γ -irradiation. In all of these experiments, the initial concentrations of triazines were kept at $10^{-3} \text{ mol dm}^{-3}$ (except of AT, which has a concentration of $10^{-4} \text{ mol dm}^{-3}$) and *t*-butyl alcohol at 0.3 mol dm^{-3} . The degradation profile obtained by HPLC as a function of dose absorbed is shown in **Figure 4**. This indicated a nearly complete disappearance of T at 3.2 kGy. However, when the $G(-T)$ value was calculated from the initial decrease in concentration of T, a very high value of $3.9 \mu\text{mol J}^{-1}$ was obtained. As the maximum expected $G(-T)$ is around $0.28 \mu\text{mol J}^{-1}$ [equal to $G(e_{\text{aq}}^-)$], such a value must be the result of some other reactions. A detailed investigation has shown that T undergoes a self-decay [due to hydrolysis (29), as expected] during the experimental time scale (which was about 2 h). Obviously, this is the reason for the high $G(-T)$ value; hence, this degradation profile is a combined effect of both radiation and thermal degradations. It is, therefore, not very useful data for the understanding of the reductive degradation of triazines. Similar HPLC analyses in the case of TMT, DHT, AT, and CA were carried out, and it was found that none of these compounds have undergone thermal decay during the experimental time scale. A clear dose-dependent decay was also observed in the case of TMT, and the HPLC analysis showed its complete disappearance at 10.1 kGy (**Figure 4**). From the initial disappearance of TMT, a $G(-\text{TMT})$ value of $0.20 \mu\text{mol J}^{-1}$ was calculated. Similarly, DHT showed a high degree of degradation (more than 70%) and a relatively low $G(-\text{DHT})$ value of $0.11 \mu\text{mol J}^{-1}$ has been obtained. Examination of the product peaks showed the presence of two major products at the λ_{max} of DHT (data not shown) whose structural details could not be determined using HPLC due to the lack of standards. AT has also shown a clear dose-dependent decay and a $G(-\text{AT})$ of $0.26 \mu\text{mol J}^{-1}$ is calculated from its initial decay. Its decay was nearly complete after about 8 kGy (**Figure 4**). CA has not shown a significant decay of its initial concentration in the initial stage as can be seen from **Figure 4**. However, at a

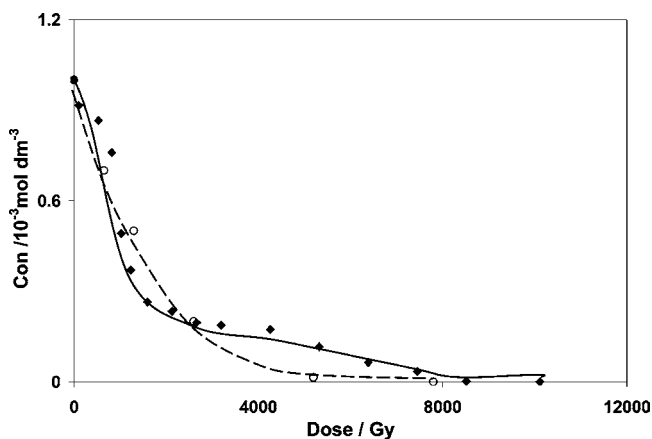


Figure 5. Comparison of the degradation profile obtained from the reaction of e^-_{aq} (◆) and of OH radicals (taken from ref 21) (○) with TMT.

higher time of irradiation (i.e., more than 6 kGy), the concentration of CA has shown a considerable decrease similar to other triazines.

These degradation studies have been carried out to understand the efficiency of degradation of triazines under reductive environment, as most of the known studies are under oxidative conditions, mostly using OH radicals (12–22). The results obtained in this study demonstrate that the degradation profile of the parent triazines is well comparable to that induced by OH radicals (22). A comparison between the decay of TMT induced by OH radicals from the previous report (22) and by e^-_{aq} in the present study is shown in **Figure 5**. In the reaction of TMT with OH radicals, a complete degradation was obtained after 5 kGy (22). In both cases, TMT was irradiated under the same conditions. Interestingly, the yield of e^-_{aq} is only half the yield of OH radicals under this condition according to reaction 4. Even then, a nearly similar decay of TMT is observed using both of the reactions. This comparison clearly establishes the potential role of e^-_{aq} in the degradation of triazines similar to OH radicals.

It must, however, be noted that a complete degradation of the aromatic ring may not be taking place under the present experimental conditions. It can be only understood that there is a transformation of the triazines to some of their products on reaction with e^-_{aq} . As indicated in the Pulse Radiolysis section, the immediate intermediate after the attack of e^-_{aq} with all of the selected triazines is the electron adduct followed by the formation of their protonated form. As the transient spectra in these cases were found to undergo a second-order decay, any stable products would be the result of a disproportionation reaction of these protonated electron adducts.



Although the second-order rate constants for the reaction of e^-_{aq} with T, TMT, AT, and CA are diffusion-controlled and well comparable, the degradation of CA is relatively slower at the initial stage (i.e., lower doses) as compared to the other three. On the other hand, DHT, although it has a rate constant lower by an order of magnitude than the other three, has a relatively faster decay as compared to CA in the initial stage. It is probable that part of the unstable intermediates in the case of CA may recombine and this may lead to the reformation of CA. At higher doses, as the radical concentration will be much higher as compared to low doses of irradiation, this may evoke an effective bimolecular interaction. This could be the reason that the degradation of CA is slow at a low dose of irradiation.

However, a fully convincing explanation for this behavior could not be given at this stage as it requires further studies on the exact nature of the intermediate (unstable) products.

In conclusion, the kinetic and mechanistic details of the diffusion-controlled reaction of e^-_{aq} with triazines are presented. Such reduction reactions of triazine derivatives are reported for the first time. The comparison of the degradation profile of TMT induced by e^-_{aq} and OH radicals highlights the potential application of the reaction of e^-_{aq} in the degradation of triazines. However, it must be noted that the contaminated water normally contains oxygen and nitrate, which can effectively react with e^-_{aq} , and this may evoke a competition for e^-_{aq} . In this context, additional steps may be required to minimize such competition reactions. Therefore, more work is needed to fully explore the applicability of this reaction in natural conditions. On the other hand, radical-mediated reductive degradation of these compounds provides an additional detoxification channel, which must be intensively explored.

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