Reaction of Sulphate Radical Anion ($SO_4^{\bullet-}$) with Cyanuric Acid: A Potential Reaction for Its Degradation?

P. Manoj, R. Varghese, V. M. Manoj, and C. T. Aravindakumar*
School of Chemical Sciences, Mahatma Gandhi University, Kottayam. 686 560, India

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A novel reaction between sulfate radical anion ($SO_4^{\bullet-}$) and cyanuric acid (CA), a non-degradable end product of the oxidative degradation of the triazine based herbicide, atrazine, is presented using laser flash photolysis and steady state radiolysis techniques at pH 5. A second order rate constant of 1.9×10^7 dm^3 mol^{-1} s^{-1} has been determined and the transient intermediate ($\lambda_{max} = 330$ nm) is assigned to a radical cation of CA ($CA^{\bullet+}$). The degradation profile indicated that about 76% of CA have been decomposed after an absorbed γ-radiation dose of 18 kGy. It is therefore proposed that the reaction of $SO_4^{\bullet-}$ could be utilised for the degradation of CA in aqueous medium which is normally stable to any Advanced Oxidation Processes.

A rapid, safe and inexpensive method for the removal of triazine derivatives which have extensively been used as herbicides, from ground and surface water forms an important part of water purification research based on Advanced Oxidation Processes (AOPs) that make use of the powerful oxidant, hydroxyl radical (${}^{\bullet}OH$).[1] Atrazine is one among the important components of triazine based herbicides and, therefore, many studies using AOPs were reported with this compound.[2–7] The product analysis of all these studies reveal that cyanuric acid (CA) is the major end product and it remains stable even after prolonged treatment with ${}^{\bullet}OH$.[5–8] In the present communication we report a novel reaction which involve the degradation of CA by sulphate radical anion ($SO_4^{\bullet-}$) produced by both photolytic and radiolytic techniques. To our knowledge this is the first report on the radical mediated degradation of CA and it is expected that this reaction could be explored for the complete degradation of CA in aqueous medium.

Laser flash photolysis experiments were carried out using a SP-Quanta ray GCR-2(10) Nd-YAG laser (266 nm with a pulse width of 5 ns and energy 50 mJ/pulse) connected with an optical absorption detection set-up.[9] $K_2S_2O_8$ can be selectively excited in presence of CA at 266 nm to get $SO_4^{\bullet-}$ as CA has practically no absorption at this wavelength. Photolytic and radiolytic (using a ^{60}Co-gamma source) production of $SO_4^{\bullet-}$ (from $S_2O_8^{2-}$) and ${}^{\bullet}OH$ in aqueous medium are shown in reactions 1-5.

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\bullet-} \tag{1}$$

$$H_2O \rightsquigarrow {}^{\bullet}OH,\ e^-_{aq},\ {}^{\bullet}H,\ H_3O^+,\ H_2O_2,\ H_2 \tag{2}$$

$$(CH_3)_3COH + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_2(CH_3)_2COH \tag{3}$$

$$e^-_{aq}/H^{\bullet} + S_2O_8^{2-} \longrightarrow SO_4^{\bullet-} + SO_4^{2-}/H^+ \tag{4}$$

$$e^-_{aq} + N_2O \longrightarrow {}^{\bullet}OH + N_2 + OH^- \tag{5}$$

A second-order rate constant of 1.9×10^7 dm^3 mol^{-1} s^{-1} was determined by monitoring the decay of absorption of $SO_4^{\bullet-}$ at 460 nm (pseudo first-order) as a function of varying concentrations of CA (Figure 1), using laser flash photolysis.

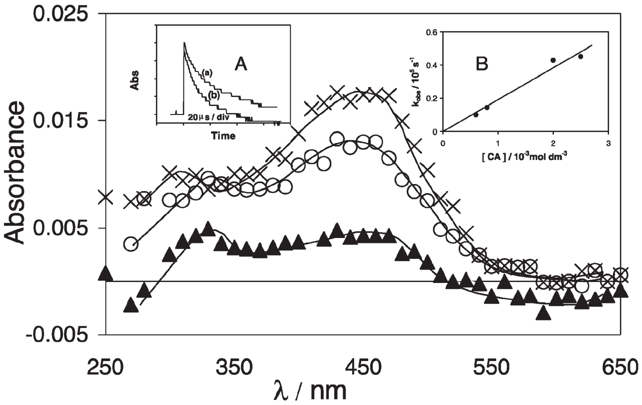


Figure 1. Transient absorption spectra obtained from the reaction of $SO_4^{\bullet-}$ with cyanuric acid at (×) 1 μs, (O) 10 μs and (▲) 40 μs after the pulse at pH 5. Inset: A. Decay traces of $SO_4^{\bullet-}$ in the absence (a) and in the presence of CA (5×10^{-4} mol dm^{-3}) (b); B. The pseudo first-order decay of $SO_4^{\bullet-}$ (k_{obs}) versus concentration of CA.

The time resolved absorption spectra have shown an evolution of a spectrum characterized by its λ_{max} around 330 nm at 10 μs after the laser flash from the initial spectrum at 1 μs (corresponds to $SO_4^{\bullet-}$ with λ_{max} at 460 nm[10]). No significant change in the spectral properties was observed when the spectra were recorded in presence of O_2. The degradation of CA after its reaction with $SO_4^{\bullet-}$ was also monitored using γ-radiolysis. An exponential decay of CA with respect to the absorbed dose was observed (Figure 2) and a pseudo first order

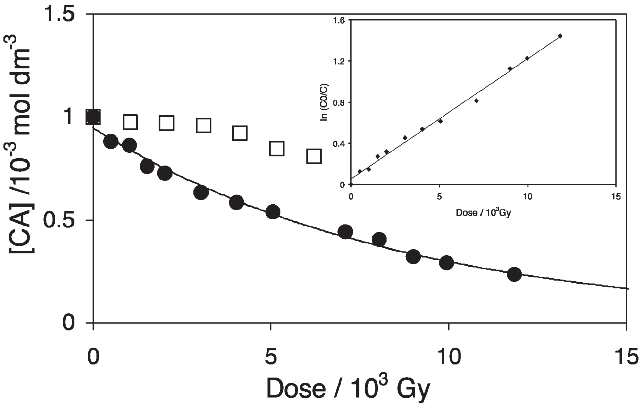
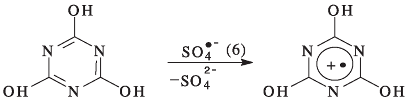


Figure 2. The degradation profile of cyanuric acid induced by $SO_4^{\bullet-}$ (●) and ${}^{\bullet}OH$ (☐) measured by HPLC after γ-radiolysis. Inset: First-order nature of the decay profile induced by $SO_4^{\bullet-}$. C_0 is the initial concentration of CA and C is that at time t. (Dose rate of the gamma source was 100 Gy/min).

rate constant was calculated as 0.011 min^{-1}. The G(-CA) value (which is the micromolar consumption of CA per joule of radiation energy), was calculated from the slope of the initial decay of CA as 0.1 μmol J^{-1}. No significant change in concentration of CA was observed on its reaction with $^{\bullet}$OH (except that at higher time of irradiation, there was a slow decrease in the concentration) under this condition (Figure 2) indicating a much lower efficiency of $^{\bullet}$OH in degrading CA.

$SO_4^{\bullet-}$ is a powerful oxidant ($E^0(SO_4^{\bullet-}/SO_4^{2-}) = 2.43$ V), similar to $^{\bullet}$OH. The $SO_4^{\bullet-}$ is proposed to undergo an electron transfer reaction with CA forming a radical cation ($CA^{\bullet+}$) in the initial step based on the earlier knowledge on its reaction with pyrimidines and substituted benzenes.[10–14] The possibility of deprotonation of $CA^{\bullet+}$ like in the case of pyrimidine derivatives,[14] may be ruled out keeping in view of its structure where there is no favorable proton for elimination (reaction 6). The spectral features and the results with O_2 (stability of the spectra in the presence of O_2) did not support the possible hydrolysis of $CA^{\bullet+}$ leading to OH-adduct as the carbon centered OH-adduct radicals of 2,4,6–trimethoxy–1,3,5–triazine (TMT) and 1,3,5–triazine (T) were reported to have different spectral characteristics[2] and the fact that generally O_2 has a high reactivity with any carbon centered aromatic neutral radicals (diffusion controlled) as well as with nitrogen centered radicals ($\sim 10^7$ dm^3 mol^{-1} s^1) forming peroxyl radicals.[15] This leads to the conclusion that the intermediate having the absorption spectra (with λ_{max} at 330 nm) possesses a radical site neither at carbon nor at nitrogen. The existence of a $SO_4^{\bullet-}$-CA adduct (precursor of $CA^{\bullet+}$) is also ruled out because such an adduct would be a carbon centered radical and it can have high reactivity towards O_2. Therefore, it is proposed that the species existing at pH 5 with λ_{max} at 330 nm is a radical cation, $CA^{\bullet+}$ (reaction 6) and its stability in the microsecond time scale is likely due to the presence of three hydroxy groups substituted in the triazine ring. The radical cations are, in general, known to react with O_2 only very slowly.[16] Relatively longer lived ($t_{1/2} \geq 1$ μs) radical cations are reported to be formed with a number of aromatic compounds in solution such as methyl substituted thymines.[14]



The decay of CA (Figure 2) is obviously initiated by a bimolecular reaction of the intermediate species, most likely the radical cation. It is not clear from the laser flash photolysis studies that this radical cation may undergo hydrolysis at a later stage (> 200 μs). On the other hand, the consumption of CA (almost 76% after 18 kGy, Figure 2) demonstrates the potential usefulness of this reaction. This study (see Figure 2) as well as from previous reports[5,7,8] has made clear that even the well known powerful oxidant, $^{\bullet}$OH, is inefficient in the degradation of CA. Undoubtedly, this difference in the efficiency of degradation is due to the difference in their mode of reactions.

In conclusion, the possibility of radical mediated degradation of CA is reported for the first time and this reaction could possibly be used for the complete degradation of CA in aqueous medium. It is also interesting to note that the high efficiency of $SO_4^{\bullet-}$ over $^{\bullet}$OH mediated degradation is a result of a different reaction mechanism compared to $^{\bullet}$OH. A detailed mechanistic study using a variety of substituted triazines are currently in progress.

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