

Role of Solvent on Formation and Stability of the Radical and Radical Cations of Organic Compounds having $(>N)_2C=S$ Moiety: A Mini Review

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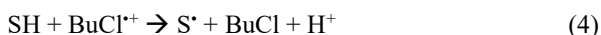
GENERAL BACKGROUND

Non-aqueous or organic solvents such as n-butyl chloride ($CH_3-CH_2-CH_2-CH_2-Cl$) (BuCl), etc., are usually employed in several studies to generate free ions and radicals of associated solutes. In this the radiolytically generated reactive species (ions and radicals of organic solvents) involve actively in electron transfer (ET) processes [1-5]. The transient species produced during radiolysis of neat BuCl are: the parent radical cations ($BuCl^{+\bullet}$), butene radical cations ($Bu^{+\bullet}$) and butyl radicals ($Bu^\bullet$) [2]. The $BuCl^{+\bullet}$ react through following reactions to produce radical cations and radicals of solute molecules (SH):



(SH contains $(>N)_2C=S$ moiety)

$SH^{+\bullet}$ undergoes deprotonation leading to $S^\bullet$,



$Bu^{+\bullet}$ has very low gas phase ionization potential (~ 1 eV) with respect to $BuCl^{+\bullet}$ (gas phase $IP_{(BuCl)}=10.7$ eV), hence not considered [1,2,6] for ET reactions under the study. Furthermore, the radicals such as $Bu^\bullet$ reactions are well differentiated from radical cations upon O_2 addition into the systems, where the $Bu^\bullet$ reacts readily with O_2 forming peroxides [7].

On the other hand, aqueous solution continues for transient chemistry studies, in which different methods such as thermal, photolysis, radiolysis and sonolysis are employed for transients' generations. The use of radiolysis (with γ -ray and e^- beam irradiation) or ultra sound permits solute transient generation indirectly via the reactions of primary solvent derived redox radicals/ions with solute molecules. Moreover, in all cases the formation of solute radical cations undergoes rapid deprotonation limiting other associate chemical investigations. Hence for such studies either organic solvents (as discussed above) or in gaseous and frozen matrices are beneficial. Extensive studies on transient

acidity (pK_a) and their chemical reactivity based on kinetic parameters such as redox potentials, reaction rate constants, etc. are generally unattainable because of the use of different environment. In this context the use of aqueous acid ($HClO_4$ or H_2SO_4) has proved to be a useful media for radiation induced generation and study of protonated transient species conveniently. [8,9].

In this review our aim is to bring together the three solvent systems: organic solvent (BuCl), normal aqueous solutions (pH 0-14) and highly acidic media (pH<0) for radiation chemical studies on transient species (radical cations and radicals) wherein thiourea (TU) is used as a model compound, which contains $(>N)_2C=S$ moiety.

DISCUSSION

The pulse radiolysis experimental set up for radiation chemical study available in the institute has been reported previously [10] wherein 7 MeV electron beam of different pulse durations (for example 200 ns; dose rate 40 Gy/pulse, determined as described elsewhere [11]) was used for sample irradiation. The dose per pulse in organic medium was calculated considering density of medium (density of $BuCl=0.886$ kg L^{-1}) [12] as explained before [13] and found 35 Gy/pulse in BuCl for 40 Gy/pulse in aqueous systems. Nevertheless, in aqueous medium, the primary species generated because of the interaction of ionizing radiation (e^- -beam) in picosecond time and diffused homogeneously throughout the medium within 0.1 μs time are: e_{aq}^- , $\bullet OH$, $H^\bullet$, H_2 , H_2O_2 , H_3O^+ . [13] Amongst these, e_{aq}^- and $H^\bullet$ are reducing and $\bullet OH$ is oxidizing species. The molecular species (H_2 and H_2O_2) are less reactive as compared to

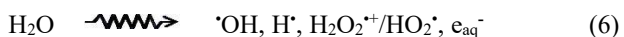
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radical species. At pH ≥ 10 , in N_2O purged systems, the primary species viz. e_{aq}^- , $H^\bullet$ ($H + H_2O \rightleftharpoons e_{aq}^- + H_3O^+$ $pK_a = 9.6$ [13]) and $\bullet OH$ remain as total $\bullet OH$ through $N_2O + e_{aq}^- \rightarrow N_2 + OH^- + \bullet OH$. Furthermore, in presence of O_2 , $H^\bullet$ and e_{aq}^- produce less reactive $HO_2^\bullet$ through ($O_2 + H^\bullet \rightarrow HO_2^\bullet$) and $O_2^\bullet$ [14] ($O_2 + e_{aq}^- \rightarrow O_2^\bullet$), allowing $\bullet OH$ to interact with TU.

Furthermore, the generation of $SO_4^{\bullet -}$ (an oxidizing radical) during radiolysis of aqueous H_2SO_4 is well known [8,9] which possesses broad absorption band with an absorption maximum (λ_{max}) at 450 nm. The reactions taking place are:



The $H_2O_2^{\bullet +}/HO_2^\bullet$ ($pK_a = 1.2$) [14] may also act as oxidant. Under highly acidic conditions $H^\bullet$ remains the only reducing radical produced through $e_{aq}^- + H_3O^+ \longrightarrow H^\bullet$. However, in oxygenated aqueous H_2SO_4 during radiolysis ($H^\bullet + O_2 \longrightarrow$

$HO_2^\bullet$), $SO_4^{\bullet -}$ remains only as reactive oxidizing species to interact with TU, and subsequently generates TU radical cations. The concentration of $\bullet OH$ vary with acid strengths and in acid solvents these radicals ($SO_4^{\bullet -}$ and $\bullet OH$) mostly represented as total oxidising radicals [9].

Figure 1 spectrum 'a' represents the transient absorption spectrum obtained in electron pulse irradiated Ar-purged 0.5 mM TU solutions in BuCl, which exhibits a λ_{max} around 300 nm. The absorbance at 300 nm increases with time leading to the formation of TU radical with slow growth. This is formed probably due to ET reaction between $BuCl^{+}$ and TU via deprotonation (reaction 3), as the growth of intermediate starts from minimal absorbance value (first component the TU radical cation) immediately after the electron pulse to high absorbance (2nd component the TU radical) at 25 μs after the electron pulse. This is concluded based on the similar studies with TU but in presence of ethanol (a radical cation scavenger) where identical yields of TU radical have been observed. Under the study because of the limitation of experimental facility the radical cation of solvent was not observed.

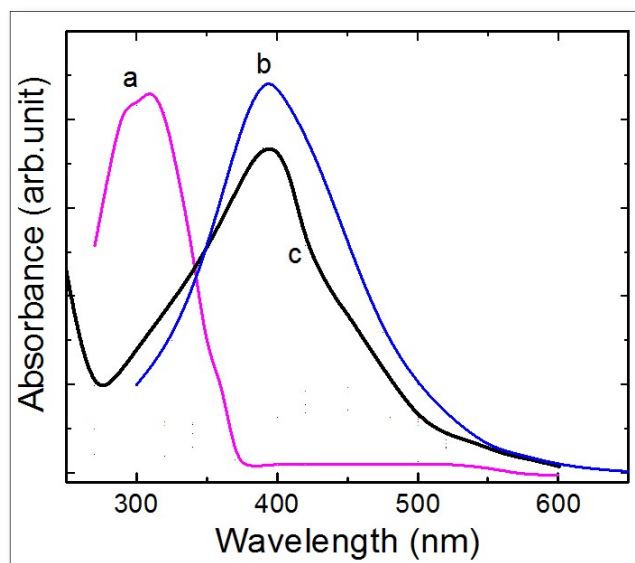


Figure 1. Transient absorption spectra obtained a: in n-butyl chloride; b: in aqueous solutions at pH 6.8 and c: in H_2SO_4 medium at $pH/H_0 = -4.1$ containing TU ('b' adopted from ref 14 and 'c' adopted [15]).

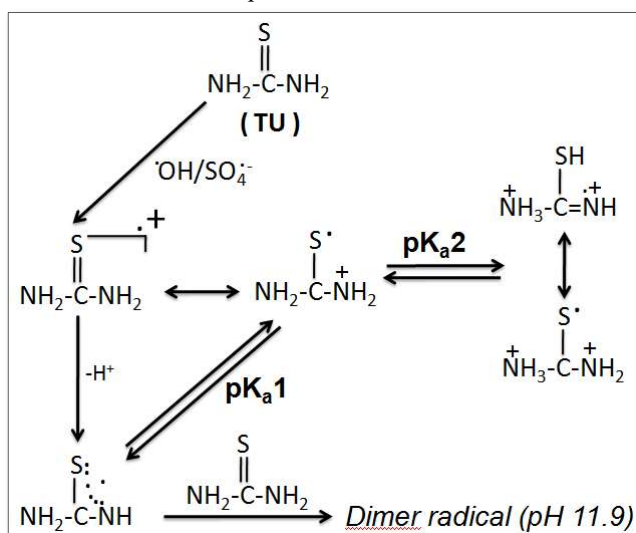
Similarly, the pulse radiolysis of N_2O -saturated aqueous solution of TU at pH 6.8 yielded an intermediate, which exhibits a strong absorption with λ_{max} at 400 nm (spectrum 'b' in **Figure 1**). This species as discussed above undergoes deprotonation rapidly resulting TU radical. Moreover, this radical reacts with parent TU to yield dimer type species only in basic media (pH 11.9), which exhibits absorption at 510 nm [15].

In the same way, the transient absorption spectra reported in electron pulse irradiated aerated 1 mM TU solutions at

$pH/H_0 = -4.1$ [16] is compared in **Figure 1**, in which the spectrum 'c' exhibits λ_{max} at 400 nm. This curve is quite similar to the peak obtained at pH 6.8 (spectrum 'b'). The rate constant for $SO_4^{\bullet -}$ reaction with TU has been reported to be $2.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is rather slow as compared to $\bullet OH$ radical reactions ($1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) [15]. The intermediate has been designated as TU radical cation, as its decay follows first order kinetics. It is noteworthy to note that at $pH/H_0 < -5.0$ HSO_4 , a protonated form of $SO_4^{\bullet -}$ takes part in oxidation reactions with low reactivity. Hence, > -5.0 H_0 is found to be better for $SO_4^{\bullet -}$ reactions study.

It is reported that the yield and the formation kinetics of the TU transients with respect to absorption at 400 nm depend on pH/H_0 of the experimental solutions. The variation of absorbance value with pH/H_0 reveals the existence of acid – base conjugate forms of the TU transients and the pK_a values -0.32 and -4.33 has been reported elsewhere [16]. TU possesses better stability at high acid strength within the present experimental conditions. The intermediate species

responsible for 400 nm absorption decays by following first order kinetics. The half-life time of TU radical cation increases with acid strength significantly [16]. In high strength acid medium 510 nm light absorbing intermediate species has not been generated revealing that the reaction for the generation of dimer radical type species are pH selective (**Scheme 1**).



Scheme I. Schematic formation of radical and radical cations of TU along with acid-base conjugate forms.

CONCLUSION

In this presentation we have demonstrated the effect of experimental media on the radiolytic generation and stability of radical and radical cations of TU. The difference in absorption peak/spectra in organic and aqueous media is due to the difference in polarity of the solvent/solutions suggesting a strong interaction of the radical cation/radical with the solvent media. Moreover, a series of TU derivatives have been studied pulse radiolytically in above mentioned three media [17-21] in which kinetics and stability of their radical and radical cations differs significantly.

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