Radical cations and radicals of thiourea and its derivatives in *n*-butyl chloride solutions: A pulse radiolysis study

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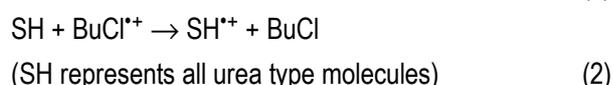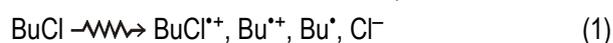
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The formation of radical cations and radicals of thiourea and its derivatives such as thiosemicarbazide, diethylthiourea, phenylthiourea in *n*-butyl chloride solutions using pulse radiolysis technique is reported. Solute radical cations generated initially produce respective radicals on deprotonation. The yields of radicals of these compounds are reduced partly upon addition of ethanol (C_2H_5OH), a radical cation scavenger, which reveals the generation of solute radical is two channel processes: one through direct reaction during the electron pulse irradiation and other through deprotonation of radical cations. The thioureayl radicals and their respective radical cations are characterized with optical absorption measurements and their kinetic analyses. The spectral absorption maximum of radical cations and radicals of thiourea and its derivatives is red shifted when we move from thiourea to phenylthiourea. Results obtained on urea exhibits no defined absorption peaks for radical cations in contrast to 320 nm peak in selenourea under identical experimental conditions. Moreover, the uniqueness of S in optical spectral characteristics of radical cations and radicals of thiourea and its derivatives is observed as compared to O and Se in urea and selenourea respectively. Quantum chemical calculations support the mechanistic interpretation and endow with the charge distributions in ureayl radical and radical cations along with their respective parent molecules. The formation of radical cations and radicals of these organic compounds using pulse radiolysis is revisited in *n*-butyl chloride in which the charge transfer reaction is more prominent.

Keywords: Thiourea, *n*-butyl chloride, radical cation, radical, urea, selenourea.

Introduction

Organic/non-aqueous solvents are normally used in several studies to generate free ions of associated solutes, wherein the radiolytically generated solvent reactive species (free ions and radicals) are actively involved in electron transfer (ET) reactions[1–6]. The generated free ions of solvent on ET reaction produce radical cations and radicals of available solutes. For example the reactive transient species produced during radiolysis of neat *n*-butyl chloride (BuCl), an organic solvent are: the parent radical cations ($BuCl^{•+}$), butene radical cations ($Bu^{•+}$) and butyl radicals ($Bu^{•}$)[2], in which the parent radical cations undergo following reactions to produce radical cations and radicals of solute molecules (thiourea/urea/selenourea molecules in this case):

$$BuCl \rightsquigarrow BuCl^{•+}, Bu^{•+}, Bu^{•}, Cl^{-} \qquad (1)$$

$$SH + BuCl^{•+} \rightarrow SH^{•+} + BuCl$$

(SH represents all urea type molecules) \qquad (2)

$$SH^{•+} \rightarrow S^{•} + H^{+} \text{ (Deprotonation reaction)} \qquad (3)$$

$$SH + BuCl^{•+} \rightarrow S^{•} + BuCl + H^{+} \qquad (4)$$

Having low gas phase ionization potential, $Bu^{•+}$ (~1 eV) is an order of magnitude less reactive as compared to $BuCl^{•+}$ (gas phase $IP_{(BuCl)}$ = 10.7 eV), therefore, $Bu^{•+}$ is not considered[1,2,7] for kinetic analyses under the study. Furthermore, radical reactions have been differentiated simply from radical cations upon addition of O_2 into the systems since the radicals such as $Bu^{•}$ are highly sensitive to O_2 forming peroxide ($Bu^{•} + O_2 \rightarrow BuO_2$)[8,9].

In addition, several reports available in the literature on pulse radiolysis studies of thiourea[10] and its derivatives[11,12] in aqueous medium emphasize the formation of intra-molecular three-electron bonded transient species through H-abstraction reaction mechanism. Their optical absorption in the visible region has been explained previously due to the delocalization of free electron in three-electron bond over

S-C-N moiety[10–12]. In highly acidic media the protonated and neutral species of these radicals have also been documented[13–15].

More recently, we have reported the effect of phenyl moiety on the formation of radical and radical cations of thioamides (-C(S)NH$_2$) in BuCl solutions[16]. As a continuation, in this work we report the formation of radical cations and radicals of organic compounds having common >N-CS-N< moiety such as thiourea (TU), thiosemicarbazide (TSC), diethylthiourea (DTU) and phenylthiourea (PTU) in BuCl solvent. For easy understanding the basic structures of all compounds used in the study are shown in Scheme 1.
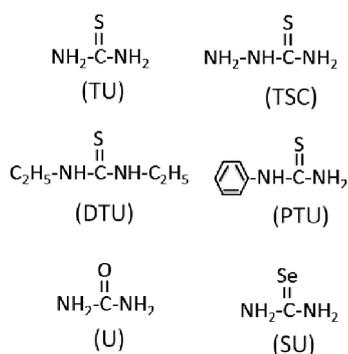
Scheme 1. Structures of all compounds.

Furthermore, in aqueous systems the solute radical cations formed undergo fast deprotonation limiting the other associated investigations on these transients. Hence for such studies organic solvent such as BuCl is beneficial.

In this solvent, BuCl$^{\bullet+}$ oxidises the available solute (TU or TSC or DTU or PTU) through ET mechanism forming respective radical cations and/or radicals. The radical cations generated in this process are normally short-lived species. The results generated on urea (U) and selenourea (SU) at identical experimental conditions are also included to explore the differences exist if any between S with O and Se substituent in >N-CS-N< moiety. Reaction pathways and the results obtained are aimed to report in this communication, which are lacking currently in the literature.

Experimental and materials

Thiourea (> 99% pure), thiosemicarbazide (> 99% pure) from E. Merck, diethylthiourea (>99% pure) from Aldrich,

phenylthiourea (> 99% pure) from Koch-Light laboratory, England, urea (> 99% pure) and selenourea (> 99% pure) from E. Merck, *n*-butyl chloride (Spectrograde) and ethanol (> 99.9% pure) from Fluka were used as received. Pulse radiolysis study was carried out with 7 MeV electron pulses of 200 ns durations from a linear electron accelerator available at BARC and the details of experimental set up has been reported earlier[17]. Aerated 0.01 *M* potassium thiocyanate solution was used for determining the absorbed dose using Gε value 2.59×10^{-4} m^2 J^{-1} at 475 nm[18]. The dose per pulse in water measured using 10 mm×10 mm square quartz cuvette was 40 Gy for 200 ns pulses. The dose per pulse in BuCl was calculated considering density of medium (density of *n*-butyl chloride is 0.886 kg L^{-1})[19] as discussed elsewhere[20] and found 35 Gy per pulse in BuCl for 40 Gy per pulse dose in water. High purity grades argon (Six Sigma Gases India Pvt. Ltd.) and oxygen (Inox Air Products Ltd.) gases were used when required for purging the experimental solutions.

Density functional theory has been utilized to calculate the ground electronic state geometry of U, SU, TU, TSC, DTU and PTU in the gas phase to understand the possible reaction site for attacking electrophilic reactants such as BuCl$^{\bullet+}$ in charge-transfer processes. The geometries of these compounds and their transient species have been optimized at B3LYP theory with the basis sets 6-311++G(2d,2p), and single point energy was calculated for the structures at MP2 level of theory with the same basis sets using the GAMESS program[21].

Results and discussion

The results obtained in pulse radiolysis studies with thiourea and its derivatives along with urea and selenourea in BuCl are discussed in the following sections.

Thiourea:

Fig. 1A represents the time resolved transient spectra obtained in electron pulse irradiation of Ar-purged 0.5 mM TU solutions in BuCl, which exhibits absorption maximum (λ_{max}) around 300 nm. It is noticed from Fig. 1A that with time the absorbance at 300 nm increases leading to the formation of secondary reaction intermediate, which also con-

tribute absorption at this wavelength. The inset time profile recorded at 310 nm shows the growth of the intermediate species of TU formed probably due to ET reaction between BuCl$^{\bullet+}$ and TU, as the growth of intermediate starts immediate after the electron pulse (initially within 1 μs ΔA = < 0.003 at 300 nm (first component), which apparently increased to 0.011 at 21 μs (second component)), hence the initial species generated might be radical cations of TU. The later time transient is probably a radical species of TU. The formation rate at 310 nm was found to be 8.2×10^4 s^{-1}. Concentrations effect (as solubility of TU in BuCl was low hence the upper TU concentration used was 0.5 mM) did not show formation of any dimer type species (see Fig. 1B) except radical cation scavenging proficiency of TU that increase the absorbance around 300 nm region. The bimolecular reaction rate constant was determined from the formation of transient intermediates absorption at 300 nm adopting the pseudo-first order reaction rate determination concept and found to be 3×10^9 mol^{-1} dm^3 s^{-1}.

The transient spectra obtained in electron pulse irradiation of oxygenated 0.5 mM TU in BuCl were quite similar to those observed in Ar-purged systems under identical conditions; hence these spectra are not shown separately. This observation indicates that the transient species generated were not oxygen sensitive, and were also not generated through radicals reactions because Bu$^{\bullet}$ radicals are highly sensitive to O$_2$[14,15]. Moreover, in aqueous systems, oxygen

has been reported inactive to three electron bonded intermediate species[7–9].

It will be useful to compare the pulse radiolytic results obtained with neat BuCl solvent under identical experimental conditions. The time resolved transient spectra recorded in electron pulse irradiated Ar-purged BuCl are shown in Fig. 1C, which exhibit only absorbance beyond 300 nm with no distinct peak. Hence, the absorbance observed below 300 nm in TU systems is probably due to the interference of solvent radiolytic products. The time profiles obtained at 250, 300 and 500 nm (Fig. 1C insets) indicate different kinetic patterns of different species at lower time scale. Moreover, the substantial change in spectra and kinetic behavior in TU systems reveal that the formation of TU intermediates is probably radical cations and radicals.

Thiosemicarbazide:

The time resolved spectra of transient species produced during the electron pulse irradiation of Ar-purged 1 mM TSC solutions in BuCl are shown in Fig. 2A, which exhibits an absorption band with λ$_{max}$ at 300 nm along with a weak absorption peak around 380 nm. With time the absorbance at 380 nm was decreased with an increase in absorbance at 300 nm. The time profiles at 300, 320 and 380 nm shown as inset of Fig. 2A exhibit different kinetics. For example the time profiles obtained at 300 nm (first order formation rate 1.1×10^5 s^{-1}) and 320 nm (first order formation rate 5.5×10^4
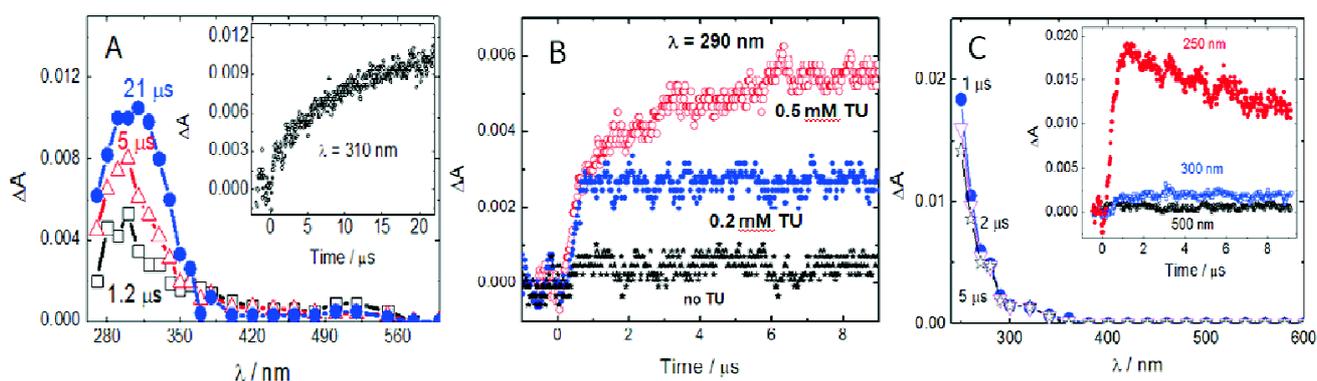

Fig. 1. The time resolved transient spectra obtained in electron pulse irradiated Ar-purged 0.5 mM TU in *n*-butyl chloride solutions (A), insets: time profiles obtained at 310; (B) timeprofiles obtained at 290 nm with and without different concentrations of TU and (C) time resolved transient spectra obtained in electron pulse irradiated Ar-purged *n*-butyl chloride. Insets: Time profiles obtained at 250, 300 and 500 nm. Dose per pulse = 35 Gy in *n*-butyl chloride.
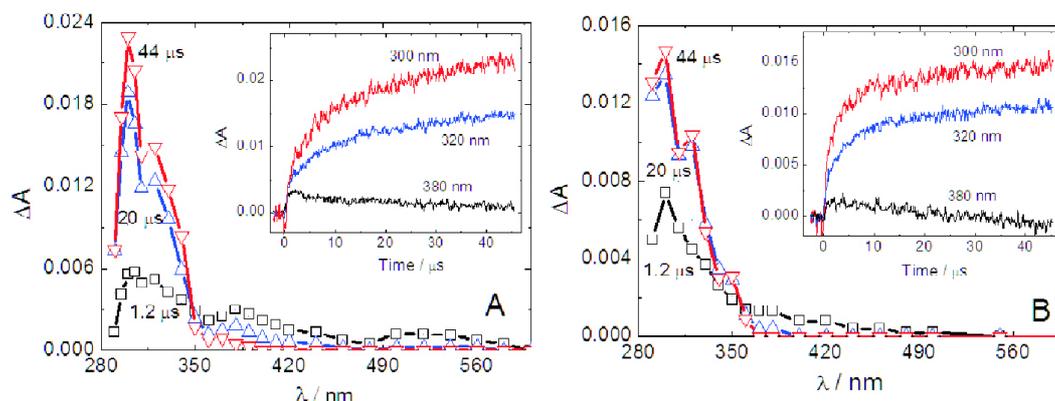
Fig. 2. The time resolved transient spectra obtained in electron pulse irradiated Ar-purged 1 mM TSC in *n*-butyl chloride solution in absence (A) and in presence (B) of 0.1 *M* ethanol. Insets: time profiles obtained at 300, 320 and 380 nm. Dose per pulse = 35 Gy in *n*-butyl chloride.

s^{-1}) were growth type with different kinetics whereas the time profile obtained at 380 nm was decay in nature. The species decayed at 380 nm following first order kinetics with k_1 value 1×10^5 s^{-1}. However, in presence of 0.1 *M* ethanol (an ionic radical scavenger) otherwise under identical conditions, the weak band at 380 nm reduced significantly, which concludes that the absorption at 380 nm is possibly caused by the formation of TSC radical cations. The absorption intensity at 300 nm was reduced from 0.022 to 0.015 at 40 µs upon 0.1 *M* ethanol addition into the system that probably refers to TSC radical formation. The inset time profiles obtained at 300 (first order formation 3.5×10^5 s^{-1}), 320 and 380 nm in ethanol containing systems are shown in Fig. 2B. The slow formation kinetics at 320 nm in absence of ethanol became faster in presence of ethanol showing the significant radical cation scavenging properties of ethanol. By this process the final yield was reduced in ethanol containing systems indicating the contribution of ionic component to TSC radical formation through slow kinetics (deprotonation reaction). In the slow growth time profile at 300 nm, the direct TSC radical formation was remained hidden in system containing no ethanol, which was only visible upon ethanol addition. Similar to TU systems, the transient spectrum and kinetics of TSC intermediates were not found oxygen sensitive.

Diethylthiourea:

Similarly, Fig. 3 depicts the time resolved transient spectra obtained in electron pulse irradiated Ar-purged 2 mM DTU solutions in BuCl both in absence and presence of 0.1 *M*

ethanol. The spectra obtained in absence of ethanol exhibit broad band peaking around 420 nm with higher absorbance value than that observed in the system containing ethanol. In DTU systems it is clear that two different absorbing intermediate species generated in BuCl, which are differentiated significantly upon ethanol addition. During the study the transient absorbance at 420 nm at 1.3 µs after the electron pulse was decreased from 0.02 to 0.009 (~45%). It was understood that the initially generated radical cations produced radical after their subsequent deprotonation. The inset time
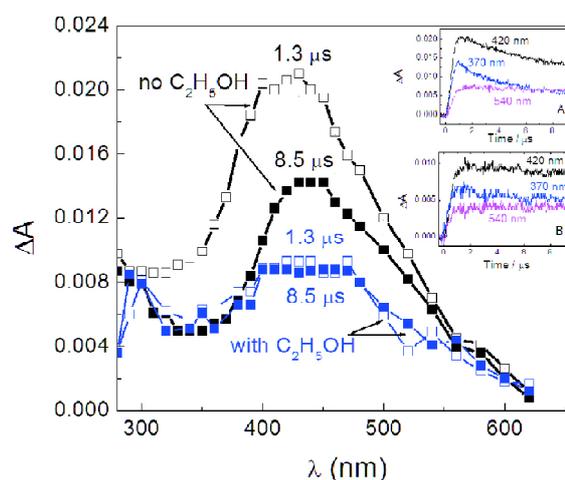

Fig. 3. The time resolved transient spectra obtained in electron pulse irradiated Ar-purged 2 mM DTU in *n*-butyl chloride solution in absence (black) and in presence (blue) of 0.1 *M* ethanol. Insets: Time profiles at 300, 370, 420 and 540 nm. Dose per pulse = 35 Gy in *n*-butyl chloride.

profiles obtained at 370 and 420 nm in both these systems demonstrate the considerable effect of a radical cation scavenger on the formation of intermediate species of DTU. In ethanol containing systems the radical yields remain almost steady. This phenomenon is clearly visible in the time profiles shown as inset B in Fig. 3. The time profiles at 370 and 420 nm (Fig. 3, inset A) exhibit significant absorption due to radical cations formation whereas at 540 nm both radical and radical cations overlap in which radical absorption dominates and the absorbance value remains steady. The first order decay of the species in absence of ethanol was found to be 3.7×10^4 s^{-1} at 420 nm revealing that the radical cation decay led to DTU radical formation through deprotonation (reaction 3). Similar to TU and TSC systems, the concentra-

species. Upon ethanol addition to the system under identical conditions Fig. 4B was generated, which shows a drastic difference in spectral nature especially in 400 nm wavelength region. Significant change in decay kinetics reveals that the existence of ionic species (radical cations) absorption in this spectral region. To explore further, two spectra obtained at 1.2 µs after the electron pulse in two different systems are compared in Fig. 5 along with their differences (spectrum denoted as 'difference' = spectrum obtained in absence of ethanol – spectrum obtained in presence of ethanol), which represents the species generated during/(immediate after) the electron pulse. These species might be produced through reaction (4) and were not sensitive to ethanol referred herein as PTU radical. The reaction nature is quite similar to TSC
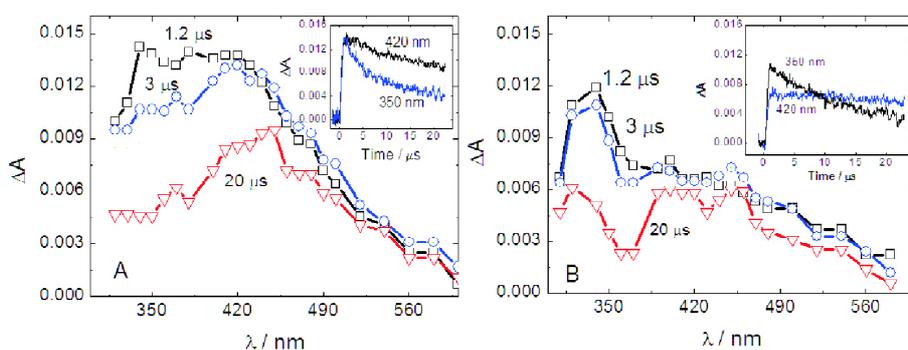

Fig. 4. The time resolved transient spectra obtained in electron pulse irradiated Ar-purged 0.5 mM PTU in *n*-butyl chloride solutions in absence (A) and in presence (B) of 0.1 *M* ethanol. Insets: Time profiles at 350 and 420 nm. Dose per pulse = 35 Gy in *n*-butyl chloride.

tion effect experiments did not show the formation of any dimer type species in DTU systems in BuCl under the study.

Phenylthiourea:

The time resolved transient spectra obtained in electron pulse irradiated Ar-purged 0.5 mM PTU in BuCl solutions in absence and in presence of 0.1 *M* ethanol are shown in Fig. 4(A) and (B). Fig. 4A exhibits two bands spectra with absorption maxima around 420 and 350 nm and the absorbance values at corresponding peaks were found decreasing with time. Moreover, the spectrum obtained at 20 µs after the electron pulse depicts one broad absorption band with maximum around 450 nm. Insets time profiles at 350 and 420 nm show different kinetics revealing the formation of dissimilar
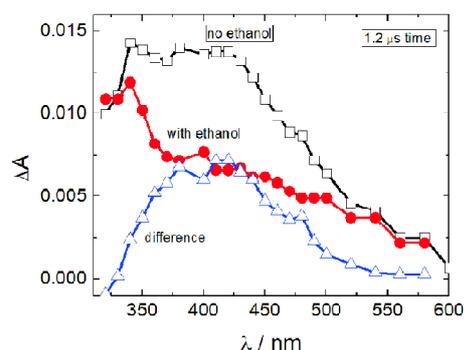

Fig. 5. The spectral difference along with two different spectra obtained in absence and in presence of ethanol at 1.2 ms after the electron pulse irradiation of Ar-purged 1 mM PTU in *n*-butyl chloride solutions. Dose = 35 Gy per pulse in *n*-butyl chloride.
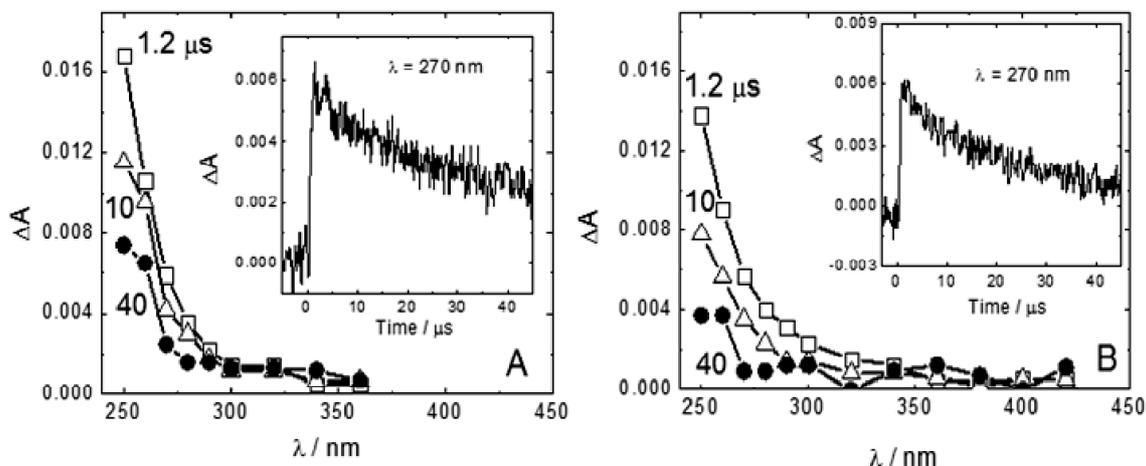
Fig. 6. Time resolved transient spectra obtained in electron pulse irradiated Ar-purged 2 mM urea in *n*-butyl chloride in absence (A) and in presence (B) of ethanol. Insets: Time profiles at 270 nm. Dose per pulse = 35 Gy in *n*-butyl chloride.

and DTU as discussed above. Furthermore on comparison of time profiles obtained in PTU systems in absence and presence of ethanol we arrived that at both wavelengths (350 and 420 nm) regions the ionic species (PTU radical cation) absorb analyzing light significantly. At 370 nm the species decayed following second order kinetics with $2k/\varepsilon l$ value 6.5×10^6 s^{-1} in PTU systems containing no ethanol. In presence of ethanol the decay of 420 nm species was found to be slow, and the 370 nm absorbing species decayed following second order kinetics with $2k/\varepsilon l$ value 1.2×10^7 s^{-1}.

It will be interesting to compare at this juncture the experimental results obtained on urea and selenourea in BuCl under similar conditions.

Urea:

In *n*-butyl chloride system, the transient species generated during the electron pulse irradiation of Ar-purged 2 mM U solutions in absence and presence of 0.1 *M* ethanol possesses spectra (see Fig. 6A and B) with optical absorption beyond 300 nm but with no distinct peak. Decay time profiles obtained at 270 nm in U containing BuCl systems both in absence and in presence of 0.1 *M* ethanol shown in Fig. 6 A and B are quite similar (decay followed first order kinetics with k_1 value 1×10^5 s^{-1}). Furthermore, in both the systems the highest absorbance at 250 nm differed marginally. With all the acquired data it is difficult to interpret the nature of transients produced in U systems under the study as solvent radiolytic products interfere in this wavelength region.

Selenourea:

Similarly, the transient spectrum (Fig. 7) obtained at 1.2 µs after the electron pulse irradiation of Ar-purged 0.2 mM SU (a 'Se' homologue of U or TU) solutions in BuCl exhibits a weak absorption band with λ_{max} at 320 nm along with continuous increase in absorbance beyond 300 nm. The growth rate at 320 nm was found to be 1.4×10^5 s^{-1}. This weak absorption does not explain any conclusive fact. Moreover, in presence of 0.1 *M* ethanol otherwise in the same system, the band at 320 nm vanishes completely, indicating the species at 320 nm was due to SU radical cation formation. The
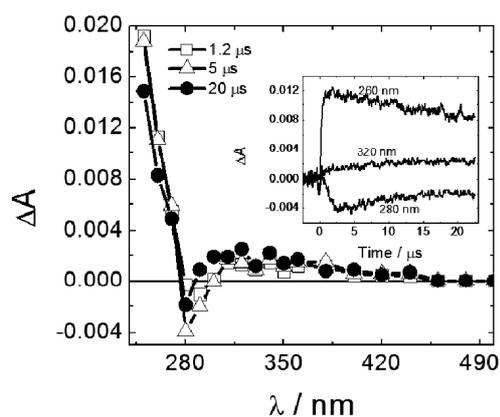

Fig. 7. Time resolved transient spectra obtained during electron pulse irradiated Ar-purged 0.2 mM SU in *n*-butyl chloride. Insets: Time profiles at 260, 280 and 320 nm. Dose per pulse = 35 Gy in *n*-butyl chloride.

bleaching at 280 nm as shown in Fig. 7 was observed due to the absorption of parent SU molecule. Because of very low solubility of SU in BuCl we could not generate additional data with high SU concentrations.

On careful analysis, it is apparent that in the case of TU, no absorbing species like radical cation was observed in the visible wavelength regions; moreover, on comparison with neat solvent systems the 320 nm time profiles in TU systems point out that the formation of TU transient species (growth type time profiles). However, it is not resolved fully even upon ethanol addition. It is important to note that 0.1 *M* ethanol in BuCl solution under deoxygenated conditions on electron beam irradiation did not lead to the formation of any such species, which possess significant absorption in 280 to 500 nm wavelength region. Moreover, in the case of TSC, diminutive information was noticed for example a small shoulder at 380 nm represents TSC radical cation as it was scavenged by ethanol; this phenomenon is more pronounced in DTU and PTU systems. In DTU, the absorption around 400 nm was suppressed drastically upon addition of ethanol which means that two different intermediates such as radical cations and radicals of DTU were generated and their optical absorptions fall in the same wavelength regions. Similarly, in PTU systems the spectral differences for radical cations and radical species were noticed. The overall results elucidate the formation of stable radical cations and radicals, which depend mainly on the structural changes in thiourea moiety. Concurrently, in DTU systems due to availability of ten H atoms in two ethyl ($-C_2H_5$) groups the stabilization of radical cations was superior hence apparent observation of radical and radical cations were noticed. Similarly, in PTU because of phenyl ($-C_6H_5$) ring; such stabilizing effect was also noticed. Due to less stabilizing effect with respect to structural arrangement in organic compounds such radical cations and radicals were not prominent in TSC in contrast to no effect in TU and U systems. Se has depicted some extent stabilizing holding criteria in SU, because of what a weak peak due to SU radical cation was noticed. The formation of radical cations of thiourea and its derivatives in organic medium has never been reported earlier. The proposed overall reaction mechanism for the formation of radical cations and radicals is summarized in Scheme 2.
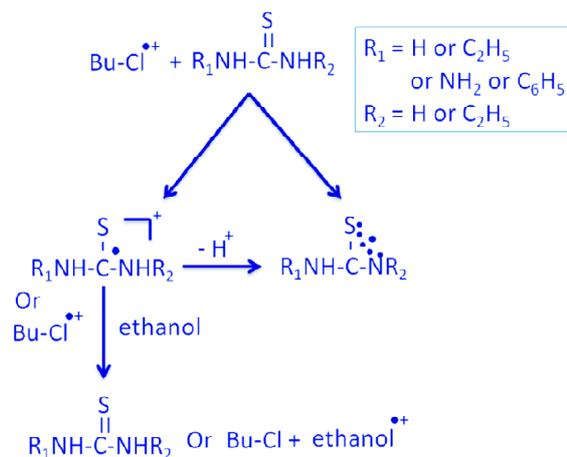
Scheme 2. Schematic presentation of solvent radical cation reactions with thioureas.

At last but not the least the formation of solute radical cations (<500 ns event) and the decay of solvent radical cations were not observed due to limitation of the experimental facility used under the study.

Computation results:

As mentioned above the GAMESS program was utilized for calculation to generate various data on parent molecules as well as intermediates species of these compounds. The stable structures were characterized as minima by vibrational analysis. Their ground state optimized structures with electronic charges (Mulliken charge) (shown in Table 1) support the proposed reaction patterns. For instance, the BuCl$^{•+}$ adduct/charge transfer reaction is possible at higher electron density in -C(X)-N- (X = O or S or Se) part preferably from S atom where the electronic charges were more (–0.598 in PTU and –0.447 in TSC) than Se (–0.073 in SU). Moreover O in urea possesses high –0.531 Mulliken charge exhibiting strong interaction with BuCl$^{•+}$ but due to not forming three electron bond type intermediate species or any such optical absorbing species of urea under the study; no absorption peak was observed in U systems. Partial planer arrangements of atoms, and high electron density at -C(S)-N- part, the reaction nature and stability of PTU were different. Similarly, the existing ten H atoms in two C_2H_5-groups help in stabilizing radical cations and radical species in DTU systems.

Table 1. Optimized structures with Mulliken charge of different forms of urea, thiourea, selenourea, thiosemicarbazide, diethylthiourea and phenylthiourea

Compounds	Neutral	Radical cation	Radical
TU			
TSC			
DTU			
PTU			
U			
SU			

Conclusions

In the present study we have demonstrated the effect of substituent in TU as well as elemental effects in $(NH_2)_2$-CX (where X represents O or S or Se) with respect to solute radical cations and radicals formation using pulse radiolysis technique in *n*-butyl chloride. In BuCl, the formations of solvent radical cations and TU radical cations were not clearly observed due to non-availability of sensitive monitoring system. Dimer types of species were not observed in TU and its other derivatives. Moreover, in TSC system the information regarding radical (major) and radical cation (minor) formation was observed, which were differentiated upon addition of ethanol. In DTU and PTU systems both radical cations and radicals possess significant optical absorption differences in the UV-Visible region and ethanol differentiates convincingly. Thus, the structural differences bring important information of intermediates formation in organic medium. Furthermore, U did not show any impressive information about the formation of radical cations and radicals, exhibiting elemental difference in U, SU, TU and other derivatives of TU.

Acknowledgements

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