Effect of phenyl moiety on the formation of radicals and radical cations of thioamides in *n*-butyl chloride: a pulse radiolysis study

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Abstract. The formation of radical cations and radicals of thioamides (**R**)(NH₂)CS, where R represents CH₃ in thioacetamide (TA) and C₆H₅ in thiobenzamide (TBA) in *n*-butyl chloride has been studied using pulse radiolysis technique. The radical cations of TA and TBA are observed in *n*-butyl chloride, and on their subsequent deprotonation, respective radicals are generated. In this study on thioamide solutions in *n*-butyl chloride, the transient species formed at 1.2 μs after the electron pulse exhibiting absorption maxima in 400 nm region are attributed to their radical cations. In the presence of 0.1 M ethanol (C₂H₅OH), a radical cation scavenger, the absorbance values at corresponding peaks are reduced substantially, revealing the formation of their respective radical cations. Moreover, at a later time, the generation of radical species takes place through deprotonation of radical cations and also through direct reactions during electron pulse irradiation. The mechanisms for the formation of radical cations and radicals of these two thioamides under pulse radiolysis have been revisited in butyl chloride medium wherein the charge transfer reactions are more prominent. Results of quantum chemical calculation support the mechanistic explanation and provide information on the reactivity of parent molecules, and the charge distribution on radical cations and radicals species of thioamides.

Keywords. Thioacetamide; thiobenzamide; *n*-butyl chloride; radical cation; radical; pulse radiolysis.

1. Introduction

Reports on the utility of organic/non-aqueous solvents such as *n*-butyl chloride (CH₃–CH₂–CH₂–CH₂–Cl (BuCl)) towards the generation of free ions of associated solutes during radiolysis are available in literature.^{1–3} It has been explained that the radiolytically generated reactive species such as free ions and free radicals of solvents have participated actively in electron transfer reaction (ET).^{1,2} The initially generated solvent free ion species, on ET reaction produce radical cations of associated solutes. The reactive transient species in neat *n*-butyl chloride produced during radiolysis are the parent cations (BuCl^{•+}), butene radical cations (Bu^{•+}), and butyl radicals (Bu[•]). These are produced through preliminary solvent molecule ionization due to high ionizing radiation (electron beam) interaction³ as shown in reaction 1.

Due to low gas phase ionization potential (~1 eV), Bu^{•+} is less reactive than BuCl^{•+} (gas phase IP_(n-BuCl) = 10.7 eV).⁴ Hence, Bu^{•+} is not taken into account for kinetic considerations under the study. Solvent radical cation BuCl^{•+} exhibits a broad absorption band with absorption maximum (λ_{max}) at 500 nm, which oxidises the available solute (S) in the system converting into solute radical cation through ET mechanism (reaction 2).³

The information of radical cations and radicals of thioamides in organic solvents are not available in the literature, which is the major aim to carry out this work. In this work, we report the formation of radical cations and radicals of thioacetamide (TA) and thiobenzamide (TBA) in *n*-butyl chloride solvent. The radical cations and radicals of TA and TBA generated in this process are short-lived species. Theoretical data such as charge distribution, bond length and absorption of their radicals and radical cations are generated to support the formation and stability of these intermediates.

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2. Experimental

Thioacetamide (>99% pure) from Loba Chemie Pvt. Ltd., thiobenzamide (>99% purity), *n*-butyl chloride (with >99% purity) and ethanol (spectroscopy grade) from Fluka Chemicals, were used as received. Pulse radiolysis studies were carried out using 7 MeV electron pulses of 50 and 200 ns durations from a linear electron accelerator, and the details of experimental setup have been reported before.⁵ The aerated 0.01 M KCNS solution in water was used to determine the absorbed dose using a G_e value of $2.59 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ at 475 nm.⁶ The doses per pulse in *n*-butyl chloride were calculated considering the density of the medium⁷ (density (ρ) of *n*-butyl chloride = 0.886 kg L^{-1})⁸ and found to be 18 and 35 Gy, respectively, for measured doses 20 and 40 Gy per pulse in water. Iolar grade Ar (Six Sigma Gases India Pvt. Ltd.) and O₂ gas (Inox Air Products Ltd.) were used to purge the solutions. All the quantitative values (kinetic parameters) measured under the study have an error within 10%.

3. Results and Discussion

As mentioned above on radiolysis of *n*-butyl chloride, BuCl^{•+} is generated, which interacts with the associated solutes such as TA and TBA under the study resulting in formation of different transient species, which is discussed in the following sections.

3.1 Thioacetamide

Figure 1A shows the time-resolved transient spectra obtained in electron pulse irradiated Ar-purged, 0.4 mM TA solution in *n*-butyl chloride, which exhibits one band absorption spectrum with λ_{max} at 400 nm. With time, the absorbance at peak (400 nm) was observed to be decreasing with the increase in absorbance beyond 350 nm. The inset time profile obtained at 400 nm shows the decay of the intermediate species of TA (TA radical cations) formed probably due to ET reaction between solvent radical cation (BuCl^{•+}) and TA. Formation of TA radical cations was assumed based on the growth of intermediate, which starts just after the electron pulse. Whereas the time profile obtained at 540 nm shows very slow formation up to 5 μs time. Later, this is followed by slow decay indicating two different species generated in this system. At this moment, it is difficult to ignore the contribution of TA radical absorption at 400 nm peak up to 20 μs after the electron pulse. Moreover, the time profiles obtained at 330 and 350 nm were different from those at 400 and 540 nm time profiles. At 330 nm the time profile shows slow growth kinetics with k_1 value = $5.6 \times 10^4 \text{ s}^{-1}$ whereas at 380 nm the kinetics nature was decay type with $2k/\epsilon l$ value $3 \times 10^6 \text{ s}^{-1}$. The 330 nm

Figure 1. The time-resolved transient spectra (a: 1.2; b: 3; c: 5; d: 10; e: 22 μs) obtained in electron pulse irradiated Ar-purged, 0.4 mM TA solution in *n*-butyl chloride in the absence (A) and in presence (B) of 0.1 M ethanol. Insets: time profiles obtained at 330, 350, 400 and 540 nm. Dose per pulse used was 35 Gy in *n*-butyl chloride and optical path length was 10 mm.

absorption is possibly due to decay products (probably a dimer or fragments) of TA radical species.

Similarly, Figure 1B shows the time-resolved transient spectra obtained in presence of 0.1 M ethanol with conditions identical to those as in Figure 1A. The inset time profile at 400 nm demonstrates the effects of a radical cation scavenger on the formation of intermediate transients especially in the earlier events (TA radical cation). In the presence of ethanol, the formation kinetics at 400 nm were different but with almost similar yields at 10 μs after the electron pulse (see spectra d of Figures 1A and B). The initial absorbance values were different. This observation reveals that the absorption around 400 nm was due to two different species (radical cation and radical of TA) as at λ_{max} (400 nm) the absorbance value decreased to 0.019 from 0.024 (~20% decrease curves 'a' in Figures 1A and B). Furthermore,

Figure 2. Time profiles obtained at 400 nm (A) in electron pulse irradiated Ar-purged, 0.4 mM TA and (B) at 480 nm in electron pulse irradiated Ar-purged 0.02 M TBA in *n*-butyl chloride solutions with and without 0.1 M ethanol. Dose per pulse used was 35 Gy in *n*-butyl chloride, and optical path length, 10 mm.

at 540 nm the nature of time profiles as well as kinetics did not alter significantly even in presence of 0.1 M ethanol (Figures 1A and B). The time profile recorded at 340 nm possesses high absorbance value whereas at 350 nm the decay nature changed considerably in contrast to TA systems with no ethanol under identical conditions. The influence of ethanol was studied in Ar-purged TA in *n*-BuCl solutions. Here, the solvent radical cations are deprotonated by ethanol and hence, the ionic channels in the reactions can be eliminated (Figure 2A). In the presence of ethanol, the build-up time profiles at 400 nm are changed in such a way that the early fast radical cation component disappeared. The difference between the time profiles obtained in TA systems, without and with ethanol, perhaps represents the radical cation of TA. Interestingly, the time profile derived from the difference follows first-order decay kinetics with k_1 value of $2.4 \times 10^5 \text{ s}^{-1}$. The possible reactions are:

TA radical formation takes place also through deprotonation.

Hence, the TA radical formation took place through two channels; first, by direct TA-BuCl^{•+} complex reaction intermediates during electron pulse irradiation (reaction 3) and second, through deprotonation of TA radical cations (reaction 4). The contribution through the latter process is ~20%, which was stopped upon ethanol addition into the system.

The spectra obtained in electron pulse irradiated oxygenated 0.4 mM TA in *n*-butyl chloride solutions are quite similar to those observed in Ar-purged systems under identical conditions and hence it is not presented separately. This observation also indicates that the radicals (as G_{radical} is very high in *n*-butyl chloride systems and radicals are extremely oxygen-sensitive)^{9,10} generated from solvent radiolysis is not responsible for the formation of transient species possessing absorption at 400 nm. Furthermore, in aqueous systems,^{11–13} oxygen has been reported as an inactive molecule to three-electron bonded intermediate radicals, which were generated in $\bullet\text{OH}/\text{SO}_4^{\bullet-}$ reactions with TA. At high acidic aqueous solutions, the protonated species of TA radical has also been reported earlier.

3.2 Thiobenzamide

Similarly, Figure 3 represents the time-resolved transient spectra obtained in electron pulse irradiated Ar-purged, 0.02 M TBA solutions in *n*-butyl chloride, which exhibits one broad band ($\lambda_{\text{max}} = 380 \text{ nm}$) along with a shoulder at 410 nm. The spectrum (curve 'a' in Figure 3) recorded at 1.2 μs after the electron pulse was considerably different from that at 5 μs and/or later time-resolved transient spectra. The inset time profiles obtained at 380, 440 and 480 nm (Figure 3) show

Figure 3. The time-resolved transient spectra (a: 1.2; b: 5; c: 10; d: 20 μ s) obtained in electron pulse irradiated Ar-purged 0.02 M TBA in *n*-butyl chloride solutions. Inset: time profiles obtained at 380, 440, and 480 nm. Dose per pulse used was 35 Gy in *n*-butyl chloride, and optical path length was 10 mm.

the decay of the intermediate species of TBA formed possibly due to ET reaction between $\text{BuCl}^{\bullet+}$ and TBA. The transient decay at 440 and 480 nm were quite faster and followed second-order kinetics with $2k/\epsilon l$ values 2.7×10^7 and $2.1 \times 10^7 \text{ s}^{-1}$, respectively, whereas the 380 nm absorbing species decayed following second-order kinetics with an order slower kinetics ($2k/\epsilon l$ values $3.4 \times 10^6 \text{ s}^{-1}$) revealing the formation of two different species. Furthermore, on careful analysis of 440 nm time profile, it was observed that there was a faster decay (first-order decay with k_1 value $2.8 \times 10^5 \text{ s}^{-1}$) which completed within 3 μ s after the electron pulse

(initial species). Beyond 3 μ s the secondary species decayed following second-order kinetics (discussed above). Therefore, it is assumed that the first order decay is due to deprotonation of TBA radical cation leading to the formation of TBA radical. It is difficult to ignore the contribution of later intermediate species in the faster decay kinetics of the preliminary species. Therefore, it is proposed that the 380 nm absorbing intermediate species undergoing slow decay corresponds to radical of TBA, whereas the initial fast decay completed within 3 μ s in 440–480 nm region represents radical cation of TBA. The time-resolved transient spectra exhibiting 380 nm peak at later times ($>5 \mu$ s) largely support the formation of radical cation (short-lived species), which exhibits absorption maximum around 410 nm (Figure 3).

Figure 2B shows the time profiles obtained at 440 nm in electron pulse irradiated Ar-purged, 0.02 M TBA solutions in *n*-butyl chloride containing 0.1 M ethanol at identical conditions of Figure 3. The time profiles at 440 nm demonstrate the effects of ethanol on the formation of an initial intermediate component. Upon addition of ethanol this faster decay component (within 3 μ s time) part vanished completely, which might be a radical cation of TBA. This observation reveals that the absorption shoulder around 410–440 nm is due to TBA radical cations. The broader peak in 420 nm region vanished gradually with time (Figure 3) indicating clearly that the 410 species was different than later time species (TBA radical).

The spectra obtained in electron pulse irradiated oxygenated 0.2 mM TBA in *n*-butyl chloride solution are quite similar to those observed in deoxygenated systems under identical conditions and this behavior is quite similar to TA systems. This indicates that the

Figure 4. The time profiles obtained with electron beam irradiated, Ar-purged *n*-butyl chloride at 400 nm at different concentrations of, (A) TA a: 0.05; b: 0.01; c: 0.2; and d: 0.4 mM and (B) TBA a: 0.0025; b: 0.005; c: 0.01; and d: 0.02 M. Dose per pulse used was 35 Gy in *n*-butyl chloride and optical path length was 10 mm.

Table 1. List of the optimized structures with relative energy (kcal/mol) and electronic charges (Mulliken charge) on S atoms of different forms of thioacetamide and thiobenzamide.

Radical cation	Relative energy = 770 Charge on S = -0.022	Relative energy = 1100 Charge on S = -0.104
Radical	Relative energy = 422 Charge on S = -0.102	Relative energy = 416 Charge on S = -0.375
Neutral	Relative energy = 0 Charge on S = -0.609	Relative energy = 0 Charge on S = -0.655
	TA	TBA

species generated in TBA systems are not sensitive to oxygen and also not originating through radical ($\text{Bu}^\bullet$) reactions.

It will be interesting to include at this point about the solute concentration effect on radical or radical cation formation in both TA and TBA systems. The time profiles obtained with electron beam irradiated Ar-purged *n*-butyl chloride containing different concentrations of TA and TBA are shown in Figures 4A and B. The higher

concentrations of TA (0.04 mM) and TBA (0.02 M) provide the ultimate information (time profiles d in both cases). In both systems, two different species were generated having different kinetics. The faster kinetics translates radical cation, which were effected in presence of ethanol, whereas later slower kinetics translates the formation of radical species. The measurements at other wavelengths in both systems also followed similar kinetics hence dimer type species were not

produced. Due to limitations of solubilities of TA and TBA further, higher concentrations were not used to verify dimer formation.

3.3 Computational results

Density functional theory has been utilized to calculate the ground electronic state geometry of thioacetamide and thiobenzamide to understand the reaction site for attacking electrophilic reactants ($\text{BuCl}^{\bullet+}$) in charge-transfer oxidation processes. Additionally, stabilizing energies of neutral, radical and radical cations of respective thioamides are also included. The geometries of neutral, radical and radical cations of TA and TBA 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 the MP2 level of theory with the same basis sets using the GAMESS program.¹⁴ The stable structures were characterized as minima by vibrational analysis. Their ground state optimized structures and electronic charges (Mulliken charge) (Table 1) support the different reaction patterns. For instance, the $\text{BuCl}^{\bullet+}$ adduct/charge transfer reaction is possible in TA/TBA at higher electron density $-\text{C}(\text{S})-\text{N}-$ part preferably from S atom where the electronic charge was more (-0.609 and -0.655 , respectively, in TA and TBA). Calculated energies of radical species were found lower than those of their respective radical cations revealing the former are more stable than the later; hence radicals possess slower decay kinetics. The respective relative energies in TA/TBA systems evaluated are neutral 0/0, radical 422/415 and radical cation 770/1100 kcal/mol. Partial planar arrangements of atoms, and high electron density at $-\text{C}(\text{S})-\text{N}-$ part the reaction nature and stability of TBA were different, which is due to the presence of phenyl ring in the molecule.

4. Conclusions

In the present study, we have demonstrated the effect of phenyl ring in the formation of radical cations and radicals of TA and TBA in *n*-butyl chloride system employing pulse radiolysis technique. In *n*-butyl chloride, the radical cation of TA exhibits absorbance similar to radical species, whereas in the case of TBA the radical cation absorbs at a higher wavelength than its radical species. Radical cations of both TA and TBA were separated from the respective radicals upon addition of ethanol. A faster decay of the 1st component (radical cation) in TBA was observed which was not seen in TA systems. Furthermore, the electronic charge distribution

represents the effect of the phenyl group in stabilizing the radical cations and radical species of TBA as compared to TA systems.

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References

1. Brede O and Naumov S 2010 Reactivity of radical cations in nonpolar condensed matter In *Charged Particle and Photon Interactions with Matter* Y Hatano, Y Katsumura and A Mozumdar (Eds.) (Boca Raton: CRC Press) p. 237
2. Mehnert R, Brede O and Naumann W 1982 Charge transfer from the solvent radical cation to solutes studied in pulse-irradiated liquid *n*-butyl chloride *Ber. Bunsenges. Phys. Chem.* **86** 525
3. Mehnert R 1991 *Topics in Molecular Organization and Engineering – Radical Ionic Systems* A Lund and M Shiotani (Eds.) (Dordrecht, The Netherlands: Kluwer Academic) p. 276
4. Lomoth R, Naumov S and Brede O 1999 Genuine pyrimidine radical cations generated by radical-induced electron transfer to butyl chloride or acetone parent-ions *J. Phys. Chem. A* **103** 2641
5. Guha S N, Moorthy P N, Kishore K, Naik D B and Rao K N 1987 One electron reduction of thionine studied by pulse radiolysis *Proc. Indian Acad. Sci. (J. Chem. Sci.)* **99** 261
6. Buxton G V and Stuart C R 1995 Re-evaluation of the thiocyanate dosimeter for pulse radiolysis *J. Chem. Soc. Faraday Trans.* **91** 279
7. Spinks J W T and Woods R J 1990 in *An Introduction to Radiation Chemistry* 3rd edn. (New York: John Wiley)
8. Density of *n*-butyl chloride. http://www.chemicalbook.com/ChemicalProductProperty_EN_CB5314609.htm. Accessed on 23 August 2018
9. Dey G R, Hermann R, Naumov S and Brede O 1999 Encounter geometry determines product characteristics of electron transfer from 4-hydroxythiophenol to *n*-butylchloride radical cations *Chem. Phys. Lett.* **310** 137
10. Hermann R, Dey G R, Naumov S and Brede O 2000 Thiol radical cations and thiyl radicals as direct products of the free electron transfer from aromatic thiols to *n*-butyl chloride radical cations *Phys. Chem. Chem. Phys.* **2** 1213
11. Dey G R 2015 Radicals and radical cations of thioacetamide and thiobenzamide in aqueous sulphuric acid media *Res. Chem. Intermed.* **41** 831
12. Dey G R, Dwibedy P, Naik D B, Kishore K and Moorthy P N 1999 Reactions of reducing and oxidising radicals with thiobenzamide: A pulse radiolysis study *Res. Chem. Intermed.* **25** 403
13. Kishore K, Dwibedy P, Dey G R, Naik D B and Moorthy P N 1998 Nature of the transient species formed during

- pulse radiolysis of thioacetamide in aqueous solutions
Res. Chem. Intermed. **24** 35
14. Schmidt M W, Baldrige K K, Boatz J A, Elbert S T, Gordon M S, Jensen J H, Koseki S, Matsunaga N, Nguyen K A, Su S J, Windus T L, Dupuis M and Jr. Montgomery J A 1993 General atomic and molecular electronic structure system *J. Comput. Chem.* **14** 1347