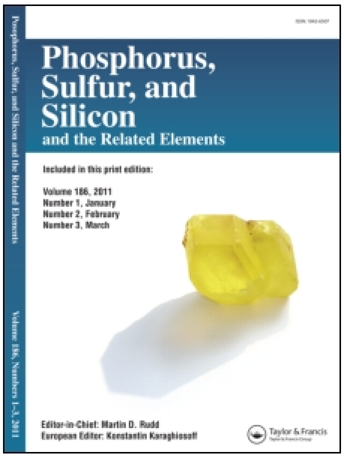

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Formation of Dimer Radical Cations of Selenourea on Oxidation: Pulse Radiolysis Studies

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Reactions of oxidizing radicals like hydroxyl ($^{\cdot}OH$*) radical, specific electron transfer agents like* $N_3^{\cdot}$*, and* $I_2^{-\cdot}$ *radicals were studied with selenourea (SeU) and compared with thiourea (ThU) using pulse radiolysis technique in microsecond time scales. Both the compounds efficiently react with* $^{\cdot}OH$ *radicals, however, SeU undergoes easier oxidation by secondary oxidants as compared to ThU. The results were supported by cyclic voltammetry studies. The radical cations of both SeU and ThU formed on oxidation undergo dimerization with the parent molecule to form two-centered three-electron-hemi bonded radical cations absorbing at 410 and 400 nm respectively with the stabilization energies of 21.1 and 20.5 kcal / mol for SeU and ThU, respectively. Preliminary studies indicated that at low concentration of SeU, the dimerization is prevented and the oxidation reaction produced metallic Se nanoparticles.*

Keywords DFT studies; nanoselenium; pulse radiolysis; radical cation; selenourea

INTRODUCTION

Sulfur and selenium compounds are biologically important molecules involved in many physiological functions. One of the factors responsible for their activity is their ability to react with reactive oxygen-free radicals like hydroxyl radicals. The free radical chemistry of sulfur compounds has been reported in the literature in detail.[1] On oxidation, many sulfides produce radical cations, which undergo unique reaction with the parent-forming dimer radical cations. Selenium belongs to the same group in the periodic table and selenium compounds have

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been shown to exhibit different chemistry.[2] To understand this we have studied in detail the reactions of hydroxyl radicals and specific one-electron transfer agents with SeU and compared with its sulfur analogue ThU. The pulse radiolysis and Density Functional Theory (DFT) studies are presented here.

MATERIALS AND METHODS

SeU and ThU were obtained from Sigma/Aldrich Chemicals. Solutions were prepared using water from nanopure system. Seven MeV electrons of 50 ns pulse width from a linear accelerator were used for the pulse radiolysis set up and the transients detected by absorption detection and thiocyanate dosimeter was employed for the dosimetry.[3,4] Typical doses were of 7–10 Gy/pulse. Hydroxyl radicals were generated by the radiolysis N_2O-saturated aqueous solutions, and $N_3^{\cdot}$ and $I_2^{-\cdot}$ radicals were generated by reaction of hydroxyl radicals with N_3^- and I^- respectively.[5] Cyclic voltammetric studies were performed on Ecochemie Auto Lab, PGSTAT 20 Model using three electrode system, i.e., glassy carbon electrode, platinum wire, and Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

$^{\cdot}OH$ radicals react with SeU and ThU with diffusion controlled rate constants (Table I). In both the cases at the concentrations of the substrates used (50–1000 μM) transients with absorption maxima at 400–410 nm were observed. Even though the reaction with primarily produced $^{\cdot}OH$ radicals is complete in <5 μs, the absorbance increased with increasing parent concentration, due to the reaction of the initially formed radical cation with parent to form a dimer radical cation. This was

TABLE I Properties of Transient of Selenourea and Thiourea in Aqueous Solution

Parameters	Selenourea	Thiourea
λ_{max} (nm)/Dimer radical cation	410	400
Bimolecular rate constant ($k \times 10^{-9}$)/M^{-1} s^{-1}	(OH) 9.9	11
	($N_3^{\cdot}$) 3.8	No reaction
	(I_2^{-}) 0.28	No reaction
Association constant/M^{-1} for dimer formation	7.9×10^{4}	8.5×10^{4}
Second order decay constant (2k)/M^{-1} s^{-1}	3.3×10^{9}	9.0×10^{8}
Peak potential/V	0.56	1.16
Stabilization energy for dimer formation/kcals mol^{-1}	21.1	20.5
Ionization potential (eV)	5.11	6.12

further confirmed by using specific one-electron oxidants. The second order decay rate constants, the absorption maxima, and the association constants for the formation of dimer radical cations for SeU and ThU are listed in Table I. The dimer radical cations decay by radical-radical reactions and probably converted to diselenide and SeU. The radical cation nature was also confirmed by following the decay in presence of added salt, whereby reactions involving charged species are accelerated by the increased ionic strength from the salt. From these studies it looks that the $^{\cdot}OH$ radical chemistry of SeU and ThU is not very different.

Reactions of less powerful oxidants like $N_3^{\cdot}$ (1.3 V) and $I_2^{\cdot-}$ radicals (1.03 V)^6 were studied with SeU and ThU. In all these cases, no reaction was observed with ThU but all of them were able to oxidize SeU. In the concentration range of 50–1000 μM, similar transient spectra were observed in all the cases. Figure 1 gives the transient spectrum of the dimer radical cation of SeU produced by one-electron oxidation by $N_3^{\cdot}$ radicals. The bimolecular rate constants for the reaction of these radicals with SeU are given in Table I. Since these radicals show higher reactivity with SeU, it is essential to know the reduction potential of these compounds. Cyclic voltammograms of these two compounds were determined (Inset (b) & (c) of Figure 1) in the voltage range from −0.25 V–1.2 V. Both showed irreversible peaks and the peak position indicates that SeU is more easily oxidizable than ThU by 0.6 V.

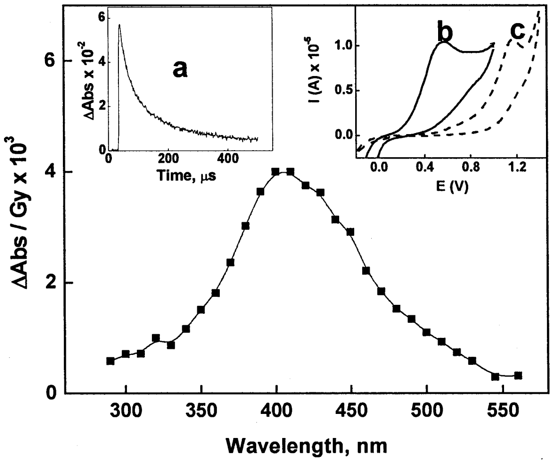

FIGURE 1 Difference absorption spectrum of the dimer radical cation of SeU produced by reaction with azide radicals. Inset a gives the decay kinetic trace of dimer radical cation at 410 nm. Inset b & c respectively give the voltammograms of SeU & ThU.

It has been reported that the sulfur-centered radical cations are unstable and form more stable dimer radical cations on reaction with the parent. Such reaction results in the formation of a new three-electron sigma bond containing two bonding σ electrons and one anti-bonding σ^* electron. Since selenium belongs to the same group as sulfur it is necessary to examine whether similar dimer radical cation formation is observed in selenium compounds. In general a Se—Se bond is weaker a than S—S bond and therefore dimer formation should be unfavorable with selenium compounds. To substantiate the experimental results, DFT studies were carried out for both SeU and ThU.[7] The first ionization potentials, absorption maxima for the dimer radical cations and the stabilization energy for the formation of dimer radical cations, were calculated and are listed in Table I. The theoretically calculated parameters agree well with the experimental results. From these studies it can be concluded that although SeU is easier to undergo oxidation than ThU, the dimer-radical cation formation is equally feasible in both SeU and ThU.

Under conditions, where SeU concentration is much less than that of the oxidants, a new reaction was observed. In the reaction of SeU in the presence of excess of oxidants like hydrogen peroxide or OH or $ABTS^-$ radicals, the solution initially turned pink, which slowly was converted into a red precipitate of metallic selenium. This suggested that at low concentrations of SeU, oxidation of SeU produced nanoparticles selenium, which is characterized by dynamic light-scattering studies. With time, these nanoparticles subsequently turned into metallic selenium. Further work on stabilization of nanoparticles by the addition proteins and their characterization is in progress.

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