

ONE-ELECTRON OXIDATION OF SELENOUREA IN AQUEOUS SOLUTION

Beena Mishra, K. I. Priyadarsini and Hari Mohan

Radiation Chemistry & Chemical Dynamics Division

Bhabha Atomic Research Centre

Abstract

One-electron oxidation of selenourea in aqueous solution has been studied using pulse radiolysis technique. The hydroxyl radicals react with a bimolecular rate constant of $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and showed the formation of a transient absorption band with λ_{max} at 410 nm. The absorbance at 410 nm is observed to depend on solute concentration. The transient showed reactivity towards oxygen ($k = 8.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). Specific one-electron oxidants (N_3^- , Br_2^- , Cl_2^- , I_2^-) and also H atom showed the formation of similar transient species. Based on these studies, the transient absorption band is assigned due to the solute dimer radical cation formed by 2-centre 3-electron bonding between two selenium atoms.

Introduction

Sulfur compounds are biologically important molecules as they are 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. On oxidation, organic sulfides produce dimer radical cations via a complex sequence of reactions involving α -thio radicals, OH-adduct and monomer radical cation [1]. The radiation chemistry of thiourea has been studied to understand its application as radioprotective agent and corrosion inhibitor. Selenium belongs to the same group and it is therefore interesting to see how selenium behaves on oxidation. With this objective, we have studied in detail the reactions of hydroxyl radicals and specific one-electron transfer agents with selenourea (SeU).

Experimental

The solutions of selenourea (Aldrich Chemicals) were prepared in nanopure water in phosphate buffers. Freshly prepared solutions were used for

each experiments. Pulse radiolysis experiments were carried with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator. An aerated aqueous solution of KSCN was used to determine the dose delivered per pulse and it was kept close to 8 Gy. The reaction of $\cdot\text{OH}$ radical was carried out in N_2O -saturated aqueous solution where e_{aq}^- is quantitatively converted to $\cdot\text{OH}$ radicals ($\text{N}_2\text{O} + e_{\text{aq}}^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{N}_2$). The reaction with specific one-electron oxidants was conducted under conditions such that the $\cdot\text{OH}$ radicals do not react with the solute and only the one-electron oxidants react with the solute. The reaction with H. atom was carried out at pH 1 in N_2 -saturated solution containing tert-butyl alcohol to scavenge $\cdot\text{OH}$ radicals ($\cdot\text{OH} + (\text{CH}_3)_3\text{COH} \rightarrow \cdot\text{CH}_2(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O}$).

Results and Discussion

Figure 1 shows the transient absorption spectra obtained on pulse radiolysis of N_2O -saturated aqueous solution of selenourea, which exhibits λ_{max} at 410 nm. The transient absorbance at

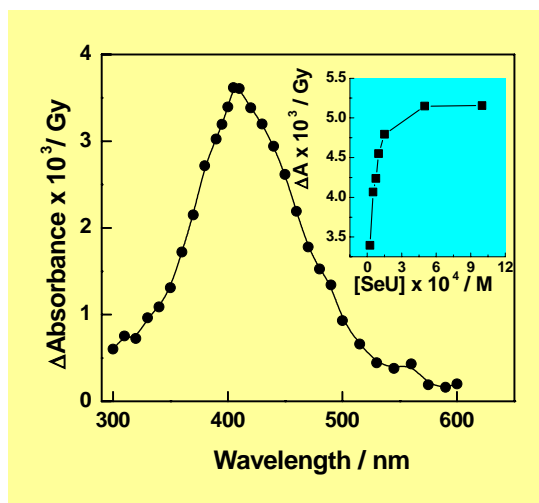


Fig. 1 Difference transient optical absorption spectrum obtained on pulse radiolysis of N₂O-saturated aqueous solution (pH 7) of SeU (50 μM). Inset show variation of absorbance at 410 nm as a function of SeU concentration.

410 nm was observed to increase with solute concentration (inset of Fig 1), suggesting the formation of a dimeric species. The rate constant for the reaction of ·OH radicals with SeU was determined by competition kinetic studies using 2-propanol (IP) as the standard solute. Using a value of $k_{IP + \cdot OH} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the bimolecular rate constant was determined to be $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1).

Table 1: Kinetic and spectroscopic properties of dimer radical cation formed on reaction of ·OH radicals with selenourea

Parameters	Values
$\lambda_{max} / \text{nm}$	410
Bimolecular rate constant / $\text{M}^{-1} \text{ s}^{-1}$	9.9×10^9
Association constant / M^{-1}	7.9×10^4
Second order decay constant (2k) / $\text{M}^{-1} \text{ s}^{-1}$	3.3×10^9

The transient absorption band at 410 nm was observed to decay by second order kinetics with a 2k value of $2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The decay was observed to be faster in the presence of oxygen (Fig 2). The pseudo-first order rate constant (k_{obs}) increased linearly with oxygen concentration (inset of Fig 2). The slope of the linear plot gave a bimolecular rate constant of $8.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

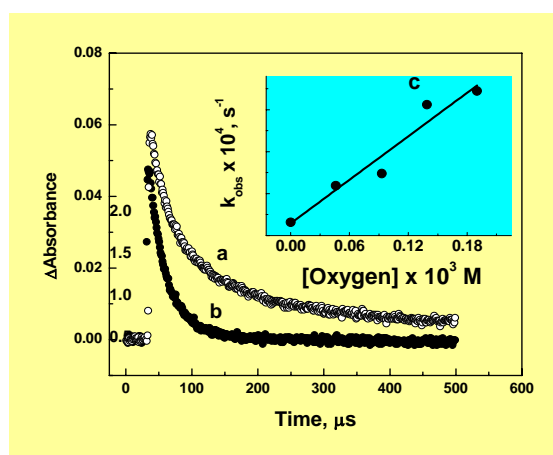


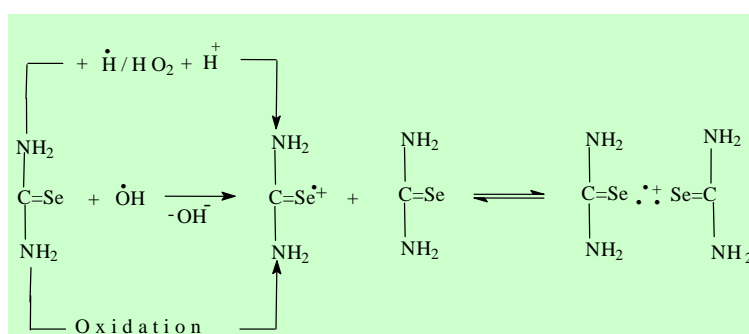
Fig. 2 Absorption-time profiles at 410 nm formed on pulse radiolysis of aqueous solution of SeU (1 mM, pH 7) in (a) N₂O and (b) N₂O-O₂. Inset shows variation of pseudo-first-order rate constant (k_{obs}) as a function of oxygen concentration.

The reaction with specific one-electron oxidants (Cl₂⁻, Br₂⁻, I₂⁻, N₃[·]) produced transient absorption spectra with λ_{max} at 410 nm and the transient absorbance was observed to increase with SeU concentration in each case. The nature of the transient optical absorption spectrum obtained on reaction of ·OH radical with SeU was similar to that obtained on reaction with specific one-electron oxidants. Therefore the transient absorption band (Fig 1) is assigned to one-electron oxidized species of SeU.

Pulse radiolysis of N₂-saturated acidic (pH 1) aqueous solution of SeU (0.3 mM) containing tert-butyl alcohol (0.3 M) showed the formation of a transient absorption band at 410 nm. The transient absorbance at 410 nm was also observed to increase with SeU concentration.

The rate constant for the reaction of H[•] atom with SeU was determined to be 2.1x10⁹ M⁻¹ s⁻¹. The HO₂[•] radical was also observed to react with SeU with the formation of transient absorption band at 410 nm.

Based on these studies and the data available in literature on organic sulfur compounds, the transient absorption band at 410 nm is assigned to dimer radical cation, formed by 3-electron bonding between two selenium atoms (scheme 1).



Scheme 1

The equilibrium constant (K) for the equilibrium process was determined by following equation [2].

$$\frac{A_0}{A} = 1 + K^{-1}[SeU]^{-1}$$

where A and A₀ are the absorbance at 410 nm at any given concentration of SeU (6x10⁻⁶ – 1x10⁻³ M) and the saturation absorbance of SeU (1x10⁻³

M) respectively. The plot of (A₀/A) – 1 against [SeU]⁻¹ gave a straight line with slope = 1/K. The equilibrium constant for the formation of dimer radical cation was evaluated to be 7.9x10⁴ M⁻¹.

Conclusions

Hydroxyl radicals and specific one-electron oxidants react with selenourea to form a transient broad absorption band at λ_{max} = 410 nm and is assigned to dimer radical cation. Unlike organic sulfur compounds, the dimer radical cation of selenourea reacts with molecular oxygen. H[•]/HO₂[•] also react to form dimer radical cation following H-abstraction reaction. The results also confirm that like sulfur, selenium formed 2-centre 3-electron bonding between two selenium atoms.

References

1. K.D. Asmus, in S-centered radicals, Z. B. Alfassi (Ed.) John Wiley: New York, p.142 (1999).
2. W. Wang, M. N. Schuchmann, H. P. Knolle, W. J. von Sonntag, C. von Sonntag, J. Am. Chem. Soc., 121, 238 (1999).

This paper was adjudged as one of the Best Posters in the National Symposium on Radiation & Photochemistry (NSRP 2003) held at IIT Kanpur during March 3 – 5, 2003.

About the authors ...

Ms Beena Mishra received her M.Sc. degree in Chemistry with specialization in Inorganic Chemistry from Institute of Science, Mumbai, in 2001. She stood second in M.Sc. in Mumbai University. She is a DAE fellow working in Radiation Chemistry & Chemical Dynamics Division, BARC. She is pursuing her Ph.D. degree in the subject entitled, "Free radical and transient studies of some biologically important organic and organometallic compounds".



Dr Indira Priyadarsini joined BARC in 1983. She obtained her Ph. D. in Radiation and Photochemistry in 1990. She has co-authored more than 70 papers in international journals on radiation chemistry, photochemistry and radiation biology. Employing fast reaction techniques, she has been studying the free radical reactions involving antioxidants, radio protectors and radio sensitizers in model systems. She is currently working on the elucidation of mechanism of antioxidant action involving natural products and herbal extracts.



Dr Hari Mohan joined BARC in 1967. Since then, he is actively involved in the study of fast reaction kinetics using accelerators and lasers. His current research interests include free radical reactions of halogenated and sulfur compounds and biomolecules of natural origin. He has co-authored more than 150 research papers in international journals. Presently he is the Head, Radiation Chemistry Section of Radiation Chemistry & Chemical Dynamics Division, BARC.