One-Electron Oxidation of Selenomethionine in Aqueous Solutions

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Abstract

Pulse radiolysis technique has been employed to study one-electron oxidation of selenomethionine (SeM) in aqueous solutions and hydroxyl radicals (\(\cdot\)OH) and specific one-electron oxidants have been used to induce oxidation. Hydroxyl radicals react with SeM at pH 7 to form transient absorbing at 380 nm, which is assigned to intra-molecularly stabilize radical cation between oxidized selenium and nitrogen. At pH 1, dimer radical cation having absorption maxima at 480 nm is formed. The pH of the solution was observed to play an important role on the nature of transient species formed on oxidation. Cyclic voltammetry and pulse radiolysis studies revealed that one-electron oxidation of selenomethionine is easier compared to methionine.

Introduction

The radiation chemistry of organic sulfur (S) and selenium (Se) compounds in aqueous solutions are of current interest as the radical species generated from these compounds are considered to be possible intermediates in redox reactions of S/Se-compound.\(^1\)\(^2\) Many of these compounds find applications as radioprotectors and are important building blocks for the synthesis of biologically important molecules.

Even though S & Se belong to the same group in the periodic table, the chemistry of Se and tellurium compounds has been found to be different due difference in ionization potential, electronegativity and polarizability. One-electron oxidation of methionine has been studied and a few reports are available in literature.\(^3\) In order to understand the effect of selenium on the oxidation mechanism of methionine, detailed radiation chemical studies on aqueous solution of selenomethionine (SeM) have been carried out.

Experimental Section

The solution of SeM (Aldrich chemicals) was prepared in nanopure water in phosphate buffers. Pulse radiolysis experiments were carried out with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator. The dose for the experiment was \(~9-10\) Gy / pulse. Reaction of \(\cdot\)OH radical was carried out in \(\text{N}_2\text{O}\) saturated aqueous solution and reaction with specific one electron oxidant. The reaction with H atom was carried out at pH 1 in presence of \(t\)-butananol to scavenge \(\cdot\)OH radical.

Results and Discussion

SeM is reported to have two \(pK_a\) values of 2.35 and 9.2 with an isoelectric point at 5.75, corresponding to COOH and \(\text{NH}_3^+\) groups respectively. It is present in different forms at different pH (scheme 1).

In the zwitterionic form the \(\text{NH}_3^+\) and COO\(^-\) are exceptional proton-donor and -acceptor groups respectively and the fast proton transfer provide enough concentration of an unprotonated amino group at neutral pH. However in acidic solutions (pH < 2), proton exchange from \(\text{NH}_3^+\) can no longer take place effectively.

Reaction of \(\cdot\)OH radicals at pH 7

The transient absorption spectrum obtained on pulse radiolysis of \(\text{N}_2\text{O}\)-saturated aqueous solution of SeM exhibits a broad absorption
band with $\lambda_{\text{max}}$ at 380 nm with a small shoulder in 280 – 290 nm region (Fig 1a). The absorption band at 380 nm decayed by first order kinetics with $k = 1.2 \times 10^4$ s$^{-1}$ and is unaffected by the presence of $O_2$, suggesting the absence of a carbon centered radical. The transient absorbance at 380 nm remained independent of solute concentration, suggesting the formation of a monomeric species. H atom reaction with SeM did not produce any transient even at pH 1, which shows that the transient spectrum (Fig 1a or 1c) is mainly due to the reaction of $\cdot$OH radicals with SeM.

Based on these studies and the data available for organic sulfur compounds, the transient absorption band at 380 nm could be due to one of the three possibilities, viz., (1) OH-adduct at selenium, or (2) intra-molecularly stabilized 5-membered ring between oxidized selenium and nitrogen, (3) intra-molecularly stabilized 6-membered ring between oxidized selenium and oxygen of either carbonyl or OH group and (4) selenium centered radical cation. In analogy with studies reported for dialky sulfides, Se centered radical cation would be highly unstable and will have high tendency to stabilize on coordination with another Se or heteroatom. Due to higher difference in the electronegativity of Se and O (1.02 eV) as compared to Se and N (0.59 eV), intra-molecularly stabilized 6-membered ring configuration is expected to be less stable.

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**Fig.1:** Fig 1a and c shows difference absorbance obtained on pulse radiolysis of $N_2O$ saturated solution of SeM (0.5 mM) at pH 7 & 1 respectively. Inset (b) shows absorbance at 380 nm (o) and 480 nm (●) as a function of pH. Inset (d) shows variation of absorbance at 480 nm as a function of SeM concentration at pH 1.
The reaction of SeM with specific one electron oxidation (Br₂⁺, (SCN)₂⁺) at pH 7 produced similar spectrum suggesting that the transient is one electron oxidized species and not OH adduct. Based on these studies, the transient absorption band at 380 nm is assigned to intramolecularly stabilized 5-membered ring formed between oxidized selenium and nitrogen (scheme 1).

**Reaction of \(^{\bullet}\)OH radicals in acidic conditions**

As the pH of the solution is decreased, the transient absorbance at 380 nm decreases with the appearance of a new band at 480 nm. The variation of absorbance at 380 and 480 nm, formed on pulse radiolysis of N₂O-saturated aqueous solution of SeM (5x10⁻⁴ M), as a function of pH (Fig 1b) gave an inflection point at 2.2. The transient absorption spectrum obtained on pulse radiolysis of N₂ saturated aqueous solution of SeM (1 mM at pH 1), showed the formation of a transient absorption band at 480 nm (Fig 1c). At pH 7, 480 nm band is almost absent. Also the absorbance at 480 nm was observed to increase with increasing concentration of SeM (Fig 1d). This increase in the absorbance is due to the reaction of initially formed transient species with SeM suggesting the formation of a dimeric species. The transient absorption band at 480 nm decayed by second order kinetics with 2k/ε value of 1.6x10⁵ s⁻¹ and remained same in N₂O/O₂ conditions. The kinetic and spectroscopic properties of the transient species formed on reaction of \(^{\bullet}\)OH radicals with SeM at pH 1 were different from those observed at pH 7. In order to identify the nature of the transient species formed on reaction of \(^{\bullet}\)OH radicals with SeM at pH 1, pulse radiolysis studies were carried out with various specific one-electron oxidants (Cl₂⁺, Ti⁺) at pH 1.

The nature of the transient absorption band at pH 1, formed on reaction with specific one-electron oxidants was similar to that formed on reaction of \(^{\bullet}\)OH radicals with SeM at pH 1. The nature of the transient species formed at pH 1, formed on reaction with specific one-electron oxidants was similar to that formed on reaction of \(^{\bullet}\)OH radicals with SeM at pH 1. The absence of any vacant orbital on the nitrogen atom of NH₃⁺ group does not allow formation of intra-molecular bonding between oxidized selenium and nitrogen. Based on these studies and also the results available in literature on organic sulfur compounds, the transient absorption band is assigned to dimer radical cation formed on p orbital overlap of oxidized Se with Se of another SeM.

**Scheme 1**
The rate constant for the reaction of $^\bullet$OH radicals with SeM at pH 1, was determined by competition kinetic studies using 2-propanol as a standard. By taking $k_{\text{OH}+IP} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ the bimolecular rate constant was determined to be $5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The equilibrium constant (K) for dimer formation is determined by equation (3).

$$\frac{1}{\Delta A_{\text{obs}}} = \frac{1}{\Delta A_{\text{max}}} + \frac{1}{\Delta A_{\text{max}} K [\text{SeM}]}$$  \hspace{1cm} (1)

where $\Delta A_{\text{obs}}$ and $\Delta A_{\text{max}}$ are the absorbance at 480 nm at any given concentration of SeM (0.2 – 2.4 mM) and the saturation absorbance of SeM (2.4 mM) respectively. The plot of $1/\Delta A_{\text{obs}}$ vs $[\text{SeM}]^{-1}$ gave a straight line with slope = $1/K\Delta A_{\text{max}}$ and intercept = $1/\Delta A_{\text{max}}$. The equilibrium constant (K) for the formation of dimer radical cation is determined to be $9.2 \times 10^3 \text{ M}^{-1}$.

**Conclusions**

The experimental studies revealed that the nature of $^\bullet$OH radical reaction with SeM depends on the pH of the solution, forming monomer radical cations in neutral pH and dimer radical cations in acidic pH region. In neutral pH, intra-molecularly stabilized 5-membered ring is formed between oxidized selenium and nitrogen. The association constant for dimer formation of SeM is higher than that of methionine, indicating higher stability of SeM dimer radical cation.

**References**


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**Table 1: Kinetic and spectroscopic properties of transient formed on reaction of selenomethionine with oxidizing radical.**

<table>
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<tr>
<th>Radical</th>
<th>pH</th>
<th>$k_f \times 10^9$/M$^{-1}$s$^{-1}$</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$k_d \times 10^4$/s$^{-1}$</th>
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<td>5.6</td>
<td>480</td>
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<tr>
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<td>---</td>
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<tr>
<td>$Br_2^\bullet$-</td>
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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 K. Indira Priyadarsini is currently working on the elucidation of mechanisms of antioxidant action involving natural products and herbal extracts with the potential application as radioprotectors, employing electron pulse radiolysis and in vitro biochemical studies. Dr Priyadarsini has co-authored more than 95 papers in peer reviewed international journals on radiation chemistry, photochemistry and radiation biology. She has been elected as the Fellow of the National academy of Sciences, India, 2003.

Dr Hari Mohan joined BARC in 1967. Since then, he was actively involved in the study of first reaction kinetics using accelerators and lasers. His research interest includes free radical reaction of halogenated and sulfur compounds and biomolecules of natural origin. He had co-authored more than 200 research papers in international journals. He superannuated in November, 2004 as Head, Radiation Chemistry Section of Radiation Chemistry & Chemical Dynamics Division of BARC.