

# RADIATION CHEMICAL STUDIES OF SELENIUM COMPOUNDS: HOW THEY DIFFER FROM SULFUR COMPOUNDS

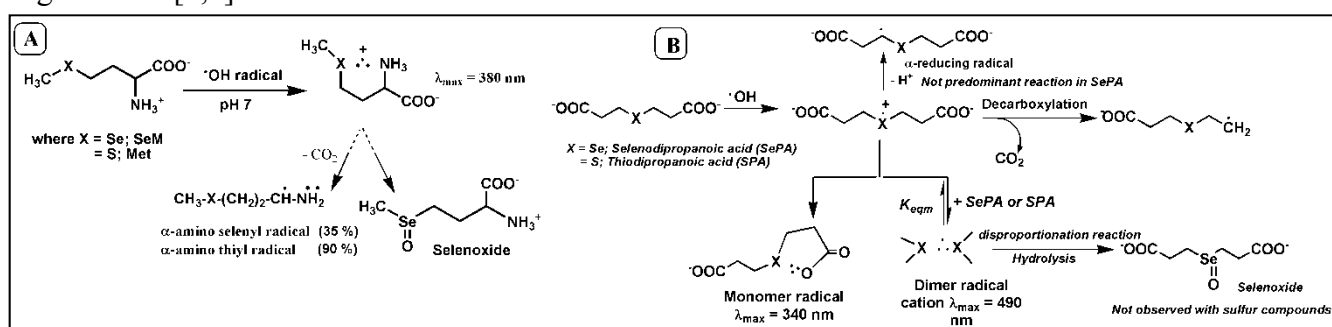
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Selenium, an essential micronutrient is being thoroughly investigated for its role in the catalytic cycle of oxidoreductase enzyme like glutathione peroxidase (GPx) and in combating oxidative stress in cells.[1] The protective ability of selenium compounds against oxidative assault has been found to be superior as compared to its lighter analogue, sulfur. In the presentation, a few examples from our studies depicting the role of physico-chemical properties of functionalized selenoether and thioether responsible for their differential reactivity will be discussed. The studies have been carried out with hydroxyl ( $\bullet\text{OH}$ ) radical, using nanosecond pulse radiolysis coupled with absorption detection

Selenomethionine (SeMet), a selenium analogue of methionine (Met) on oxidation with  $\bullet\text{OH}$  radical at pH 7 generates a monomer radical cation ( $\text{SeMet}^{\bullet+}$ ). A fraction of  $\text{SeMet}^{\bullet+}$  radicals undergo decarboxylation to produce 3-methyl selenopropyl radicals that are reducing in nature (Scheme A). Comparison of the reducing ability of these radicals with that from Met, indicated that  $\text{SeMet}^{\bullet+}$  radicals are comparatively weak electrophile, which results in its lower degradation. [2]

Functionalized selenoethers like bis(propyl)selenides substituted with either alcohol or carboxylate group, reacts with  $\bullet\text{OH}$  radical mainly to form dimer radical cation ( $>\text{Se}::\text{Se}<^+$ ), intramolecular-stabilized radical cation ( $>\text{Se}^{\bullet+}$ ) and minor quantity of  $\alpha$ -reducing radical. The dimer radical cations were subsequently converted to their corresponding selenoxides (Scheme B). Estimated yield of these products showed effect of neighbouring group participation in stabilizing the selenium centred radicals, which correlated well with their antioxidant ability. Comparing these results with those for sulfur analogues indicated that the extent of non-bonding interaction ( $E_{\text{nb}}$ ) in sulfur compounds with neighbouring group is higher than analogous selenium compounds, resulting in their higher oxidative degradation. [3,4]



Scheme: Comparative  $\bullet\text{OH}$  radical reactions of functionalized seleno- and thio-ethers

These studies emphasize the role of redox potential, neighbouring group participation and non-bonding interaction in antioxidant activity of selenium compounds.

## References

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