

# THEORETICAL CALCULATIONS AND EXPERIMENTAL DATA ON SPECTRAL, KINETIC AND THERMODYNAMIC PROPERTIES OF SE.:N AND S.:N THREE-ELECTRON-BONDED, STRUCTURALLY STABILIZED $\sigma^2\sigma^*$ RADICALS IN AQUEOUS ENVIRONMENT.

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A complementary quantum mechanical and experimental study has been undertaken on the reactivity, formation and properties of Se.:N and S.:N  $\sigma^2/\sigma^*$  three-electron-bonded radical species, generated upon one-electron oxidation of Se- and S-methionine and structurally related compounds. The quantum-chemical calculations were based on Density Functional Theory (DFT) Hybrid B3LYP and BHandHLYP methods with basis sets ranging from 6-31G(d) to 6-311+G(d,p). Solvent effects, which play an important role concerning structure and energy of ground and excited states, were taken into account as dielectric continuum as well as explicit water molecules. They fully confirm new and previously obtained experimental results concerning the Vis/near-UV absorptions and thermodynamic stability. Special emphasis was put on a comparison between selenium and sulfur. The calculations clearly confirm the higher thermodynamic stability of the Se.:N radical species relative to the S.:N ones, and also corroborate the observed much higher kinetic stability of the former. Concerning optical absorptions, the calculations predict the Se.:N transients to exhibit a blue-shift by about 20 nm relative to the S-based analogues, confirming the few experimental data available so far. The theoretical study includes a comparison of various calculation levels and the influence of the solvent environment, also in relation to vacuum, in which the transients are generated. New experimental data within the scope of this study have been obtained on *intramolecularly* formed (S.:N)<sup>+</sup> radical cation moiety, structurally stabilized by a rigid norbornane backbone. The methionine-related species, with an endo-2-amino, exo-2-carboxyl, and endo-6 methylthio substitution, for example, exhibits almost identical optical and kinetic stability properties as the corresponding species from free methionine. Its optical absorption depends on the protonation state of the carboxyl group, with  $\lambda_{\max}$  at 410 nm for the carboxylate (zwitterionic) form and at 390 nm for the overall cationic form with the protonated carboxyl group. The short lifetimes with  $t_{1/2}$  of 490 ns and 2  $\mu$ s pertain to the decarboxylation of the respective species. A much longer-lived S.:N species with  $t_{1/2} > 500 \mu$ s and 2.order decay kinetics ( $\lambda_{\max}$  465 nm) was obtained from an endo-2-anilino norbornane analogue which does not carry a carboxyl group. In conclusion, selenium enhances the thermodynamic and kinetic stability of its radical transients, relative to the sulfur analogues.