

Supplementary Materials

Unexpected Reaction Pathway of the Alpha-Aminoalkyl Radical Derived from One-Electron Oxidation of S-Alkyl-Glutathiones

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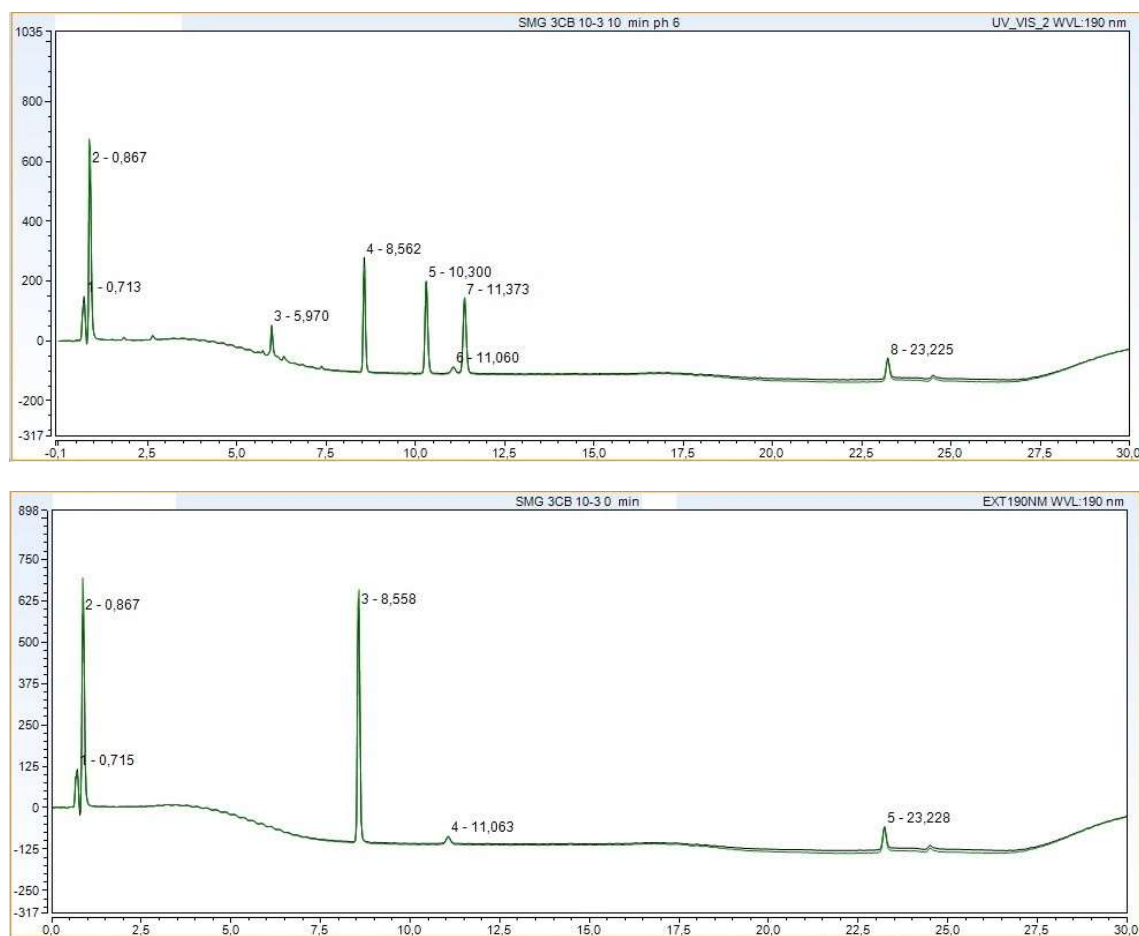


Figure S1. HPLC-DAD chromatogram of non-irradiated (upper) and irradiated for 10 minutes (lower) 3CB (3 mM) - S-Me-Glu (10 mM) system at pH 6.0. Only traces (as compared with pH 11) of the irradiation products at m/z 259 can be seen at retention time of approximately 2.5 min.

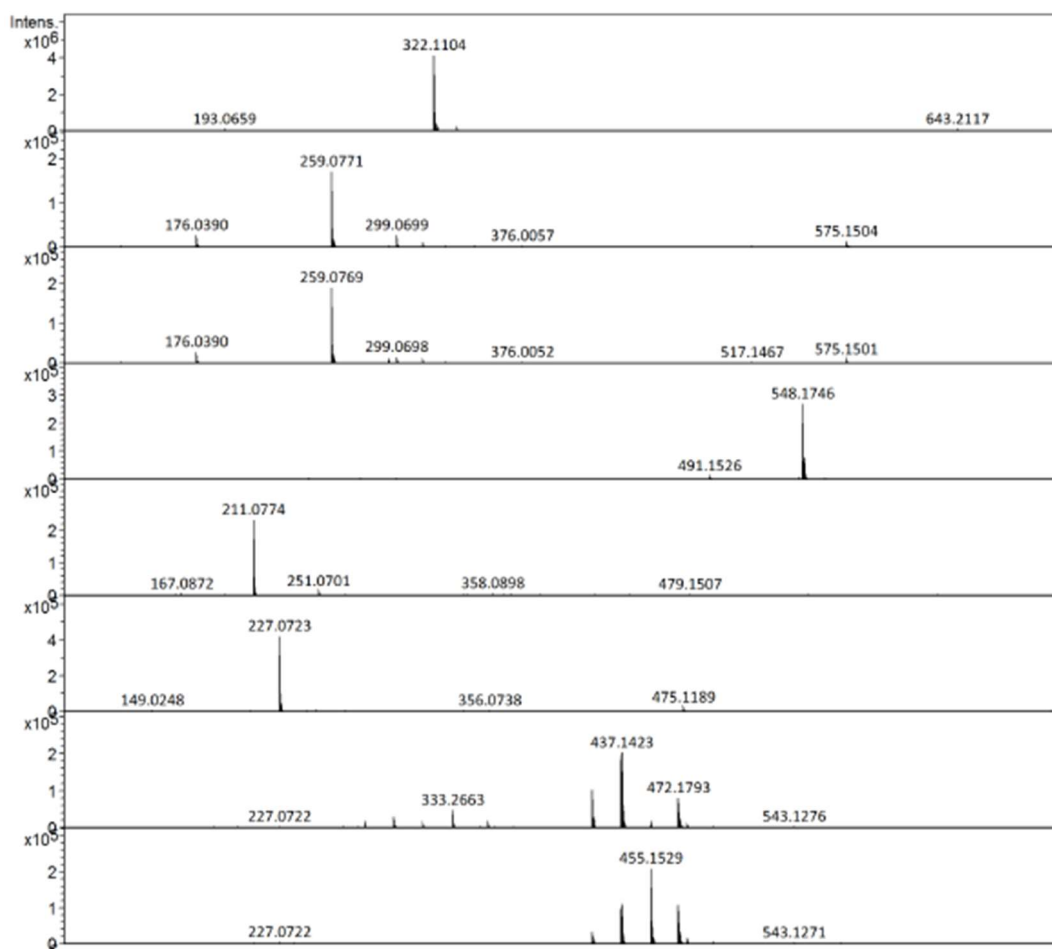


Figure S2. 3CB + S-Me-Glu, irradiation time 10 min—mass spectra of the LC-MS chromatogram for all detected peaks with their retention times.

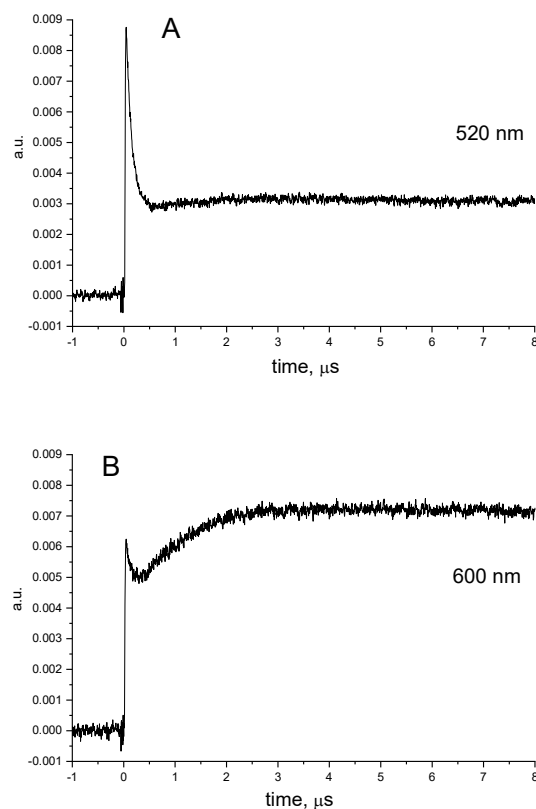


Figure S3. LFP kinetic traces monitored at 520 nm (A) and 600 nm (B). The 3CB triplet state is quenched efficiently by S-Me-Glu, shortening its lifetime to approximately 100 ns ([3CB] = 4 mM, [S-Me-Glu] = 10 mM, pH = 11.2).

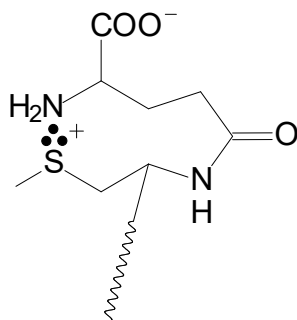
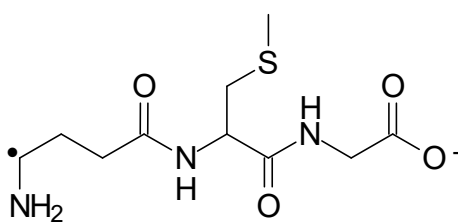
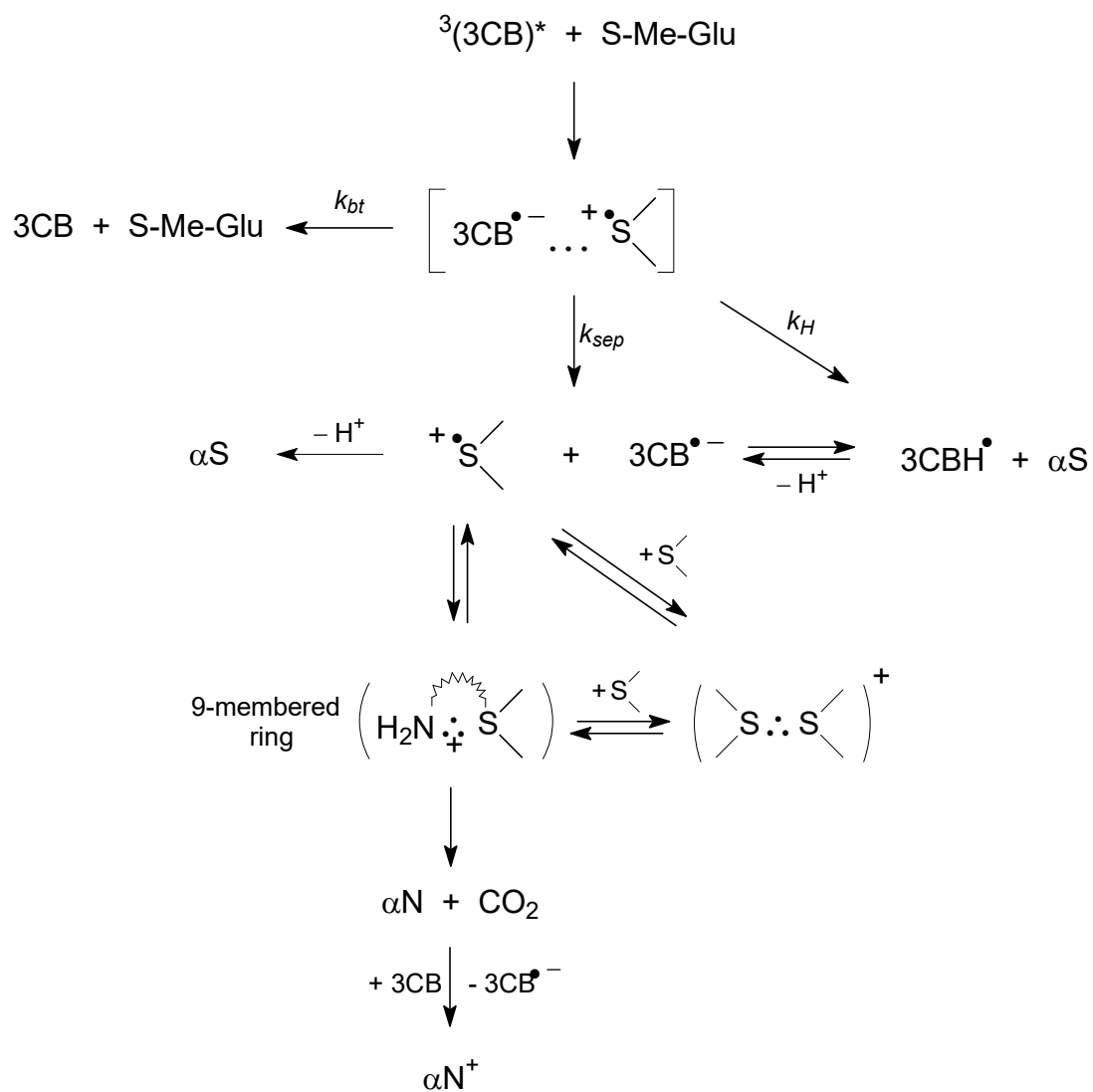


Figure S4. Structure of a 9-membered cyclic (S...N)-bonded radical cation.



α -aminoalkyl radical (α N)

Figure S5. Structure of α -aminoalkyl radical derived from S-Methyl-Glutathione (S-Me-Glu).



Scheme SI. Mechanism of primary reactions in 3CB sensitized photooxidation of S-Me-Glu at pH = 11.2.

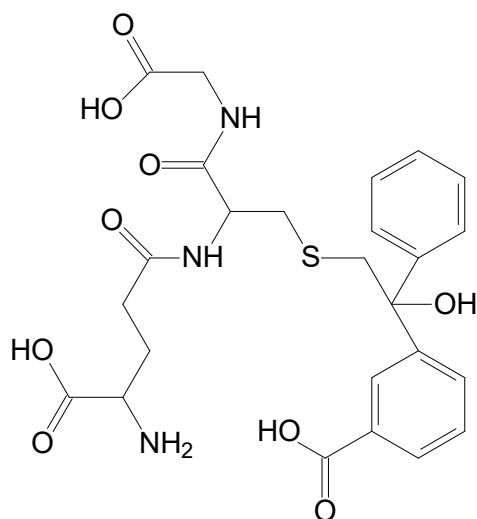
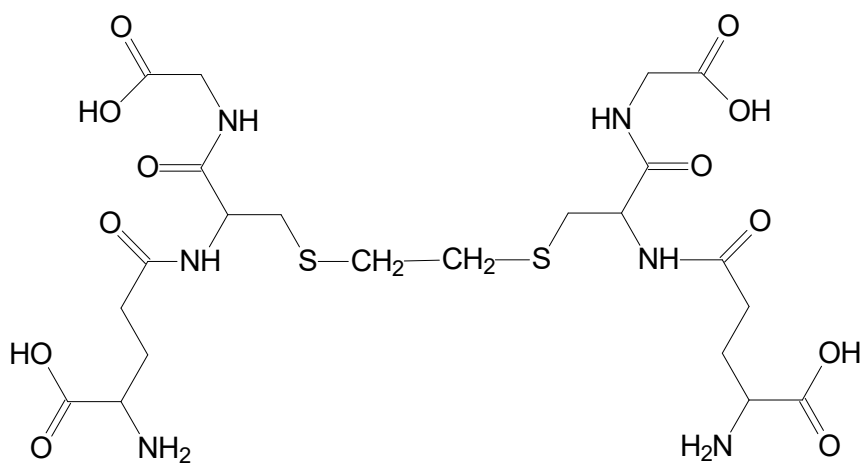
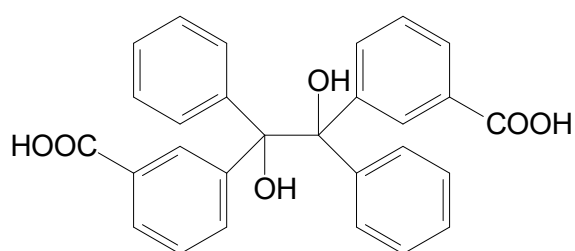
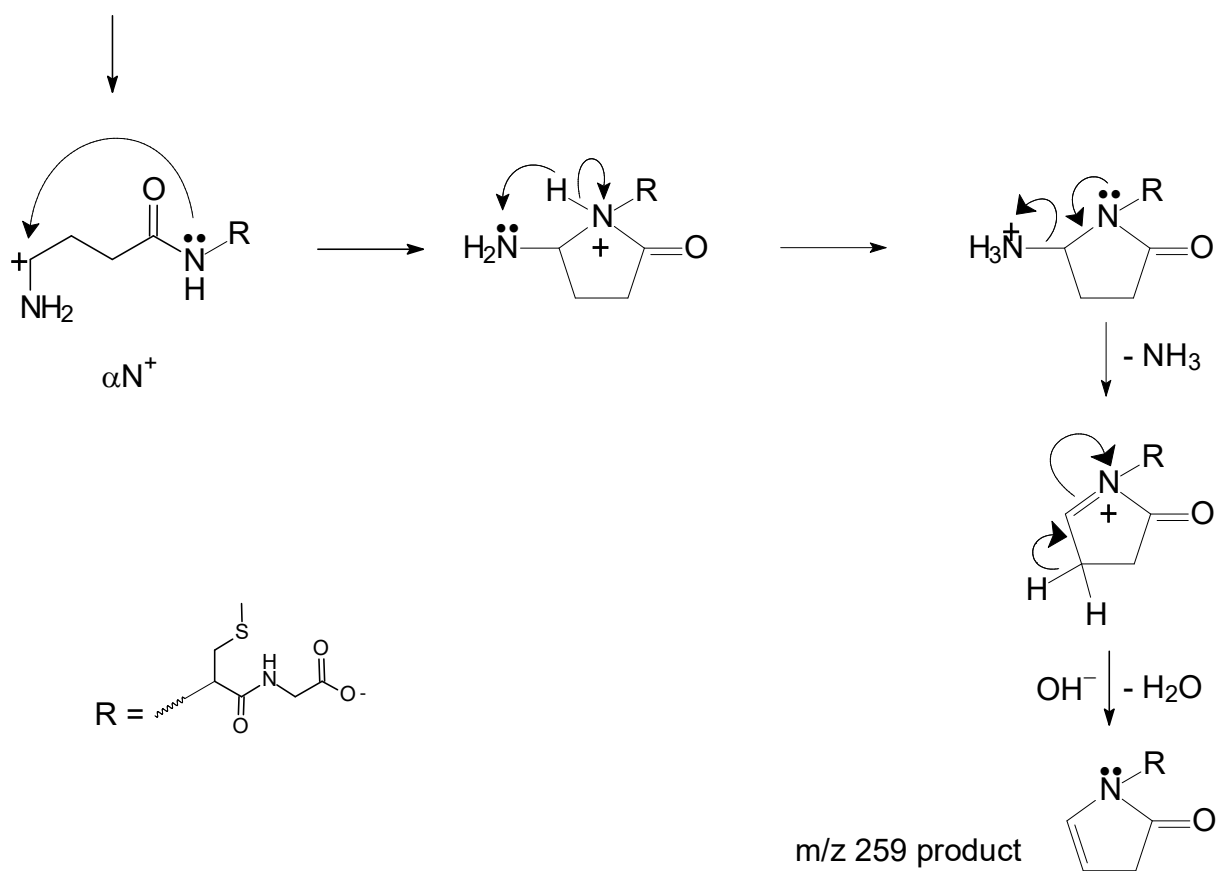
**P2** α S-Sens m/z 548**P3** α S- α S m/z 641**P4** Sens-Sens m/z 455

Figure S6. Suggested structures of products: **P2** m/z 548 - adduct of S-Me-Glu α -thioalkyl radical (α S) with 3CB ketyl radical; **P3** m/z 641 - α S radical dimer; **P4** m/z 455 - 3CB ketyl radical dimer.

from Scheme SI



Scheme SII. Suggested mechanism of cyclic product formation from the αN^+ derived from S-Me-Glu.

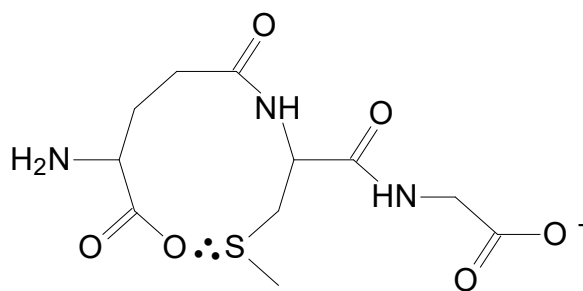


Figure S7. Structure of a 10-membered cyclic (S...O)-bonded transient postulated in the work of [32].