

Decay Kinetic Studies of the Superoxyl Radical Adduct of the Cyclic Nitron 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide (BMPO)

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Although the nitron 5-diethoxyphosphoryl-5-methyl-1-pyrroline N-oxide (DEPMPO) proved to be superior in trapping superoxyl radicals than the conventionally used DMPO, DEPMPO faces several drawbacks such as difficulty in purification, multiple splitting resulting in low peak intensity, and susceptibility of phosphoryl groups to reduction. A novel solid nitron, 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide (BMPO), was reported by Kalyanaraman et al.¹ Since BMPO is solid, it offers some advantages such as ease of purification thus preventing co-distillation of nitroxide impurities. An improved synthesis of the nitron BMPO that allows direct conversion of the aldehyde to nitron without dioxalane synthesis will be presented. Although the synthesis and biochemical application of BMPO has been reported, no kinetic studies of its stability has been done. The decay kinetics of BMPO-superoxyl radical was performed using O₂-riboflavin/light as the superoxyl radical source and decay was monitored using EPR spectroscopy. The decay of the BMPO-superoxyl adduct at pH 5.6, 7.0 and 8.2 were monitored giving first order rate constants ranging from 5.2×10^{-4} to $9.2 \times 10^{-4} \text{ s}^{-1}$ comparable to that of DEPMPO of $3.8\text{-}11.0 \times 10^{-4} \text{ s}^{-1}$. The decay kinetics was analyzed using a decay rate equation containing first and second order terms. Half-lives of the superoxyl adducts at various pH were calculated and found to be 1265s, 910s, and 850s at pH 5.6, 7.0 and 8.2, respectively. These half-lives show that BMPO-superoxyl adduct has comparable stability to DEPMPO in aqueous media. Spin adduct stability in organic solvents and biological conditions will also be presented.

[1]. Kalayanaraman, B. et al., Free Rad. Biol. Med. 2001, 31, 599-606.