EPR characterization of the hetero-atom radical adducts of DEPMPO and DMPO: Nitrogen Centered radicals.

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In order to develop the spin trapping technique for the detection of N-centered radicals, two well-known spin traps, DMPO (5,5'-dimethyl-1-pyrroline 1-oxide) and DEPMPO (5-diethoxy-phosphoryl-5-methyl-1-pryyoline N-oxide) which are widely used for the active oxygen trapping, have been applied for the detection of chemically generated N-centered radicals in aqueous solutions. Detection and identification of N-radicals produced in the catalytic reaction of enzymes often provides decisive evidences for the competence of the system, e.g. direct catch of NO from Nitrogen Oxide Synthase. To date, very few studies have been reported for the N-radical trapping with nitron spin traps in physiological conditions. Examined N-radicals are nitrogen monoxide generated from nitrite by the dithionite reduction and simple alkyl aminyl radicals derive from oxidation of alkyl amines. Both DMPO and DEPMPO yielded stable NO adducts. EPR spectra of the produced nitroxides did not show the hyperfine splitting due to the nitrogen nuclei of trapped radicals (a-$N_?$) as confirmed by ^{15}NO trapping. EPR spectrum of NO-DEPMPO exhibited extra hf splitting (0.42 gauss, 6H) but NO-DMPO did not. Among prim-, sec-, and tert-methyl and ethyl amines, only dimethylamine yielded N-radical adducts both with DMPO and DEPMPO as a single product. Ethyl amine also provided N-radical adduct as a major product. These N-adducts showed obvious $N_?$ splitting (1.8-2 gauss) discriminating from the NO adducts. In addition, the alkyl aminyl adducts were more unstable than NO adduct. The magnitude of both a-N and a-$H_?$ of the nitroxide from N-radical adducts with DMPO and $H_?$ of the DEPMPO adducts falls between those of oxygen-centered radical adducts and carbon-centered radical adducts.