

# Spin trapping of superoxide and peroxy radicals with 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline N-oxide (DEPMPO). Characterization of the high-resolution ESR spectra

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It has been previously reported that spin trap 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline N-oxide (DEPMPO) can form stable radical adducts with superoxide and peroxy radicals. However, the presence of two diastereomers of DEPMPO radical adducts complicates the interpretation of the ESR spectra. Moreover, conformational exchange between conformers with slightly different phosphorus couplings has been suggested to cause line-width alternation in the ESR spectra of DEPMPO radical adducts. In this work we have studied high-resolution ESR spectra of superoxide and peroxy radical adducts. Subtraction of ESR spectra at different time points revealed a superoxide-derived decomposition product without a beta-hydrogen, which has a six-line superhyperfine structure had been previously assigned as part of the DEPMPO/OOH spectrum. Formation of this decomposition product was studied utilizing nucleophilic synthesis of DMPO, TMPO and DEPMPO radical adducts. One of the products of DEPMPO nucleophilic synthesis revealed identical superhyperfine structure as the decomposition product of DEPMPO/OOH. DMPO formed a product with similar ESR spectrum as decomposition product of DEPMPO/OOH, while TMPO did not. Thus, g- protons at the 3rd position are likely to be involved in the formation of the decomposition product. Therefore, ESR spectra previously assigned to DEPMPO/OOH consist of two diastereomers of DEPMPO/OOH and its decomposition product and can be simulated as 3-species. We have examined formation of DEPMPO radical adducts with tert-butyl, ethyl and cumyl peroxy radicals. In contrast to DMPO, adducts of DEPMPO with organic peroxy radicals were sufficiently stable to be detected at room temperature. ESR spectra of DEPMPO/OOR were simulated similar to DEPMPO/OOH as a combination of two diastereomers of DEPMPO radical adduct and its decomposition product with superhyperfine structure. It is important to note that the superhyperfine structure of DEPMPO/OOR ESR spectra depend on peroxy radical, which may provide information about the structure of trapped peroxy radical. It was shown that DEPMPO/OOR were not as stable as DEPMPO/OOH decomposing to corresponding DEPMPO/OR radical adducts. We have studied the role of conformational exchange in line-width alternation in the ESR spectra of DEPMPO/OOH and DMPO/OOH radical adducts. Asymmetric shape of the DMPO/OOH ESR spectrum at 4 C revealed presence of two conformers, while at 67 C fast exchange collapses the different hyperfine coupling constants, which resulted in symmetrical ESR spectrum. Variation of temperature affected hyperfine-coupling constants of one b- and one g- protons of DEPMPO/OOH similar to DMPO/OOH. At the same time it did not affect superhyperfine structure of DEPMPO/OOH ESR spectra, which implies that superhyperfine structure of DEPMPO/OOH ESR spectra does not result from conformational exchange as it was previously suggested. Therefore, the interpretation of ESR spectra from the spin trapping of superoxide and peroxy radicals by DEPMPO requires the inclusion of a nitroxide decomposition product.