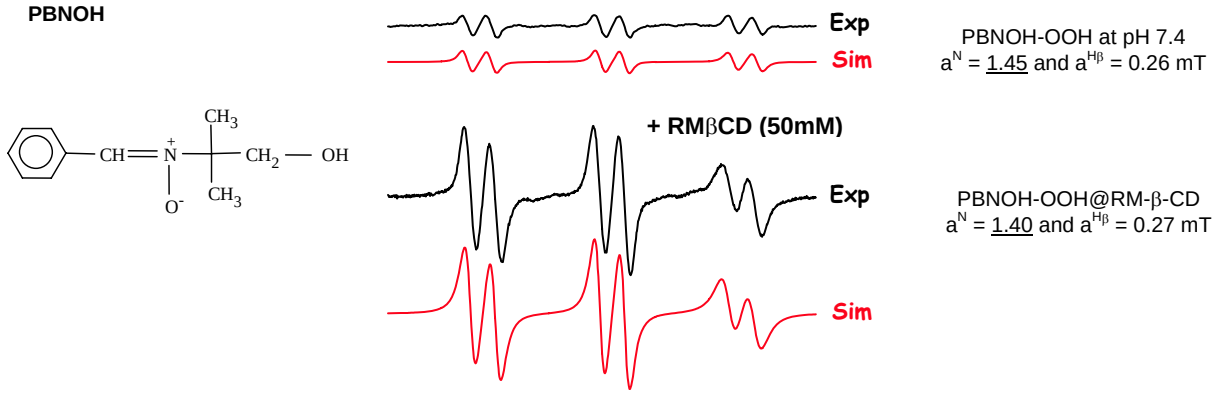
Use of Cyclodextrins in ESR-Spin Trapping Experiments of Superoxide

Hakim Karoui,[a] David Bardelang,[a] Antal Rockenbauer,[b] Jean-Pierre Finet [a] and Paul Tordo [a]

[a]Laboratoire SREP, UMR "Chimie, Biologie et Radicaux Libres" CNRS 6517, Faculté des Sciences de Saint-Jérôme, Université de Provence, Marseille, France
[b]Chemical Research Center, Institute for Chemistry, H-125 Budapest, PO Box 17 Hungary. *E-mail:* hakim.karoui@up.univ-mrs.fr

Cyclodextrins are versatile biocompatible macrocycles based on 1,4-glucopyranose units with a truncated cone shape, which present outside hydrophilic sites and an inside hydrophobic cavity allowing the complexation of a wide variety of compounds in aqueous solution including stable nitroxides.[1]

We used DMPO, DEPMPO and PBN to trap superoxide in the presence of methylated β-cyclodextrins.[2] The presence of β-cylodextrins greatly stabilizes the PBN-superoxide spin adduct which is usually hardly detected.[2b] The same phenomenon was observed with PBN analogues, DEPMPO,[2a] EMPO and DMPO-superoxide spin adducts. PBN- and DEPMPO-superoxide adducts were partially protected against L-ascorbate monoanion reduction.[2,3] In order to design the best candidate (spin trap – cyclodextrin) for our ESR spin trapping experiments, we studied the parameters concerning the associations' cyclodextrins-spin traps and cyclodextrins-nitroxides. The interactions between the simple linear traps (nitrones) and DM-β-CD were studied by NMR techniques to determine the stoechiometry. Binding constants were further evaluated by using ^{1}H NMR titrations. Secondly, ESR-spin trapping titrations in the presence of increasing cyclodextrin concentrations provided specifically spectral changes. Data from ESR titrations were analyzed by a novel two dimensional-ESR simulation program to afford stoechiometry and binding constants of the spin adduct@cyclodextrin systems. All the studied spin traps as well as spin adducts form inclusion complexes with DM- and RM-β-CD. All the spin trap@cyclodextrin complexes presented a 1:1 stoechiometry. Most of all the nitroxides could form 1:1 and 1:2 complexes depending on the nitroxide structure and the cyclodextrin concentration. Superoxide spin adduct ESR signal intensity depended on the nitrone-cyclodextrin association. Based on the different results we got, we studied the complexation of various stable nitroxides with different β-CD and prepared covalent nitroxide and nitrone-β-CD.



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