MULTIFREQUENCY ELECTRON PARAMAGNETIC RESONANCE MEASUREMENTS OF ORGANIC RADICALS IN THE PRESENCE OF METAL IONS

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Introduction

Carotenoids (C_{48}H_{36}) appear to be intermediate electron carriers in the reduction of the photosystem II primary electron donor P680(+). Carotenoid radical cations and dications formed during the process greatly facilitate subsequent carotenoid isomerization which is dependent on the surrounding matrix. Studies of the electron transfer efficiency for carotenoids in metal substituted (Fe, Ni, Mn, Cu), MCM-41 molecular sieves required electron paramagnetic resonance measurements at high fields (3.8 T to 23.3 T or 109 GHz to 670 GHz EPR (EMR) frequencies) and pulsed measurements at 9 GHz. The radical species formed in the reactions of heme proteins with hydroperoxides is of interest in elucidating the origin of the lipid peroxidation and the structural perturbations of proteins. The location of the peroxyl radical in oxidized horse heart myoglobin has been identified by use of multifrequency EPR spectroscopy.

Experimental

The 95-287 GHz EPR measurements were carried out at the NHMFL Lab in Tallahassee, FL using the 15 T Oxford Instruments superconducting magnet. Since the spectrometer was operated in a single-pass transmission mode without a resonator, similar sized quartz samples (4 mm) could be measured at all frequencies. The 356 GHz to 670 GHz measurements were carried out on an in-house constructed spectrometer which used a far - infrared laser as the microwave source and a resistive bitter-type Keck magnet which can reach a maximum magnetic field of 25 T. Pulsed EPR measurements of predeuterated β-carotene were obtained at 9 GHz using a Bruker ELEXSYS E580 FT/CW pulse X-band spectrometer with a (0.01 - 1T) electromagnet.

Results and Discussion

The pulsed EPR measurements (ESEEM) showed that the Cu^{2+} coordination in MCM-41 most likely occurs at the 15, 15' carbon of β-carotene at a distance of 2.8 Å from the center of the C=C double bond. This is an unusually short distance when compared to distances reported for smaller molecules. For instance, ethylene is coordinated in MCM-41 at distances of 3.8 Å. Variable high frequency EPR measurements (95, 181, 282, 356, 416, 502, 516 and 630 GHz) showed that electron transfer occurs from the carotenoid to Mn(II) but not to the Mn clusters formed in MnMCM-41. The broad powder Mn EPR signal observed at 282 GHz resolved into a cylindrical powder pattern at 416 GHz. The exchange-coupled oxoferryl-protein radical pair exhibited g values of 2.0356, 2.0083 and 2.0024, and a dipolar coupling corresponding to a distance of 8.3 Å between the protein and the oxoferryl iron. The peroxyl radical location appears to be at the Tyrosine residue at position 146 in oxidized myoglobin.

Conclusions

High field EPR measurements (> 95 GHz) are critical for the identification of radical species and their location in systems containing high spin metal ions such as Fe(III), Ni(II), Ni(I), Mn(II). The availability of high field EPR measurements have made it possible to study metal clusters, metal centers distant to a spin = 1/2 system and to detect the presence of high spin systems in catalysis.

Acknowledgements

The Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Science, Office of Science, U. S. Department of Energy, and the NSF Instrumentation Programs are thanked for financial support.