

Time-Resolved EPR Spectroscopy in the Q-Band Microwave Region.

2. Magnetic Field Effects on CIDEP in Radicals, Biradicals, and Spin-Correlated Radical Pairs*

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Investigations of chemically induced dynamic electron spin polarization (CIDEP) in free radical, biradical, and spin-correlated radical pair electron paramagnetic resonance (EPR) spectra at two microwave frequencies are reported. Time-resolved EPR spectra in both organic and aqueous solutions were obtained at X-band (9.5 GHz) and at Q-band (35 GHz). Comparison of CIDEP patterns at the two frequencies shows that the external magnetic field greatly influences both the shape and the time evolution of the EPR spectra. Hydrogen atom abstraction in the acetone/2-propanol system, and Norrish I α -cleavage of several alkyl and benzyl ketones are used to give examples of these unusual effects in doublet state spectra of radical pairs. Acyl-alkyl and bis(alkyl) biradicals from the cleavage of 2,2,12,12-tetramethylcyclododecanone show dramatic magnetic field effects in their EPR spectra, the former from the large g -factor difference between the radical centers, and the latter due to field dependent state-mixing of singlet and triplet sub-levels. A spin-correlated radical pair, obtained via the abstraction of hydrogen atoms by benzophenone- d_{10} triplet from the alkyl chain interior of a sodium dodecyl sulfate (SDS) micelle, also exhibits minor magnetic field effects. Aqueous solution and variable temperature flow TREPR spectroscopy at Q-band are described.

Es wird über chemisch induzierte dynamische Elektronenspinpolarisation (CIDEP) von freien Radikalen, Biradikalen, und spinkorrelierten Radikalpaaren berichtet, die mit ESR-Spektroskopie bei zwei verschiedenen Mikrowellenfrequenzen untersucht wurde. Zeitaufgelöste ESR-Spektren in organischen wie wäßrigen Lösungen wurden sowohl im X-Band (9.5 GHz) wie im Q-band (35 GHz) erhalten. Ein Vergleich der CIDEP-Muster bei den beiden Frequenzen zeigt, daß das externe Magnetfeld sowohl die spektrale Intensitätsverteilung der ESR-Spektren wie auch ihre Zeitentwicklung stark beeinflußt. H-Atom-Abstraktion im Aceton/Isopropanol-System und Norrish I α -Spaltung einiger

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