Reaction Kinetics Studied Via EPR

Photostability is important for taste stability in many foods and beverages. Using spin trapping, at least 3 photochemical products are identified upon UV irradiation of a hop extract by using the SpinFit simulation module. A field vs. time experiment coupled with the SpinCount module for concentration measurement offers the food scientist insights into extending the shelf-life of such ingredients.

Introduction

The world is a very dynamic place, never in equilibrium. Much of these dynamics are chemical reactions involving the transfer of one electron. Each electron transfer results in an unpaired electron creating paramagnetic free radicals. EPR (Electron Paramagnetic Resonance) is the ideal spectroscopic technique to measure these species as well as to monitor the time behavior of their creation and disappearance. EPR solely has the ability to detect free radicals unambiguously.

These radicals and the reactions in which they are involved are very important in many different fields such as:

- Enzyme Reactions
- Oxidative Stability of Foods and Beverages
- Materials such as Polymers and Paints
- Photochemistry
- Catalysis
- Electrochemistry
- Redox Chemistry
- Reactive Oxygen Species
- Antioxidants

Challenge

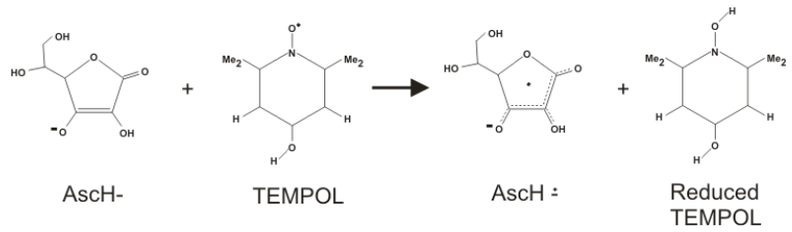
Transient species are short-lived which makes their detection challenging. Spectral overlap between different radical signals is frequently a major problem.

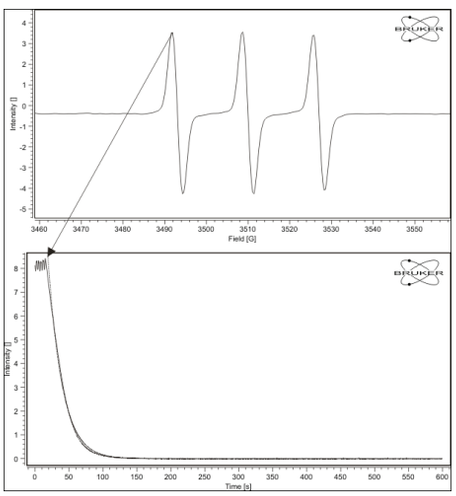
Solution

Two methods of monitoring and quantifying short-lived radical species are directly recording the EPR spectrum with fast field sweeps or indirectly detecting the species through their reactions with an added EPR visible probe. For direct detection, simulation and fitting of the EPR spectrum aides in the identification and quantification of the radical species. For indirect detection, fast acquisition schemes where the signal is monitored as a function of time are critical for kinetic studies.

Equipment

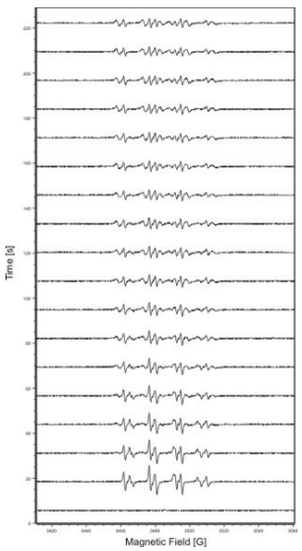
The EMXnano spectrometer ensures high precision results with superior sensitivity thus enabling researchers and students with limited EPR experience to use the power of EPR spectroscopy to identify and monitor reactions rates of free radical reactions in many fields of study.

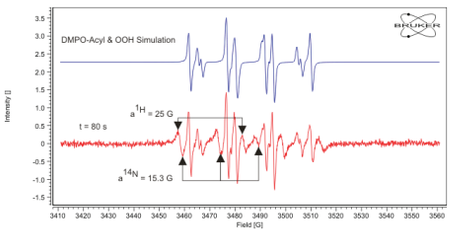


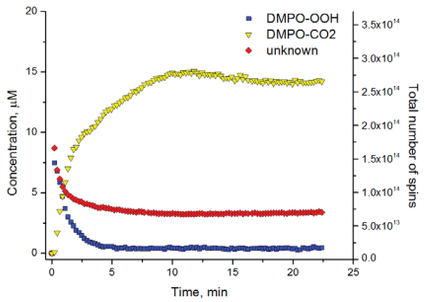


- Experimental data of the reduction of the nitroxide TEMPOL by ascorbate (vitamin C).
- Antioxidants such as Vitamin C are important in neutralizing dangerous free radicals in living things and kinetics indicates their effectiveness.

- Experimental data from irradiating a hop extract (used in beer brewing) with the spin trap DMPO using the UV lamp accessory.
- Photochemistry and photophysics cause the flavor to go bad in the presence of light.
- Three species (THAA (Tetrahydroiso-alpha-acids), superoxide, and an unknown radical) can be monitored simultaneously as a function of time and their concentration can be individually determined.







Key Features include:

- Easy-to-use software
- 1D Time sweep experiments to monitor the kinetics of a single species
- 2D EPR field vs. time experiments to monitor the kinetics of multiple species
- Fitting routines to analyze kinetics
- SpinFit module to simulate and identify multiple radicals in the sample
- SpinCount module to quantify the total number of spins and to determine the radical concentration

- Simulate the multiple DMPO radical adducts using SpinFit and the spin trap database.
- SpinCount provides a report of the fit species concentrations during the time course of the experiment.
- The report can be saved as an ASCII file for further evaluation.

References for further reading

1. Mark W. Ruszczycky, Sei-hyun Choi, and Hung-wen Liu, PNAS, Vol. 110(6), 2088-2093, (2013) EPR-kinetic isotope effect study of the mechanism of radical-mediated dehydrogenation of an alcohol by the radical SAM enzyme DesII
2. Wibke Meiser, Michael Buback and Alana Sidoruk, Macromolecular Chemistry and Physics,Volume 214(18), 2108–2114, (2013) EPR Investigations into the Kinetics of Trithiocarbonate-Mediated RAFT-Polymerization of Butyl Acrylate
3. Sergey I. Dikalov, Igor A. Kirilyuk, Maxim Voinov, and Igor A. Grigor'ev Free Radic Res., 45(4): 417–430 (2011) EPR Detection of Cellular and Mitochondrial Superoxide Using Cyclic Hydroxylamines

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