ELECTRON PARAMAGNETIC RESONANCE IMAGING OF ELECTROCHEMICALLY GENERATED p-PHENYLENEDIAMINE RADICALS

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Abstract Two-dimensional spectral-spatial electron paramagnetic resonance (EPR) imaging was used to measure the spatial distribution of p-phenylenediamine radicals that were generated electrochemically in the EPR cavity. The multi-line EPR spectrum obtained from a spectral slice through the image was in good agreement with the non-gradient spectrum. A spatial slice showed that the radicals were localized in the vicinity of the working electrode.

Key words electron paramagnetic resonance, spectral-spatial imaging, electrochemistry, p-phenylenediamine

Electron paramagnetic resonance (EPR) imaging permits determination of the spatial distribution of paramagnetic species [1]. In a two-dimensional spectral-spatial EPR image, the full hyperfine EPR spectrum is displayed as a function of one spatial dimension. In the spectral-spatial plane the angle $\alpha = 0^\circ$ is defined as zero gradient and $\alpha = +90^\circ$ is defined as infinitely large gradient [4,6]. The length of the spatial axis of an image, L , is related to the length of the spectral axis (ΔH), the maximum angle at which data are collected ($\alpha_{\max}$), and the maximum gradient ($G_{\max}$) by equation (1)

$$L = \tan(\alpha_{\max})\Delta H/G_{\max} \quad (1)$$

The magnetic field sweep width at a projection angle α is given by equation (2)

$$\text{sweep width} = \sqrt{2}\Delta H/\cos(\alpha) \quad (2)$$

An incomplete set of projections can be used to maximize the spatial resolution of the image for a particular combination of maximum gradient available and desired spectral window [4,6]. The "missing" projections are estimated iteratively.

Two-dimensional spectral-spatial EPR imaging in conjunction with electrochemical generation of radicals has been used to demonstrate the simultaneous production of different radicals at the working and reference electrodes [2] and the production of p-benzosemiquinone from hydroquinone in a two-step process in which the hydroquinone is first oxidized to quinone and then reduced to the semiquinone [3]. In these examples the EPR spectra consisted of at most 5 hyperfine lines. Typical computer-collected EPR data use between 1024 and 4096 data points to define a spectrum. In EPR images there usually are less than 1024 points per projection and less than 1024 projections per data set. Indeed, a data set with 256 points per projection and 128 projections is large by recent EPR imaging standards. It is therefore important to examine the how much information is retained in spectral slices obtained from spectral-spatial images of radicals with multiple hyperfine lines.

EXPERIMENTAL

Apparatus The electrochemical cell that was used for these experiments had internal dimensions 3.5 x 1.0 x 0.4 cm. It was oriented in the cavity with the 1.0-cm dimension along the direction of the external magnetic field,

which is also the direction along which the magnetic field gradient was generated. The working and auxiliary electrodes were 0.25 mm diameter Pt wires. The reference electrode was 0.1 mm diameter Ag wire. The distances between the working and reference electrode and the reference and auxiliary electrodes was about 4 mm, which gave a distance between the working and auxiliary electrodes of about 8 mm. Electrodes were repositioned in the cell for each measurement, which caused some variability in the distances between the electrodes. The electrochemistry was controlled with a Bioanalytical Systems CV-27 Instrument. The oxidation potential for ferrocene in DMF in this cell was 0.96 V. A slow purge of nitrogen gas was used to avoid oxygen broadening of the EPR spectra and to increase the lifetime of the radicals.

EPR spectra were recorded on a Varian E9 spectrometer. The experimental conditions for data collection were 9.480 GHz, 5 mW microwave power, 0.63 G modulation amplitude, 100 kHz modulation frequency, 5.0×10^3 gain, 0.008 sec time constant and 20 second scan time. The magnetic field gradients were generated with a Hewlett Packard HP6010A power supply and anti-Helmholtz coils mounted on the magnetic pole faces as described previously [4]. A current of 4 amps generated a gradient of 400 G/cm, which was the maximum gradient used in these experiments. Gradient control and magnetic field sweeps were performed with a VAXstation II and Stanford Research SR245 computer interface.

Reagents p-Phenylenediamine was decolorized twice with carbon black, recrystallized twice from water, and then sublimed in vacuum. The melting point of the purified material was 137°C (lit. 140°C [5]). Dimethylformamide (DMF) was distilled prior to use. The DMF solutions that were used in the imaging experiments were 0.2 M in tetraethylammonium perchlorate supporting electrolyte and 10 mM in p-phenylenediamine. Freshly prepared solutions were used for the measurements. The average concentration of radicals in the cell was substantially less than 1 mM, as judged from the intensity of the EPR signals, although as illustrated below, there was a concentration gradient in the cell.

Fig. 1. Spectral-spatial EPR image of p-phenylenediamine cation radicals generated electrochemically. The image was reconstructed iteratively from 120 experimental and 8 "missing" projections on a 256 x 256 grid. The maximum gradient was 400 G/cm. The ridges that run vertically through the image are due to changes in the radical concentration during the time required for data collection.

Fig. 2. A) Spatial slice through the image in Fig. 1, which displays the spatial distribution of radicals. B) First derivative of a spectral slice through the image shown in Fig. 1 at a spatial location in the vicinity of the working electrode. C) EPR spectrum of sample that was used in the EPR imaging experiment, defined by 256 data points.

Procedure p-Phenylenediamine was oxidized at the working electrode at a potential of 0.87 V. The potential was applied for about 10 minutes prior to the start of data collection to achieve a steady-state distribution of radicals in the cell. To permit time for heat removal from the gradient coils, which are heat-sunked to the poles of the magnet, there is a variable waiting time between scans. The longest wait occurs after the highest gradient scans. The waiting time added about 50% to the total experiment time. The data for each image consists of 120 experimental projections and 8 "missing" projections with 256 points/projection. Images were reconstructed on the VAXstation II with 5 cycles of the iterative algorithm [6] and a Hamming filter parameter of 0.9 for the first four iterations and 0.55 for the final iteration.

RESULTS AND DISCUSSION

A spectral-spatial image of the cation radicals generated by oxidation of p-phenylenediamine is shown in Fig. 1. To facilitate image reconstruction, the spectral dimension is presented as the absorption spectrum rather than the first-derivative display that is traditionally used in EPR. A spatial slice through the image at a magnetic field that corresponds to the peak of the central line in the EPR spectrum is shown in Fig. 2A. The EPR signal is localized predominantly in the vicinity of the working electrode and lower concentrations of radical are observed throughout the cell. The first derivative of a spectral slice through the image at a spatial location adjacent to the electrode is shown in Fig. 2B. An EPR spectrum collected with 256 data points and the same spectrometer operating parameters that were used to obtain the image is shown in Fig. 2C. There is good agreement between the slice from the image and the scan of the EPR spectrum. Both spectra give resolution of about half of the 75 lines that have been observed for p-phenylenediamine [7]. The data for the image and for the scan shown in Fig. 2C were obtained with a modulation amplitude of 0.63 G. The large modulation amplitude was used to deliberately broaden the EPR lines such that the line widths were greater than the sampling interval in the lowest-gradient spectra used to obtain the image. If this criterion is not satisfied, sharp lines would not be adequately sampled in the low-gradient projections and the spectral dimension of the image would be distorted. This compromise between various spectral distortion mechanisms is inherent in the imaging spectroscopy process.

CONCLUSION

Samples containing radicals with multiple hyperfine lines can be successfully imaged with EPR spectral-spatial imaging provided that care is taken such that the linewidths of the lines are at least as great as the sampling interval in the projections.

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