UV/EPR Spectrosopy of Imidazolyl and Phenoxyl Radicals.

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Photooxidation of imidazole, phenol, and their cross-linked compounds were investigated using optical absorption/EPR spectroscopy in an effort to characterize effects of substitution on electronic properties of radicals. Photooxidation was carried out in frozen glasses by light from a high-power D_2 lamp. Exponential global fitting analysis of absorption changes with exposure revealed the presence of several, often competing phases for all model compounds investigated.

Photooxidation of imidazole involved initial small changes in the 200-230 nm region, followed by development of a strong absorption band at ~250 nm and a weaker band at ~500 nm. This species was followed by two other species with a progressive red shift of major UV transition. EPR measurements at the time of maximal intensity at 250 nm revealed the presence of a paramagnetic species with a broad, multiline EPR spectrum.

Tyrosine and 4-imidazolyl-phenol (**4Im♦Ph**) showed similar kinetics: initial broad absorption phase at 600 nm was followed by a red shift of the dominant UV transition (by 35 and 65 nm, respectively) and formation of a new transition in the 410-430 nm region. Additional photoproducts followed for both compounds, typically exhibiting a further red shift in their spectra. Effect of imidazole moiety on spectral properties of **4Im♦Ph** in the ground state and the first photooxidized species was limited, in comparison to **Tyr**, to an overall ~20 nm red shift of its optical spectra and loss of hyperfine EPR structure from C_β protons.

Methylation of phenol oxygen in 4-imidazolyl-methoxyphenyl caused significant changes in the spectra of photooxidized species. Two forms were observed following typical broad 600 nm species, both exhibiting ~100 nm red shift of the 250 nm band—significantly larger than observed for **4Im♦Ph**. The first of these two species showed additional absorption at ~240 and 500 nm—positions seen upon oxidation of imidazole. EPR measurements confirmed the presence of an imidazole-based radical. EPR spectra appear to be contributed by two radical species: one virtually identical to isolated imidazole radicals and another similar to traditional phenol-type radical. Our results provide the first direct observation of imidazole radicals and stress the critical role of protons in controlling biological oxidation processes.