

Magnetic Resonance in Chemistry 2006 vol.44 N6, pages 594-605

Electron spin resonance study of radicals generated in cellulose/N- methylmorpholine solutions after flash photolysis at 77 K

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Abstract

The processes of radical formation in N-methylmorpholine-N-oxide monohydrate (NMMO) and cellulose/NMMO solutions were studied by ESR at 77 K under high-power UV ($\lambda = 248$ nm) excimer laser flash photolysis. Radicals mainly generated were attributed to the nitroxide type radicals $\text{-CH}_2\text{-NO}$, $\text{-CH}_2\text{-}$ and $\text{-CH}_2\text{-NO}$ -CH_3 at the first step and methyl .CH_3 and formyl .CHO radicals at the second step of the photoreaction. Kinetic studies of these radicals revealed that formation and recombination rates of the radicals depend on the cellulose concentration in cellulose/NMMO solutions and the concentration of additional ingredients, e.g. Fe(II) and propyl gallate. Even at frozen state temperature, acceleration or quenching of radical reaction processes was found. The proposed scheme of UV light-induced NMMO degradation during irradiation based on ESR data correlates well with independently obtained results based on high-performance liquid chromatography (HPLC). The analysis of degradation products by HPLC, e.g. aminoethanol and acetaldehyde, supports the assumption concerning a radical-initiated ring opening of NMMO. Copyright © 2006 John Wiley & Sons, Ltd.

<http://dx.doi.org/10.1002/mrc.1795>

Keywords

Aminiumyl radical, Cellulose, ESR, Flash photolysis, High-performance liquid chromatography (HPLC), N-methylmorpholine-N-oxide, Nitroxide radical, Radical kinetics