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The Detection of Oxalate Free Radicals by EPR Spin Trapping in the Photolysis of Tris(oxalato)iron(III)*

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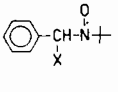
The complex $(phenH)_3[Fe(ox)_3]\cdot 5H_2O$ (phen = 1,10-phenanthroline; H_2ox = oxalic acid) was found to be photosensitive even in the solid state. The tris(1,10-phenanthroline)iron(II) complex is formed during the photolysis, but the mechanism of this reaction has remained obscure [1].

In order to get some information concerning the free radicals formed during the reaction we have carried out EPR spin trapping experiments, which are reported here.

Experimental

$(phenH)_3[Fe(ox)_3]\cdot 5H_2O$ has been prepared after Thomas *et al.* [1]. The spin trap phenyl-N-tert.butyl nitrone (*PBN*) was obtained by condensation of benzaldehyde with tert.butylhydroxylamine [2]. Powdered samples of $(phenH)_3[Fe(ox)_3]\cdot 5H_2O$ were placed in an EPR sample tube, and chloroform or benzene solutions of *PBN* were added. The solutions were deoxygenated by bubbling with nitrogen before irradiation. EPR spectra were recorded at room temperature with a JES-3BQ Jeol spectrometer during the irradiation with a HBO-200 high pressure mercury lamp (VEB Narva, Berlin).

TABLE I. *EPR* Parameters of Spin Adducts 

Species	X	Solvent	a_H (mT)	a_N (mT)
I	ox^-	$CHCl_3$	0.115 ± 0.015	1.415 ± 0.015
II	CO_2^-	$CHCl_3$	0.230 ± 0.015	1.443 ± 0.017
I	ox^-	C_6H_6	Not determined	
II	CO_2^-	C_6H_6	0.229 ± 0.015	1.398 ± 0.015

Results

EPR spectra of two nitroxide radicals (see Table I) could be detected. The β-hydrogen hyperfine splitting is much lower than for alkyl spin adducts. It is assumed that these nitroxides are formed by the addition of oxalate (species I) and formate radical (species II) to *PBN*, respectively. Furthermore a dependence of the relative signal intensity of the two radicals upon the concentration of the spin trap was observed. At low *PBN* concentration the species II is the only radical observed. In chloroform solution at very high concentrations of *PBN* (*ca.* 1 *M*) the signal intensity of II decreased and the species I became predominant. In benzene solution even at high *PBN* concentrations the signal of II is much more intensive than that of I. This is probably due to the trapping of oxalate radicals by benzene. So the hyperfine splitting of I could not have been determined in this solvent.

From these spin trapping experiments it can be concluded that oxalate free radicals are (probably) the primary products in the photolysis of $[Fe(ox)_3]^{3-}$, whereas the formate radicals are formed in a secondary reaction.

References

1 Ph. Thomas, M. Benedix, and H. Hennig, *Z. Chem.*, *17,* 114 (1977).
2 W. Rundel, Houben-Weyl, Georg-Thieme-Verlag Stuttgart (1968) Bd. X/4.

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