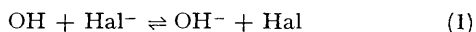


ClOH⁻ Radical: Electron Spin Resonance Evidence from γ -Irradiated Barium Chloride Hydrate

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KINETIC and spectroscopic studies of irradiated aqueous solutions have shown that hydroxy-radicals are important intermediates¹ and that, in the presence of halide ions (Hal⁻), a reaction of the following type occurs^{2,3}



Anbar and Thomas³ and Raef,⁴ in order to explain certain kinetic features have tentatively postulated the formation of the species HalOH⁻ as an intermediate in reaction (1), but no spectroscopic evidence has so far been reported.

We have detected two radicals in γ -irradiated BaCl₂·2H₂O, the less thermally stable being a normal Cl₂⁻ ion and the other being a radical having e.s.r. properties in accord with the formulation ClOH⁻. The data for both radicals are given in the Table and the similarity of the *g*- and ³⁵Cl-hyperfine tensors can be seen. That the isotropic

doublet is a result of hyperfine coupling to a proton was established by studying BaCl₂·2D₂O.

*E.s.r. parameters of Cl₂⁻ and ClOH⁻ found in γ -irradiated BaCl₂·2H₂O. (The *A*-tensor is in gauss.)*

	Cl ₂ ⁻	ClOH ⁻
<i>g</i> _L	2.0380	2.0174
<i>g</i>	2.0027	2.0053
<i>A</i> _L (³⁵ Cl)	ca. 9	16.4
<i>A</i> (³⁵ Cl)	100	58
<i>A</i> _L (H)		24.6
<i>A</i> (H)		25.0

We conclude that ClOH⁻ is a σ -radical of the same type as the *V*_K-centres and that the spin density is distributed to give about 0.4 on the chlorine atom. Hence the radical should have chemical properties similar to those of hydroxy-radicals, which was one of the requirements stipulated by Anbar and Thomas.³

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