$ClOH^-$ 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 intermediates[1] and that, in the presence of halide ions (Hal^-), a reaction of the following type occurs[2,3]

$$OH + Hal^- \rightleftharpoons OH^- + Hal \quad (1)$$

$$Hal + Hal^- \rightarrow Hal_2^- \quad (2)$$

Anbar and Thomas[3] 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 $BaCl_2,2H_2O$, the less thermally stable being a normal Cl_2^- 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 ^{35}Cl-hyperfine tensors can be seen. That the isotropic doublet is a result of hyperfine coupling to a proton was established by studying $BaCl_2,2D_2O$.

E.s.r. parameters of Cl_2^- *and* $ClOH^-$ *found in γ-irradiated* $BaCl_2,2H_2O$. (The *A*-tensor is in gauss.)

	Cl_2^-	$ClOH^-$
$g_\perp$	2·0380	2·0174
$g_\parallel$	2·0027	2·0053
$A_\perp(^{35}Cl)$	*ca.* 9	16·4
$A_\parallel(^{35}Cl)$	100	58
$A_\perp(H)$		24·6
$A_\parallel(H)$		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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