# Conversion of ·OH radicals into $O^-$ Ions on Cooling: A Radiation–E.s.r. Study

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*Summary* When hydroxyl radicals, formed in ice or various aqueous systems by ionizing radiation, are cooled from *ca.* 30 to 4 K they are extensively converted into $O^-$ ions, as judged by e.s.r. spectroscopy, the conversion being almost complete for ·OD in $D_2O$.

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SOME years ago we suggested a new interpretation for the e.s.r. spectrum of ·OH radicals trapped in ice crystals at 77 K.[1,2] We concluded that some librational averaging was occurring at this temperature, and confirmed this conclusion by showing that the predicted parameters were indeed obtained for ·OH radicals at *ca.* 15 K.[3] In this study, a weak low-field line grew on cooling which we thought at the time was probably due to a trace of some transition metal ion impurity.

Recently, Johnson and Moulton have demonstrated conclusively that this new line at $g = 2{\cdot}08$ is not due to an impurity and, therefore, must be due to radicals formed from water.[4] They suggested that $H_2O^+$ cations were responsible, but did not extract the principle values of the $g$-tensor nor did they detect any $^1H$ hyperfine coupling.

It seemed to me that $H_2O^+$ could not possibly be responsible for the 2·08 feature, because this implies a greater degree of orbital angular momentum than is exhibited by ·OH radicals in the same medium. As we have stressed previously[1,2] well-defined features relatively close to $g = 2$ can only be expected for ·OH radicals if the orbital degeneracy is strongly lifted by precise hydrogen bonding. However, $H_2O^+$ is a bent molecule with no orbital degeneracy and hence is expected to have $g$-values much closer to the free-spin $g$-value. This is indeed the case for a species thought to be $H_2O^+$ discussed previously,[5] and is also the case for the isoelectronic radical, $NH_2$.[6]

However, the conjugate base, $O^-$, has an enhanced degeneracy and hence could well be responsible. We detected this species some years ago in irradiated aqueous alkaline glasses,[7] and found $g_\perp \approx 2{\cdot}07$ and $g_\parallel = 2{\cdot}002$.

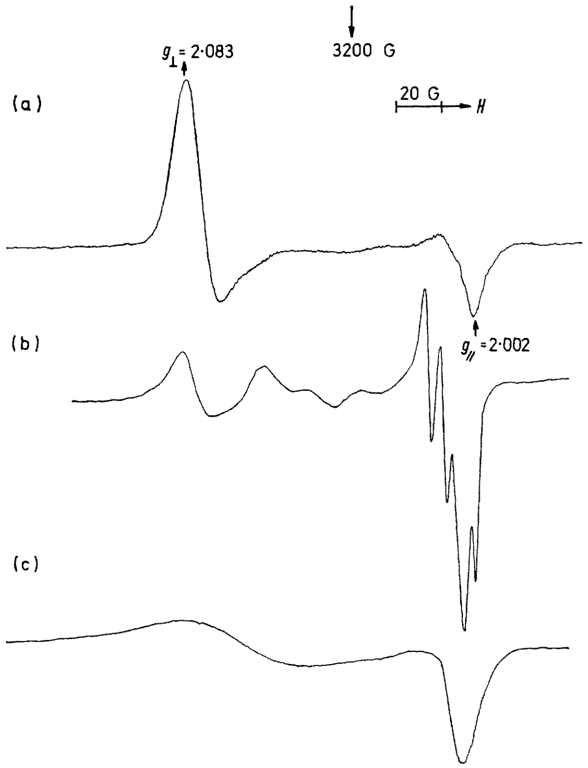

FIGURE. First derivative $X$-band e.s.r. spectra for (a) $\gamma$-irradiated ice ($D_2O$) at 4·2 K, showing features assigned to $O^-$ ions; (b) as (a) at 15 K, showing loss of ·$O^-$ features and gain of ·OD features, and (c) for aqueous KOH (*ca.* 8 M) at 4·2 K, showing features assigned to $O^-$ ions.

It therefore seemed worthwhile to measure the $g$-tensor components of the '$g = 2{\cdot}08$' species. Our results show that there is a clear interconversion between ·OH radicals and this new species with *ca.* 50% conversion at 4·2 K for

$H_2O$ However, for $D_2O$, the conversion was *ca* 80% Furthermore, •OH (•OD) radicals were saturated preferentially at high powers, such that only the features for the new species were resolved (Figure *a*) The form of this spectrum is very similar to that for $O^-$ ions in a $KOH/H_2O$ glass (Figure *c*), with $g_\perp = 2{\cdot}083$ and $g_\parallel = 2{\cdot}002$ I conclude firmly that the species is $O^-$, presumably formed by the equilibrium (1)

$$\cdot OH + H_2O \rightleftharpoons O^- + H_3O^+ \qquad (1)$$

This reaction is not a special property of ice crystals since very similar results were obtained for •OH radicals in a clear glass of $H_2O + MgCO_3$ and also for •OH in $CaSO_4{\cdot}2H_2O$ Proton acceptors are clearly necessary, since •OH radicals in irradiated $AuCl_4{\cdot}H_2O$ crystals showed no sign of conversion into $O^-$ at 4·2 K The fact that $g_x = g_y$ is also significant, since it implies remarkably selective hydrogen bonding The fact that the perpendicular features are far narrower than those for $O^-$ in aqueous KOH confirms that hydrogen bonding is precise, and a further decrease in width for $O^-$ in $D_2O$ confirms that hydrogen bonding is extensive

This is a novel result of some significance It means that the effective p$K_a$ of •OH radicals must fall markedly from its room temperature value on cooling, but it is not clear why this should be I suggest tentatively that it is to do with contraction on cooling This shortens the average hydrogen bond lengths to •OH and hence leads to an increase in hydrogen bond strength Thus the bonds to oxygen become stronger and hence favour $O^-$ formation, and also the •OH - - - O bond becomes stronger, thus moving towards proton transfer Probably the $H_3O^+$ ion moves away from the $O^-$ site to some more favourable location by chain proton-transfer

(*Received*, 18*th April* 1980, *Com* 399 )

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