

## Initial fate of Hydrogen Atoms and Hydroxyl Radicals in the Radiolysis of Frozen Aqueous Solutions of Alkali Halides

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**Summary.** After exposure to  $^{60}\text{Co}$   $\gamma$ -rays, aqueous glasses containing sodium or potassium fluoride, chloride, bromide, or iodide gave e.s.r. spectra containing features characteristic of the radicals  $\text{H}\cdot$ ,  $\text{MH}^+$ ,  $\cdot\text{OH}$ , and  $\text{halOH}^-$ .

SOLVATED electrons, hydrogen atoms, and hydroxyl radicals are the chemically important initial intermediates in the radiolysis of fluid aqueous solutions. In considering subsequent reactions of these radicals with alkali halides, the

sulphate crystals,<sup>1</sup> the spectra being characterised by a 500 G proton doublet, each component being split into a quartet by coupling to the alkali metal nucleus having  $I = 3/2$ . We have also shown by e.s.r. that the radical  $\text{ClOH}^-$  is formed in irradiated  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,<sup>2</sup> and that  $\text{BrOH}^-$  and  $\text{IOH}^-$  can be detected in irradiated frozen aqueous solutions of bromides and iodides.<sup>3</sup>

Clear evidence for the radicals  $\text{NaH}^+$  and  $\text{KH}^+$  in addition to normal trapped hydrogen atoms has now been obtained

TABLE  
E.s.r. parameters for the  $(\text{Na}^+ \dots \text{H})$ ,  $(\text{K}^+ \dots \text{D})$  centres and  $\text{FOH}^-$  species

Radical	$g_{av}$	Alkali-metal/fluorine hyperfine tensor (G)			Hydrogen/deuterium hyperfine tensor (G)		
		$A_{11}$	$A_{\perp}$	$A_{iso}$	$A_{11}$	$A_{\perp}$	$A_{iso}$
H atoms in gas phase	2.0022						507.3
$(\text{Na}^+ \dots \text{H})$ in $\text{H}_2\text{O}^a$	2.002	21.2	14.0	16.4	513.1	510.7	511.5
$(\text{Na}^+ \dots \text{H})$ $(\text{BaSO}_4)^b$	2.001	21.4	15.1	17.2	513.2	510.7	511.5
$(\text{K}^+ \dots \text{D})$ in $\text{H}_2\text{O}^a$	2.002	8.7	5.0	6.9	79.2	78.7	78.9
$(\text{K}^+ \dots \text{H})$ $(\text{BaSO}_4)^b$	2.001		4.0				500
$\text{FOH}^-$	$g_{11} = 2.10$ $g_{\perp} = 2.007^a$	$A_z = 7$	$A_x = 33$ $A_y = 7.5$		$A_z \sim 0$	$A_x = -25$ $A_y = -40$	
$\cdot\text{OH}$	$g_{11} = 2.06$ $g_{\perp} = 2.007^c$				$A_z = 0 \pm 6$	$A_x = -26$ $A_y = -44$	

<sup>a</sup> This work. <sup>b</sup> Ref. 1. <sup>c</sup> J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, and D. O. Williams, *J. Chem. Soc. (A)*, 1969, 791.

species  $\text{halOH}^-$  are rarely considered and have not been detected directly, and, so far as we know, the species  $\text{MH}^+$  have never been considered. We have previously shown that  $\text{NaH}^+$  and  $\text{KH}^+$  can be detected by e.s.r. in doped barium

in frozen glasses containing molar quantities of sodium and potassium salts. The derived data are given in the Table. In addition, improved e.s.r. spectra for  $\text{BrOH}^-$  and  $\text{IOH}^-$  have been obtained, together with good evidence for the

formation of  $\text{ClOH}^-$  and  $\text{FOH}^-$  in irradiated aqueous glasses containing chlorides and fluorides.

The  $\text{MH}^+$  species seem to have about the same stability as normal trapped hydrogen atoms, judging by their relative rates of decay on annealing. Thus they probably have only a subtle mechanistic significance in fluid solutions. However, the hydroxyl radical-halide ion adducts seem to have fair stability, and except for fluoride, the e.s.r. results show that there is considerable delocalisation of the unpaired electron in the halogen-oxygen  $\sigma^*$  orbital. The

results for  $\text{FOH}^-$  show that this species differs markedly from the remainder since its e.s.r. spectrum closely resembles that for normally trapped hydroxyl radicals (Table). This suggests that little or no extra stabilisation results in this case.

All these irradiated glasses were intensely blue or purple, indicating the presence of trapped electrons. The spectra and properties of these species are currently being studied.

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<sup>1</sup> M. B. D. Bloom, R. S. Eachus, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1971, 833.

<sup>2</sup> R. C. Catton and M. C. R. Symons, *J. Chem. Soc. (A)*, 1969, 446.

<sup>3</sup> I. Marov and M. C. R. Symons, *J. Chem. Soc. (A)*, 1971, 201.