Unstable Intermediates. Part CV.[1] Radiolysis of Frozen Aqueous Solutions of Alkali-metal Halides: Electron Spin Resonance Spectra for MH^+ and $HalOH^-$

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Exposure of glassy aqueous solutions of alkali-metal halides to ^{60}Co γ-rays at 77 K gave species identified by their e.s.r. spectra as H•, MH^+, OH, $HalOH^-$, and Hal_2^-. The effect of gradual annealing is outlined and aspects of the damage mechanism discussed. The fact that H• is preferentially trapped by the metal cations whilst OH is trapped by the halide ions is rationalised in terms of the electronic structures of the resulting radicals.

THE main purpose of this and subsequent studies of aqueous solutions is to investigate reactions between the initial radiation products for water (e_t^-, H•, and •OH) and various substrates, particularly inorganic ions, using e.s.r. and u.v. spectroscopy. Much attention has recently been given to optical studies of fluid, aqueous solutions immediately following radiation pulses but, in general, it has not been possible to apply the more searching technique of e.s.r. to probe the nature and structure of the radical intermediates involved. This can be done, in principle, by using aqueous glasses at sufficiently low temperatures together with subsequent controlled heating.

In previous studies of this type, care has not always been taken to ensure that glassy materials were studied. This is a particularly important factor for aqueous solutions because of the strong tendency for water to give pure ice crystals on freezing with consequent phase separation. If this occurs then, in general, radiation damage results in e.s.r. spectra characteristic of the separate phases, and are not directly relevant to the present study. It is often not possible to gauge the occurrence of such phase separation by direct observation, and we have, therefore, devised various tests to detect phase separations. When these were positive, minimum concentrations of certain additives were included to assist in glass formation. These were chosen, as far as possible, so as to avoid unwanted side reactions.

In the present study, we have confined our attention to the alkali-metal halides. Of the species detected by e.s.r. spectroscopy, the hydrogen atom alkali-metal adducts MH^+ have previously been detected in irradiated barium sulphate crystals doped with alkali-metal ions.[2] The ion $ClOH^-$ was first detected in γ-irradiated $BaCl_2,2H_2O$,[3] and $BrOH^-$ and IOH^- have subsequently been reported.[4] It is significant that none of these species has been detected in pulse-radiolysis studies, but kinetic evidence for the involvement of $ClOH^-$ ions has been adduced.[5]

EXPERIMENTAL

The alkali-metal halide salts were Reagent grade and were used without further purification. Solutions of NaI, NaBr, KCl, and KF were prepared in water which had been doubly distilled from alkaline permanganate. Solution concentrations ranging from 2M to saturation level were prepared. In addition, aqueous solutions of the remaining potassium, sodium, and lithium halide salts were studied. Samples were also prepared in D_2O supplied by Koch–Light (99·7% D).

Tests for Glassification.—Samples containing low concentrations of Mn^{2+} were frozen in the form of beads and their e.s.r. spectra were obtained at 77 K. When phase separation occurred, a very broad single-line spectrum for Mn^{2+} was obtained. Samples which formed good glasses, *e.g.* aqueous solutions of LiI, LiBr, LiCl, and NaCl, gave well resolved Mn^{2+} spectra at 77 K.

Aqueous solutions were γ-irradiated at 77 K using a ^{60}Co Vickrad source (4 Mrad/h) to a total dose of 2 Mrad. All e.s.r. spectra were obtained on a Varian E.3 spectrometer. Annealing experiments were carried out by allowing samples to warm for fixed times and then re-cooling them to liquid-nitrogen temperature.

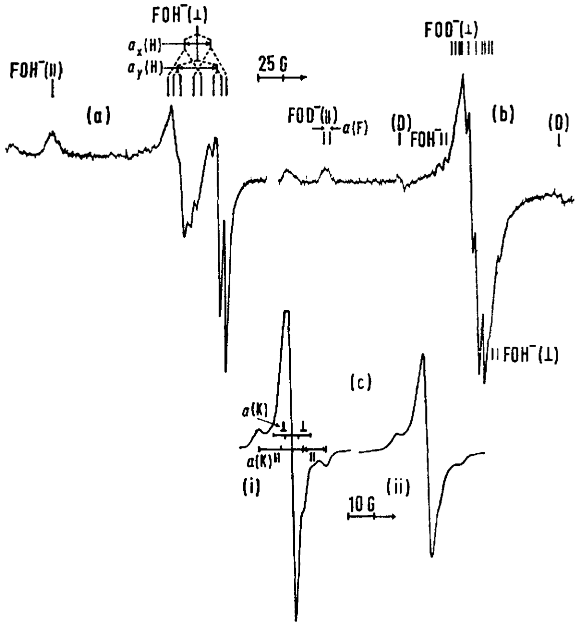

FIGURE 1 E.s.r. spectra of *a* FOH^- in γ-irradiated aqueous KF; *b* FOD^- from γ-irradiated KF in D_2O—extra features due to FOH^- and D• are marked; *c* $M_I = -1$ feature for the ($K^+ \cdots D$) centre formed in KF–D_2O—(i) 0·32 mW, (ii) 5·0 mW

RESULTS AND DISCUSSION

Results are summarised in the Tables 1 and 2, and typical spectra, with an indication of our analyses, are given in Figures 1—4. Only single lines in the normal

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[1] Part CIV, R. Catterall, I. Hurley, and M. C. R. Symons, preceding paper.

[2] M. B. D. Bloom, R. S. Eachus, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 833.

[3] R. C. Catton and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1969, 446.

[4] I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 201.

[5] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 3829.

TABLE 1

E.s.r. parameters for the ($Na^+ \cdots H$), ($K^+ \cdots D$) centres

		Alkali-metal hyperfine tensor (G)			Hydrogen–deuterium hyperfine tensor (G)		
Radical	g_{av}	$A_\parallel$	$A_\perp$	A_{iso}	$A_\parallel$	$A_\perp$	A_{iso}
H atoms in gas phase	2·0022						507·3
($Na^+ \cdots H$) in H_2O [a]	2·002	21·2	14·0	16·4	513·1	510·7	511·5
($Na^+ \cdots H$) ($BaSO_4$) [b]	2·001	21·4	15·1	17·2	513·2	510·7	511·5
($K^+ \cdots D$) in D_2O [a]	2·002	8·7	5·0	6·9	79·2	78·7	78·9
($K^+ \cdots H$) ($BaSO_4$) [b]	2·001		4·0				500
($F^- \cdots H$) (CaF_2) [c]	2·002	(^{19}F) 62·0	(^{19}F) 24·6				522·5

[a] This work. [b] Ref. 2. [c] Ref. 13.

TABLE 2

E.s.r. data for radicals formed in γ-irradiated aqueous solutions of alkali-metal halides at 77 K

	g-Tensor		Hyperfine tensor data (G)				Spin densities	
Radical	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	A_{iso}	$2B$	a^2s %	a^2p %
FOH^- [a]	2·1	2·009	A_z (^{19}F) = ±7 A_z (^1H) ~ 0	A_x (^{19}F) = 33 A_x (^1H) = −25 A_y (^{19}F) = ±7 A_y (^1H) = −40	15·8 6·4	17·2 ($A_\perp > 0$) 26·6 ($A_\perp < 0$)	0·09 0·04	1·6 2·5
•OH [d]	2·06	2·007	A_z (^1H) = 0 ± 6	A_x (^1H) = −26 A_y (^1H) = −44				
IOH^- [a]	1·98	2·13	517	70	172 [b,c]	345	2·4	76·2
IOH^- [e]	1·98	2·13	480	70	155	310	2·1	70·0
I_2^- [a]	1·93	2·18	418	120	155	263	2·1	58·1
I_2^- [e]	1·975	2·175	433	120	193	240	2·6	53·0
$BrOH^-$ [a]	2·00	2·08	(^{81}Br) 405	50	137	268	1·6	54·3
$BrOH^-$ [e]	2·00	2·08	425	50	142	283	1·7	57·3
Br_2^- [a]	1·99	2·09	469	85	194	275	2·3	55·5
Br_2^- [e]	1·98	2·09	470	85	195	275	2·3	55·5
Cl_2^- [a]	2·000	2·04	(^{35}Cl) 102	(^{35}Cl) 10	40·8	61·2	2·4	58·2
Cl_2^- [f]	2·0027	2·038	(^{35}Cl) 100	(^{35}Cl) 9	39·9	61·2	2·4	58·2
$ClOH^-$ [a]	2·004	2·017	(^{35}Cl) 59 (^1H) 25	(^{35}Cl) 16 (^1H) 25	9	50	0·5	48·0
$ClOH^-$ [f]	2·0054	2·0174	(^{35}Cl) 59 (^1H) 25·0	(^{35}Cl) 16·4 (^1H) 24·6	8·8	50·2	0·5	48·0

[a] This work. [b] Values corrected for orbital magnetism when necessary as indicated in ref. 4. [c] Refs. 8, 9. [d] $A_\parallel$ is always taken to be positive. The sign of $A_\perp$ is ambiguous, and reasons for choosing the signs given have been discussed in ref. 4. Ref. 4. [f] Ref. 3.

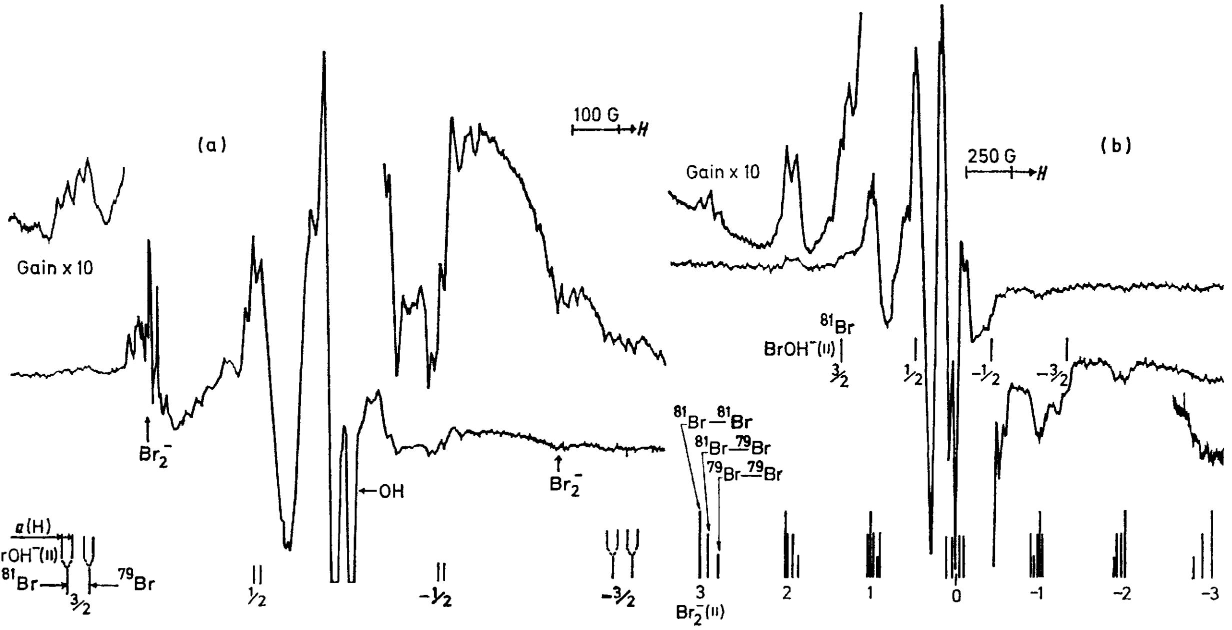

FIGURE 2 E.s.r. spectra of *a* $BrOH^-$ formed in γ-irradiated aqueous NaBr—the additional features are due to Br_2^- and •OH; *b* Br_2^- formed in same solution—the central features are obscured by •OH. The main parallel features are indicated in each spectrum

region for hydrogen atoms were detected in irradiated glasses containing Cs^+, and no hydrogen atoms were obtained from solutions containing ammonium ions. The features for MH^+ ions formed in solutions prepared from 90% D_2O were narrower and better resolved. Those associated with the $M_I = \pm 1$ lines for MD^+ ions were identical with those for MH^+. In general, the lowest possible power level was used (*ca.* 0·3 mW).

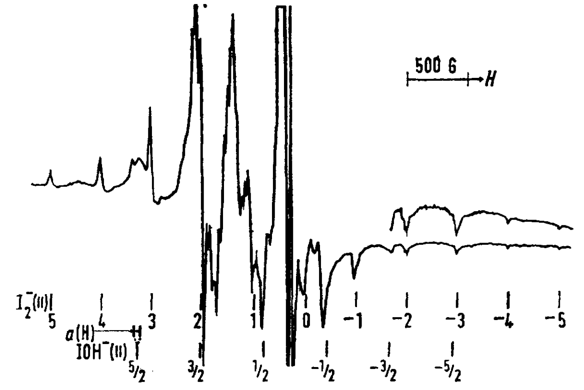

FIGURE 3 E.s.r. spectra of IOH^- and I_2^- in γ-irradiated aqueous NaI. The parallel features are marked

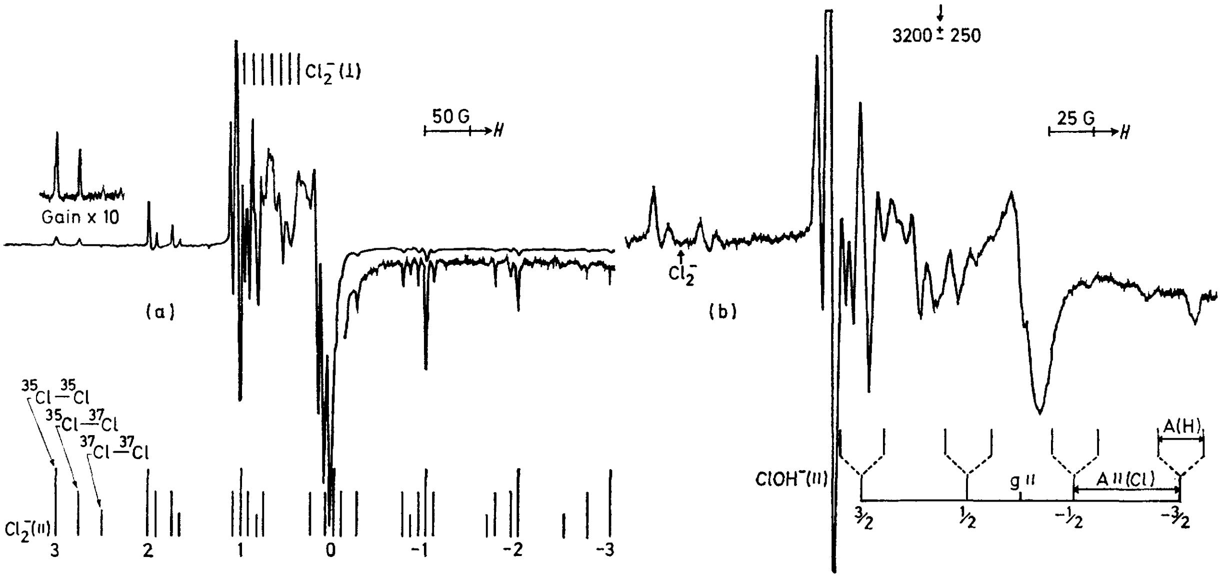

FIGURE 4 E.s.r. spectra of *a* Cl_2^- from γ-irradiated KCl in D_2O —central features are obscured by $\cdot OD$ spectrum; *b* $ClOH^-$ from KCl in 5M-KOH. The parallel features are indicated in each spectrum

Spectra assigned to Cl_2^-, Br_2^-, and I_2^- were all well resolved (*cf.* Figures 2—3) and normal in that both halogen atoms were strictly equivalent, in contrast with results sometimes obtained for these centres in crystalline halides.[3]

Spectra for IOH^- and $BrOH^-$ were better resolved than those previously reported,[4] and the parameters have been slightly revised (Table 2). Spectra for $ClOH^-$ were always largely masked by that for Cl_2^- under conditions which were varied as much as possible within the requirement that the solids were glasses. Indeed, identification of this species would have been impossible had we not known the regions in which strong features were to be expected from previous studies of $ClOH^-$ in $BaCl_2,2H_2O$.[3]

In contrast, no features for F_2^- were ever detected, whilst those assigned to FOH^- (Figure 1) were always strong. We do not understand why this difference was found.

Annealing.—Hydroxyl radicals were lost first in all cases, but we were unable to detect any concomitant increase in the concentration of the $HalOH^-$ ions because of changes in line widths and, in some cases, partial loss of signal strength for these species also. The $HalOH^-$ and Hal_2^- ions were lost at roughly comparable rates when they could be studied together. However, the MH^+ radicals were lost more readily than the ' normal ' trapped hydrogen atoms in all cases.

Electronic Structure.—The $HalOH^-$ ions, in general, resemble the V_K centres in having their unpaired electrons in σ* orbitals. Attention has already been drawn to various trends in computed spin-densities for these iso-structural species.[3,4,6] However, our results for the new radical FOH^- are quite different, and the radical is, in many ways, better described as an hydroxyl radical weakly interacting with a fluoride ion. A similar description was proposed[6] for the anion FO^{2-}[7] which has been identified in irradiated CaF_2 crystals.

Considerable difficulty was experienced in interpreting the powder e.s.r. spectra, and the interpretation used in Figure 1 is the one that gives the most internally consistent set of results, both for FOH^- and FOD^-. The

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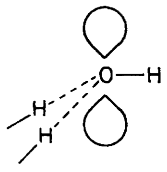
[6] M. C. R. Symons, *Advances in Chemistry Series*, 1968, **82**, 1.

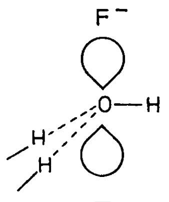
[7] H. Bill and R. Lacroix, *J. Physique* (*Suppl.*), 1967, **28**, CH. 138.

results can be interpreted in terms of an FOH bond angle of *ca.* 90°. This is consistent with the concept of a weak, long, σ bond between oxygen and fluorine, the unpaired electron remaining primarily in an oxygen $2p$ orbital perpendicular to the $\cdot$OH bond. Thus the proton coupling remains close to that for hydroxyl radicals in pure ice crystals [8,9] and the fluorine coupling corresponds to only *ca.* 2·5% delocalisation. In particular, the form of the anisotropy for the ^{1}H and ^{19}F tensors agree with this model, the $A_{\parallel}(^{19}F)$ features coming with the intermediate coupling for ^{1}H, *etc.*

The form of the g-tensors for FOH^- is as predicted, but it is surprising that g_z (that is, the g-value along the O–H bond direction) is actually greater than that for 'normal' OH radicals in ice.[8,9] For the latter, orbital motion is largely quenched by asymmetric hydrogen bonding, (I), whilst for the former, the fluoride ion must also be considered. The effect of hydrogen bonding as in (I) is to constrain the filled $p(\pi)$ orbital towards the protons, leaving the unpaired electron as remote as possible from these. The fluoride ion is surely expected to enhance this trend, thus increasing the energy gap between the $p(\pi)$ levels and decreasing $\Delta g_{\parallel}$. In fact, the opposite occurs—this may be taken as evidence for weaker hydrogen bonding in (II), possibly because the parent water molecule hydrogen bonded to fluoride is less closely bound into the water network.



(I)



(II)

The fact that the [MH$^+$] can approximately equal or even exceed that of 'normal' trapped hydrogen atoms despite the fact that [H$_2$O] $\gg$ [M$^+$] strongly suggests that these units are energetically preferred. However, annealing studies show that they are destroyed at appreciably lower temperatures, as was found in earlier work on these species in barium sulphate crystals.[2] Also *ab initio* calculations [10] suggest that the unit NaH$^+$ is dissociative. An alternative explanation is that the cations provide the best trapping sites because of their effect on water structure. Normal ice is very closely knit and, in fact, hydrogen atoms are not trapped therein at 77 K. The interaction between cations such as Na$^+$ and water is weaker than that between water and water,[11] and also there is likely to be a somewhat disordered region of water surrounding the cations which can provide cavities for the hydrogen atoms. It is significant, in this context, that Cs$^+$ gave no noticeable interaction with hydrogen atoms. This may be because the orbitals are too disparate to interact strongly, but we recall that CO_2^- radicals interact with Cs$^+$ just as effectively as with the smaller cations.[12] Alternatively, the organisation of water around the Cs$^+$ ions may be less conducive to trapping.

We consider the fact that hydrogen atoms are preferentially trapped at cation sites and hydroxyl radicals at anion sites to be especially significant. The bonding situations for these centres and the alternatives in which H· and ·OH are trapped at anion and cation sites respectively are compared in Figure 5. The unpaired electron in the anion centres is predominantly in a σ^*-orbital whilst that in the cation centres is in a σ-orbital. Thus in the former there is electron transfer from the anion to the radical and in the latter, from the radical to the cation. This is, we suggest, the main reason for the observed selectivity since hydroxyl radicals are definitely electrophilic whilst hydrogen atoms are not. (Units such as NaOH$^+$ could be present, but we would have expected to detect hyperfine coupling to ^{23}Na.)

We have previously drawn attention to the remarkable fact that although there is appreciable delocalisation of the unpaired electron onto the cation, the proton hyperfine coupling for MH$^+$ radicals is slightly greater than that for the free atoms.[2] The most easily understandable explanation is that the radial extension of the 1s orbital for the hydrogen atom is strongly dependent upon the environment, and the hyperfine coupling is very sensitive to small changes in the former and hence also in the latter.[2] The effect of the positive charge was then postulated to result in a small reduction in the radial extension and hence in a compensating increase in $A_{iso}(^{1}H)$.

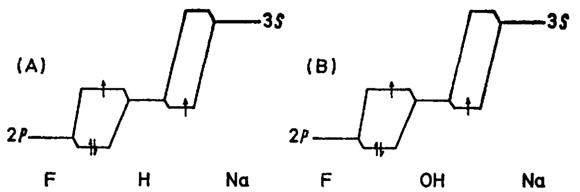


FIGURE 5 Bonding schemes for H· *a*; and ·OH *b* where H· and ·OH are trapped at cation (Na$^+$) or anion (F$^-$) sites

It is interesting to compare our results with those for hydrogen atoms trapped in calcium fluoride crystals.[13] Here also, $A_{iso}(^{1}H)$ is slightly greater than that for the free atoms despite the fact that there is apparent delocalisation onto eight equivalent fluorine atoms. The usual model for these centres is that the hydrogen atoms are trapped interstitially in sites that are surrounded by eight fluoride ions. If the hyperfine coupling (also given in Table 1) to ^{19}F is taken to be positive, and allowance is made for the direct dipole coupling from spin on hydro-

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[8] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 2112.

[9] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, and D. O. Williams, *J. Chem. Soc.* (*A*), 1969, 719.

[10] T. A. Claxton and D. McWilliams, *Trans. Faraday Soc.*, 1970, **66**, 513.

[11] R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 1969, **65**, 2559.

[12] R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 1969, **65**, 945; J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3075.

[13] J. L. Hall and R. T. Schumacher, *Phys. Rev.*, 1962, **127**, 1892.

gen (*ca.* 2 G), then the apparent spin-density on each fluorine is *ca.* 2%, giving *ca.* 16% delocalisation in total. If interaction with each fluoride is as pictured in Figure 5 (this might involve rapid migration *via* HF^- units, for example) then some electron transfer towards hydrogen must occur and we would have predicted an orbital expansion and hence an exaggerated decrease in the ^1H hyperfine coupling. This may be outweighed by other factors, or just possibly, it may arise because the trapping site is at a calcium ion rather than a cavity. In that case, coupling to ^{19}F may be less direct, possibly involving spin polarisation rather than σ-delocalisation. It would be interesting to search for coupling to ^{43}Ca in these centres.

Mechanism of Formation.—Damage to water is thought to involve mainly electron loss (1) followed by electron trapping (hydration) (2), and reaction to give hydrogen atoms (3) and (4).

$$H_2O + \gamma \longrightarrow H_2O^+ + e^- \qquad (1)$$

$$e^- + \text{cavity} \longrightarrow e_t^- \qquad (2)$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (3)$$

$$e^- + H_3O^+ \longrightarrow H + H_2O \qquad (4)$$

Direct interaction with halide ions is also reasonable:

$$Hal^- + \gamma \longrightarrow Hal + e \qquad (5)$$

which may be followed by

$$Hal + Hal^- \longrightarrow Hal_2^- \qquad (6)$$

All the paramagnetic species listed in (1)—(6) apart from H_2O^+ and Hal were detected, if it is allowed that the intense blue–violet colours were indicative of e_t^-.[14] To these reactions we must now add

$$M^+ + H \longrightarrow MH^+ \qquad (7)$$

(or possibly, $M^+,H_2O + e^- \longrightarrow MH^+ + OH^-$)

and $$OH + Hal^- \longrightarrow HalOH^- \qquad (8)$$

Neither of these reactions (7) and (8) are normally considered in liquid-phase studies: it may be that (7) is not of kinetic significance in view of the weakness of the interaction, but (8) certainly should be important except for FOH^-, when the bonding is again thought to be weak.

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[14] B. G. Ershov and A. K. Pikaev, *Radiation Res. Rev.*, 1969, **2**, 1.