1071. *Unstable Intermediates. Part XX.** *Hydrogen Atoms Trapped in Phosphates.*

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The electron-spin resonance spectra of various γ-irradiated phosphates show that hydrogen atoms are trapped, the centres being stable at room temperature in some cases. A model of the trapping site is suggested which accounts qualitatively for the observed hyperfine interaction and g-tensors, and for the observed increase in stability with increase in basicity of the anion.

Various crystalline orthophosphates, after exposure to ^{60}Co γ-rays, contain relatively high concentrations of trapped hydrogen atoms which have been recognised by their characteristic electron-spin resonance absorption spectrum. The trapping is remarkably deep, for in some cases the half-life of the trapped atoms is a matter of months even at room temperature. This contrasts with observations on a wide range of other oxysalts which, on exposure to γ-rays, almost certainly give hydrogen atoms as one initial product, but these are not detected even at 77°K. Hydrogen atoms have previously been trapped in rare-gas matrices at 4°K,[1] in irradiated sulphuric acids,[2] silica gel,[3] and hydride-doped alkali halides [4] at 77°K, and in calcium fluoride at room temperature.[5]

Bernstein [6] has recently presented thermodynamic arguments which suggest that hydrogen atoms might be stabilised by a form of " hydrogen-bonding " to " closed-shell " nucleophiles. His model is comparable with that developed independently in the present work.

Experimental and Results

Most orthophosphates were kindly supplied by Dr. Chapman of Albright and Wilson (Mfg.) Ltd., and were used without further purification. Water-soluble phosphates were deuterated by direct exchange in 98% D_2O. Lithium orthophosphate was baked at 120° for 20 hr. but the sources of hydrogen atoms on irradiation were not removed under these conditions.

Samples were exposed at 77°K and room temperature, to a 1900-c ^{60}Co source, the total dose being about 6·5 mrad.

Electron-spin resonance spectra were obtained at X-band frequencies with a spectrometer described previously [7] and with a Varian V4502 spectrometer.

Parameters given in Tables 1 and 2 have been corrected for the intermediate field case, the magnetic energy levels being given by solutions of the Breit–Rabi equation: [8]

$$W_{I\pm\frac{1}{2}} = \frac{-\Delta W}{2(2I+1)} + g_I\beta HM \pm \frac{\Delta W}{2}\left(1 + \frac{4Mx}{2I+1} + x^2\right)^{\frac{1}{2}}, \qquad (1)$$

where $\Delta W = \frac{1}{2}(2I+1)A$, A being the hyperfine splitting energy, and M the magnetic quantum number of $\boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I}$. The parameter $x = (g_J - g_I)\beta H/\Delta W$, where g_J and g_I are the electronic and nuclear g-factors, β is the Bohr magneton, and H the magnetic field strength.

Results are given in Tables 1 and 2. In all cases other radicals were also detected and will be discussed in a later paper. Hydrogen atoms were not trapped in $Na_3PO_4,12H_2O$,

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* Part XIX, *J.*, 1963, 1189.

[1] Foner, Cochran, Bowers, and Jen, *J. Chem. Phys.*, 1960, **32**, 963; Adrian, *J. Chem. Phys.*, 1960, **32**, 972.
[2] Livingston, Zeldes, and Taylor, *Discuss. Farad. Soc.*, 1955, **19**, 166.
[3] Kazansky, Pariisky, and Voevodsky, *Discuss. Farad. Soc.*, 1961, **31**, 203.
[4] Delbecq, Smaller, and Yuster, *Phys. Rev.*, 1956, **104**, 599.
[5] Hall and Schumacker, *Phys. Rev.*, 1962, **127**, 1892.
[6] Bernstein, *J. Amer. Chem. Soc.*, 1963, **85**, 484.
[7] Brivati, Keen, and Symons, *J.*, 1962, 237.
[8] Breit and Rabi, *Phys. Rev.*, 1931, **38**, 2082.

TABLE 1.

Experimental results for hydrogen atoms trapped in phosphates.

Lattice	Temp. (°K)	Hyperfine splitting (Mc./sec.)	g-Value	κ_{obs}
Li_3PO_4	300	1411·3	2·0052	340
	77	1408·4	2·0066	230
$Ca_3(PO_4)_2$	300	1409·7	2·0048	400
$AlPO_4$	77	1407·8	2·0045	440
$CaHPO_4,2H_2O$	77	1409·1	2·0042	510
$Ca(H_2PO_4)_2,H_2O$	77	1419·7	2·0034	855
NaH_2PO_4	77	1413·7	2·0041	550
$Na_3HP_2O_7$	77	1407·0	2·0039	617
$Na_2H_2P_2O_7$	77	1401·5	*ca.* 2·006	*ca.* 260
$Na_2H_2P_2O_6$	77	1406·2	2·0039	620

TABLE 2.

Experimental results for deuterium atoms trapped in phosphates.

Lattice	Temp. (°K)	Hyperfine splitting (Mc./sec.)	*g*-Value	κ_{obs}	Lattice	Temp. (°K)	Hyperfine splitting (Mc./sec.)	*g*-Value	κ_{obs}
$CaDPO_4,2D_2O$...	77	77·2	2·0011	—	Na_2DPO_4 ...	77	77·6	2·0035	831
$Ca(D_2PO_4),D_2O$	77	77·2	2·0032	1100	$Na_2D_2P_2O_7$	77	76·4	2·0021	—
NaD_2PO_4	77	77·2	2·0026	3307	$Na_3DP_2O_7$...	77	77·1	2·0025	3300

$Zn_3(PO_4)_2,4H_2O$, $Cd_3(PO_4)_2$, $Na_4P_2O_7$, $Na_2HPO_4,12H_2O$, $Na_3HPO_3,5H_2O$, and $M(H_2PO_2)_2$ where M = Mg, Ca, or 2Na, and those trapped in Li_3PO_4 were stable to baking at 120°.

DISCUSSION

Identity of the Radicals.—The doublets observed had a splitting of about 500 gauss and *g*-values close to that of the free spin. These properties are characteristic of hydrogen atoms both when in the gas phase and when trapped in various matrices. A phosphorus-containing radical could also show a large hyperfine splitting, but for a splitting as large as 500 gauss the unpaired electron would need to have appreciable 3*s*-character on the phosphorus. Such radicals would be HPO_2^{2-}, PO_3^{2-}, and PO_2; the spectra due to the first two species are well known [9,10] and the last, by analogy [11] with NO_2, would probably give a doublet with a splitting of about 500 gauss. Since several of the salts studied were ostensibly anhydrous our preliminary assignment was to rotating PO_2 radicals.

However, since in all cases where it was possible to replace water by deuterium oxide the doublet was largely replaced by a triplet characteristic of deuterium atoms, the conclusion that the species is a trapped hydrogen atom is confirmed. Refluxing with deuterium oxide had no effect on the spectra of the compounds which formally contained no hydrogen-bearing species initially, such as lithium and calcium orthophosphates, Li_3PO_4 and $Ca_2(PO_4)_3$, but since the parameters conform to the species containing a replaceable hydrogen atom, the trapped species are assumed to be hydrogen atoms.

The Tables show that the deviation from the free-atom *g*-value is positive and that from the free-atom hyperfine splitting is negative. These observations differ from those observed in previous cases [1-5] and indicate a difference in trapping mechanism. Also, in contrast with the results of others,[1,5] considerable anisotropy was detected in several instances. In his treatment, Adrian [1] considers two effects on the trapped hydrogen atoms by the matrix, one due to van der Waals forces and the other due to Pauli exclusion forces. The former effectively expands the hydrogen 1*s* wave function and consequently the hyperfine splitting is reduced. The second effect entails the use of a hydrogen 1*s* function which is orthogonalised to the matrix particle wave function; the effect of this

[9] Atkins, Keen, and Symons, *J.*, 1963, 250.
[10] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 475.
[11] Atkins, Keen, and Symons, *J.*, 1962, 2873.

is two-fold, the hyperfine interaction is increased and, owing to admixture of matrix $2p$ wave functions into the hydrogen $1s$ orbital during the orthogonalisation, the deviation of the g-value from that of the free-spin is negative.

Our results are not accommodated either quantitatively or qualitatively by this model and we suggest that the centre is a hydrogen atom very weakly bonded to a saturated phosphate ion. This arrangement is similar to that proposed by Bernstein.[6] The ion PO_4^{3-} is probably sufficiently nucleophilic to be able to behave as such an acceptor, and it is to be remarked that only crystals containing PO_4^{3-} stabilise hydrogen atoms at room temperature, HPO_4^{2-} and $H_2PO_4^-$ acting as " traps " only at 77°K.

We suppose that the hydrogen atom is sufficiently close to one oxygen atom of a phosphate group for bonding to occur *via* the lone-pair electrons on that oxygen. We can, very simply, consider the species as $(HO\text{-}X)^{2-}$ with the unpaired electron in a σ^* localised molecular orbital. The unpaired electron would be expected to reside largely on the hydrogen atom, and the bonding pair largely on the oxygen. The splitting due to the hydrogen nucleus would therefore approach that for the free atom, the more so the weaker the overall bonding. This extent of localisation of an electron is supported, for example, by the electron distribution in HCl in which an important contributing structure is H^+Cl^-, in HCO in which the fraction of unpaired electron[7] on the proton is 0·25, and in HPO_2^- where the fraction is 0·18.[9] The effect of the polarisation of the σ-bonding pair by the unpaired electron is difficult to assess, but it will probably induce a positive spin density at the proton and thereby increase the hyperfine splitting. This effect would decrease to the free-atom value as the bond weakened.

Although the concept of σ^*-electrons in bonds containing hydrogen is novel, the presence of σ^*-electrons has been convincingly demonstrated for species such as Cl_2^-, F_2^-, and F_3^{2-} in irradiated alkali-halide crystals.[12,13]

Since the wave function for the unpaired electron has some oxygen $2p$-character a deviation from the free-spin g-value would be expected, at least in the direction perpendicular to the H–O bond. A simple molecular-orbital derivation can indicate the sign and magnitude of the shift to be expected.

If overlap is neglected, the σ^* molecular orbital has the form

$$\psi(\sigma^*) = a_H\psi(1s) - a_0\psi(2p_z), \tag{2}$$

where $\psi(1s)$ is a $1s$-orbital on the hydrogen and $\psi(2p_z)$ is a $2p$-orbital on the oxygen directed along the internuclear axis. The energies of the σ- and σ^*-orbitals, ε_σ and ε_σ^*, respectively, are obtained as solutions of a secular determinant

$$\begin{vmatrix} \alpha_H - \varepsilon & \beta \\ \beta & \alpha_0 - \varepsilon \end{vmatrix} = 0, \tag{3}$$

where α_i is the coulomb integral on the i'th atom and β the O–H exchange energy. The non-bonding orbitals on the oxygen have an energy $\varepsilon_n = \alpha_0$. The coefficients in expression (2) are given by

$$a_H^2 = (\alpha_0 - \varepsilon^*)^2/N^2 \text{ and } a_0^2 = \beta^2/N^2$$

where N^2 is a normalising constant. As the bond lengthens, β approaches zero and the electron becomes increasingly localised on the hydrogen, as required. The shift, $\Delta g_\perp$, in the perpendicular g-value from the free-spin value, is due to spin–orbit coupling on the oxygen mixing some $n(\pi)$-component into $\psi(\sigma^*)$, and has the value

$$\Delta g_\perp = 2a_0^2\lambda_0/(\varepsilon_\sigma^* - \varepsilon_n)$$

Consequently, with $\alpha_0 = \varepsilon_n$,

$$a_s^2 = (\varepsilon_\sigma^* - \varepsilon_n)^3\Delta g_\perp/2\beta^2\lambda_0, \tag{4}$$

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[12] Castner and Kanzig, *Phys. and Chem. Solids*, 1957, **3**, 178.

[13] Symons, *J.*, 1963, 570.

where λ_0 is the spin–orbit coupling constant on the oxygen atom. The sign of $(\varepsilon_\sigma^* - \varepsilon_n)$ is necessarily positive, as also is β^2 and λ_0; since a_s^2 must be positive it follows that $\Delta g_\perp$ is positive, as observed. The value of λ_0 is 151 cm.$^{-1}$ and β is about -2 ev. An estimate of the value of $(\varepsilon_\sigma^* - \varepsilon_n)$ may be obtained from a knowledge of the energy of the $\sigma^* \longleftarrow n$ transition in the hydroxide ion. This is uncertain but is probably about 50,000 cm.$^{-1}$, although for such a long bond as we envisage this value would be considerably reduced, as also would that of β. In this way it is possible to make a crude estimate of κ, in the relation $a_s^2 = \kappa\Delta g_\perp$, of about 1000. The actual values of κ (κ_{obs}) are given in the Tables. For stronger bonds, κ should decrease; we would therefore expect a smaller κ in the trapping sites stable at room temperature than those stable only at 77°K. This is observed. The variation of the κ-function with O–H distance may be computed from the secular determinant, with overlap included, when reasonable values of the constants are inserted and by scaling β proportional to the overlap integral of $\psi(1s)$ and $\psi(2p_z)$. The variation is then as given in Fig. 1, when using the values $\alpha_H = -1{\cdot}3$ ev, $\alpha_0 = -2{\cdot}2$ ev, and scaling β from the value $\beta_{CC} = 0{\cdot}96$ ev in a carbon–carbon bond. It is seen that the κ-values we observe correspond to an O–H distance about 1 Å longer than the observed bond length [14] in $H_2PO_4^-$.

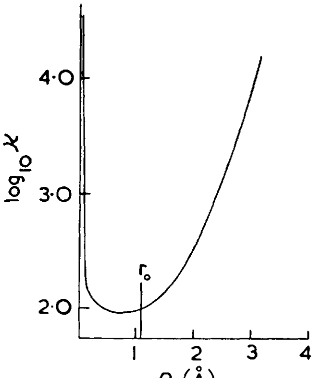

FIG. 1.

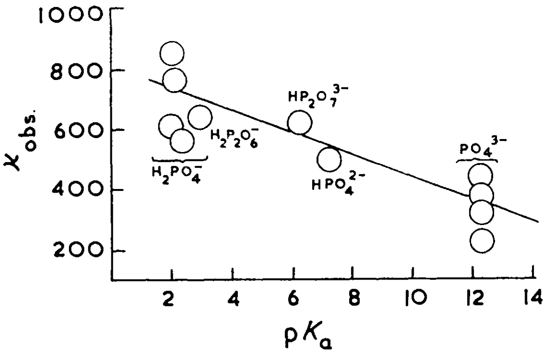

FIG. 2.

FIG. 1. Variation of the κ-function with interatomic distance, $R_{(OH)}$.

FIG. 2. Variation of κ with pK_a of the protonated anion.

If our proposed method of trapping conforms to that proposed by Bernstein [6] the depth of trapping should vary with the nucleophilic character of the anion in the crystal lattice. A measure of this is the pK_a value of the acid radical, and for H • • • X one would expect the trap depth to increase, and hence the κ-value to decrease, as the pK_a value of the acid HX increases. There is such a trend, as is shown in Fig. 2. The κ/R_{OH} curve is very steep in the region with which we are concerned and this could account for the rather large scatter in the points observed. Only the species with a large pK_a value are stable at room temperature, in accord with expectation.

The discussion so far has dealt only with the variation in the perpendicular *g*-value; on the present model the parallel component should have the free-spin value. However, the effect of the moiety X in H • • • OX on the *g*-value anisotropies, although difficult to determine, would probably separate the perpendicular components to give a completely anisotropic tensor, with all the elements above the free-spin value. The effect of this removal of axial asymmetry of the $(HOX)^{2-}$ fragment was observed only in Li_3PO_4, where the *g*-tensor is estimated to have the form $g = (2{\cdot}009,\ 2{\cdot}005,\ 2{\cdot}002)$ which is compatible

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[14] Sutton *et al.*, " Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, No. 11, 1958.

with our conclusions. The hyperfine splitting was isotropic within experimental error for this salt.

One can consider the reaction, $O_3POH^{2-} + e \longrightarrow O_3POH^{3-}$, in this context. It might have been supposed that the " outer " electron in O_3POH^{3-} would be accommodated in an orbital centred considerably on phosphorus, such as the phosphorus 3*d*-, 4*s*-, or 4*p*-levels or one of the antibonding molecular orbitals of phosphate. In fact, the present model, if correct, shows that the acceptor level is the localised σ^* O–H bond.

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