arise from the conventional assumption that crystal field effects arise from the electrostatic field of the ligands. This assumption is known to be over-simplified.[24]

The formation constants of some of the complexes undergoing exchange are also given in Table VII. The lability of copper complexes is quite at variance with the thermodynamic stability and shows that a special mechanism must be operating. For the rest, the rates correlate well with the stability data, manganese being the most labile and least stable and nickel being least labile and most stable. Compared to cobalt, however, nickel shows a slower rate of reaction than indicated by stability constants alone. This is a valid indication of crystal field, or ligand field, stabilization. Regardless of the factors which produce crystal field effects,[24] the octahedral configuration must be very well suited to a d^8 system. Any change in structure produces substantial loss of d-orbital energy. The activation energy for the first-order dissociation of $Ni(en)_3{}^{2+}$ is 18 kcal.,[11] which may also be considered in connection with the data of Table III.

The results for glycol exchange given in Table I call for some special comment. First of all, the rates for exchange of this chelate molecule are about the same as those previously reported for the unidentate methanol.[4a] This is understandable in terms of the mechanism of a solvent assisted dissociation. The intermediate IV guarantees exchange after only one end

IV
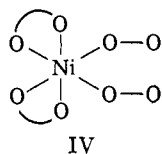
of the chelate has dissociated. A five-coordinated intermediate, V, would lead to the prediction of a greatly

(24) R. G. Pearson, *Record Chem. Progr.*, **23**, 53 (1962).

reduced exchange rate for glycol compared to methanol because of rapid reclosing of the chelate ring.

V
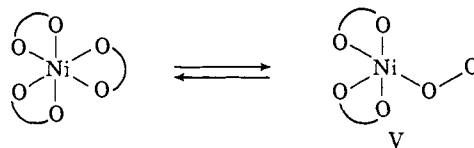
It is an interesting fact that when coordination of a paramagnetic ion occurs to oxygen compared to nitrogen, it is much more likely that rates of relaxation rather than rates of exchange are being measured by line broadening of proton n.m.r. signals. Thus $T_{2B} > \tau_B$ for oxygen coordination and $T_{2B} < \tau_B$ for nitrogen coordination. The inversion is due more to changes in T_{2B} than τ_B. Thus values of T_{2B} for oxygen coordination range from 10^{-3} to 10^{-5} sec. usually. For the same metal ions coordinated to nitrogen, T_{2B} is in the range from 10^{-5} to 10^{-7} sec. The difference may be attributed to the greater polarizability of nitrogen compared to oxygen. Thus a higher unpaired spin density due to isotropic contact interaction[25] will appear on N than on O. By polarization this spin density will be transferred to the proton bound to N and produce relaxation, shortening T_{2B}. Benson, *et al.*, have shown that N transmits spin densities more efficiently than does O.[26]

(25) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

(26) R. E. Benson, D. R. Eaton, A. D. Josey, and W. D. Phillips, *J. Am. Chem. Soc.*, **83**, 3714 (1961).

Formation and Reactions of Radiation-Produced Electrons and Atomic Hydrogen in γ-Irradiated Ice

BY L. KEVAN, P. N. MOORTHY,[1] AND J. J. WEISS

Hydrogen atoms have been found in γ-irradiated ice at 77°K. containing acid salts such as potassium dihydrogen orthophosphate and sodium bisulfate. It has been shown that they are also produced, although with lower yield, in ice containing neutral salts such as sulfates, phosphates, and carbonates. The hydrogen atom yields were found to be linear with solute concentration from 0.01 M up to saturated solutions and with radiation dose up to 8 megarads but attained a stationary value at about 13 megarads. Solutes which can act as scavengers for the radiation-produced electrons (polarons), such as nitrate, nitrite, acetone, and cupric salts, decreased the hydrogen atom yields in ices containing the mononegative ions, but were ineffective in the case of polynegative oxyanion solute. Relative rates of reactions of the electron with $H_2PO_4{}^-$ and competing scavengers such as nitrate and nitrite ions and acetone have been determined. These reactions can be interpreted by the following mechanism: the radiation-produced electron reacts with an acid anion, e.g., $HSO_4{}^-$ or $H_2PO_4{}^-$, either by electron or by proton transfer leading eventually to the formation of a hydrogen atom; in the case of the neutral salts, the stabilized hydrogen atoms are formed only from those water molecules which are in the solvation shells of the anions.

Introduction

Hydrogen atoms have been found to be formed in the radiolysis of ice at 77°K. containing certain acids such as sulfuric, phosphoric, hydrofluoric, fluorosilicic, and fluoroboric acid.[2] In neutral ice no hydrogen atoms were observed on irradiation at 77°K. However, they have been detected at 4°K. and were found

(1) On leave from A.E.E.T., Bombay, India.

(2) R. Livingston, H. Zeldes, and E. H. Taylor, *Discussions Faraday Soc.*, **19**, 166 (1955).

to decay upon warming.[3] More recently, it has been reported[4a] that atomic hydrogen is produced and can be detected by electron spin resonance (e.s.r.) in γ-irradiated ice at 77°K. containing various solutes such as $H_2PO_4{}^-$, $HPO_4{}^{-2}$, $PO_4{}^{-3}$, $HSO_4{}^-$, and $SO_4{}^{-2}$ and that the hydrogen atom yields increased linearly with solute

(3) D. H. Piette, R. L. Rempel, M. E. Weaver, and S. Siegel, *J. Chem. Phys.*, **30**, 1623 (1959).

(4) (a) L. Kevan, P. N. Moorthy, and J. J. Weiss, *Nature*, **199**, 689 (1963); (b) J. J. Weiss, *ibid.*, **186**, 751 (1960).
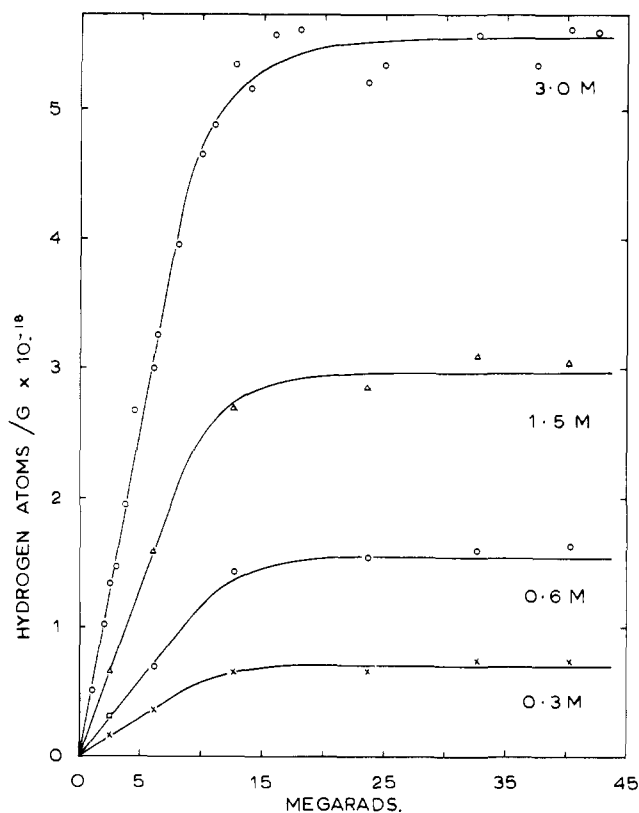
Fig. 1.—Yield–dose plots for hydrogen atom formation at 77°K. in γ-irradiated ice containing different concentrations of NaH_2PO_4 as solute.

concentration up to saturated solutions. It has been proposed[4a,b] that some of these hydrogen atoms observed at 77°K. may arise by the reaction of an electron (polaron) with a proton or a Brönsted acid solute. Such a reaction should be affected by an electron scavenger. Preliminary findings[4a] indicated this to be the case and a more detailed study is reported here. Previously, in a study of irradiated acids, Livingston and Weinberger[5] have also reported a few results on the scavenging of hydrogen atoms by nitric acid.

Experimental

Analar grade chemicals were used as obtained. Pure water, triply distilled over alkaline permanganate and dilute H_3PO_4, was used to make all solutions.

The solutions were rapidly frozen in 2 mm. i.d. Pyrex tubes in liquid nitrogen to give opaque crystalline solids. The required lengths were cut off from these and the ice cylinders were pushed out into 4 mm. i.d. Pyrex tubes for irradiation; the specimens were in contact with liquid nitrogen during irradiation. The samples weighed about 0.03 g. and were 1.5 cm. long.

Degassed samples were prepared in a two-necked 100-ml. flask. An inverted 2-mm. sample tube was attached to one neck and the other attached to a vacuum line through which degassing was accomplished by several cycles of the freeze–pump–thaw method. After degassing, the flask was inverted, filling the sample tube, and sample cylinders were prepared as above. Some samples were deoxygenated by bubbling argon through the solution for 1 hr. Both methods of removing oxygen from the solution were found to have no effect on the e.s.r. signals and the data reported here are based on samples which were not subjected to these treatments.

It is believed that a homogeneous distribution of solute in the solid was obtained. The following points support this: the reproducibility was good—cutting different sections from the same sample tube gave identical results, and the color after irradiation, when present, was uniform; the hydrogen atom yields were linear with solute concentration over a large range; freezing was complete in about 6 sec.

The irradiations were carried out around a cylindrical 600 curie Co[60] source at a dose rate of 0.17 megarad per hour as measured by the ferrous sulfate dosimeter taking $G(Fe^{III})$ =

(5) R. Livingston and A. J. Weinberger, *J. Chem. Phys.*, **33**, 499 (1960).

15.5. The irradiation tubes were centered in dewars filled with liquid nitrogen.

After irradiation the specimens were transferred, without allowing to warm up, into an e.s.r. dewar with a thin-walled quartz tip (outer tube 6 mm. o.d., inner tube 3 mm. i.d.) which fits into the reflection type H_{012} rectangular cavity of a Microspin e.s.r. spectrometer (Microwave Instruments, Ltd). The spectrometer operates at a nominal frequency of 9.2 kMc./sec., employs 100 kc./sec. field modulation and phase sensitive detection, and records the first derivative of the absorption signal on a 10 in. potentiometric strip chart recorder. A stream of dry nitrogen gas entered one side of the cavity to prevent moisture condensation on the dewar tip. A 3 hr. or longer warm up time for the spectrometer was allowed before using it.

All comparisons of hydrogen atom formation and scavenger effects were made against standards irradiated and examined simultaneously. The hydrogen atom signals were found to be stable at 77°K. over a period of a month by periodic comparison with freshly irradiated samples. Data for a complete dose saturation curve could be obtained from one sample by interrupting the irradiation periodically and comparing its hydrogen signal with a set of three standard samples. All measurements on any one system were made under identical experimental conditions of microwave power, modulation current, time constant, and sweep speed with only the spectrometer gain being varied. When the gain control was varied the multiplication factor for conversion of the signal amplitude from one gain setting to another was determined empirically, thus improving the accuracy of the results. It was found that the rotational orientation of the e.s.r. dewar in the cavity affected the reproducibility appreciably and accordingly this was kept constant. Reproducibility was obtained within ±15% and the relative errors are estimated to be less than ±20%. Absolute yields were determined by comparison with glassy 0.200-mole fraction sulfuric acid taking $G(H)$ = 1.66 as described previously.[4a]

To obtain maximum sensitivity, high modulation currents and microwave powers were used. For the low field hydrogen atom, line modulation broadening occurred above a modulation amplitude of 2.5 amp. (2.5 gauss peak to peak); in the absence of microwave power saturation the line width between points of maximum slope increased from 4.0 to 4.3 gauss for a change in modulation amplitude from 2.5 to 5.0 amp. Saturation of the signal was found to occur at microwave powers above 50 μw. Absolute comparisons were made in the absence of these two effects, but relative comparisons were not since both signals are affected similarly.

In addition to the characteristic hydrogen atom doublet split by about 505 gauss, other paramagnetic signals are usually detected near $g = 2.00$. Some colors were also observed: phosphates gave a red color and bisulfate a light yellow. These phenomena are presently being studied.

Results and Discussion

Hydrogen Atom Formation.—Hydrogen atom yields in γ-irradiated ices containing various solutes are given in Table I. These yields were found to be identical in the sodium, potassium, and ammonium salts indicating that the monovalent cation has no effect. No detectable yield was observed in KNO_3 or KNO_2 for which an upper limit of $G(H) \leq 1 \times 10^{-4}$ may be given. This is not surprising since nitrate and nitrite ions are good electron scavengers.[6]

TABLE I

HYDROGEN ATOM YIELDS, $G(H)$ (= ATOMS/100 E.V.), IN γ-IRRADIATED ICE AT 77°K. CONTAINING VARIOUS SOLUTES

Solute, 1.0 M	$G(H)$	Solute, 1.0 M	$G(H)$
$NH_4H_2PO_4$	0.25	$NaHSO_4$	0.14
NaH_2PO_4	.27	Na_2SO_4	.04
KH_2PO_4	.27	$NaHCO_3$	.01
Na_2HPO_4	.07[a]	K_2CO_3	.006
Na_3PO_4	.03[a]	$NaClO_4$	.02

[a] Extrapolated linearly to 1.0 M.

Dose Saturation Effects.—The yield of hydrogen atoms is linear with dose up to about 8 megarads in ice containing various concentrations of $H_2PO_4^-$. It approaches a stationary value at about 15 megarads (Fig. 1). At 3.0 M $H_2PO_4^-$ the stationary concentration is 5.6 × 10^{18} hydrogen atoms per gram. This

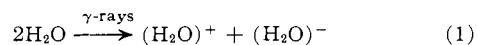(6) J. Jortner, M. Ottolenghi, J. Rabani, and G. Stein, *J. Chem. Phys.*, **37**, 2488 (1962).

Table II

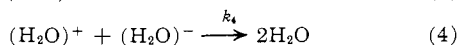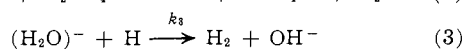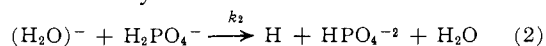Effect of Scavengers on the Hydrogen Atom Yields in γ-Irradiated Ice Containing Various Solutes at 77°K.[a]

Scavenger	H₂PO₄⁻	HPO₄⁻²	PO₄⁻³	HSO₄⁻	SO₄⁻²	HCO₃⁻	CO₃⁻²	ClO₄⁻
CH₃COCH₃	Yes	No	No	Yes	No	Yes	No	Yes
NO₃⁻	Yes	No	No	Yes	No	Yes	No	Yes
NO₂⁻	Yes	No	No	***	No	Yes	No	Yes
Cu⁺²	*	*	*	Yes	No	*	*	Yes
N₂O	Yes	...	...	...	...	...	...	...
CO₂	Yes	...	...	...	...	...	...	...
O₂	**	...	...	**	...	...	...	...

[a] Yes, hydrogen atom yield was reduced in presence of the scavenger; no, hydrogen atom yield was not reduced in presence of the scavenger; *, precipitation occurred on mixing the two reactants; **, concentration was too low to determine an effect; ***, decomposition occurred on mixing the two reactants; ..., not tried.

corresponds to 0.36% of the $H_2PO_4^-$ ions giving rise to hydrogen atoms. The stationary values of the hydrogen atom yields are found to be proportional to the solute concentration. This dose saturation is evidently due to the attainment of a steady state for the production and disappearance of the hydrogen atoms. The formation of hydrogen atoms is suggested[4a] to be by reaction of the negative polaron with the solute anion according to eq. 2. On the other hand, the reaction of the negative polaron with hydrogen atoms according to reaction 3 would provide a mechanism for their disappearance. The mechanism can thus be represented as: positive and negative polarons, henceforward denoted by $(H_2O)^+$ and $(H_2O)^-$, are formed primarily by the action of the γ-rays according to

$$2H_2O \xrightarrow{\text{γ-rays}} (H_2O)^+ + (H_2O)^- \tag{1}$$

which is followed by

$$(H_2O)^- + H_2PO_4^- \xrightarrow{k_2} H + HPO_4^{-2} + H_2O \tag{2}$$

$$(H_2O)^- + H \xrightarrow{k_3} H_2 + OH^- \tag{3}$$

$$(H_2O)^+ + (H_2O)^- \xrightarrow{k_4} 2H_2O \tag{4}$$

By considering reactions 1 to 4 one obtains for the stationary concentration of hydrogen atoms, $[H]_s$, the relation

$$[H]_s = (k_2/k_3)[H_2PO_4^-] \tag{5}$$

which shows that $[H]_s$ is proportional to the concentration of the solute.

The line widths of the hydrogen atom e.s.r. signals increased upon dose saturation as has been observed before[5] but remained constant once the limiting value for the hydrogen yield was reached. The width between points of maximum slopes increased from 4.0 to 4.9 gauss. These values have been corrected for microwave power saturation and modulation broadening. This increase is probably due to spin–spin interaction between trapped paramagnetic species and ceases to increase when the concentration of trapped paramagnetic centers reaches a limit. It has been observed that the other paramagnetic species also show a similar dose saturation behavior.

Scavenging Effects.—If, as suggested above, some of the hydrogen atoms are formed by the reaction of negative polarons with the solute, it is expected that a second solute which can also react with the polarons will set up a competition. If this second solute does not lead to hydrogen atoms, the yield of the latter should decrease. Various solutes which are considered to be good electron scavengers in aqueous solutions have been tried, and the results are shown in Table II. Generally, solutions 1.0 M in solute and scavenger were used except when the solubilities required the use of lower concentrations.

Scavenging action is not recorded when equimolar concentrations of solute and scavenger irradiated to

7.5 megarads gave no reduction in the hydrogen atom yield, within experimental error. With the mono-negative anions $H_2PO_4^-$, HSO_4^-, HCO_3^-, and ClO_4^- as solutes all of the scavengers were found to decrease the yield of hydrogen atoms. On the other hand, hydrogen atoms produced in systems containing the polyvalent anions were not affected by the presence of these scavengers.

Mechanism of Hydrogen Atom Formation and Stabilization.—It is known that the primary chemical processes in the action of ionizing radiations on water are: (a) the formation of positive and negative polarons by the action of the radiation according to reaction 1[4] and (b) the (direct) formation of hydrogen atoms and hydroxyl radicals for example by the dissociation of excited water molecules[7]

$$H_2O^* \longrightarrow H + OH \tag{6}$$
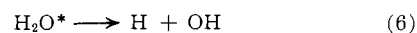
The same considerations would seem to apply also to the case of ice. In the absence of scavenging solutes most of the positive and negative polarons will recombine according to reaction 4. However, reactions such as

$$2(H_2O)^+ \longrightarrow H_2O_2 + 2H^+ \tag{7}$$

and

$$2(H_2O)^- \longrightarrow H_2 + 2OH^- \tag{8}$$
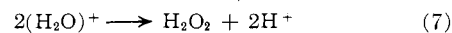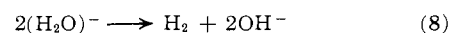
may also occur. Although there is no direct evidence for these in the case of ice, they could be responsible at least for part of the molecular hydrogen peroxide[8] and hydrogen[8] yields observed upon warming γ-irradiated ice. When a Brönsted acid solute such as HSO_4^- or $H_2PO_4^-$ is present in the ice, hydrogen atoms are formed by the reaction of the negative polarons according to eq. 2 and these hydrogen atoms are stable at 77°K. and below. Hydrogen atoms and hydroxyl radicals produced in equivalent yields according to reaction 6 have been observed by e.s.r. in irradiated ice at 4°K.[9] On warming to 77°K. or in irradiated ice at 77°K. only hydroxyl radicals are observed,[9] the yield of these being lower at this temperature. The decay kinetics of hydrogen atoms and hydroxyl radicals upon warming in the temperature range 4–77°K.[10] indicates that the directly produced hydrogen atoms and hydroxyl radicals may recombine in a pairwise fashion

$$H + OH \longrightarrow H_2O \tag{9}$$
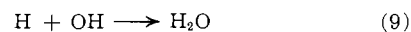
However, if this was the only process taking place one would not expect to find hydroxyl radicals in pure ice either at 77°K., or after irradiation at 4°K. and subsequent warming to 77°K. Reaction 9, therefore, would account only for part of the loss of hydrogen atoms. The rest of the hydrogen atoms must disappear by a different mechanism not involving the hydroxyl

(7) J. J. Weiss, Ann. Rev. Phys. Chem., 4, 143 (1953).

(8) J. A. Ghormley and A. C. Stewart, J. Am. Chem. Soc., 78, 2934 (1956).
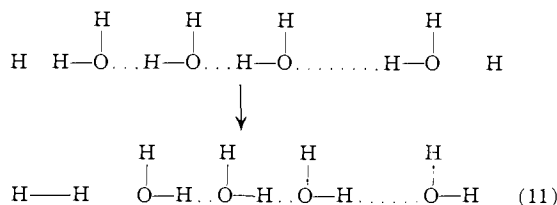
(9) S. Siegel, J. M. Flournoy, and L. H. Baum, J. Chem. Phys., 34, 1782 (1961).

(10) J. M. Flournoy, L. H. Baum, and S. Siegel, ibid., 36, 2229 (1962).

radicals. An obvious process would be the bimolecular recombination of hydrogen atoms

$$2H \longrightarrow H_2 \qquad (10)$$

However, such a process, involving the diffusion of two hydrogen atoms as the initial step, does not appear feasible at 77°K. and below, for, if they could diffuse and recombine at 77°K. one would not observe the hydrogen atoms formed by reaction 2. However, there may be a possibility that, in the ice lattice, two hydrogen atoms form a molecule of hydrogen by an electronic rearrangement in the hydrogen-bonded network according to the scheme[11] represented by eq. 11: a process which does not require the diffusion of the reacting partners as the initial step.

$$
\begin{array}{ccccc}
& H & H & H & H \\
& | & | & | & | \\
H & H—O\ldots H—O\ldots H—O\ldots\ldots H—O & & & H
\end{array}
$$

$$\downarrow$$

$$
\begin{array}{ccccc}
& H & H & H & H \\
& | & | & | & | \\
H——H & O—H\ldots O—H\ldots O—H\ldots\ldots O—H & & & (11)
\end{array}
$$

In eq. 11 the full and broken lines represent, respectively, the covalent bonds and the hydrogen bridges, and the dots imply the presence of additional water molecules.

When an oxyanion solute is present in the ice the hydrogen atoms formed are located within the solvation shell of the oxyanions, where the water molecules are arranged with their hydrogens oriented toward the anion. Thus, the hydrogen-bonded network of water molecules as present in pure ice or at larger distances from the anion in ice containing solutes does not exist. For the mechanism represented by eq. 11 the thermal vibrations of the lattice may be sufficient to provide the necessary activation energy for such a rearrangement. This may no longer be so at 4°K. and below, thus accounting for the stability of the hydrogen atoms in pure ice at these lower temperatures. In principle, a similar scheme can be written for the formation of hydrogen peroxide from two hydroxyl radicals and such a process may be responsible for the observed decay of these species[12] above 100°K. However, the stability of hydroxyl radicals in pure ice between 77 and 100°K. requires that such a process does not occur below 100°K.

The recombination reaction 9 may be inhibited to a greater or lesser extent at 77°K. if such a radical pair is formed in the hydration shell of certain anions when the hydroxyl radical can react with the anion. Then a process such as reaction 12

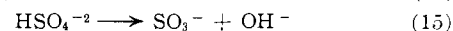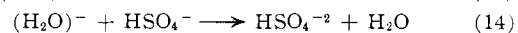$$SO_4^{-2} + OH \longrightarrow SO_4^- + OH^- \qquad (12)$$
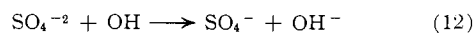
might lead to the stabilization of the hydrogen atom formed in the solvation shell of the anion. There appears to be some experimental support for this since the hydroxyl radical yield is independent of the anion concentration, whereas the hydrogen atom yield is proportional to it. No definite e.s.r. evidence for the SO_4^- species could be found in irradiated ice containing Na_2SO_4 because the strong hydroxyl radical signal dominates the center of the e.s.r. spectrum.

From Table II it appears that the effect of electron scavengers may be connected with the strength of the electrostatic field around the anion. Each anion exerts an electrostatic field on its solvation shell; this field may act to stabilize a free hydrogen atom formed in the solvation shell in a way similar to that proposed

for hydrogen atoms adsorbed on silica gel,[13] in addition to stabilization against the possible formation of molecular hydrogen by mechanism 11. An electron may penetrate the electrostatic field of a mononegative anion and react directly with the solute anion, but this is much less probable in the case of di- and trinegative anions owing to the stronger repulsive field. The experimental observations are then explained as follows.

For the mononegative anions which can act as Brönsted acids (e.g., $H_2PO_4^-$, HSO_4^-, and HCO_3^-) the negative polaron may react with the anion via a proton transfer to form a hydrogen atom as in reactions 2 and 13 or to form a paramagnetic species as in reactions 14 and 15.

$$(H_2O)^- + HSO_4^- \longrightarrow H + SO_4^{-2} + H_2O \qquad (13)$$

$$(H_2O)^- + HSO_4^- \longrightarrow HSO_4^{-2} + H_2O \qquad (14)$$

$$HSO_4^{-2} \longrightarrow SO_3^- + OH^- \qquad (15)$$

Paramagnetic species were in fact observed in the e.s.r. spectrum, although they were usually considerably obscured by the spectrum of the OH doublet. In HSO_4^- ice a singlet or possibly an unresolved doublet (splitting less than 20 gauss) occurs which may be attributed to SO_3^- or HSO_4^{-2} (Fig. 2, curve a). The spectrum of SO_3^- has been studied at room temperature[14] and is reported to be a singlet with $g = 2.004$. In ice containing HSO_4^-, the resonance is near $g = 2.01$. In $H_2PO_4^-$-ice a central doublet arises which overlaps the OH doublet and in HCO_3^--ice a singlet is observed.

In the case of mononegative anions such as ClO_4^-, the polaron apparently interacts with the water molecules in the solvation shell. Since the "acidity" in the solvation shell of an anion may be greater than in the bulk, the reaction of a negative polaron with $(H_3O)^+$ in the solvation shell may lead to the formation of hydrogen atoms.

With di- or trinegative anions, the increased strength of the electrostatic field in the solvation shell may produce two different effects. Firstly, it could act to repel the negative polaron, thus inhibiting reactions involving this species, and secondly it may help to stabilize hydrogen atoms which are formed directly in the solvation shell according to reaction 6 by an electron transfer corresponding to reaction 12.

The reaction leading to hydrogen atoms via a mobile electron (polaron) should be affected by electron scavengers. From Table II it will be seen that the hydrogen atoms formed in $H_2PO_4^-$, HSO_4^-, HCO_3^-, and ClO_4^- systems are all scavengeable. On the other hand, the yield of hydrogen atoms formed by the direct dissociation of excited water molecules in the solvation shell of the polynegative anions should be unaffected by electron scavengers, which also agrees with the results in Table II.

From the above discussion it is evident that irradiation of ice containing solutes such as $H_2PO_4^-$ and HSO_4^- should lead, in addition to scavengeable hydrogen atoms from reactions 2 or 13, to a much lower yield of nonscavengeable hydrogen atoms from HPO_4^{-2} and SO_4^{-2} which are in equilibrium with $H_2PO_4^-$ and HSO_4^-, respectively. This has been found to be the case with HSO_4^- for which the dissociation constant is high enough to give a sufficiently large concentration of SO_4^{-2} ions, which could lead to detectable yields of the nonscavengeable hydrogen atoms. The detection of these nonscavengeable hydrogen atoms was facilitated by their microwave power saturation characteristics which are different from those of the scavengeable

(11) P. T. Emmerson, P. N. Moorthy, and J. J. Weiss, unpublished results.

(12) S. Siegel, L. H. Baum, S. Skolnik, and J. M. Flournoy, J. Chem. Phys., 32, 1249 (1960).

(13) V. B. Kasanskii and G. B. Pariiskii, The Sixth Intern. Symp. on Free Radicals, Cambridge, Eng., 1963, Preprint P.

(14) G. W. Chantry, A. Horsfield, J. R. Morton, J. R. Rowlands, and D. H. Whiffen, Mol. Phys., 5, 233 (1962).

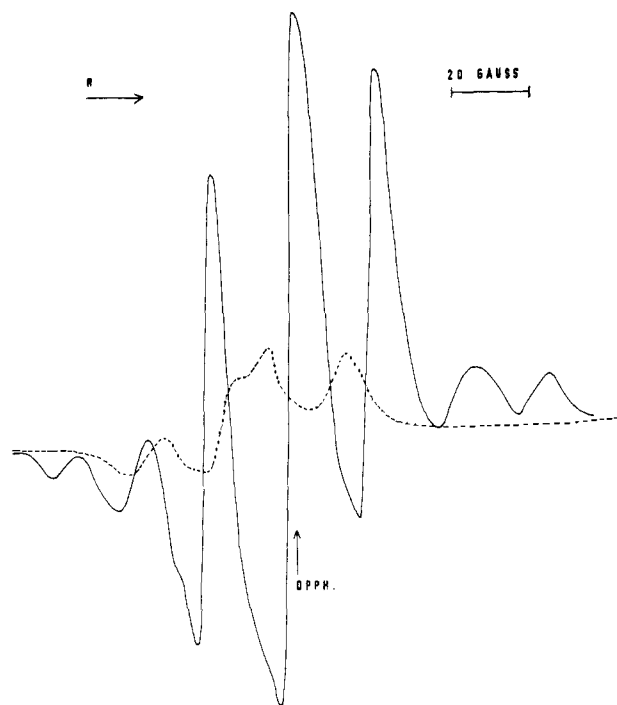Fig. 2.—First derivative e.s.r. spectrum of ice at 77°K. irradiated with γ-rays: – – – –, 1.0 M NaHSO$_4$ as solute (curve a); ————, 1.0 M NaHSO$_4$ + 1.0 M acetone as solute (curve b).

hydrogen atoms but are similar to those of hydrogen atoms from SO$_4$$^{-2}$–ice. Since the dissociation constant of H$_2$PO$_4$$^{-2}$ is several orders of magnitude smaller than that of HSO$_4$$^{-}$, the nonscavengeable hydrogen atoms from the correspondingly lower concentration of HPO$_4$$^{-2}$ in equilibrium with H$_2$PO$_4$$^{-}$ could not be detected at the sensitivities realized in our experiments.

Nature of the Mobile Species.—The diffusing species are considered to be negative and positive polarons. The alternative possibility, namely that the hydrogen atoms are the diffusing species as implied by previous workers,[5] is ruled out on the following grounds. Assuming that hydrogen atoms are formed both by a direct and an indirect action of the radiation on the anion and then diffuse to a "stabilization site" (the latter must again be associated with the anions since no hydrogen atoms are found in pure ice irradiated at 77°K.), the yield of hydrogen atoms should depend on the square of the anion concentration. However, the yields follow a good linear plot over a wide range of anion concentrations.[4a] Therefore this scheme is not applicable. Hydrogen atoms formed in the bulk of the ice by reaction 6 could diffuse to a "stabilization site" associated with an anion. This would give the observed linear dependence on anion concentration, but it would not agree with or explain the fact that the hydrogen atoms are scavengeable in the case of ClO$_4$$^{-}$ but not in the case of SO$_4$$^{-2}$, CO$_3$$^{-2}$, and PO$_4$$^{-3}$.

It was hoped that the additional paramagnetic species formed by the reaction of a scavenger with the polarons would help to identify them. This has not proved to be unambiguous but does seem to reinforce the assumption of mobile electrons (polarons). With nitrate and nitrite ions as scavengers a triplet probably due to interaction with the nitrogen nucleus is formed which shows some additional anisotropic or hyperfine structure. By using the D$_2$O system, it has been shown that this species contains no interacting proton, and it is thought that it arises from the reaction of an electron with the scavenger anion.

With acetone as scavenger a seven-line spectrum was obtained for the species produced from the acetone.
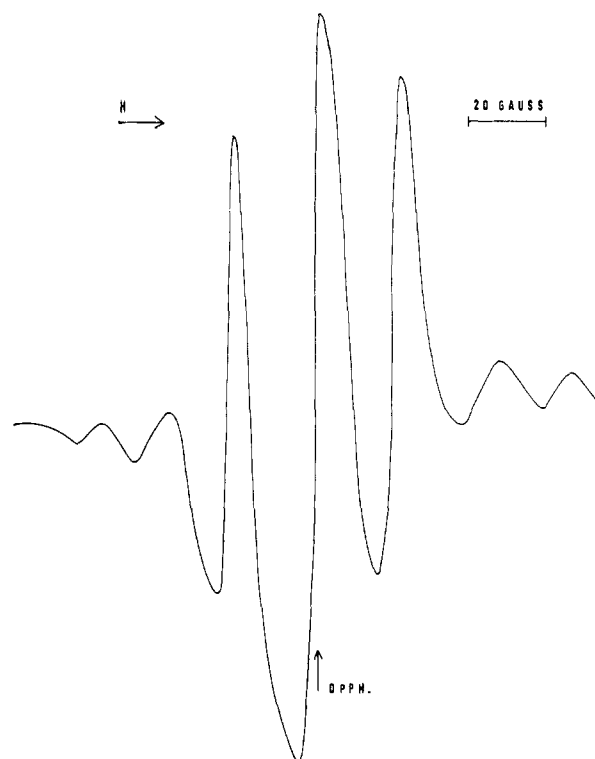

Fig. 3.—First derivative e.s.r. spectrum of the paramagnetic species from acetone (obtained on point by point subtraction of curve a from b in Fig. 2).
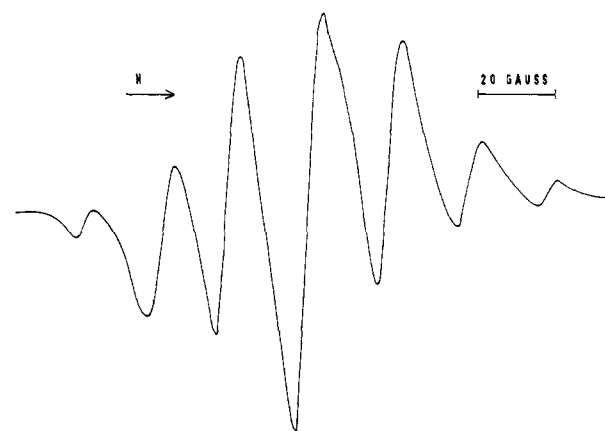

Fig. 4.—First derivative e.s.r. spectrum at 120°K. for 0.3 M NaH$_2$PO$_4$ + 0.3 M acetone previously irradiated with γ-rays at 77°K.

In Fig. 2, curve a is the central spectrum of irradiated bisulfate–ice, and curve b is the spectrum in the presence of acetone. Point by point subtraction leads to a seven-line spectrum with splitting of 22 gauss as shown in Fig. 3. The same type of spectrum is obtained in the H$_2$PO$_4$$^{-}$ ice containing added acetone which upon warming to 120°K. results in the decay of OH radicals,[12] and the seven-line spectrum is observed directly as seen in Fig. 4. These spectra can be attributed to the reaction product of an electron with an acetone molecule, i.e., the acetone negative ion, in which the unpaired electron interacts with the six protons. The approach to a binomial intensity distribution is much closer for the directly observed spectrum at 120°K. than for the one obtained by point by point subtraction at 77°K. There may also be a change in the relative line intensities with temperature which reflects the nonequivalence of the protons.[15]

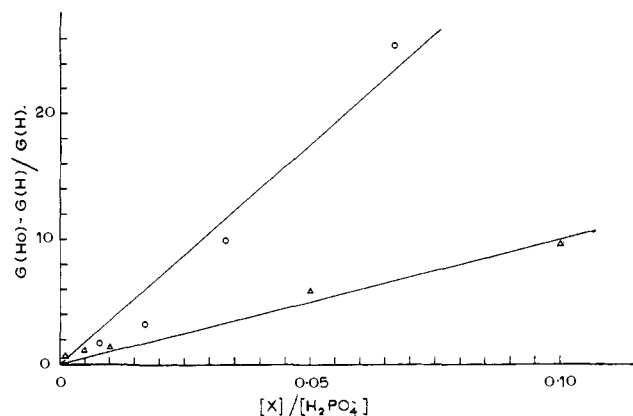(15) H. Zeldes and R. Livingston, J. Chem. Phys., **30**, 40 (1959).

Fig. 5.—γ-Irradiated ice at 77°K.: kinetic plots for competition of electrons between $H_2PO_4^-$ and NO_3^- (O) or acetone (Δ).

Fig. 6.—γ-Irradiated ice at 77°K.: kinetic plot for competition of electrons between $H_2PO_4^-$ and NO_2^-.

The addition reaction of a hydrogen atom with acetone would give the isopropyl alcohol radical which would also give a seven-line spectrum[16] with about the same splitting, but this reaction is very slow at room temperature in aqueous solution[6] and then would be expected to be even slower in ice at 77°K.

By utilizing ultraviolet (λ 2537 Å.) photolysis, direct evidence for the reaction of mobile electrons (polarons) was obtained.[17] Low energy ultraviolet photolysis does not generate electrons in pure water, but the photolysis of aqueous iodide solutions is known[6] to do so via reaction 16:

$$I^-(aq.) + h\nu \longrightarrow I + (H_2O)^-   (16)$$
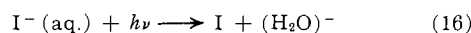
In the solid phase this method of electron generation is limited to transparent specimens; 6 M H_2SO_4 forms a transparent matrix on rapid cooling to 77°K., and when this contains 10^{-2} M KI, exposure (30 min.) of this system to a low pressure mercury vapor lamp gives strong hydrogen atom signals; no signals are observed in the absence of potassium iodide.

From these results one may conclude that the scavengeable hydrogen atoms are formed by a reaction involving mobile electrons (polarons). It is to be expected that the polaron in ice is physically not quite identical with the polaron in aqueous solutions, although it may have many similar chemical characteristics.

Kinetics of Competition Reactions.—By following the decrease in the hydrogen atom yields with scavenger concentration, the competition for the electron between a solute and a second solute, a scavenger, may be studied. Assuming that homogeneous kinetics apply, from eq. 2 and 17

$$(H_2O)^- + X \xrightarrow{k_{17}} \text{products}   (17)$$
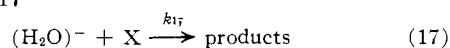
one obtains the expression

$$\{G(H)_0 - G(H)\}/G(H) = k_{17}[X]/k_1[S]   (18)$$

(16) J. F. Gibson, D. J. E. Ingram, M. C. R. Symons, and M. G. Townsend, *Trans. Faraday Soc.*, **53**, 914 (1957).
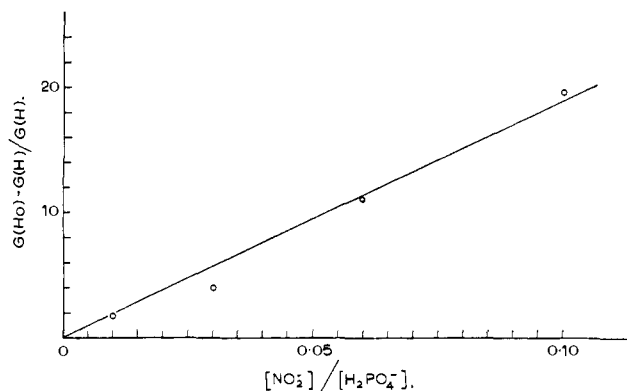
(17) Results to be published.

where [X] and [S] are the scavenger and solute concentrations, respectively, and $G(H)_0$ and $G(H)$ the yields of hydrogen atoms in the absence and presence of the scavenger. Plots of $\{G(H)_0 - G(H)\}/G(H)$ vs. $[X]/[H_2PO_4^-]$ are shown for X = NO_3^-, NO_2^-, and acetone in Fig. 5 and 6. Each point is the average of three runs. Linear plots are also obtained with HSO_4^- as solute and NO_3^-, Cu^{+2}, and acetone as scavengers. The kinetics in ices containing N_2O and CO_2 as scavengers could not be followed because of the limited solubility of these gases in aqueous solutions. In Table III the relative rate constants obtained from the slopes in Fig. 5 and 6 have been compared with those determined for electrons (polarons) in aqueous solution.[6] The polaron in ice is probably more reactive than in water. This may lead to a smaller difference in the relative rates of reaction of the polaron in ice as is shown from Table III. It is of interest to note that the

Table III

Comparison of Relative Rates of Reaction of the Negative Polaron in Aqueous Solutions and in Ice

Solute, X	$k\{(H_2O)^- + X\}/k\{(H_2O)^- + H_2PO_4^-\}$ (K) Aq. soln., 20°	Ice, −196°	Ratio $K_{20°}/K_{-196°}$
NO_3^-	1300	350	3.7
NO_2^-	770	185	4.2
Acetone	570	100	5.7
			4.5 ± 0.7

trend in the rate constant ratios of the different solutes is the same in both phases; this would indicate that the reacting species are somewhat similar, though not identical.