BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2383—2385(1972)

On the Mechanism of H-Atom Formation by Reaction of Electrons in Frozen Acidic Solutions at 77°K[1]

Shin-ichi OHNO, Teikichi SASAKI, and Mitsuru KOIKE
Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken

(Received November 13, 1971)

A model for the reaction of radiation-produced electrons in frozen acidic solutions is presented to explain anomalies. It does not assume the inertness of the hydrogen ion as an electron scavenger in the solid phase but involves a process in which an H-atom, the product of the (e^-+H^+) reaction, is transferred to an adjacent water molecule through an H-bonded network until it finds a suitable site where it can be trapped or a species with which to react. Results from ESR-measurements on photolysed frozen solutions of ferrocyanide ions in the presence of nitrate ions and 2-propanol as well as the data on H/D isotope effects were used as evidence supporting the model.

It is generally believed that radiation-produced electrons are converted into hydrogen atoms on reacting with the hydrogen ion in both liquid[2] and gas phases.[3]

$$e^- + H_3O^+ \longrightarrow H_3O \longrightarrow H + H_2O \qquad (1)$$

However, the above mechanism does not seem to hold in the solid phase, because of three anomalies: (1) The yield of H-atoms in ice is not as high as might be expected from the experimental results in the liquid phase.[4] (2) In a solvent consisting of D_2O and H_2O where both H- and D-atoms are produced, the product ratio H/D in the solid phase is quite different from that in gas or liquid phase.[5] (3) Paramagnetic relaxation experiments on γ-irradiated frozen aqueous systems have shown that the trapped H-atoms are distributed uniformly in the irradiated sample,[6] while the trapped electrons are non-uniformly distributed.

Some authors assume that the electron does not react with the hydrogen ion at 77°K,[4,7] but the trapped H-atoms found in irradiated acidic ice result from the reactions of the electron either with undissociated acids or with water molecules in the hydration layer of the added solute.[4,7] However, many other solutes, inorganic and organic, react with the electron as effectively in the solid as in the liquid phase.[4,8,9] The hydrogen ion would be the only exception for which no reason was given.[8]

The purpose of this paper is to present a model for the reaction of electrons in acidic ice which would reasonably explain the anomalies, not assuming the exceptional inertness of the hydrogen ion as an electron scavenger.

Experimental and Results

Electrons were generated from ferrocyanide ions by photolysis at 254 nm. The merit of this method over the radiolysis method is that other reactive species (*e.g.* OH, H, H_2O^+, or H_2O_2) are not produced, thus eliminating the complex reaction sequences. Details of the experimental procedures were the same as described.[5] ESR spectra of UV-irradiated frozen solutions (at 77°K) of 10^{-2}M potassium ferrocyanide containing various concentrations of sodium nitrate and 2-propanol are shown in Fig. 1. In the liquid phase, the electron (e_{aq}^-) reacts rapidly with both H_3O^+ and NO_3^- (rate constants$\approx 10^{10}$M^{-1}s^{-1}) but not with 2-propanol,[10] while the H-atom reacts with both NO_3^- and 2-propanol (rate constants$\approx 10^{7}$M^{-1}s^{-1}) but only slowly with H_3O^+.[10] Thus, one might expect that, in a frozen solution containing 10^{-3}M NO_3^- and 10^{-1}M 2-propanol, the electron reacts only with NO_3^- to

---

[1] Presented at 4th Intern. Conf. Radiation Res., Evian, 1970.

[2] E. J. Hart, "Actions Chemiques et Biologiques des Radiations," Ed. by M. Haissinsky, Masson & Cie., (1966). Ser. **10**, Chap. 1.

[3] G. R. A. Johnson and M. Simic, "The Chemistry of Ionization and Excitation," Ed. by G. R. A. Johnson and G. Scholes, Taylor & Francis Ltd., (1967), p. 211.

[4] L. Kevan, "Radiation Chemistry of Aqueous Systems," Ed. by G. Stein, Weizmann Science Press, (1968), p. 21.

[5] S. Ohno, This Bulletin, **41**, 1301 (1968).

[6] J. Zimbrick and L. Kevan, *J. Chem. Phys.*, **47**, 5000 (1967).

[7] L. Kevan, P. N. Moorthy, and J. J. Weiss, *J. Amer. Chem. Soc.*, **86**, 771 (1964).

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

[9] L. Kevan, *J. Amer. Chem. Soc.*, **89**, 4238 (1967).

[10] M. Anbar and P. Neta, *Intern. J. Appl. Radiation Isotopes*, **18**, 493 (1967).

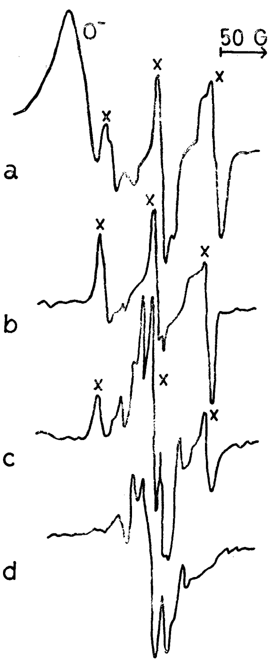


Fig. 1. ESR spectra of UV-irradiated frozen solutions (at 77°K) of 10^{-2} M $K_4[Fe(CN)_6]$ containing various concentrations of $NaNO_3$ and 2-propanol.

Medium	$[NO_3^-]$, M	[2-propanol], M
(a): 5N NaOH	0.001	0.1
(b): 1N H_2SO_4	0.01	0.01
(c): 1N H_2SO_4	0.001	0.1
(d): 1N H_2SO_4	0	0.2

Lines (×) refer to the signals due to the NO_2 radical.

give NO_2 radical. This was found to be the case with an alkaline medium (Fig. 1, a), but not with an acidic medium (Fig. 1, c) where the signals due to the NO_2 radicals are largely replaced by one due to the 2-propanol radical.[11] This suggests that the electron is converted into an H-atom on going from an alkaline to an acidic medium.

One of us (S. O.) observed[5] the product ratio H/D arising from the reaction between the electron and the hydrogen ion in a solvent composed of light and heavy water (the atom ratio in the solvent $(H/D)_{water}=1$) in the liquid phase as a function of temperature (2—40°C) and also in the solid phase at 77°K. Since it is known that H-atoms are fractionated over D-atoms in the hydronium ion, the observed isotope effect (S_{all}) will comprise two consecutive isotope effects; the equilibrium isotope effect (K) in the formation of hydronium ion from water and the kinetic isotope effect (S_{ion}) in the formation of hydrogen atom from the hydronium ion.

$$S_{all} = K \times S_{ion} \tag{2}$$

The value of the equilibrium isotope effect at various temperatures can be calculated with data by Heinzinger and Weston.[13] The observed overall isotope effects together with the kinetic isotope effects thus calculated for the liquid phase system are plotted in Fig. 2 against the reciprocal of absolute temperature. The value obtained at 85°C by Meyerstein[14] and the gas phase datum at 140°C reported by Johnson and Simic[3] are also given.

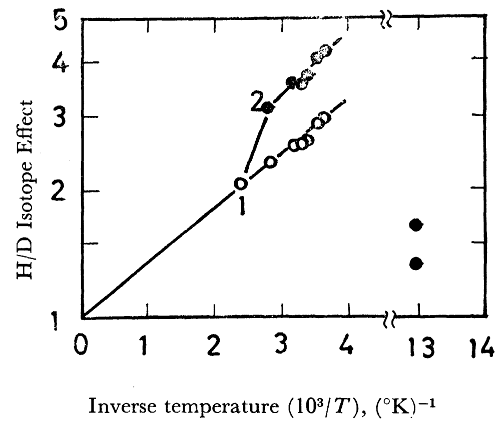


Fig. 2. Temperature dependence of the isotope effects on H/D atom production.
Point (1) refers to the gas phase datum obtained by Johnson and Simic at 140°C (Ref. 3). Point (2) is that due to Meyerstein (Ref. 14). The other values of S_{ion} (●) are from Ref. 5. For S_{all} (○), see text.

Discussion

The straight line (in Fig. 2) throughout the liquid and gas phase regions which is obtained when $\log(S_{ion})$ is plotted against $1/T$ indicates that the same reaction mechanism holds in both phases and that the relative rates of O–H and O–D bond breakages k_H/k_D can be given by

$$\frac{k_H}{k_D} = \exp\left(\frac{E_D - E_H}{RT}\right) \tag{3}$$

where E_H and E_D are the activation energy of O–H and O–D breakages, respectively. The slope of the straight line in Fig. 2 gives $E_D - E_H = 0.6$ kcal/mol. A value of this order of magnitude might be appropriate for the difference in zero-point energy between O–H and O–D bonds in the intermediate complex such as H_2DO.

On the other hand, the observed isotope effect in the solid phase is strikingly low ($S_{all} \approx 1.5$), suggesting that the H-atom trapping process in the solid differs a great deal from liquid phase reactions.

---

[11] ESR signals ascribed to NO_2 and 2-propanol radicals are identical with those reported by Chachaty and Hayon.[12]

Figure 1, a, shows the presence also of O^- radical ion. They can be formed as follows:

$$e^- + NO_3^- \longrightarrow NO_3^{2-}$$

$$\begin{cases} NO_3^{2-} + H_2O \longrightarrow NO_2 + 2OH^- \\ NO_3^{2-} \longrightarrow NO_2^- + O^- \end{cases}$$

[12] C. Chachaty and E. Hayon, *J. Chim. Phys.*, **60**, 1115 (1964).

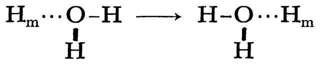
[13] K. Heinzinger and R. E. Weston, *J. Phys. Chem.*, **68**, 744 (1964).

[14] D. Meyerstein, Ph. D. Thesis, Hebrew Univ. 1965, quoted by M. Anber and D. Meyerstein, in Ref. 4, p. 109.

The results shown in Fig. 1 indicate that photodetached electrons from ferrocyanide ions are converted into H-atoms in sulfuric acid ice. Fletcher and Freeman observed that the trapped H-atom yields, $G(\mathrm{H_t})$, found in γ-irradiated sulfuric acid glasses can be reduced from 1.3 to 0.24 by the presence of 10^{-3} mol fraction of ethanol.[15] This demonstrates that the precursor of $\mathrm{H_t}$ in the acid glass which can react with ethanol might be an H-atom rather than an electron. Recent observations that the presence of sulfuric acid in frozen aqueous solutions of a number of organic compounds enhances the yield of the radiation-produced organic radical[16] also suggest the conversion of the electron into an H-atom in acidic ice.

Concerning H-atom trapping in irradiated ice, the following facts are well-known. H-atoms are not stabilized in pure water at 77°K, though they are stable near 4°K.[4] At 77°K, only aqueous systems containing ions of a certain type such as $\mathrm{ClO_4^-}$, $\mathrm{SO_4^{2-}}$, or $\mathrm{PO_4^{3-}}$ can stabilize H-atoms.[17] Acids such as HF, $\mathrm{CCl_3COOH}$, $\mathrm{H_2SO_3}$ do not give stabilized H-atoms when irradiated at 77°K.[17] This would indicate that at 77°K H-atoms can migrate through the water structure until they reach a trapping site which can stabilize an H-atom. The structure of this particular trap in the ice cannot be precisely visualized as yet, but it is probably associated with an oxyanion. According to Ultee and Kepford,[17] the site involves a hydrated $\mathrm{MO_4^-}$-type ion, which in aqueous solution should provide a tight three-dimensional lattice, destroying the open structure of ice rather than providing a specific site.

We feel that reaction (1) takes place irrespective of the phase, *i.e.*, even in the solid phase. An H-atom, the product of reaction (1) in the solid phase, will be transferred through the hydrogen-bonded network of the ice and be trapped stably at the site which can stabilize the $\mathrm{H_t}$.



$$\mathrm{H_m\cdots \underset{\displaystyle H}{\overset{}{O}}\!-\!H \longrightarrow H\!-\!\underset{\displaystyle H}{O}\cdots H_m} \tag{4}$$

Here, a moving H-atom is designated by $\mathrm{H_m}$. An H-atom transfer of this type can be caused by the thermal vibration of the lattice at 77°K, but not at 4°K. The process may be so slow that in the liquid phase the H-atom would predominantly diffuse about in the usual sense to be scavenged by the solute added. Such a transfer would prevail only in the solid phase where all the atoms can be assumed to be immobilized.

Our model would explain the three anomalies associated with the solid phase. Assuming that the observed $\mathrm{H_t}$ is caused by reaction (1) alone, not including an H-atom transfer, an H/D isotope effect as large as 50 would be expected at 77°K if Eq. (3) holds. In fact, a value of about 1.5 was obtained. The value of $\mathrm{H_t/D_t}$ by the present model would be a consequence of the H/D atom ratio eventually present in the trapping site. The isotope effect of this kind does not arise from competing reactions and will not make the value of H/D largely differ from unity. It is thus not surprising that a marked difference in the magnitude of the isotope effect is found between the solid and the liquid phases.

One may expect that, in an acidic ice, competition occurs between the solute(S) and the trapping site(T) for the moving H-atom through the H-bonded chain-($\mathrm{H_m}$):

$$\mathrm{e^- + H_3O^+ \longrightarrow H_m}\begin{cases}\mathrm{+\,T \longrightarrow H_t}\\ \mathrm{+\,S \longrightarrow [SH]}\end{cases} \tag{5}$$

[SH] would decompose to give more stable species in the matrix. If as an example $\mathrm{NO_3^-}$ and 2-propanol are taken for S, the decomposition would be:

$$\mathrm{[NO_3H^-] \longrightarrow NO_2 + OH^-\ \text{or}\ NO_2^- + OH} \tag{6}$$

$$\mathrm{[(CH_3)_2CHOH_2] \longrightarrow (CH_3)_2COH + H_2} \tag{7}$$

Reaction (7) is a possible process producing the alcohol radical by an attack of a diffusing H-atom.[18] If we assume that the order of magnitude for the concentration of T in an acidic glass to be 10^{-2}M, any solute which is involved in the H-bonded chain and which can scavenge $\mathrm{H_m}$ could reduce the yield of $\mathrm{H_t}$, even though its concentration is small compared to that of the acid. This is why the hydrogen ion does not apparently react with the electron in frozen matrices.

The wider distribution from the point of energy deposit of the trapped H-atoms than that of the trapped electrons may also be understood.

It is of interest to note that the mobile energy in 5.3M $\mathrm{H_2SO_4}$ glass, assumed by Dainton and Gopinathan,[21] which can liberate $\mathrm{Cl^-}$ ion from chloracetic acid (with a *G*-value of about 2), and which is incapable of reacting with nitrous oxide is possibly the mobile H-atom through hydrogen bonds.

---

[15] J. W. Fletcher and G. R. Freeman, *Can. J. Chem.*, **45**, 635 (1967).

[16] P. N. Moorthy, G. Gopinathan, and K. N. Rao, *Radiation Effects*, **2**, 175 (1970).

[17] C. J. Ultee and C. R. Kepford, *J. Chem. Phys.*, **52**, 3462 (1970).

[18] Hagopian and Johnsen showed that thermal energy H-atoms produced by a heated tungsten-filament do not abstract α-H from ethanol at 77°K,[19] whereas many other authors observed that the $\mathrm{H_t}$ in sulfuric acid glass disappears, in the presence of organic substances, to be replaced by organic radicals.[15,16,20] The latter observation may be explained in terms of the $\mathrm{H_m}$-scavenging process by organic compounds.

[19] A. K. E. Hagopian and R. H. Johnsen, *J. Phys. Chem.*, **72**, 1949 (1968).

[20] W. Köhnlein and D. Schulte-Frohlinde, *Radiation Res.*, **38**, 173 (1969).

[21] F. S. Dainton and G. Gopinathan, *Trans. Faraday Soc.*, **65**, 143 (1969).