BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1301—1307 (1968)

The H/D Isotope Effect in the Conversion of the Electron into a Hydrogen Atom in Aqueous Acid Solutions at 300 and 77°K[1]

Shin-ichi OHNO

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki

(Received December 18, 1967)

The isotope effect in the formation of hydrogen atoms as a result of the reaction of the photochemically-produced electron in an acidified solution of hexacyanoferrate(II) has been investigated in both the liquid and solid phases. The magnitude of the effect (H/D) in the liquid phase, determined by a mass-spectrometric analysis of the hydrogen gas evolved from CH_3OH-containing solution, ranges from 3 to 4, and it depends on the temperature. The corresponding H/D ratio in acidic ices (at 77°K), determined by comparing the relative intensities of the ESR signals of the H and D atoms, is rather low ($\sim$1.5). Possible mechanisms by which the electron is converted into a hydrogen atom in aqueous acid solutions in both phases are discussed.

Electrons which are generated either by the ionization of water molecules (in radiation chemistry) or by photo-detachment from the solute (in photochemistry) have been shown to react with a variety of substances.[2,3] Many of these reactions in an aqueous solution are diffusion-controlled and may, therefore, be expected to occur even at low temperatures, provided that the reactants can encounter each other. The reaction:

$$e_{aq}^- + H_3O^+ \rightarrow H + H_2O \qquad (1)$$

is one such fast reaction.

The H/D isotope effect in the formation of hydrogen atoms as a result of the reaction of the photochemically-produced electron in an acidified solution of $[Fe(CN)_6]^{4-}$ by way of Reaction (1) has previously been reported;[4] the magnitude of the effect depends slightly on the temperature. Although, these experiments might be helpful in the understanding of the above reaction, no

---

[1] Presented at the 10th Symposium of Radiation Chemistry, Hiroshima, October, 1967.

[2] a) "Solvated Electron," *Advances in Chemistry Series*, No. 50, American Chemical Society, Washington, D. C., 1965. b) E. J. Hart, The Hydrated Electron, in "Actions Chimiques et Biologiques des Radiations," ed. by M. Haissinsky, Masson and Cie., Paris, 1966, Series 10, Chap. 1.

[3] S. Ohno, This Bulletin **38**, 2018 (1965).

[4] S. Ohno, *ibid.*, **39**, 2560 (1966).

details of the experimental results were given, nor was there any detailed discussion of them. The present author has since measured the ratio of the H/D atoms produced in UV-irradiated acidic ices (at 77°K) containing $[Fe(CN)_6]^{4-}$ by comparing the relative intensities of the ESR signals of the H and D atoms. The H/D ratio observed in an equi-molar mixture of H_2O-D_2O ice is rather low (~1.5) as compared with the corresponding value (~3.5) in the fluid phase. This paper will present these results and will consider the reaction mechanism of the electron in both phases.

Experimental

A low-pressure mercury lamp of the spiral type was used as the light source.[5] The light of wavelengths below 2000 Å was eliminated using a 0.1 M NaCl solution as a filter. Solutions were prepared from laboratory-distilled water. The heavy water (99.7%) was from Showa Denko Co., Ltd. The other chemicals used were of the purest grade available.

Liquid-phase Experiments. Irradiations were carried out in a quartz cylindrical vessel 3 cm in diameter employing 30 or 50 *ml* of the solution. The vessel immersed in a thermostat was connected to a vacuum system. The solution was evacuated as has been previously described.[5] The solution was irradiated for 30 min, during which period it was stirred by a magnetic stirrer. After irradiation, the evolved gas (~0.7 cm^3) was analysed by a CEC 103 mass spectrometer after having passed through a trap cooled to −196°C. The peak heights were determined in the order of m/e: 2, 3, 2, in order to take into account pressure changes in the mass spectrometer. The D_2 ($m/e=4$) was not observed at any time during the experiment. No correction for the fractionation in the mass spectrometer was made, as this is identical for all the samples and was found to be small (an absolute error <10%).[6]

Solid-phase Experiments (ESR Measurements). The electron spin resonance spectra were obtained with a JEP-1 spectrometer operating at 9.4 kMc and with 100 kc/s field modulation. The spectra recorded, after phase-sensitive detection, form the first derivative of the absorption curves.

Sample solutions, after having been flushed with argon, were rapidly frozen in 0.4-cm-diam. quartz tubes in liquid nitrogen. All the frozen samples appeared opaque, except for the 10 N NaOH-solutions, which appeared glassy. The samples weighed about 0.1 g; freezing was complete in about 10 sec. The quartz tube was then placed inside a quartz Dewar flask filled with liquid nitrogen and positioned in the center of the spiral lamp. After irradiation the specimens were transferred, without having been allowed to warm up, into liquid nitrogen in a quartz tipped-Dewar flask, which fits into the ESR cavity. A stream of nirogen gas was passed through the cavity in order to prevent condensation of moisture on the tip of the dewar.

Results

H/D Isotope Effects in the Liquid Phase. When an aqueous acidic solution of potassium hexacyanoferrate(II) containing 1 M CH_3OH is irradiated by light with a wavelength of 2537 Å, the following reactions occur:[5]

$$[Fe(CN)_6]^{4-} + h\nu \rightarrow [Fe(CN)_6]^{3-} + e_{aq}^- \qquad (2)$$

$$e_{aq}^- + H_3O^+ \rightarrow H + H_2O \qquad (1)$$

$$H + CH_3OH \rightarrow H_2 + CH_2OH \qquad (3)$$

$$CH_2OH + [Fe(CN)_6]^{3-} \rightarrow H^+ + HCHO + [Fe(CN)_6]^{4-} \qquad (4)$$

In an H_2O-D_2O mixture where the hydrogen ion exists as H_3O^+, H_2DO^+, HD_2O^+ and D_3O^+, both H and D atoms are formed in Reaction (1). Its isotope effect may be measured from the evolved H_2/HD ratio, as the hydrogen atoms thus produced, H and D, react with CH_3OH by Reaction (3) to yield H_2 and HD respectively. The results obtained at a constant temperature (*ca.* 27°C) using various sulfuric acid concentrations are presented in Table 1. In this table, $(H/D)_{water}$ means the H *vs.* D atom ratio in the solution; $(H/D)_{atom}$ means that of the hydrogen atom produced, which is measured as the observed H_2/HD ratio; S is the $(H/D)_{atom}/(H/D)_{water}$ ratio, and is commonly called the separation factor.[7] Table 2 presents the results obtained at $[H_2SO_4]=0.1$ N and $(H/D)_{water}=1.1$, but at various temperatures of irradiation.

It should be noted that the interaction of H and D atoms with the solvent does not contribute to the isotope effect in the present case, since the exchange reaction:

$$D + H_2O \rightarrow H + HDO \qquad (5)$$

was found to be slow ($k=2$ sec^{-1} at pH 2).[8] Formaldehyde, which is produced by Reaction (4),

TABLE 1. H/D ISOTOPE EFFECTS AS A FUNCTION OF SULFURIC ACID CONCENTRATION AT CONSTANT TEMPERATURE (*ca.* 27°C)

$[H_2SO_4]$, N	$(H/D)_{water}$	$(H/D)_{atom}$	S
1.2	1.94	6.78	3.5
0.6	1.92	6.90	3.6
0.35	1.11	3.49	3.1
0.12	1.90	6.85	3.6
0.07	1.11	3.52	3.2
0.05	1.12	4.3	3.9
0.01	1.11	3.16	2.9
0.001	1.11	1.88	1.7

---

[5] S. Ohno, *ibid.*, **40**, 1770 (1967).

[6] This was checked using the standard hydrogen gas sample prepared by Zn-decomposed water mixtures (H_2O-D_2O). The author wishes to thank Dr. Takuji Komori, Analytical Division, Japan Atomic Energy Research Institute, for his kindly offering the samples.

[7] J. Jortner and G. Stein, *Intern. J. Appl. Radiation Isotopes*, **7**, 198 (1960).

[8] H. L. Friedman and A. H. Zeltman, *J. Chem. Phys.*, **28**, 878 (1958).

TABLE 2. H/D ISOTOPE EFFECTS AS A FUNCTION OF THE TEMPERATURE, OBSERVED AT $[H_2SO_4]=0.1$ N AND $(H/D)_{water}=1.1$

Temp., °C	L	$K(=L^{1/6})$	S	$S_{ion}(=S/K)$
2.0	9.43	1.45	4.35	3.00
10.4	8.94	1.44	4.16	2.89
21.6	8.36	1.42	3.80	2.68
25	8.20	1.42	—	—
30.2	7.97	1.41	3.64	2.58
40.8	7.54	1.40	3.61	2.58

shows a rather low reactivity toward e_{aq}^- and H atoms.[9]

In a solvent composed of light and heavy water, the isotopic composition of the hydrogen ion differs from that of the solvent.[10-12] These two quantities are related by the equilibrium constant;

$$K = (H/D)_{hydrogen\ ion}/(H/D)_{water} \qquad (6)$$

which determines the fractionation effect. The K constant corresponds[13] to $L^{1/6}$, L being the equilibrium constant for the reaction:

$$2\,D_3O^+ + 3\,H_2O = 2\,H_3O^+ + 3\,D_2O,\ L \qquad (7)$$

if one assumes that the proton is solvated in the H_3O^+ form.[14] The value of L has been evaluated by different methods; these have been reviewed and discussed by Heinzinger and Weston[10] and by Schaleger, Salomaa and Long.[11] Following these authors, here we take the value of 8.2 for L at 25°C. The values at other temperatures can be calculated using an approximate value of -1000 cal mol^{-1} for ΔH[10] for Reaction (7). The results of these calculations are included in Table 2. Fortunately, the uncertainty of this temperature coefficient is not at all serious when $K(=L^{1/6})$ is considered. The last coulmn of Table 2 refers to the isotopic fractionation (S_{ion}) due to the production of hydrogen atoms from the hydrogen ion (in Reaction (1)), calculated from the relation:

$$\begin{aligned} S &= (H/D)_{atom}/(H/D)_{water} \\ &= \left[\frac{(H/D)_{atom}}{(H/D)_{hydrogen\ ion}}\right]\times\left[\frac{(H/D)_{hydrogen\ ion}}{(H/D)_{water}}\right] \\ &= S_{ion}\times K \end{aligned} \qquad (8)$$

ESR Measurements of Frozen Alkaline and Neutral Solutions. The irradiation of the $[Fe(CN)_6]^{4-}$ ions (10^{-2}—10^{-3} M) in 10 N NaOH at 77°K with a light with a wavelength of 2537 Å gave an intense blue-violet color and an ESR signal consisting of a single narrow line at $g=2.00$ and with a maximum slope-linewidth of 17 gauss (Fig. 1, (a)). On exposure to visible light, both the blue-violet color and the ESR signal are lost (Fig. 1, (a), dotted curve); this ESR line is identical with the well-known signal of the trapped electron, e_t^-.[15-19]

The same solution, however, if irradiated with light of 3660 Å, gave no blue-violet color and no ESR signal attributable to e_t^-. Instead, there appeared an unidentified signal (Fig. 1, (b));

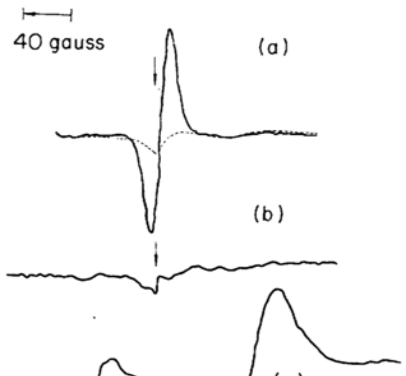


Fig. 1. ESR spectra of UV-irradiated frozen solutions of 10^{-2} M $[Fe(CN)_6]^{4-}$ at 77°K. Arrows show the field value of the DPPH signal. (a) 2537 Å, 10 N NaOH; (b) 3660 Å, 10 N NaOH; (c) 2537 Å, 10 N NaOH containing 10^{-2} M NO_3^-; (d) 2537 Å, neutral ice containing 10^{-2} M $ClCH_2COOH$

---

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

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

11) L. L. Schaleger, P. Salomaa and F. A. Long, in "Chemical Physics of Ionic Solutions," ed. by B. E. Conway and R. G. Barradas, John Wiley and Sons, Inc., New York (1966), p. 237.

12) A. J. Kresge and A. L. Allered, *J. Am. Chem. Soc.*, **85**, 1541 (1963); V. Gold, *Proc. Chem. Soc.*, **1963**, 141.

13) This simplification results from the assumption of the rule of the geometric mean as applied to the isotopically homologous series H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+, as well as to the series H_2O, HDO, and D_2O. See, for example, Ref. 10 or 11.

14) It has been shown that the various estimates of L are compatible with the results of proton magnetic resonance experiments (Ref. 12) only if the proton is formulated as H_3O^+. This by no means excludes the model for the hydrogen ion in which a hydronium ion is further solvated by three water molecules, *i. e.*, $H_9O_4^+$. See Refs. 10 and 11.

15) D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, **17a**, 445 (1962); *ibid.*, **18a**, 99 (1963).

16) T. Henriksen, *Radiation Res.*, **23**, 63 (1964).

17) P. N. Moorthy and J. J. Weiss, *Phil. Mag.*, **10**, 659 (1964).

18) P. B. Ayscough, R. G. Collins and F. S. Dainton, *Nature*, **205**, 965 (1965).

19) M. J. Blandamer, L. Shields and M. C. R. Symons, *J. Chem. Soc.*, **1964**, 4352.

this is a strong confirmation of the previous findings that the d-d excitation of $[Fe(CN)_6]^{4-}$ does not lead to an electron-detachment,[5,20] while the charge-transfer excitation results in an electron release.

It should be noted that the presence of 10^{-2} M NO_3^- in an UV(2537 Å)-irradiated 10 N NaOH solution of $[Fe(CN)_6]^{4-}$ reduced completely the signal due to the e_t^-; instead, there appeared a more complex signal (Fig. 1, (c)), with the specimen turning yellow. The presence of 10^{-2} M N_2O in the same system, on the other hand, caused no significant change.

Moreover, in an UV(2537 Å)-irradiated neutral ice containing 10^{-2}—10^{-3} M $[Fe(CN)_6]^{4-}$ and $ClCH_2COOH$, the signal attributable to the radical, CH_2COOH,[18] is observed (Fig. 1, (d)):

$$e + ClCH_2COOH \rightarrow Cl^- + CH_2COOH \qquad (9)$$

H/D Isotope Effects in Frozen Solutions. The electron is converted to the hydrogen atom in frozen aqueous acid solutions.[16,21-23] Figure 2 shows the ESR signals of the H and D atoms thus produced in an H_2O—D_2O mixture at 77°K. A doublet of 509 gauss and a triplet of 153 gauss (end-to-end) are due to the H and D atoms respectively. The origin of the small signal in the center portion of the spectrum is not known. In both the H and D atom spectra, the low-field lines are somewhat more intense than the high-field lines.

The relative concentrations of H and D atoms can be determined by calculating the sums of the hw^2 values of the H and D lines respectively, where h is the height of the line and w, its width at a maximum slope of the first derivative curve. In effect, the signal intensities were calculated simply from the heights of the lines, as the linewidths and shapes for the H and D lines in the H_2O-D_2O (50% D) system were nearly identical (the linewidth: about 4 gauss). The satellite lines appeared in some cases (Fig. 3), as is often observed in γ-irradiated ice,[16,23b,24] but this, too, was identical in both the H and D spectra.

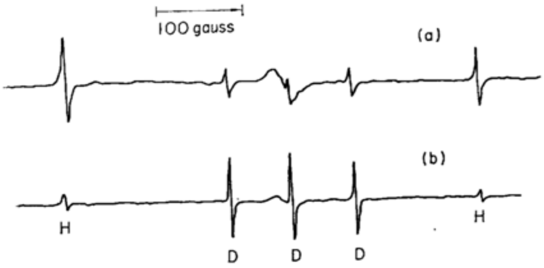


Fig. 2. ESR spectra of UV(2537 Å)-irradiated acid solutions (H_2O-D_2O) of 10^{-3} M $[Fe(CN)_6]^{4-}$ at 77°K.
(a) $[H_2SO_4]=0.01$ N, $(H/D)_{water}=1$
(b) $[H_2SO_4]=0.6$ N, $(H/D)_{water}=0.05$

Fig. 3. The high field atomic D line in a frozen solution ($(H/D)_{water}=1$) of 1 N H_2SO_4 showing weak satellites.

Because of the well-known phenomenon of the microwave power saturation of the H atom signal,[16,25] it was necessary to check the saturation modes of both the H and D signals. Both of them

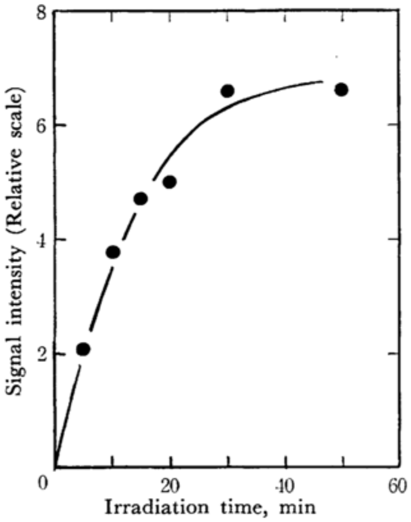


Fig. 4. Signal intensity of H-atoms as a function of irradiation time; Irradiation at 2537 Å and 77°K of a 10^{-3} M $[Fe(CN)_6]^{4-}$ solution containing 1 N H_2SO_4.

---

[20] S. Ohno and G. Tsuchihashi, This Bulletin, **38**, 1052 (1965).

[21] J. J. Weiss, *Nature*, **186**, 751 (1960); L. Kevan, P. N. Moorthy and J. J. Weiss, *ibid.*, **199**, 698 (1963).

[22] F. S. Dainton and F. T. Jones, *Trans. Faraday Soc.*, **61**, 1681 (1965).

[23] a) R. Livingston and A. J. Weinberger, *J. Chem. Phys.*, **33**, 499 (1960). b) R. Livingston, H. Zeldes and E. H. Taylor, *Discussions Faraday Soc.*, **19**, 166 (1955).

[24] H. N. Rexroad and W. Gordy, *Phys. Rev.*, **125**, 242 (1962).

[25] S. Siegel, J. M. Flournoy and L. H. Baum, *J. Chem. Phys.*, **34**, 1782 (1961); H. S. Jueikis, J. M. Flournoy and S. Siegel, *ibid.*, **37**, 2272 (1962).

were found to be nearly in the region of power saturation, even at the lowest crystal current employed. However, the signal heights for the H and D lines relative to each other are constant within the limits of experimental error at crystal currents below 0.2 mA. The actual measurements were made within this range.

No decay in the H and D signals was seen over a period of several days at the temperature of liquid nitrogen.

In all the systems examined, the signal intensities increased with the irradiation time, reaching a more or less steady value upon prolonged irradiation (Fig. 4). The signal intensities, resulting from irradiation for 15 min, on the linear part of the yield-time curve were used to calculate the relative yields of H and D atoms.

The results obtained with photolysed H_2O-D_2O mixtures containing 10^{-3} M $[Fe(CN)_6]^{4-}$ and varying amounts of sulfuric or perchloric acid are shown in Table 3. The error included may be small (±10%), as the conditions under which the spectra were obtained were exactly identical with those for the H and D atoms in each measurement.

TABLE 3. H/D ISOTOPE EFFECT IN THE FORMATION OF THE HYDROGEN ATOMS ORIGINATING FROM THE REACTION OF THE ELECTRON IN ACID ICES AT 77°K
Obtained at $(H/D)_{water}=1.0$ and $[Fe(CN)_6{}^{4-}]10^{-3}$ M

	Acid concn., N	S, (H/D)
H_2SO_4	1	1.33
H_2SO_4	0.5	1.46
H_2SO_4	0.1	1.42
H_2SO_4	0.05	~2.2*
$HClO_4$	1	1.86
$HClO_4$	0.1	1.56

* Hydrogen atom yields are low by a factor of ten.

Discussion

Possible Mechanisms for Observed Isotopic Effects in the Liquid Phase. In a previous communication,[4] the relative rates of O–H and O–D breakages, k_H/k_D, from the isotopic hydronium ion were computed on the simple assumptions that the $H_nD_{3-n}O^+$ species ($n=0$, 1, 2, or 3) gives the H or D atom in the $H/D=nk_H/(3-n)k_D$ ratio, and that the reactivity of $H_nD_{3-n}O^+$ with e_{aq}^- does not depend on the value of n. There, however, the implausibly high k_H/k_D value of 4—5 was obtained, in comparison with the low value observed ($S=1.2$)[26] for the isotope effects in the vapor-phase radiolysis of water, where monomolecular decompositions of the excited H_2O or the neutralization of the H_3O^+ ion are probably involved,[26,27] according to the following reactions:

$$H_2O^* \rightarrow H + OH \quad (10)$$

$$H_2O \rightarrow H_2O^+ + e \quad (11)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (12)$$

$$H_3O^+ + e \rightarrow H + H_2O \quad (13)$$

In the condensed medium, where interaction with another water molecule can easily occur, the mode of H-atom production may be very complex.

The rate constant of Reaction (1)[28,29] is 2—2.3 $\times 10^{10}\ M^{-1}sec^{-1}$; its activation energy is 3.2 kcal/mol.[30] This latter value is nearly identical with that of the diffusion-controlled neutralization reaction (14), namely, 3.5 kcal/mol:[31]

$$H_3O^+{}_{aq} + OH^-{}_{aq} \rightarrow 2\,H_2O \quad (14)$$

Yet Reaction (1) proceeds 6—7 times less rapidly than Reaction (14) ($k_{14}=1.4\times10^{11}\ M^{-1}sec^{-1}$ [32]). The most rapidly diffusing species in both of these reactions is likely to be $H_3O^+{}_{aq}$ presumably by a mechanism of H transfer along the chain of hydrogen-bonded waters,[33] since the diffusion coefficient of the e_{aq}^- ($4.7\times10^{-5}\ cm^2sec^{-1}$ at 25°C[34]) is rather low compared with that of $H_3O^+{}_{aq}$ ($9.5\times 10^{-5}\ cm^2sec^{-1}$).

It may be speculated that the proton interacting with the negative charge due to the e_{aq}^- forms an intermediate complex, *i. e.*, $(H_3O^+\cdot e^-)_{aq}$, which then decomposes either to give the H atom or to regenerate e_{aq}^-:[35]

$$H_3O^+{}_{aq} + e_{aq}^- \rightarrow (H_3O^+\cdot e^-)_{aq} \quad (1a)$$

$$(H_3O^+\cdot e^-)_{aq} \rightarrow e_{aq}^- + H_3O^+ \quad (1b)$$

$$\searrow H + H_2O \quad (1c)$$

---

26) J. Y. Yang and I. Marcus, *J. Am. Chem. Soc.*, **88**, 1625 (1966).

27) J. H. Baxendale and G. P. Gilbert, *Discussions Faraday Soc.*, **36**, 186 (1963); F. Fiquet-Fayard, *J. Chim. Phys.*, **57**, 453 (1960); G. R. A. Johnson and M. Simic, *J. Phys. Chem.*, **71**, 1118 (1967); I. Santar and J. Bednar, *Collection Czechoslov. Chem. Commun.*, **32**, 953 (1967).

28) J. P. Keene, *Radiation Res.*, **22**, 1 (1964).

29) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963).

30) J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).

31) M. S. Matheson in Ref. 2a; G. Ertl and H. Gerisher, *Z. Elektrochem.*, **66**, 560 (1962).

32) M. Eigen and L. DeMaeyer, *ibid.*, **59**, 986 (1955).

33) R. A. Horne and E. H. Axelrod, *J. Chem. Phys.*, **40**, 1518 (1964).

34) K. H. Schmidt and W. L. Buck, *Science*, **151**, 70 (1966).

35) Melton and Joy has recently reported the existence of H_3O in the gas phase evidenced by a mass-spectrometric study. If such a species exists in an aqueous solution, then one might consider the H_3O in place of $(H_3O^+\cdot e^-)_{aq}$ in the present argument. See C. E. Melton and H. W. Joy, *J. Chem. Phys.*, **46**, 4275 (1967). The theoretical calculation of Bishop does not predict the existence of H_3O, however; D. M. Bishop, *J. Chem. Phys.*, **45**, 2474 (1966).

Reaction (1a) is expected to proceed at a diffusion-controlled rate (the same as Reaction (14); thus, $k_{1a}=1.4\times10^{11}$ M^{-1}sec^{-1}).[36] In this scheme, the observed rate of Reaction (1), k_1, is expressed by:

$$k_1 = \frac{k_{1a}k_{1c}}{k_{1b}+k_{1c}} \tag{15}$$

Using the reported value for k_1[28,29] and the assumed value for k_{1a} as above, one gets $k_{1b}/k_{1c}=5$. The value of k_{1b}/k_{1c} might be different for each isotopic hydronium ion, $H_nD_{3-n}O^+$, where $n=0$—3, thus causing some part of the isotopic effects observed.

The results shown in Table 2 would indicate that the isotope effect for H-atom *vs.* D-atom production by way of Reaction (1c) ranges from 2.6 to 3, and that it depends slightly on the temperature. Even if the highest possible value for the ΔH of Reaction (7), namely, $\Delta H=-2000$ cal/mol,[10] is adopted, this causes only slight changes (1% or less) in the value of K and, thus, in the value of S_{ion}. Other systematic errors in obtaining S_{ion} are all identical for all the results. One may thus conclude that decreasing the temperature results in an enhancement of the isotope effect.

The isotope effect found here is too large to be attributed to a diffusion isotope effect. It can not be due to a difference in the vibrational frequencies of O–H and O–D bonds, either, since this would cause an isotope effect of only 1.4 or so and since this should be independent of the temperature. On the other hand, the large H/D isotope effect can be explained in terms of a difference in the activation energy for the O–H and O–D bond dissociations in the $(H_3O^+\cdot e^-)_{aq}$. As a result of the difference in zero-point energies,[37] more energy should be required to remove the D than the H. This would also account for the slight temperature dependence of the isotope effects seen in Table 2.

A similar intermediate, $(H_3O^+\cdot e^-)_{aq}$, has been considered by Hart[38] in a different connection. In the $(H_3O^+\cdot e^-)_{aq}$ complex, one of the water molecules in the hydration structure of the e^- may be incorporated in the outer shell of H_3O^+. This complex, which can be regarded as a closely-coupled unit, could either produce a hydrogen atom (Reaction (1c)) or decompose into H_3O^+ and e_{aq}^- (Reaction (1b)). These processes are caused by either a proton movement toward an adjacent hydrogen-bonded water molecule or rotations of the water molecules in the hydration sphere of the electron.

It should be emphasized here that, in the vapor-phase radiolysis, the H_3O-radical, if formed by the $(H_3O^+ + e^-)$ reaction, decomposes probably in the first vibration, and that, therefore, the relative probability of the dissociation of O–H and O–D bonds is closely related to the relative bond-stretching vibrational frequency, that is, 1.4.

Possible Reaction Mechanisms and Isotope Effects in the Solid State. The isotope separation factor which we have obtained for the frozen acid solution containing $[Fe(CN)_6]^{4-}$ and illuminated with ultraviolet light at 77°K (Table 3) is much smaller than the corresponding values of 3—4 obtained in the liquid phase. The present author considers this to be evidence that different mechanisms of the production of hydrogen atoms are operative for the two phases.

Dainton and Jones[22] have reported that the photo-detached electron, though differing from the radiolytically-formed electron in having much less kinetic energy, becomes a mobile electron in a frozen system. In a rigid medium, where the relaxation time for the orientation of the water dipoles is much longer than in a fluid medium, the electron could not easily polarize the surrounding medium; this would cause the electron to move larger distances from its point of origin. Moreover, the Coulombic repulsion between the ejected electron and the remaining species in the present case, namely $[Fe(CN)_6]^{3-}$, may be more effective than in a liquid phase, since the Coulomb interactions in a frozen solution at 77°K are, in an extreme case, mainly governed, not by the static dielectric constant (~80), but by the optical dielectric constant (~1.7).

The mobile electron moves through the medium until it finds a suitable site at which to be trapped (*e. g.*, a hydroxide anion vacancy[19,39]) or a species with which to react. The reaction of the electron in γ-irradiated frozen solutions has been studied in many works.[19,21,22,40,41] The trend in the rate-constant ratios at 77°K of the solutes, NO_3^-, NO_2^-, and acetone, with respect to $H_2PO_4^-$ was found to be the same as in an aqueous solution at 300°K.[40,41] More recently, the quantitative correlation of the rates in both phases for the electron reaction with Cd^{2+}, Cu^{2+}, CrO_4^{3-}, Zn^{2+}, and $ClCH_2COO^-$ ions has been verified further.[42] Unfortunately, no data on the H_3O^+ as well as on O_2 and N_2O have yet been given.

From the known values of the rate constants at *ca.* 25°C of Reactions (1) and (9), namely, $k_1=2.3\times10^{10}$ and $k_9=6.5\times10^9$ M^{-1}sec^{-},[7] one may

---

[36] Schwarz estimated the value of k_{1a} as 10.4×10^{10} M^{-1} sec^{-1} on the basis of a simple model of the diffusion-controlled reaction developed by Debye; H. A. Schwarz, *Radiation Res. Suppl.*, **4**, 89 (1964).

[37] The difference in zero-point energy between O–H and O–D bonds in the $(H_3O^+\cdot e^-)_{aq}$ complex may not be largely different from that in the hydronium ion, namely 1.2 kcal/mol (see Ref. 4); a value of this order of magnitude is responsable to the temperature dependence shown in Table 2.

[38] E. J. Hart in Ref. 2b, p. 32. See also E. J. Hart, *Science*, **146**, 19 (1964).

[39] L. Kevan, *J. Am. Chem. Soc.*, **87**, 1481 (1965).

[40] P. N. Moorthy and J. J. Weiss, in Ref. 2a.

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

[42] L. Kevan, *ibid.*, **89**, 4238 (1967).

expect that, in a frozen solution containing equal amounts of $ClCH_2COOH$ and H_3O^+, Reaction (1) occurs predominantly over Reaction (9). However, the results shown in Table 4 indicate that considerably high concentrations of the sulfuric acid are needed to suppress Reaction (9). An apparent unreactivity of the hydrogen ion toward the electron in an ice has been previously reported by Weiss *et al.*[40,41] In order to explain the marked differences in the H atom yields in 1 M solutions of $HClO_4$, H_2SO_4, H_3PO_4, and HCl, these authors suggested[41] that Reaction (1) is rather insignificant compared with the reactions of the electron with the anions (HX^-) and with the undissociated acid molecules (H_2X):

TABLE 4. COMPETITION BETWEEN H_2SO_4 AND $ClCH_2COOH$ FOR THE ELECTRON

a. $[Fe(CN)_6{}^{4-}] = 10^{-2}$ M, $[ClCH_2COOH] = 10^{-2}$ M

H_2SO_4, N	H	CH_2COOH
0.1	−	+
0.5	+	±
1	+	−

b. $[Fe(CN)_6{}^{4-}] = 10^{-3}$ M, $[ClCH_2COOH] = 10^{-3}$ M

H_2SO_4, N	H	CH_2COOH
10^{-2}	±	+
0.1	+	±
1	+	−

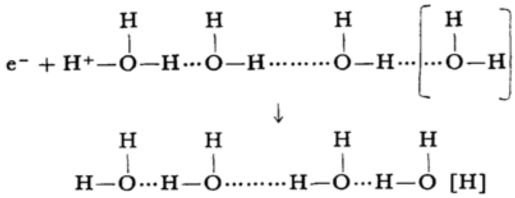
+ Signals appeared; − Signals not appeared;
± Signals appeared slightly.

$$e^- + HX^- \rightarrow H + H_2O + X^{2-} \tag{16}$$

$$e^- + H_2X \rightarrow H + H_2O + HX \tag{17}$$

The isotope effect of the production of H atoms *vs.* D atoms in this model must be governed by the isotopic fractionation between the solvent and the reacting species, HSO_4^-, H_2SO_4, or $HClO_4$. However, the reason for the relative insignificance of Reaction (1) compared with Reactions (16) and (17) at 77°K is not clear.

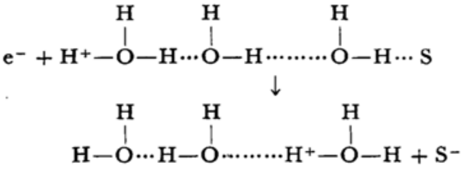
An alternative model for the production of hydrogen atoms as a result of the reaction of electrons in an acidic ice may be as follows: the electron reacts with the hydrogen ion, but in the hydrogen-bonded network, through which the hydrogen atom is transferred according to:



$$\begin{aligned} &e^- + H^+\text{—}\overset{H}{\overset{|}{O}}\text{—}H\cdots\overset{H}{\overset{|}{O}}\text{—}H\cdots\cdots\cdots\overset{H}{\overset{|}{O}}\text{—}H\cdots\left[\cdots\overset{H}{\overset{|}{O}}\text{—}H\right] \\ &\qquad\qquad\qquad\downarrow \\ &H\text{—}\overset{H}{\overset{|}{O}}\cdots H\text{—}\overset{H}{\overset{|}{O}}\cdots\cdots\cdots H\text{—}\overset{H}{\overset{|}{O}}\cdots H\text{—}\overset{H}{\overset{|}{O}}\ [H] \end{aligned} \tag{18}$$

in which [ ] represents the site in the solid which can stabilize the hydrogen atom. The thermal vibrations of the lattice may be sufficient for such an H-atom transfer.[43] The hydrogen isotope separation factor by this model would be governed by the isotopic effect in the formation of the H atom from a water molecule at the trapping site. It is, thus, not surprising that a marked difference in the magnitude of the isotope effect is found between the solid and liquid phases.

Morevoer, it may be possible, by the mechanism of Eq. (18), for an electron transfer to a solute to take place easily if the solute is involved in the same hydrogen-bonded chain as the hydrogen ion initially reacting the electron:



$$\begin{aligned} &e^- + H^+\text{—}\overset{H}{\overset{|}{O}}\text{—}H\cdots\overset{H}{\overset{|}{O}}\text{—}H\cdots\cdots\cdots\overset{H}{\overset{|}{O}}\text{—}H\cdots S \\ &\qquad\qquad\qquad\downarrow \\ &H\text{—}\overset{H}{\overset{|}{O}}\cdots H\text{—}\overset{H}{\overset{|}{O}}\cdots\cdots\cdots H^+\text{—}\overset{H}{\overset{|}{O}}\text{—}H + S^- \end{aligned} \tag{19}$$

where S denotes the solute. Reactions (18) and (19) would compete with each other. Thus, one might expect that, in an acidic ice ($H_3O^+ >$ 1 M), competition between the solute and the H-atom-trapping site for the electron (or the H-atom moving by the above mechanism) occurs. This mechanism would predict the relative ineffectiveness as an electron scavenger of the solute which does not couple with the H-bonded unit. Such electron scavengers as O_2 or N_2O might be such cases.

The author is greatly indebted to Professor Shizuo Fujiwara, the University of Tokyo, for his useful suggestions and kind guidance throughout this work. The stimulating discussions of Dr. Kenji Ishida are also acknowledged.

---

[43] A similar mechanism of H-transfer was suggested in Ref. 40 for a possibility that two hydrogen atoms form a molecule of hydrogen in an ice at 77°K without the diffusion of the two H-atoms.