The Hydrogen Isotope Effects Arising from the Reaction of Hydrated Electrons

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The measurement of hydrogen isotope effects has been applied to the elucidation of the reactions occurring during the radiolysis of water.[1-3] The question still remains unclear, however, because of the complicated set of reaction processes involved. This communication will present the isotope effect in the formation of H atoms arising from the reaction between e^-_{aq} and proton donors.

In a H_2O-D_2O mixture containing 1 M methanol, the photochemically-produced electron from 10^{-3} M $K_4[Fe(CN)_6]$[4] reacts with the added solute, SH:

$$e^-_{aq} + SH \rightarrow \begin{matrix} H + S^- \\ \searrow \\ D + S^- \end{matrix} \qquad (1)$$

The hydrogen atoms thus produced, H and D, react with CH_3OH to yield H_2 and HD respectively, the observed value of (H_2/HD) giving directly the hydrogen atom ratio, $(H/D)_a$, arising from Reaction 1. The separation factors defined by $S=(H/D)_a/(H/D)_{solvent}$ are given in Table I. The value for the hydrogen ion (H_2SO_4) confirms the values previously arrived at using radiation chemical data.[2,3] The hydrogen ion exists as H_3O^+, HD_2O^+, H_2DO^+ and D_3O^+; the estimated fraction of each species can be obtained from the literature.[5]

Table I. Isotope separation factors for the hydrogen atom formation from some solutes

[SH]	pH	S
0.01—1.2 N H_2SO_4	—	3.5±0.2
0.01—0.2 M KH_2PO_4	—	7.7
0.5—1 M NH_4Cl	—	11.0
0.1—0.8 M HCN, KCN	7.4—9.0	1.8
0.1—0.36 M H_3BO_3, $Na_2B_4O_7$	7.2—7.5	10.4

On the assumption that each species has an equal probability of reaction with e^-_{aq}, one can compute the relative rate of bond breaking, (k_H/k_D), where:

$$e^-_{aq} + HD_2O^+ \begin{matrix} \xrightarrow{k_H} H + D_2O \\ \xrightarrow{k_D} D + HDO \end{matrix}$$

An Arrhenius plot of $\log(k_H/k_D)$ vs. $1/T$ (the data of Table II) gave a value of 1340±20 cal. mol^{-1} for the difference in the activation energy of O–H and O–D bond fission in the hydronium ion. This value is close to the value (~1200 cal. mol^{-1}) which the infrared evidence gives[6] for the difference in zero-point energy between O–H and O–D bonds in the hydronium ion. One may further predict that the activation energy for the reaction of e^-_{aq} with D_3O^+ is about 4.5 kcal. mol^{-1}, since the pulse radiolysis study[7] has shown that the activation energy for the reaction, $e^-_{aq}+H_3O^+$, equals 3.2 kcal. mol^{-1}.

Table II. The effect of temperature on the isotope effect in the case of hydrogen ion

Temp., °C	2.0	10.4	21.6	30.2	40.8
S	4.35	4.16	3.80	3.64	3.61
k_H/k_D	5.40	5.07	4.36	4.09	4.03

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