

The Hydrogen Isotope Effects Arising from the Reaction of Hydrated Electrons

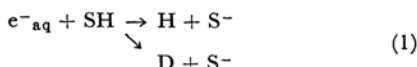
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The measurement of hydrogen isotope effects has been applied to the elucidation of the reactions occurring during the radiolysis of water.¹⁻³⁾ The question still remains unclear, however, because of the complicated set of reaction processes involved. 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:



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

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 $\left. \begin{matrix} HCN \\ KCN \end{matrix} \right\}$	7.4–9.0	1.8
0.1–0.36 M $\left. \begin{matrix} H_3BO_3 \\ Na_2B_4O_7 \end{matrix} \right\}$	7.2–7.5	10.4

1) J. H. Baxendale and G. Hughes, *Z. Phys. Chem.*, **14**, 306 (1958).

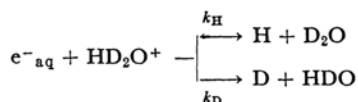
2) C. Lifshitz, *Can. J. Chem.*, **41**, 2175 (1963).

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4) S. Ohno and G. Tsuchihashi, *This Bulletin*, **38**, 1052 (1965).

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⁾

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:



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 gives⁶⁾ 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 study⁷⁾ 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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7) J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).