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The Isotope Effect in Hydrogen Formation by the Reaction between Two Aqated Electrons

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THE photolysis of hydroxide ions at 1850 Å was shown to produce hydrated electrons.¹⁻³ This is consistent with the charge-transfer-to-solvent spectrum assigned to the 1920 Å band of OH⁻.⁴ Hydrated electrons were shown to react with each other at a diffusion-controlled rate⁵ to give hydrogen as the product.⁶ Hydrogen is therefore formed, in the presence of an efficient OH scavenger, as product of the photolysis of a hydroxide solution. The mechanism of the $e_{aq}^- + e_{aq}^-$ reaction, which involves the formation of $(e_{aq}^-)_2$ ⁷ in the transition state or as an intermediate, has not yet been elucidated. H/D isotope effects in H₂O-D₂O mixtures have been shown to be helpful in the understanding of the e_{aq}^- reactions with H₃O⁺, NH₄⁺, and H₂PO₄⁻.^{8,9} It was of interest, therefore, to measure the H/D isotope effect involved in the hydrogen formed from the photolysis of hydroxide solutions in H₂O-D₂O mixtures.

Aqated electrons were produced in alkaline solution (pH = 14), containing 0.025 M-CD₃OH, by illumination with ultraviolet light at 185 mμ, at 25° C. CD₃OH was used as an OH radical scavenger to suppress the reaction of OH with H₂.

The fate of e_{aq}^- under our conditions is determined by two competing processes, $e_{aq}^- + e_{aq}^- \rightarrow H_2$; and $e_{aq}^- + H_2O \rightarrow H$. The hydrogen atoms formed are converted into e_{aq}^- by the reaction $H + OH_{aq}^- \rightarrow e_{aq}^-$, alternatively they may react with the CD₃OH to give HD. This competition for hydrogen atoms

depends upon the ratio $[OH_{aq}^-]/[CD_3OH]$. The overall yield of H₂/HD from solutions of CD₃OH in H₂O is therefore dependent on the light intensity. A mercury discharge tube with a light output of the order of 10⁻⁶ einstein/cm.² min. was used. Owing to the high extinction coefficient of OH_{aq}⁻ at 185 mμ,⁴ 99% of the light was absorbed in a layer of less than 0.02 mm., giving a high steady-state local concentration of e_{aq}^- (of the order of 10⁻⁶ M). Under these conditions only 2% of the hydrogen produced originated from hydrogen abstraction (CD₃OH in H₂O gave HD/H₂ = 0.02). The formation of hydrogen by deuterium abstraction from CD₃OH introduces a small systematic error, slightly lowering the measured value of the isotope effect.

The isotope effects were calculated by comparing the isotopic composition of the evolved hydrogen with that of the water.⁸ The experimental procedure of the isotopic analysis was as earlier described.⁸

The H/D isotope effects measured for the $e_{aq}^- + e_{aq}^-$ reaction were 3.9 ± 0.2 , 4.7 ± 0.2 , and 5.5 ± 0.2 for solutions containing 25, 50, and 75 atom percent deuterium respectively. These values are the lower limits for the isotope effects, as the ratio $R = [HD]^2/[H_2] \times [D_2]$ was higher than 4, the statistical value, in all the experiments. The values of R ranged between 4.7 and 6.0 for different samples. The increase in R cannot be accounted for by the $H + CD_3OH$ reaction alone, and it is

probably due to the reaction between the OH radicals and the hydrogen molecules formed, the isotope effect of which causes an increase in R owing to a preferential depletion of the lighter isotope.

The observed isotope effect is much higher than expected for the formation of hydrogen by a diffusion controlled reaction. The $e_{\text{aq}}^- + e_{\text{aq}}^-$ interaction is diffusion controlled as measured by pulsed radiolysis,⁵ thus the observed rate is most probably that of the formation of the $(e_{\text{aq}}^-)_2$ centre. This is an intermediate with a finite lifetime which subsequently decomposes to give $\text{H}_2 + 2 \text{OH}^-_{\text{aq}}$, with a preferential cleavage of H-O as opposed to D-O bonds. The involvement of several water molecules in the $(e_{\text{aq}}^-)_2$ centre may explain the change in the value of the isotope effect with the concentration of deuterium.

Hydrogen is one of the primary products in the radiolysis of water. In the presence of appropriate scavengers, the "molecular" hydrogen formed from water alone can be isolated. The $e_{\text{aq}}^- + e_{\text{aq}}^-$ has been suggested as a possible mechanism for its formation.^{6,10-13} The H/D isotope effect in the formation of the "molecular" hydrogen was measured at pH = 14 by the radiolysis of the same water mixture, used in photolysis, and found to be 2.3 ± 0.1 at 50% D at 25° c. The same isotope

effect has been previously observed in neutral and acid solutions.⁸

The isotope effect in the formation of "molecular" hydrogen formed in the radiolysis of water is significantly smaller than that observed for the $e_{\text{aq}}^- + e_{\text{aq}}^-$ reaction. It has thus to be concluded that the $e_{\text{aq}}^- + e_{\text{aq}}^-$ reaction is not liable for the formation of the major part of the "molecular" hydrogen. This conclusion is in accordance with previous arguments deduced from the measurements of other isotope effects⁸ and from the effect of scavengers on the yield of "molecular" hydrogen.⁹ The $e_{\text{aq}}^- + e_{\text{aq}}^-$ reaction is, however, the main source of the "molecular" hydrogen according to the diffusion model.^{12,13} It has also been demonstrated that the "residual" hydrogen atoms produced in neutral radiolysed solutions are not formed by the $e_{\text{aq}}^- + \text{H}_3\text{O}^+$ reaction⁸ as deduced in the diffusion model.^{12,15} Further, evidence was presented that a major part of the "molecular" hydrogen peroxide originates from a different reaction than $\text{OH} + \text{OH}$.¹⁶ The latter process is the only source for "molecular" H_2O_2 in the diffusion model.¹² These findings imply the necessity for a revision of the diffusion model as presently conceived.

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