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Activation Energy for the Mobility of the Hydrated Electron

INFORMATION about the activation energy for the mobility of the hydrated electron, e_{aq}^- , is important for the elucidation of the process of migration of e_{aq}^- in water. Although the mobility of e_{aq}^- was estimated several years ago¹, the activation energy for its mobility has not been determined.

I have used values of activation energies for e_{aq}^- reactions which do not require energy in excess of that for the transfer of e_{aq}^- and the substrate, such as e_{aq}^- reactions with nitrobenzene, $C_6H_5NO_2$, *p*-nitrophenol, $HOC_6H_4NO_2$, hydrogen ions, H_{aq}^+ , nitrate ions, NO_3^- , and thallous ions, Tl^+ (ref. 2), to estimate the activation energy for the mobility of e_{aq}^- . For these reactions the bimolecular rate constant, k_{diff} , is given by the Debye equation³

$$k_{diff} = 4\pi \times 10^{-3} N(D_{e^-} + D_s)(r_{e^-} + r_s)Q \quad (1)$$

and Q is given by the relationship

$$Q^{-1} = \int_{(r_{e^-} + r_s)}^{\infty} \exp \left[\frac{U(r)}{kT} \right] \frac{dr}{r^2} \quad (2)$$

where $D_{e^-} + D_s$ and $r_{e^-} + r_s$ are the sum of the diffusion coefficients and radii of the e_{aq}^- and substrate, N the Avogadro number, and $U(r)$ the potential function between the reactants. If the substrate is an ion, $U(r)$ is coulombic and $U(r) = -Z_se^2/\epsilon(r_{e^-} + r_s)$; if the substrate is a dipole, such as $C_6H_5NO_2$ or $HOC_6H_4NO_2$, $U(r) = -\mu e/\epsilon(r_{e^-} + r_s)^2$, where μ is the dipole moment, ϵ the dielectric constant, Z_s the number of positive or negative charges on the substrate, and e the electronic charge.

The sum $r_{e^-} + r_s$ can be regarded as independent of temperature. By differentiating equation (1) logarithmically and remembering that the activation energy, E , is given by

$$E = RT^2 \frac{d \ln k_{diff}}{dT}$$

the following relationship for the activation energy, E , is obtained

$$E = RT^2 \frac{dD_{e^-}/dT + dD_s/dT}{D_{e^-} + D_s} + RT^2 \frac{d \ln Q}{dT} \quad (3)$$

where T is the absolute temperature in degrees (K) and R is the gas constant.

The diffusion coefficient, D , can be expressed as $D = A \exp [-E_D/RT]^4$. Differentiating this expression logarithmically gives

$$\frac{dD}{dT} = D \frac{E_D}{RT^2} \quad (4)$$

When relation (4) is substituted in equation (3), the activation energy is given by

$$E = \frac{D_{e^-}}{D_{e^-} + D_s} E_{D,e^-} + \frac{D_s}{D_{e^-} + D_s} E_{D,s} + RT^2 \frac{d \ln Q}{dT} \quad (5)$$

where the subscripts e^- and S refer to the e_{aq}^- and substrate.

I have evaluated the term $RT^2 d \ln Q/dT$ for a typical approach distance $r_{e^-} + r_s = 0.5$ nm, dipole moment $\mu = 4$ Debye and one negative or positive charge on the substrate. The value of $RT^2 d \ln Q/dT$ does not exceed 0.2 kcalories mol^{-1} for a temperature range from 10° C to 80° C, that is, the range of measurements². The experimental uncertainty in the values of the activation energies of e_{aq}^- reactions, E , is 0.2 to 0.3 kcalories mol^{-1} . Therefore the contribution of the term $RT^2 d \ln Q/dT$ to equation (5) may be neglected and equation (5) reduces to

$$E = \frac{D_{e^-}}{D_{e^-} + D_s} E_{D,e^-} + \frac{D_s}{D_{e^-} + D_s} E_{D,s} \quad (5a)$$

The activation energy for diffusion of substrates, $E_{D,s}$, except that of the H_{aq}^+ , can be assumed to be equal to that for viscous flow of water⁵, 4.2 kcalories mol^{-1} at 18° C (ref. 6). For E_{D,H_{aq}^+} the mean value of published results^{4,7} was used (2.6 kcalories mol^{-1}). The values of the activation energies for the e_{aq}^- reactions with $C_6H_5NO_2$, $HOC_6H_4NO_2$, H_{aq}^+ , NO_3^- and Tl^+ have been determined². The diffusion coefficient of e_{aq}^- is known ($D_{e^-} = 4.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) (ref. 1); those of the substrates were estimated. The diffusion coefficients of ions were calculated from ionic mobilities $D = ukT/e$, where u is the mobility of the ion⁸ ($D_{NO_3^-} = 1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{Tl^+} = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{H^+} = 9.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). The diffusion coefficients of nitrobenzene and *p*-nitrophenol were assumed to be equal to that of phenol⁹ ($DC_6H_5OH = DC_6H_5NO_2 = DHOC_6H_4NO_2 = 0.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). On the basis of these data the activation energy for the mobility of e_{aq}^- , E_{D,e^-} , can be calculated from equation (5a). The mean value of E_{D,e^-} is 2.0 kcalories mol^{-1} , with a maximum deviation of the individual estimates of ± 0.4 kcalories mol^{-1} .

The activation energy for the mobility of e_{aq}^- is about 2 kcalories lower than that for the diffusion of conventional solutes in water, or viscous flow of water. This supports the suggestion that hydrated electrons may diffuse by migrating between existing potential traps^{10,11} instead of through the creation of new holes, as in conventional diffusion⁴.

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