Some Thermodynamic Properties of the Hydrated Electron

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Recent determinations of rate constants in both directions permit an estimate of the free energy change at 25° for the process $H_2O(l) + e_{aq}^- = H_{aq} + OH_{aq}^-$. This value can be combined with estimates of absolute thermodynamic properties of individual ions to indicate that $\Delta G° = -39.4$ kcal/mole when electrons in the gas phase are transferred to water at the same concentration (provided any electrostatic potential change at the interface has been compensated). This quantity is smaller in magnitude than for other ionic species and indicates that the charge of the hydrated electron is dispersed in a region of radius about 3.0 A. Data on other anions have been extrapolated to this radius and used to estimate the comparatively small entropy change accompanying hydration. The calculations permit the prediction that the acid dissociation of aqueous hydrogen atom proceeds with positive $\Delta H°$ and negative $\Delta S°$ and with rate constant about 4 sec^{-1}. They also predict that the unimolecular decomposition of the hydrated electron has an activation energy between 4 and 13 kcal/mole and probably not near either limit. In view of the rapid bimolecular decomposition of solvated electrons in water, it is not clear why this species is so inert to the same sort of process in ammonia.

Introduction

The solvated electron has long been known as a metastable species in alkali metal solutions in ammonia, aliphatic amines, and ethers.[1] More recently, its transient existence in water has been demonstrated unequivocally by pulse radiolysis studies.[2-5] The absorption spectrum of the solvated electron has been discussed previously on the basis of a phenomenological continuum model,[6] but available experimental data have not permitted estimates of the thermodynamic properties of the ground state in aqueous solution.

Hart and Gordon[7] have recently reported that in highly purified water the first-order rate constant for the disappearance of the hydrated electron at 25° could be reduced to a limiting value of 890 sec^{-1}. They assumed that they were observing the net reaction

$$H_2O(l) + e_{aq}^- \longrightarrow H_{aq} + OH_{aq}^- \qquad (1)$$

Matheson and Rabani[8] have shown that the rate constant for the reverse of reaction 1 is 1.8×10^7 l./mole sec at the same temperature. Combination of these data indicates that $\Delta G° = 5.87$ kcal/mole for reaction 1 written as an equilibrium in which the standard state of water is pure liquid and the standard states of the other species are ideal 1 *m* solutions.

In the present paper, we show how these data can be combined with other quantities in order to estimate changes in thermodynamic properties associated with some equilibrium reactions of the hydrated electron

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(1) See, for example, "Metal Ammonia Solutions," G. Lepoutne and M. J. Sienko, Ed., W. A. Benjamin, Inc., New York, N. Y., 1964.

(2) G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, **66**, 471 (1962).

(3) E. Collinson, F. S. Dainton, D. R. Smith, and S. Tazuké, *Proc. Chem. Soc.*, 140 (1962).

(4) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

(5) J. P. Keene, *Nature*, **188**, 843 (1960); **197**, 47 (1963).

(6) J. Jortner, S. A. Rice, and E. G. Wilson, "Metal Ammonia Solutions," ref 1, p 222.

(7) E. J. Hart and S. Gordon, XXth Congress of International Union of Pure and Applied Chemistry, Moscow, U.S.S.R., July 14, 1965.

(8) M. S. Matheson and J. Rabani, *J. Phys. Chem.*, **69**, 1324 (1965).

and also to make some very rough estimates of yet unmeasured kinetic parameters.

Thermodynamics of Electron Hydration

Noyes[9] has previously estimated that $\Delta G° = 103.81$ kcal/mole at 25° for the process

$$^1/_2H_2(g) + aq = H_{aq}^+ + [e^-](aq) \quad (2)$$

In this equation, the standard state of H_2 is one atmosphere fugacity, and that of H^+ is ideal 1 *m* aqueous solution. The symbol $[e^-](aq)$ denotes electrons in a hypothetical state having zero entropy, enthalpy, and free energy and in a vacuum at the bulk electrostatic potential of the interior of a body of water.

The following free energy changes are well known

$$^1/_2H_2(g) = H_g \quad (\Delta G° = 48.575 \text{ kcal/mole}) \quad (3)$$

$$H_2O(l) = H_{aq}^+ + OH_{aq}^- \quad (\Delta G° = 19.10 \text{ kcal/mole}) \quad (4)$$

The free energy change is not known for the process

$$H_g + aq = H_{aq} \quad (5)$$

However, $\Delta G°$ is 4.67 kcal/mole for the corresponding solution of He and is 4.24 kcal/mole for the corresponding solution of H_2. It can hardly be a serious error to assume $\Delta G° = 4.5$ kcal/mole for reaction 5.

These processes can be combined to give a free energy of formation, $\Delta G_f° = -37.5$ kcal/mole for the process

$$[e^-](aq) + aq = e_{aq}^- \quad (6)$$

Although the state $[e^-](aq)$ is probably the most convenient standard state to adopt for the electron when free energies of formation of charged aqueous ions are being considered,[10] comparison with hydration of other gaseous ions makes it more interesting to consider the process

$$e_g^-(\text{mole/l.}) + aq = e_{aq}^- \quad (7)$$

where e_g^-(mole/l.) denotes gaseous electrons at one mole per liter (but at the electrostatic potential corresponding to bulk water). Since the free energy at 25° of the state e_g^-(mole/l.) is[11] 1.89 kcal/mole, we estimate that $\Delta G° = -39.4$ for reaction 7. A very similar estimate of this quantity by Baxendale[12] did not consider standard states so specifically.

It is hoped that this estimate of $\Delta G°$ for reaction 7 is accurate to within 1 or 2 kcal/mole; it seems certainly reliable enough to state that the free energy decrease associated with hydrating the electron is very much less than that for hydrating any other gaseous anion. The charge on this interesting species must be very highly dispersed.

The methods developed previously[9,13] permit an estimate of this dispersion and of the other thermodynamic properties associated with hydration. Data for halide ions indicate that when singly charged gaseous anions at 25° are transferred to ideal aqueous solution at the same concentration

$$\Delta G° = 1.58r^2 - 0.568 - 163.89/r + 19.79/r^2 \quad (8)$$

where *r* is the radius of the anion in angstroms and the computed value is in kilocalories per mole. The numerical value of the $1/r$ term is uniquely determined by the macroscopic dielectric constant of the medium, and the term independent of *r* is the *PV* change associated with the process. The other two numerical values are empirical, although the magnitude of the term in r^2 is close to the surface free energy per unit area of the medium.

If it is assumed that the same equation will apply to the charge distribution for the hydrated electron, a $\Delta G°$ of -39.4 kcal/mole is what would be expected for an *r* value of 2.98 A. Jortner[14] has performed calculations of a completely independent type indicating that this quantity lies between 2.5 and 3.0 A. Since *r* is a rather insensitive function of $\Delta G°$, the radius of the charge distribution can hardly differ much from 3.0 A if eq 8 is applicable to this system.

A similar treatment[9] of entropy data leads to

$$\Delta S° = 1.48r^2 - 9.720/r - 47.25/r^2 \quad (9)$$

where numerical values are in calories per mole degree and the process is the same as that for eq 8. For a radius of 2.98 A, this equation gives a $\Delta S°$ of 4.5 cal/mole deg. Combination with the computed gaseous entropy[11] indicates that the entropy of the hydrated electron in ideal 1 *m* solution is 3.1 cal/mole deg greater than that of pure solvent. These results can be combined to give $\Delta H° = -38.1$ kcal/mole for the process of eq 7.

The thermodynamic properties computed for the hydrated electron are summarized in Table I. As has been indicated, the subscript f refers to formation from the state $[e^-](aq)$ by reaction 6, and the subscript hyd refers to hydration from gas phase at a standard state of 1 atm fugacity. The standard states selected

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[9] R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 971 (1964).

[10] R. M. Noyes, *J. Chem. Educ.*, **40**, 2, 116 (1963).

[11] The calculation assumes an enthalpy of $^5/_2RT$ and an entropy computed for translation and spin.

[12] J. H. Baxendale, *Radiation Res. Suppl.*, **4**, 139 (1964).

[13] R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

[14] J. Jortner, *Radiation Res. Suppl.*, **4**, 24 (1964).

for these processes correspond to those most often used when discussing similar thermodynamic properties of other chemical species.

Table I: Estimated Thermodynamic Properties of Hydrated Electron

$\Delta G_f°$	−37.5 kcal/mole
$\Delta H_f°$	−36.6 kcal/mole
$S°$	3.1 cal/mole deg
$\Delta G°_{hyd}$	−37.5 kcal/mole
$\Delta H°_{hyd}$	−38.1 kcal/mole
$\Delta S°_{hyd}$	−1.9 cal/mole deg

If the free energy change for process 1 has been correctly assigned, the free energy values in Table I can hardly be seriously in error. The estimates of entropy and enthalpy are based on a model that is open to more serious question. However, the small free energy of hydration indicates a charge dispersal that requires a small entropy of hydration. Hence moderately reliable enthalpies can be estimated from free energy data whether or not eq 9 is really applicable to the system. The values in Table I should be regarded as working estimates until better ones are available.

Acid Dissociation of Hydrogen Atoms

Hart, Matheson, *et al.*,[7] have already pointed out that the aqueous hydrogen atom can be regarded as a very weak acid and that the rate data referred to in the Introduction imply a p*K* of 9.7 for the dissociation

$$H_{aq} = H_{aq}^{+} + e_{aq}^{-} \qquad (10)$$

Estimates of changes in other thermodynamic functions require values for the solvation of hydrogen atoms (reaction 5). We have chosen $\Delta H° = -1.0$ kcal/mole for this reaction; the figure is intermediate between observed values for He and H_2 and can hardly be seriously in error. Application of other known thermodynamic properties and the values for e_{aq}^{-} derived above give for reaction 10 $\Delta H° = 11.1$ kcal/mole and $\Delta S° = -7.1$ cal/mole deg. Hence reaction 10 belongs to the comparatively rare class for which standard enthalpy and entropy changes have opposite signs.

It is hardly surprising that the reverse of reaction 10 is very fast with a rate constant[15] of 2.2×10^{10} l./mole sec. This latter figure can be combined with the equilibrium constant to give a rate constant of 4 $\sec^{-1}$ for reaction 10 in the forward direction. Since the rate of the reverse of reaction 10 is probably controlled to considerable extent by diffusion of reactants together, and since the measurement of rate constant was performed on a nonequilibrium distribution of reactants, the rate constant in the forward direction refers to dissociations in which the proton and electron actually escape from each other and do not recombine by diffusion.[16]

Unimolecular Decomposition

As was indicated in the Introduction, forward and reverse rate measurements indicate that $\Delta G° = 5.87$ kcal/mole for the equilibrium of reaction 1. The values in Table I permit enthalpy and entropy changes to be estimated for the same reaction. The calculations require previous estimates[9] for absolute thermodynamic properties of individual ions and also the estimate for hydration of hydrogen atoms discussed in connection with reaction 10.

The calculations indicate that for reaction 1, $\Delta H° = 2.2$ kcal/mole and $\Delta S° = -12.1$ cal/mole deg. The opposition of signs is probable but not as certain as for reaction 10. Since the reaction is very close to thermoneutral, a major factor in the equilibrium is the entropy decrease when the dispersed charge of the hydrated electron becomes concentrated upon a single hydroxide ion.

As is indicated by the p*K* of reaction 10, the hydrated electron is unstable with respect to reaction 1 in acid and neutral solution, but it is not difficult to make a solution sufficiently alkaline that the electron is stable with respect to decomposition to *atomic* hydrogen. This kind of stability is even more pronounced in liquid ammonia. A calculation based on a previous rough estimate by Jortner[17] indicates that the ammonia analog of reaction 1 is endothermic by about 28 kcal/mole. The much greater ease with which solvated electrons can be kept in ammonia than in water is obviously due at least in part to the big difference in thermodynamic stability with respect to unimolecular decomposition.

These calculations also permit some rough estimates of the enthalpies of activation for the forward and reverse reactions of process 1. The forward rate constant of 890 $\sec^{-1}$ indicates a free energy of activation, $\Delta G^{\ddagger} = 13.4$ kcal/mole. Since this rather simple reaction proceeds with a considerable decrease in entropy, some of this decrease is undoubtedly reflected in the formation of the transition state. If $\Delta S^{\ddagger}$ is negative, $\Delta H^{\ddagger}$ is less than 13.4 kcal/mole and probably is distinctly less.

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(15) For references, see L. M. Dorfman and M. S. Matheson, *Progr. Reaction Kinetics*, in press.

(16) R. M. Noyes, *ibid.*, **1**, 129 (1961).

(17) J. Jortner, *J. Chem. Phys.*, **30**, 839 (1959).

For the reverse of reaction 1, $\Delta G^{\ddagger} = 7.5$ kcal/mole. Since this reverse process involves bringing two particles together, it could conceivably involve a negative entropy of activation, but the entropy loss could hardly be more than the 19.6 cal/mole deg entropy of translation of gaseous hydrogen atoms at the same molar concentration. This restriction indicates that $\Delta H^{\ddagger}$ for the reverse reaction is at least 1.7 kcal/mole, and entropy changes associated with charge dispersal will probably make this quantity distinctly greater.

When these limits are combined with the estimate of $\Delta H^{\circ} = 2.2$ kcal/mole for the equilibrium reaction, we conclude that $\Delta H^{\ddagger}$ for the forward rate of process 1 lies between 3.9 and 13.4 kcal/mole and probably is not close to either limit. Experiments that we understand are in process[18] should permit a direct test of this prediction. If activation energies can be measured for the rates of process 1 in both directions, it will also be possible to test the internal consistency of the entries in Table I.

Bimolecular Decomposition Reaction

Hydrated electrons can also decompose by the process

$$2H_2O(l) + 2e_{aq}^- \longrightarrow H_2(aq) + 2OH_{aq}^- \qquad (11)$$

Matheson and Rabani[8] report a rate constant of 5.5×10^9 l./mole sec for this reaction indicating that it is essentially diffusion controlled. Since the estimates of this paper indicate that reaction 11 is exothermic by about 100 kcal/mole, it is hardly surprising that the reaction is quite rapid.

In liquid ammonia, solvated electrons can conceivably react in pairs to form molecular hydrogen by a completely analogous process. Since this reaction is also estimated[17] to be exothermic by about 50 kcal/mole, it is not clear why electrons in this solvent are so much more inert than in water with respect to decomposition to *molecular* hydrogen.

Discussion

Alternative Decomposition Mechanisms. The entire argument has been based on the assumption that reaction 1 does indeed describe the mechanism of unimolecular decomposition of the hydrated electron. Dainton[19] has questioned this assumption and has argued that the process

$$H_2O(l) + e_{aq}^- \longrightarrow H_2(aq) + O_{aq}^- \qquad (12)$$

may be favored. It is possible but by no means certain that the equilibrium products of process 12 may be favored over those of process 1, but the transition state for process 12 would involve incipient bonding between hydrogen atoms of the same molecule[20] and would undoubtedly be quite strained. In addition, calculations by Noyes[21] indicate that an incipient H–H bond contributes a smaller fraction of its energy to the stabilization of a transition state than does any other chemical bond considered.[22] For these reasons, we believe that the interpretation based on process 1 is proper and that the conclusions of this paper can be considered reasonable working hypotheses.

Comparison of Water and Ammonia as Solvents. As has been discussed elsewhere,[6,14] electron binding in a polar solvent can be treated phenomenologically by regarding the medium as a continuous polarizable dielectric. This simplified treatment properly handles the long-range interaction between the electron and the medium, but the short-range interactions are not properly included. The model of an electron localized in a cavity of radius 3–3.5 A is well established for dilute metal ammonia solutions.[1,6] The cavity size in polar solvents is governed by the short-range electron–solvent repulsions and by the surface tension energy associated with the cavity formation. It should be stressed that for the localized electron center in liquid ammonia there is a substantial leakage of the electron charge outside the solvent cavity boundary.[6] In spite of the large region of negative charge distribution in water, it is reasonable to assume that the cavity size (if a solvent cavity exists at all) is substantially smaller in this strongly hydrogen bonded solvent than it is in liquid ammonia.[14,23] In the limit of zero solvent cavity size, the heat of hydration of the electron is given by[6]

$$\Delta H_f^{\circ} = -\frac{25}{512}\left(1 - \frac{1}{D_s}\right)^2 \text{ atomic units} \qquad (13)$$

where D_s is the static (low-frequency) dielectric constant. The calculated value of $\Delta H = -30.4$ kcal/mole is in reasonable agreement with the experimental value of -36.6 kcal/mole derived above from thermochemical data.

It is also interesting to speculate on the relative reactivities of solvated electrons in water and in am-

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(18) E. J. Hart, private communication.

(19) F. S. Dainton, discussion following paper of ref 7.

(20) Because of bond energy values, a transition state involving two water molecules and leading to $H_2 + OH + OH^-$ would almost certainly have a higher energy than the transition state of reaction 1 leading to $H + OH^-$. It is possible in principle to devise complicated transition states in which protons or hydrogen atoms are transferred simultaneously around a ring, but they seem fanciful.

(21) R. M. Noyes, unpublished results.

(22) The failure to observe a bimolecular mechanism for ortho–parahydrogen conversion is related to this conclusion.

(23) L. Onsager, *Radiation Res. Suppl.*, **4**, 34 (1964).

monia with respect to the bimolecular decomposition reaction. As we have pointed out, the fast bimolecular decomposition in water is not at all surprising. On the other hand, dilute metal ammonia solutions are remarkably inert with respect to this bimolecular decomposition. The reason for this big difference in behavior may involve the different short-range local solvent structure arising because the solvent cavity size in liquid ammonia is substantially larger than in water. In liquid ammonia, the disappearance of the solvent cavity may require a large negative entropy of activation which makes the solvated electron in this system inert to bimolecular as well as to unimolecular decomposition.

Optical Excitation Energy. Finally, it is interesting to consider the relation between the heat of solvation and the optical excitation energy of the solvated electron. It has been noted that the energy of the absorption peak of the hydrated electron (39.5 kcal/mole), which was assigned to the 1s → 2p transition,[6] corresponds closely to the absolute value of the heat of solution (38.1 kcal/mole).

The excitation energy for the 1s → 2p transition can be expressed in the form[6]

$$h\nu_{1s\rightarrow 2p} = -\Delta H^{\circ}_{\mathrm{hyd}} + E_{2p(1s)} \tag{14}$$

where $E_{2p(1s)}$ is the total energy of the system in the excited 2p state but in the nuclear configuration corresponding to the ground state. Due to these restrictions imposed by the Franck-Condon principle, the energy $E_{2p(1s)}$ in polar solvents is smaller than 0.1 ev,[6,14] leading to the close correspondence between the heat of solution and the optical excitation energy of the solvated electron.

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