THE DISSOCIATION CONSTANT OF HYDROGEN PEROXIDE AND THE ELECTRON AFFINITY OF THE HO_2 RADICAL

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Measurements are described on the dissociation constant of hydrogen peroxide in aqueous solution and from these measurements at different temperatures the heat of dissociation is evaluated. This value has enabled us to estimate the electron affinity plus the solvation energy of the O_2H radical. Values of ΔG, ΔH and ΔS for the dissociation of water and hydrogen peroxide are compared. Measurements are also reported on the proton affinity of H_2O_2. Calculations based on existing data are given for the electron affinities and solvation energies of OH, O_2H, O_2 and O_2^-

Introduction.—The strengths of the various bonds in molecules and radicals of oxygen and hydrogen atoms are of importance in discussions of the energetics of many oxidation reactions both in the gas phase and in solution. The electron affinities of radicals and the solvation energies of the ions are quantities which are required in considering many electron-transfer reactions in solution. In this paper we present new measurements concerning the dissociation constant and the proton affinity of hydrogen peroxide in aqueous solution and use these values together with existing data to obtain some of the fundamental quantities referred to above. Many of these quantities have been evaluated by Weiss[1] but the data which are now available enable one to make more certain estimates.

The Dissociation Constant of Hydrogen Peroxide.—In 1912 Joyner[2] evaluated the hydrolysis of $NaHO_2$ by measuring (*a*) the ratio of saponification of ethyl acetate in the presence of $NaHO_2$, (*b*) the distribution of undissociated hydrogen peroxide between water and amyl alcohol, and (*c*) the conductivity of a solution of $NaHO_2$.

He obtained the following values for the acid dissociation of hydrogen peroxide in dilute aqueous solution at 0° C:

METHOD (*a*)	METHOD (*b*)	METHOD (*c*)
0.77×10^{-12}	0.59×10^{-12}	0.64×10^{-12}

He also measured the heat of the reaction,

$$H_2O_2 \rightarrow H_3O^+ + O_2H^-$$

at 0° C, by direct thermochemical measurement of the heat of neutralisation and obtained a value of $\Delta H^\circ = + 8.6$ kcal. The lack of any consideration of the influence of ionic strength in Joyner's experiments has necessitated a re-determination of the dissociation constant of H_2O_2 taking into account the influence of the ionic strength of the solution.

It has been shown by Reichert and Hull[3] that the glass electrode is

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[1] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 966 and 668.

[2] Joyner, *Z. anorg. Chem.*, 1912, **77**, 103.

[3] Reichert and Hull, *Ind. Eng. Chem.* (*Anal.*), 1939, **11**, 311.

suitable for the measurement of pH in peroxide solutions. We have used aqueous solution of H_2O_2 up to 2 M concentration and in this range we consider that the ions present are hydrated H_3O^+, OH^- and HO_2^-, and that the concentration of $H_3O_2^+$ is negligible. We can, therefore, treat the system as a dissociating weak acid and have used the Alki glass electrode which is now applicable over a pH range of 9-14. We have measured the pH of an H_2O_2—NaOH mixture at various concentrations of sodium perchlorate and at different temperatures. For the evaluation of the pK of dilute H_2O_2 up to 2 M the modified Henderson buffer equation has been used :

$$\text{pH} = \text{pK} + \log \frac{[\text{Na}^+]}{[H_2O_2]_0\,[\text{Na}^+]} - 0{\cdot}5\sqrt{\mu} + C'\,\mu \quad . \qquad . \quad (1)$$

It should be added that under the working concentrations the reaction $OH^- + H_2O_2 \rightarrow HO_2^- + H_2O$ can be regarded as practically complete and thus eqn. (1) is applicable. Fig. 1 shows the dependence of the pH

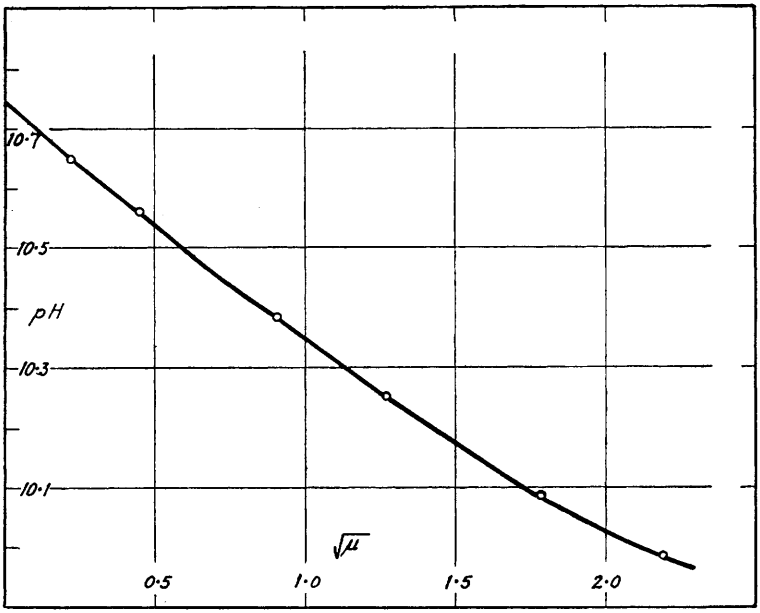

FIG. 1.—$[H_2O_2] = 0{\cdot}55$ M, [NaOH] = 0·05 M, pH = (pK − 1) − $0{\cdot}5\sqrt{\mu} \pm 0{\cdot}08\mu$.
Curve corresponding to pH = (pK − 1) − $0{\cdot}5\sqrt{\mu} + 0{\cdot}08\mu$.

at constant concentrations of 0·05 M NaOH and 0·55 M H_2O_2 at a constant temperature of 20° C on the square root of the ionic strength. The variation of the ionic strength of the solution was effected by the addition of sodium perchlorate as neutral electrolyte. From these data the values of C' and pK have been calculated ; the pK value was found to be 11·75 ± 0·02, which corresponds to a dissociation constant of

$$1{\cdot}78 \pm 0{\cdot}1 \times 10^{-12}$$

at 20° C ($C' = 0{\cdot}08$).

The variations in the value of K at 20° C determined under the same experimental conditions are shown in Table I. The error in the estimation of the dissociation constant is about ± 5 %. The average value of K at 20° C at zero ionic strength is $1{\cdot}78 \times 10^{-12}$.

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[4] Jenkins, *Trans. Faraday Soc.*, 1945, **41**, 138.

TABLE I

Expt.	Solution	K (20° C, μ = 0)	pK
1	0·55M H_2O_2 + 0·05M NaOH	$1·75 \times 10^{-12}$	11·76
2	,,	$1·79 \times 10^{-12}$	11·75
3	,,	$1·70 \times 10^{-12}$	11·77
4	,,	$1·88 \times 10^{-12}$	11·73

The complete function for the temperature dependence of K for a weak acid has the form,[3]

$$\log \mathrm{K} = A/T + \frac{B \log T}{T} + \frac{C \log^2 T}{T} + D.$$

In this case with the large value of A we can neglect B and C in the small temperature interval between 15° and 35° C. The Alki glass electrode proved suitable for measurement between 15° and 40° C only. Above 35° C, however, the hydrogen peroxide decomposition is too rapid, so that the effective range for our measurement was within the above-mentioned limit. A straight line is obtained when pK is plotted against $1/T$ (Fig. 2). The value ΔH for the reaction

$$H_2O_2 \rightarrow H_3O^+ + O_2H^-$$

calculated from the slope of the graph corresponds to + 8·2 kcal. The values obtained are generally in good agreement with those of Joyner.[2]

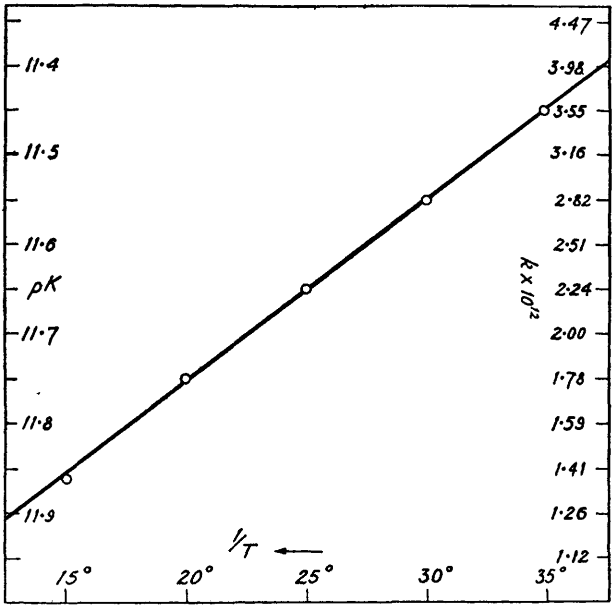

FIG. 2.

At high concentrations of H_2O_2 *a striking increase* in the hydrogen ion activity has been found. This corresponds to the effect of super-acidity observed also in concentrated acetic acid.[5] This suggests that $H_3O_2^+$ is formed and that H_2O_2 is a weaker base than H_2O.

[5] Glasstone, *Electrochemistry of Solutions* (3rd Ed., 1945), p. 181.

The Proton Affinity of H_2O_2.—The above observation suggests that in the reaction

$$H_3O_2^+ + H_2O \rightarrow H_2O_2 + H_3O^+ \qquad . \quad . \quad . \quad (1)$$

the equilibrium lies over on the right. We have measured the heat of the above change in this following way. Firstly, the heat of dilution of 88 % and 96 % H_2O_2 in a large excess of water was measured and by extrapolation a value for the heat of dilution of pure H_2O_2 obtained. Secondly, the heat of mixing was measured of a normal perchloric acid solution in 40 M H_2O_2 with a large excess of N $HClO_4$ solution in water. The temperature increases were measured on a Beckmann thermometer, and the thermal capacities of the systems measured electrically. The results obtained for the heats of dilution are shown in Table II.

TABLE II

Conc. H_2O_2	Reaction	ΔH (kcal./mol.)
88 %	$H_2O_2 \rightarrow H_2O_2$ (aq.)	$-$ 0·65
96 %	$H_2O_2 \rightarrow H_2O_2$ (aq.)	$-$ 0·71
100 %	$H_2O_2 \rightarrow H_2O_2$ (aq.)	$-$ 0·74

$H_3O_2^+ + H_2O \rightarrow H_3O^+ + H_2O_2$, $\Delta H = 4\cdot2 \pm 1\cdot2$ kcal./mol.

In the determination of the heat of dilution of pure hydrogen peroxide ($\sim$ 43 M) the increase in temperature on diluting the hydrogen peroxide with the twelve-fold excess of water was of the order of 2°. The difference in the temperature increase, however, caused by the heat of dilution of $\sim$ 40 M H_2O_2 and that of N $HClO_4$ in 40 M H_2O_2, with a twelve-fold excess of water in the first case and with a solution of N $HClO_4$ in water in the second was of the order of 0·25°-0·30° only. Hence the latter result involves a considerable experimental error. From the difference between these two heats of dilution and extrapolation to pure H_2O_2 the heat of the above reaction can be calculated. The experimental results are given in Table II. ΔH for the above reaction was evaluated as $-$ 4·2 ± 1·2 kcal./mol. The value of ΔH, which is a measure of difference between the proton affinity of H_2O_2 and H_2O, is in keeping with the observation that H_2O_2 is a weaker base than H_2O. If the entropy change in reaction (1) is negligibly small, then $\Delta G^\circ \sim \Delta H^\circ$ and $-$ 4·2 kcal. and the equilibrium constant $K \approx 10^3$.

The Electron Affinity and Solvation Energy of the OH and HO_2 Radicals. (*a*) Baughan, Evans and Polanyi [6] gave a cycle from which the electron affinity could be obtained from the solvation energy of OH. In the light of new data we now revise this cycle.

$$\begin{tikzcd}
(H_2O)_g \arrow[r, "-120\cdot7", "-D_{\mathrm{HO}\ldots\mathrm{H}}"'] & H + OH \arrow[r, "-312+E_{\mathrm{OH}}", "-I_{\mathrm{H}}+E_{\mathrm{OH}}"'] & H^+ \arrow[d, "+282"', "S_{\mathrm{H}^+}"] & + & OH^- \arrow[d, "S_{\mathrm{OH}^-}"] \\
(H_2O)_l \arrow[u, "-10\cdot6", "-\lambda"'] \arrow[rr, "-13\cdot7", "Q"'] & & (H^+)_{\mathrm{aq.}} & + & (OH^-)_{\mathrm{aq.}}
\end{tikzcd}$$

The revised value of $D_{\mathrm{HO}\,.\,.\,\mathrm{H}}$ is obtained from the heat of formation of water [7] and the value of $D_{\mathrm{H}\,.\,.\,\mathrm{O}}$ of Dwyer and Oldenburg.[8] This leads to a value $(E_{\mathrm{OH}} + S_{\mathrm{OH}^-}) = 147\cdot6$ kcal.

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[6] Baughan, Evans and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377.

[7] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (New York, 1936).

[8] Dwyer and Oldenburg, *J. Chem. Physics*, 1944, **12**, 357.

(*b*) The value of $(E_{O_2H} + S_{O_2H^-})$ can be obtained from the following cycle.

$$\begin{tikzcd}
(H_2O_2)_g \arrow[r, "-D_{HO_2\ldots H}"'] & H + O_2H \arrow[r, "-I_H + E_{O_2H}"'] & H^+ \arrow[d, "+S_{H^+}"'] & + \; O_2H^- \arrow[d, "+S_{O_2H^-}"] \\
(H_2O_2)_{aq.} \arrow[u, "-\lambda - S_{H_2O_2}"] \arrow[rr, "Q"] & & (H^+)_{aq.} & + \; (O_2H^-)_{aq.}
\end{tikzcd}$$

$$Q = -\lambda - S_{H_2O_2} - D_{HO_2\ldots H} - I_H + S_{H^+} + (E_{O_2H} + S_{O_2H^-}).$$

The value $Q = - 8{\cdot}2$ kcal./mol. is given in § 1 of this paper. The latent heat of vaporisation of pure H_2O_2 is given by Bichowsky and Rossini[7] as $+ 11{\cdot}6$ kcal./mol.; S the heat of dilution of pure H_2O_2 from our own experiments, is $+ 0{\cdot}74$ kcal./mol.

The value of $D_{HO_2\ldots H}$ corresponding to the heat of the reaction

$$H_2O_2 \rightarrow HO_2 + H - D_{HO_2\ldots H}$$

is uncertain. On the assumption that the energy of the –O–O– bond is the same in HO_2 as in H_2O_2 a value of $D_{HO_2\ldots H}$ of 100 kcal. is obtained. Sokolov,[9] however, suggests that the energy of the O–O– bond in HO_2 is increased by about 2 kcal. over that in H_2O_2.[10] This would give a value of $D_{HO_2\ldots H}$ of 102 kcal. Walsh[11] on the other hand suggests a value of the energy of the –O–O– bond in HO_2 of 80-90 kcal. which would lead to a value for $D_{HO_2\ldots H}$ of 70-80 kcal. Using the above values for the bond energy, the values of $(E_{O_2H} + S_{O_2H^-})$ obtained range over 136 to 106 kcal. It is not possible at present to give a more certain value of $(E_{O_2H} + S_{O_2H^-})$.

It is interesting to compare the entropy change of dissociation of H_2O and H_2O_2. The thermodynamical constants at 20° C for the two reactions are given in Table III.

TABLE III

Reactions	pK	ΔH (kcal.)	ΔS (cal./deg.)	ΔG (kcal.)
$H_2O \rightarrow H_3O^+ + OH^-$	15·81	13·7	−25·5	21·2
$H_2O_2 \rightarrow H_3O^+ + HO_2^-$	11·75	8·2	−25·7	15·8

We note that the difference in ΔG° is determined almost entirely by the difference in ΔH° and that the value of ΔS° for the two reactions is practically identical. This would seem to indicate that the solvation of the two ions OH^- and O_2H^- in water is very similar and that the difference between $(E + S)$ for OH and O_2H is mainly a difference in the electron affinity.

The Electron Affinity of Oxygen.—(*a*) A value of this can be obtained from the cycle,

$$\begin{tikzcd}
(M)_g + O_2 \arrow[r, "-I_M + E_{O_2}"] & M^+ + O_2^- \arrow[d, "U_0"] \\
(M)_s + O_2 \arrow[u, "-\lambda_M"] \arrow[r, "Q"] & (M^+O_2^-)_s
\end{tikzcd}$$

if the latent heat of vaporisation λ of the metal M, the ionisation potential I_M of M and the heat of formation Q of the ionic $(M^+O_2^-)$ can be calculated.

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[9] Sokolov, *Acta Physicochim.*, 1944, **19**, 208.
[10] Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645.
[11] Walsh, *J. Chem. Soc.*, 1948, 331.

The heats of formation of KO_2, RbO_2 and CsO_2 have been determined as 67·5, 68·8 and 70·5 kcal. respectively.[7, 12]

The crystal structure of these solids have been investigated by Helms and Klemm.[13] The solids have been found to be of the sodium chloride type, the O_2^- ion is, however, an asymmetric ion having a major axis of 4·04 Å and a minor of 3·02 Å. The asymmetry of the ion necessitates an evaluation of the Madelung constant for such a lattice. This was determined by summing the terms z^2e^2/d for the interaction between the ion at the origin and the other ions within a cube, the faces of which cut through the planes of atoms, and summing the rapidly converging energy series which is obtained by this method, when the cube is extended. The recent investigation by Helms and Klemm referred to above provided us with the necessary interionic distance. The lattice energy U_0 is given by

$$U_0 = \frac{Ne^2 A}{(r_{M^+} + r_{mi})}\left(1 - \frac{1}{n}\right)$$

in which N is Avogadro's number, $A = 1{\cdot}644$ the Madelung constant for this distorted sodium chloride type lattice, r_{M^+} the radius of the positive ion, r_{mi} the minor radius of the oxygen ion and n, the Born exponent, $= 10$. Table IV gives the data used in the Born-Haber cycle, the calculated lattice energies and the resulting electron affinity of the oxygen molecule in the gas phase.

TABLE IV

Solid	λ_M	I_M	Q	r_{M^+}	U_0	E_{O_2}	Mean E_{O_2}
KO_2	21·7	99·6	67·5	1·33	172·2	16·6	15·8
RbO_2	19·9	95·9	68·8	1·48	168·2	16·4	
CsO_2	19·1	89·4	70·5	1·69	164·5	14·5	

The solvation energy of the O_2^- ion has been calculated assuming free rotation of the ion in solution, and treating the ion as a sphere of average radius 1·70 Å. The value obtained in this way is 70·0 kcal. Thus the value of $(E + S)_{O_2} = 85{\cdot}8$ kcal.

(*b*) The second electron affinity of the oxygen molecule can be obtained from a similar cycle to the one above involving the heats of formation of solids of the type $M^{++}O_2^=$. The crystal structures of the Ba, Sr and Ca peroxides have been determined by Bernal and all have the calcium carbide type lattice. The $O_2^=$ ion is an ellipsoid with major and minor axial diameters of 5·12 Å and 3·34 Å respectively. The Madelung constant of such a lattice has been evaluated as 1·636 and in the same way as used above the lattice energies have been calculated. Table V gives the data used in the Born-Haber cycle and the resulting values of the energy change in the reaction,

$$O_2 + 2e \rightarrow O_2^= + E_{12}.$$

TABLE V

Solid	λ_M	$(I_1 + I_2)_M$	Q	$r_{M^{++}}$	U_0	E_{12}	Mean E_{12}
BaO_2	49·1	349·0	144·2	1·36	647	−104·7	−112·5
SrO_2	47·0	383·8	154·9	1·13	998	−115·5	
CaO_2	475	412·9	155·5	0·99	735	−117·3	

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[12] Machu, *Das Wasserstoffperoxyd und die Perverbindungen* (Wien, 1937).
[13] Helms and Klemm, *Z. anorg. Chem.*, 1939, **241**, 97.

It is interesting to note that whereas the first electron affinity of the oxygen molecule in the gas phase is positive the sum of the first and second electron affinities is negative.

We have evaluated the heat of solution of the O_2^- ion in water using a mean ionic radius of 1·97 Å as $S_{O_2} = 210$ kcal. Thus we have

$$(E_{12} + S_{O_2}) = +97{\cdot}5 \text{ kcal.}$$

From these figures we would expect the second dissociation of H_2O_2 to be extremely small due to the high endothermicity ~ 100 kcal. of the step,

$$HO_2^- \rightarrow H^+ + O_2^=.$$

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