[Contribution from the Becco Chemical Division of the Food Machinery and Chemical Corporation, and the Department of Chemistry of the Illinois Institute of Technology]

Chain Conductance of the Solvated Proton in Water–Hydrogen Peroxide

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Cells have been designed to make conductance measurements of electrolytes in water–hydrogen peroxide systems. The results indicate that the high mobility of H_3O^+ and OH^- in aqueous solution disappears as water is replaced by hydrogen peroxide. The results with potassium hydroxide are explained in terms of the replacement of the hydroxyl ion by the hydroperoxide ion. This anion appears to have a higher mobility than the hydroxyl ion in solutions containing high concentrations of hydrogen peroxide.

Introduction

In 1946 there was suggested by Edward S. Shanley[1] the possibility that the proton behaves "normally" in water–hydrogen peroxide as contrasted with its abnormally high conducting power in water solutions. The present paper reports conductance data on salts and acids in water–hydrogen peroxide mixtures to support this view in regard to the water solvated proton.

Experimental

Apparatus.—Conductance cells for use with hydrogen peroxide pose difficult problems of construction. Most of the metals suitable for use in contact with hydrogen peroxide solutions such as aluminum, zirconium, tantalum, etc., have rectifying properties and are consequently useless for electrodes. The metals commonly used for electrodes in aqueous solutions such as platinum and gold, decompose hydrogen peroxide, as do most other common metals except tin. The body of each cell consisted of a one inch length of two inch diameter Pyrex pipe (standard Pyrex spacer ring). The electrodes were machined from disks of pure tin metal, cast in glass beakers. These were clamped to the glass ring with backing flanges and bolts. Thin polythene gaskets were used between the electrodes and the glass ring. Inlet and exit tubes of Pyrex were ground to fit holes drilled through opposite sides of the glass ring. These cells while well adapted for the intended use were difficult to construct and were rather fragile. The final assembly consisted of two cells mounted one above the other: the lower having a cell constant of about 0.023 and the upper about 0.112.

The cell assembly was placed in a short section of 3.5 in. glass tubing with inlet and outlet pipes and electrical leads protruding. Then the tubing was filled with monomeric Selectron which was caused to polymerize in place. The result was rigid, non-conducting support for the cell assembly and leads. This whole unit was then encased in a water jacket through which thermostated water was pumped. The completed apparatus was suspended on a counterweighted cable over a thermostat, so that the lower tube could be dipped at will into any of a number of thermostated solution samples. The samples were filled into the cells by vacuum.

This somewhat unusual conductance cell assembly had the following desirable attributes for the problem at hand: 1. Only tin and Pyrex and a very small area of polythene contacted the solutions. 2. The tin electrodes were reasonably free from attack by mildly acid or alkaline solutions. 3. The cells were free from the Parker effect. There was no parallel capacitance path through the thermostat fluid. 4. This cell design made most efficient use of the filling volume, since there was no "dead" space. 5. Satisfactory temperature control (*ca.* 0.05°) could be obtained by first establishing the desired temperature in the solution and then drawing up the solution into the jacketed cell assembly.

Electrical Measuring Apparatus.—The basis of the measuring circuit was a General Radio Type 650 conductance bridge. This was equipped with the General Radio 1000 cycle vacuum tube oscillator and a single stage amplifier. Auxiliary equipment included a 4000 cycle generator of conventional design and good wave form, a Wagner grounding device, and a telephone headset for audio detection of the balance point. A precision decade resistance box (General Radio Type 602N) was eventually substituted for the slide wire in the bridge, in order to increase the precision of setting.

Calibration of Conductance Cells.—The cell constants of the special tin cells were determined by comparison with a conventional cell. The conventional cell was first standardized by means of measurements with carefully prepared 0.01 *M* potassium chloride. The salt was dried at 110°. The solution was made up using careful volumetric technique, including control of the temperature of the solution during dilution. Potassium chloride solutions of about 0.01 *M* and about 0.001 *M* were used to standardize the two tin cells. The appropriate solution was thermostated, and drawn into the cell for measurement. The solution was then discharged directly into the standardized conventional cell. This cell was immersed in a beaker of oil which in turn was immersed in the thermostat. The resistance values in the two cells, together with the known cell constant of the conventional cell, allowed calculation of the tin cell constants.

Preparation of Solutions.—In order to make an extensive series of measurements with several electrolytes at a range of peroxide concentrations, it was desirable to have a very substantial quantity of extremely pure hydrogen peroxide. All of the measurements reported here were carried out with one batch of hydrogen peroxide, which by a combination of fractional distillation and fractional crystallization, had been brought to about 99.7% in H_2O_2 content and to an extremely high purity. About 50 lb. of this pure peroxide were consumed in the investigation.

Once distilled water was passed through a monobed ion exchanger using Amberlite IR 120 and IRA 400. Water with a conductance of less than 1×10^{-6} ohm^{-1} cm.$^{-1}$ was consistently available by this means.

Electrolytes.—A portion of 70.20% perchloric acid was diluted with 99.7% H_2O_2 to make up a master solution (0.01000 *N*) and additional dilutions of this solution with 99.7% H_2O_2 yielded solutions 0.0055, 0.0025 and 0.00060 *N* in $HClO_4$. Corresponding solutions were also prepared in 75, 50, 25% H_2O_2 and in conductivity water.

In similar fashion solutions of sulfuric acid, potassium sulfate and potassium perchlorate were prepared.

A 20% aqueous solution of reagent grade potassium hydroxide was treated with about 1% of its weight of C.P. light magnesia. After stirring for about an hour, the magnesia suspension was allowed to settle (four days) until a clear solution could be drawn off. This procedure is known to remove heavy metal trace impurities. The solution was then freed from carbonate by treating with a *slight* excess of specially purified barium hydroxide. The resulting pure KOH solution was kept in Pyrex, under ascarite. The desired measurements were completed within one week after this preparation was completed.

The concentration of this solution as determined by careful titration was diluted to 250 ml. with 99.7% H_2O_2 to make up an 0.01 *N* solution and further diluted and solutions of corresponding concentrations in the five solvents prepared.

Measuring Technique.—Because of the inherent instability of hydrogen peroxide solutions, the conductance measurements were always carried out within a few hours after preparation of the solutions. Generally, only one set of solutions was handled at a time, a "set" being the four dilutions of 0.0100, 0.0055, 0.0025, 0.00060 *N* in one solvent. The four solutions were placed in the 25° thermostat imme-

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[1] Paper presented before the Division of Physical and Inorganic Chemistry at the 110th meeting of the American Chemical Society, Chicago, Illinois, September 9–13, 1946.

diately after making. Measurements were begun as soon as temperature equilibrium was established. Both cells were usually filled and measurements made on the one giving the more favorable resistance value. Polarization was appreciable because of the necessity to use bright metal electrodes. Measurements were always made at both 1000 cycles and at 4000 cycles, so that the appropriate correction for polarization could be made.[2]

Experimental Results

The data for perchloric acid in water, 25, 50, 75 and 99% H_2O_2 are given in Fig. 1. No solvent correction was made and except for water and 99% H_2O_2, the 0.006 M points are omitted as they fall way out of line. The solid lines are calculated Onsager slopes using the dielectric constant and viscosity data of Table I.

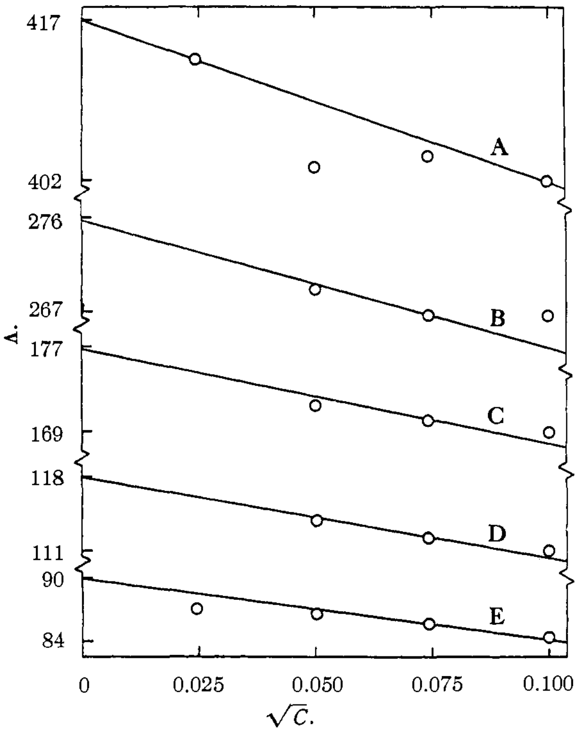

Fig. 1.—Equivalent conductance of perchloric acid in water–peroxide mixtures: A, 0% H_2O_2; B, 25% H_2O_2; C, 50% H_2O_2; D, 75% H_2O_2; E, 99% H_2O_2.

TABLE I

PHYSICAL CONSTANTS FOR WATER–HYDROGEN PEROXIDE AT 25°

Wt. % H_2O_2 nominal	Refractive index n_D	Wt. % H_2O_2 actual	Specific conductance $\times 10^7$, ohm^{-1} cm.$^{-1}$	Dielectric constant, D	Viscosity η, μpoise
0	1.3325	0	0.90	78.5	0.00895
25	1.3481	24.2	4.32	80.0	.00958
50	1.3656	49.2	5.13	81.0	.01055
75	1.3846	74.4	4.02	76.5	.01132
99	1.4054	99.4	0.51	73.0	.01055

The intercepts are given in Table II and it is evident that the equivalent conductance decreases as water is replaced by hydrogen peroxide. The corresponding results for potassium perchlorate are presented in Fig. 2. The equivalent conductances at infinite dilution are given in Table II and show a decrease as we go from pure water to 99% hydrogen peroxide. It is also significant that the equivalent conductance of perchloric acid is somewhat less than that of potassium perchlorate in 99% hydrogen peroxide. This is interpreted to mean that the mobility of the solvated proton is less than that of potassium ion analogous to our findings for the solvent anhydrous hydrofluoric acid.[3] As we have no transference numbers at present the ratios of the mobilities of the ions cannot be computed. However, the ratios of the equivalent conductances are given in Table II.

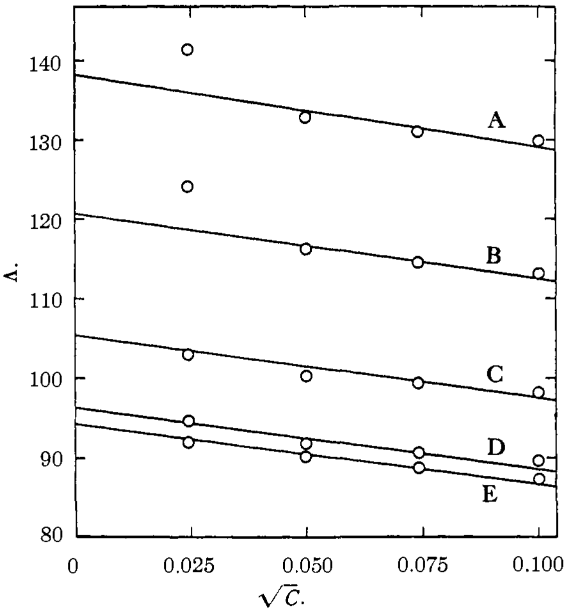

Fig. 2.—Equivalent conductance of potassium perchlorate in water–peroxide mixtures: A, 0% H_2O_2; B, 25% H_2O_2; C, 50% H_2O_2; D, 75% H_2O_2; E, 99% H_2O_2.

TABLE II

RATIO OF THE EQUIVALENT CONDUCTANCES AT 25°

H_2O_2, %	Λ_0 $HClO_4$	Λ_0 $KClO_4$	Ratio $\frac{\Lambda HClO_4}{\Lambda KClO_4}$
0	417	138	3.02
25	276	121	2.28
50	177	105	1.68
75	118	96	1.23
99	90	94	0.96

Similar experiments were carried out with sulfuric acid, potassium sulfate and potassium hydroxide. It was not possible to use the Onsager extrapolation for the sulfate solutions without some assumptions in regard to the transference numbers of the ions in the water–peroxide mixtures, as these are not known. We have assumed that the transference numbers of potassium and sulfate are the same as in water. The limiting equivalent conductances were determined by extrapolation using the square root law. Figure 3 gives the data for sulfuric acid and Fig. 4 those for potassium sulfate.

The intercepts Λ_0 and the ratios of the equivalent conductances are given in Table III.

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[2] G. Jones and G. M. Bollinger, THIS JOURNAL, **57**, 280 (1935).

[3] M. Kilpatrick and T. J. Lewis, *ibid.*, **78**, 5186 (1956).

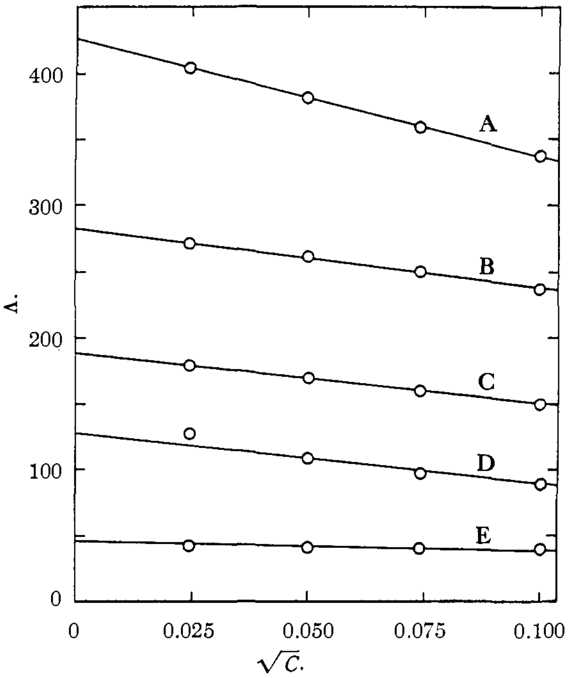

Fig. 3.—Equivalent conductance of sulfuric acid in water–peroxide mixtures: A, 0% H_2O_2; B, 25% H_2O_2; C, 50% H_2O_2; D, 75% H_2O_2; E, 99% H_2O_2.

The ratio of the equivalent conductances of sulfuric acid to potassium sulfate shows the same trend as given in Table II but the low value of the ratio in high concentrations of hydrogen peroxide indicates another explanation. Since hydrogen peroxide is a relatively basic solvent and the dielectric constant is about the same as water, the assumption was made that perchloric acid is a strong electrolyte. The same assumption is valid for sulfuric acid for the first dissociation step, but since the second dissociation constant ($K_2 = 10^{-2}$) in water is probably smaller in the water–peroxide systems, the species present, in addition to the solvated proton, are HSO_4^- and $SO_4^{=}$. Since K_2 includes the water concentration, it should decrease 100-fold in going from water to 99% hydrogen peroxide and, quite apart from the basic nature of the solvent, we can no longer consider complete dissociation to sulfate but must consider dissociation to bisulfate and partial reaction to sulfate. Therefore, we cannot expect agreement between the experimental slopes and those calculated from the Onsager relation, assuming complete dissociation.

Table III

Ratio of the Equivalent Conductances at 25°

H_2O_2, %	Λ_0 H_2SO_4	Λ_0 K_2SO_4	Ratio $\frac{\Lambda H_2SO_4}{\Lambda K_2SO_4}$	Ratio $\frac{\Lambda K_2SO_4}{\Lambda KClO_4}$
0	426	152	2.80	1.10
25	282	133	2.12	1.10
50	188	118	1.59	1.12
75	127	111	1.14	1.16
99	46	111	0.41	1.18

The determination of the conductance of potassium hydroxide presented real difficulties, especially in water and low concentration peroxide, due to decomposition of the hydrogen peroxide and the reaction of the electrodes with the caustic. The data are given in Table IV.

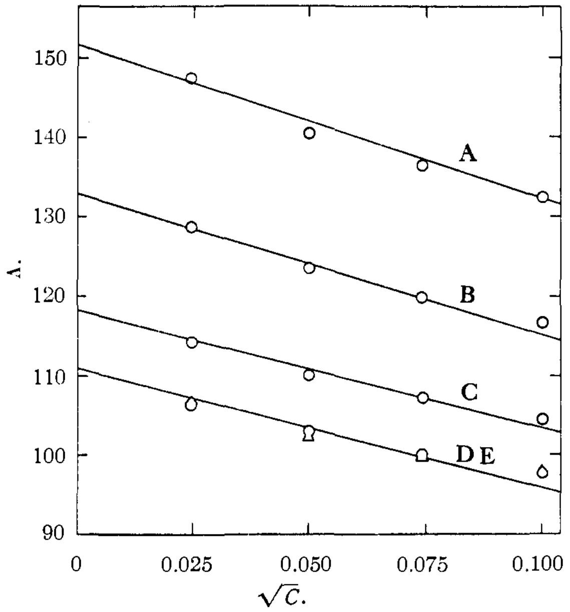

Fig. 4.—Equivalent conductance of potassium sulfate in water–peroxide mixtures: A, 0% H_2O_2; B, 25% H_2O_2; C, 50% H_2O_2; D, O, 75%; E, Δ, 99% H_2O_2.

Table IV

Equivalent Conductance of Potassium Hydroxide in Water–Hydrogen Peroxide

Peroxide, %	KOH, equiv./l. 0.01	0.0055	0.0025	0.0006	Λ_0	Ratio $\frac{\Lambda_0 KOH}{\Lambda_0 KClO_4}$
0	256.8	254.1	245.1	213.5	271[a]	1.96
25	104.1	105.0	105.9	110.5	108	0.89
50	106.8	118.2	108.5	113.8	111	1.05
75	83.5	87.3	93.0	126.3	128	1.33
99	172.5	172.6	173.1	173.5	174	1.83

[a] From the literature using Pt electrodes.

Column seven gives the ratio of the limiting equivalent conductances of potassium hydroxide to potassium perchlorate. There is a minimum in the ratio at or before 25% hydrogen peroxide, and the ratio at 99% peroxide is not much lower than that in water.

The logical explanation is that, as hydrogen peroxide replaces water, the "abnormal" conductance of hydroxyl ions disappears. However, hydrogen peroxide gives up a proton to the hydroxyl ion to form the hydroperoxide ion.

$$H_2O_2 + OH^- = H_2O + HOO^-$$

This ion, like the fluoride ion, HFF^-, has a higher mobility[3] than other anions including the hydroxyl ion in hydrogen peroxide containing some water.

The results confirm the belief that mixed solvents are more complicated than pure solvents,[4] and emphasize the importance of the structure of the solvent. It may be that the solvated proton H^+·

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(4) M. Kilpatrick, *Chem. Revs.*, **30**, 159 (1942).

H_2O_2 in anhydrous hydrogen peroxide shows "chain conductances" but this is greatly reduced in the presence of water.[5]

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CHICAGO, ILL.

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[5] Private communication, W. K. F. Wynne-Jones.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAPE TOWN]

Electrochemical Behavior in Anhydrous Formic Acid. II. Polarographic Investigation of Some Inorganic Cations

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The half-wave potentials of bismuth, antimony, lead, tin, cadmium, thallium, indium, nickel and zinc with a variety of supporting electrolytes in anhydrous formic acid have been measured. These elements were found mostly to give very well defined waves and, with the exception of nickel to undergo reversible reduction. Except in the case of tin and indium, which form weak formato complexes, formic acid showed itself to be a solvent with small solvating power. The series of half-wave potentials was found to follow closely that in aqueous solution with the exception of nickel, zinc and cadmium. The potentials of these elements were more positive than in aqueous solution, a phenomenon which was attributed to hydration of the ions in aqueous solution as opposed to the absence of solvation in formic acid. The diffusion current constants of the elements studied were found to be appreciably lower in formic acid than in water. Anomalous behavior was observed for the half-wave potential of thallium which was found to shift appreciably to more positive values on increase of the supporting electrolyte concentration.

Introduction

Although anhydrous formic acid exhibits all the properties required by a solvent for ideal polarographic characteristics, no study of the dropping mercury electrode in this medium has hitherto been described. Formic acid, besides having a high dielectric constant (56.1 at 25°[1]) and considerable ionizing properties, also exhibits a strong solvent action upon many organic compounds. Furthermore, it has been shown by Pleskov[2] to be a solvent with small complexing power, a feature which enhances its value for the examination of ions which are normally hydrated in aqueous solution. The above author also showed that the standard electrode potentials in formic acid of the elements he studied differed little from the values found in aqueous solution. Exceptional behavior was shown by zinc and cadmium, the potentials of which were displaced to more positive values. This shift was attributed to hydration of the ions in aqueous solution as opposed to the absence of solvation in formic acid.

The present investigation embodies the determination of the half-wave potentials of nine inorganic cations in a variety of supporting electrolytes in anhydrous formic acid and the diffusion current constants for each.

Experimental

Materials.—The purification of the formic acid used is described in a previous paper.[3] The best value of the conductivity found for formic acid was 6.734×10^{-5} mho/sq. cm. All samples of acid used froze at 8.40° and when examined polarographically showed residual currents which were small. To determine the amount of water absorbed by the solvent during a complete polarographic measurement the water content of the anhydrous formic acid after use in a run, was estimated by measurement of the depression of the freezing point and by Karl Fischer titrations. Both methods showed close agreement, a maximum value of 0.07% of water being found.

The following reagents were dried by heating in an oven at 130° for 5 hours and cooled over anhydrous calcium chloride: potassium chloride, tartar emetic, nickel chloride hexahydrate, sodium tartrate, sodium formate, stannous chloride, sodium bromide and cadmium chloride. Sodium citrate was dried at 180° for 3 hours, oxalic acid at 90° for 2 hours and lead acetate at 100° for 3 hours. Ammonium formate was recrystallized from absolute alcohol and then desiccated over concentrated sulfuric acid *in vacuo*. Zinc chloride was dried at 130° for 5 hours and cooled in a stoppered bottle over phosphorus pentoxide. Indic chloride was prepared by treatment of metallic indium with aqua regia and purified by sublimation and dried at 120° for 5 hours. The remainder of the salts used were dried in a desiccator over anhydrous calcium chloride for 5 days.

Apparatus.—All potentials were measured with reference to the quinhydrone-in-formic acid electrode (Q.F.A.E.); the same polarographic cell was used as in the measurements on this electrode previously described.[3] The capillary tube used had an internal radius of 0.0409 mm. and was 12.45 cm. long. All measurements were carried out at 25.00 ± 0.01°. Nitrogen, dried over phosphorus pentoxide, was bubbled through a tube of anhydrous formic acid before being passed through the polarographic cell to remove dissolved oxygen. As it previously had been shown that the measured and calculated values of the drop rate of mercury in formic acid agreed to within 1%, all subsequent values were calculated as described by Kolthoff and Lingane.[4]

Results

The results are tabulated in Table I where the potentials quoted are referred to the saturated calomel-in-formic acid electrode (S.C.F.A.E.). These values were obtained by subtracting −0.538 volt from the potential as measured against the quinhydrone-in-formic acid electrode. Thus the half-wave potential of lead using a 0.5 *M* sodium formate supporting electrolyte was -0.76^2 volt *vs.* Q.F.A.E. and therefore -0.22^4 volt *vs.* S.C.F.A.E. A measure of the reversibility of the electrode reaction was obtained by plotting *E vs.*

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[1] J. F. Johnson and R. H. Cole, THIS JOURNAL, **73**, 4536 (1951).

[2] V. Pleskov, *Acta Physicochim. URSS*, **21**, 41 (1946).

[3] T. A. Pinfold and F. Sebba, THIS JOURNAL, **78**, 2095 (1956).

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 80.