THE BEHAVIOUR OF MIXTURES OF HYDROGEN PEROXIDE AND WATER

PART 3. THE IONIC PRODUCTS

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The significance of the ionic product of a mixed solvent is discussed and the ionization of mixtures of hydrogen peroxide and water is considered in relation to the acidity and basicity of the components. The ionic products of these mixtures have been measured by two independent methods and the results are represented as a function of the mole fraction of hydrogen peroxide.

It was first shown by Maass 1 and later confirmed by us that hydrogen peroxide is a solvent very similar to water. We have also shown by the use of the glass electrode that hydrogen ions (in the solvated or "lyonium" form) exist in mixtures of hydrogen peroxide and water. By analogy with water we would expect the auto-ionization of pure peroxide to take place by the reaction

$$H_2O_2 + H_2O_2 = H_3O_2^+ + O_2H^-.$$
 (1)

In mixtures of hydrogen peroxide and water, however, the *acidity* of peroxide and the *basicity* of water will play the dominant roles and the ionization of a mixture must take place essentially according to the reaction

$$H_2O_2 + H_2O = H_3O^+ + O_2H^-.$$
 (2)

Evans and Uri,² in a paper which is often quoted as "evidence" for the existence of the ion $H_3O_2^+$, *postulated* its existence in a predominantly aqueous medium : this is quite impossible, at least at any appreciable concentration, because as we shall show in a later communication, water is more than a million times as basic as hydrogen peroxide in such solutions. Of course, at very high concentrations of peroxide we shall have appreciable amounts of the ion $H_3O_2^+$ just as in virtually pure water we have the ion OH⁻ formed by hydrolysis of O_2H^- .

The reaction represented by eqn. (2) is analogous to the auto-ionization of a pure solvent and the equilibrium constant $K_{\rm M} = a_{\rm H_3O^+}a_{\rm O_2H^-}$ can be treated exactly as the ionic product of a solvent and will similarly control "hydrolytic" or "lyolytic" equilibria. The determination of this ionic product for all mixtures is therefore a matter of importance, since a great deal of chemistry, including the stability of salts in solution, will be affected by the variation of the ionic product with solvent composition.

The ionic product of a pure solvent can be regarded as the product of the acidity and basicity constants defined by the relations

$$K_{A(1)} = a_{H^+}C_{S^-}f_{S^-},$$

 $K_{B(1)} = \frac{C_{SH^+}f_{SH^+}}{a_{H^+}},$

where C_{SH^+} is the concentration of lyonium ions, C_{S^-} the concentration of lyate ions and a_{H^+} the proton activity. We can define similar acidity and basicity

constants for a solvent mixture in which the concentrations of lyate and lyonium ions will be the sum of the concentrations of the ions formed from the various solvent molecules.

$$K_{A(M)} = a_{H^+} \sum C_S - f_S -,$$

 $K_{B(M)} = \frac{\sum C_{SH^+} f_{SH^+}}{a_{H^+}}.$

If we make the assumption that the acidity and basicity constants for each type of molecule in the solvent mixture vary as the mole fraction of that species, we can express the ionic product for a two-component mixture as

$$K_{\mathbf{M}} = \{(1-x)K_{\mathbf{A}_{1}} + xK_{\mathbf{A}_{2}}\}\{(1-x)K_{\mathbf{B}_{1}} + xK_{\mathbf{B}_{2}}\}$$

and, where one component is much more acid and much less basic than the other, this simplifies to

$$K_{\rm M} = (1-x)^2 K_{\rm M_1} + x(1-x) K_{\rm A_1} K_{\rm B_2} + x^2 K_{\rm M_2},$$

the ion concentrations being expressed as mole fractions. The second term is so much greater than the other two over most of the range of composition that it determines the values of $K_{\rm M}$. If the acidity and basicity constants are assumed to be independent of the solvent this relation leads to a symmetrical curve with rather a flat maximum. Our results are in qualitative agreement with this prediction but the actual variation of $K_{\rm M}$ with composition is incompatible with the assumption of constancy of the acidity and basicity constants of hydrogen peroxide and water respectively. In a further communication we propose to show how these two parameters vary with composition.

We have noted the importance of the ionic product for lyolytic equilibria and we can illustrate this by comparing the lyolysis of the salt of a weak acid in water and in 80 % hydrogen peroxide. We have found experimentally that the dissociation constant of a weak acid in 80 % H_2O_2 is about 10^{-3} times the value in water; and on the other hand, the value of $K_{\rm M}$ is approximately 10⁴ times as great, hence

$$\Delta \mathbf{p}\mathbf{K}_{\mathbf{L}} = \Delta \mathbf{p}\mathbf{K}_{\mathbf{M}} - \Delta \mathbf{p}\mathbf{K}_{\mathbf{A}} = -7.0,$$

i.e. the lyolytic constant $K_{\rm L}$ in 80 % H_2O_2 is 10⁷ times the hydrolytic constant $K_{\rm H}$ in water. This very large increase can have marked effects for the existence of salts, for example, the ion HPO₄²⁻ which exists in water since its hydrolytic constant is approximately 10⁻⁷, cannot exist in 80 % H_2O_2 where the value of $K_{\rm L}$ is about 1 and lyolysis into $H_2PO_4^-$ and O_2H^- is almost complete.

There are several methods which may be used for the determination of the ionic product of a solvent but, at the outset of this work, it seemed advisable to avoid the use of alkaline solutions in concentrated hydrogen peroxide and we therefore decided to use a method in which the lyolysis of the anion of a weak acid and the dissociation of the weak acid are combined to give the ionic product. By suitable choice of acid we were able to obtain reliable results by this method, but as it seemed more important to cover the whole range of solvent composition with moderate accuracy than to obtain a few very precise results, we abandoned this method for the simple and rapid one of potentiometric acid-alkali titration which, surprisingly, does not appear to have been used for such determinations.

SALT HYDROLYSIS METHOD

The dissociation constant K_A , of a weak acid, HA, is given by

$$K_{\mathbf{A}} = \frac{C_{\mathbf{H}} + C_{\mathbf{A}}}{C_{\mathbf{H}\mathbf{A}}} \frac{f_{\mathbf{H}} + f_{\mathbf{A}}}{f_{\mathbf{H}\mathbf{A}}} = K'_{\mathbf{A}} \frac{f_{\mathbf{H}} + f_{\mathbf{A}}}{f_{\mathbf{H}\mathbf{A}}}.$$

In a solution of the salt NaA, the anion A^- reacts with the solvent SH, according to the equation

$$A^- + SH = S^- + HA,$$

HYDROGEN PEROXIDE AND WATER

and the lyolytic constant $K_{\rm L}$ is given by

$$K_{\mathrm{L}} = \frac{C_{\mathrm{S}} - C_{\mathrm{HA}}}{C_{\mathrm{A}}} \frac{f_{\mathrm{S}} - f_{\mathrm{HA}}}{f_{\mathrm{A}}},$$

where $C_{S^-} = C_{HA}$ but $f_{S^-} \neq f_{HA}$.

The ionic product $K_{\mathbf{M}}$ of the solvent is given by

$$K_{\rm M} = C_{\rm H^+}C_{\rm S^-}f_{\rm H^+}f_{\rm S^-}.$$
$$C_{\rm S^-} = \frac{K_{\rm M}}{C_{\rm H^+}f_{\rm H^+}f_{\rm S^-}} = C_{\rm HA},$$

Thus

$$K_{\rm L} = \frac{(K_{\rm M})^2 f_{\rm S} - f_{\rm HA}}{(C_{\rm H} + f_{\rm H} + f_{\rm S} -)^2 C_{\rm A} - f_{\rm A} -}$$

 $K_{\rm M} = K_{\rm L} K_{\rm A},$

and But as

and

$$K_{\rm M} = \frac{(K_{\rm M})^2 K'_{\rm A}}{(C_{\rm H^+})^2 f_{\rm H^+} f_{\rm S} - C_{\rm A} -}$$

$$\frac{K_{\rm M}}{f_{\rm H^+}f_{\rm S^-}} = \frac{(C_{\rm H^+})^2 C_{\rm A^-}}{K'_{\rm A}} = K'_{\rm M},$$

where K'_{A} is the concentration ionization product of the weak acid, $C_{H^{+}}$ is the concentration of hydrogen ions, $C_{A^{-}}$ the concentration of the anions from the sodium salt of the acid, and K'_{M} is the ionic concentrations product of the solvent. K'_{A} , $C_{H^{+}}$ and K'_{M} are measured at the same ionic strength. The expression may be written in the form

$$pK'_{M} = 2pH - pK'_{A} - \log C_{A}.$$
(3)

Thus if the dissociation of a weak acid and the pH of a solution of its sodium salt in a solvent mixture are known, the ionic product of the solvent can be calculated directly from eqn. (3).

EXPERIMENTAL

The method of measuring the pH of hydrogen peroxide solutions has been described elsewhere.³ The dissociation constant of a weak acid was determined in the following way. Buffer solutions of known ionic strength were prepared volumetrically from stock solutions of the acid, its sodium salt, sodium perchlorate, hydrogen peroxide and water. For each solvent mixture a series of three buffer solutions in which the buffer ratio C_{HA}/C_{A-} varied between 4 and 1 were used. The ionic strength of the solution was maintained constant at 0.1 by the addition of sodium perchlorate. Along with each series of solutions a "blank" was made up from hydrogen peroxide and water. The concentration of hydrogen peroxide was estimated from the density of the blank solution.⁴ The pH of the buffer ratios drawn. This line has slope unity and pK'_A is read off directly from it since pK'_A = pH when log B.R. = 0. For the measurements in aqueous solution an Alki glass electrode was used. When not in use the electrode was stored in 0.1 N sodium metaborate and immediately before use was standardized in 0.05 N borax solution.

MATERIALS.—A.R. chemicals, with the exception of the salts required for direct measurement of pH of salt solutions, were used without further purification. Constant boiling hydrochloric acid ⁵ was used to standardize sodium hydroxide solution which was then used to standardize perchloric acid and acetic acid solutions. Methyl red was used as indicator for perchloric acid and thymol blue for acetic acid solutions.

Sodium acetate.—A.R. sodium acetate was recrystallized three times from cold distilled water and stored in a vacuum desiccator over sodium hydroxide pellets. Samples of the partially dehydrated material were further purified and dried by repeated extractions with (i) dry benzene and (ii) dry ether in a Soxhlet apparatus. The benzene was dried over phosphorus pentoxide and the ether over sodium metal. About 30 ml liquid was used in each extraction and refluxing was continued for about 30 min. Between each operation the sodium acetate was tipped into a dish and transferred to a vacuum desiccator

826

containing sodium hydroxide pellets and for the experiments using benzene also some shredded paraffin wax. The sodium hydroxide and wax were frequently replaced.

Sodium p-nitrophenate.—Sodium p-nitrophenate was prepared by adding aqueous sodium carbonate solution in excess to a warm aqueous solution of p-nitrophenol. The salt was filtered off, dried with suction then recrystallized three times from hot water and dried over sodium hydroxide in a vacuum desiccator. It was further purified by extraction with ether in the manner described for sodium acetate. A sample of sodium p-nitrophenate which was bright orange in colour and fairly readily soluble in water was finally obtained.

Sodium borate.—The hydrated salt $Na_2B_4O_7$. 10 H₂O was dried to constant weight in a desiccator over a saturated sodium bromide solution as recommended by Dole.⁶

Piperidine.—Stability tests were carried out on solutions of piperidine at various concentrations in approx. 96 % (w/w) hydrogen peroxide. 1 N solutions were found to decompose rapidly. 0.1 N solutions were fairly stable over short periods of time at room temperature and could be delivered accurately from a microburette. Approx. 0.1 N piperidine solutions were prepared by weighing out 0.2 g piperidine into a weighing bottle and then adding immediately before the solution was required about 22 ml hydrogen peroxide solution. The solution was stirred gently and left unstoppered but protected from the atmosphere with a cover dish.

Hydrogen peroxide.—Hydrogen peroxide was purified by the method described in an earlier paper.³ The concentration of hydrogen peroxide was estimated by determination of the refractive index. Refractive indices were measured at 25° C with a simple Abbé refractometer using sodium light. We measured the refractive indices of a series of hydrogen peroxide solutions of known concentration. The agreement of our results with those published by Giguère ⁷ was good and showed that we could estimate the concentration of an aqueous hydrogen peroxide solution with an error of less than ± 0.3 % in the percentage (w/w).

Water.—Laboratory distilled water was twice distilled in a Pyrex glass apparatus, the first time from a trace of potassium permanganate.

RESULTS

To test the applicability of the method, measurements were made using acetic acid and sodium acetate. We found that to prepare sodium acetate free from acetic acid was difficult and consequently the values obtained for pK'_{W} were much lower than those generally accepted: the best value we obtained was $pK'_{W} = 12.6$. The salt of a weaker acid should be more easily purified so we decided to use *p*-nitrophenol and its sodium salt, and from determinations of K_A and K_L we obtained the value 13.745 for pK'_{W} . This is in fair agreement with the value of 13.785 quoted by Harned and Owen ⁸ for this constant in 0.1 N sodium chloride solution.

For mixtures of hydrogen peroxide and water the ionization was so much greater that the effect of traces of free acid in the sodium salt was negligible and we were able to make measurements with both sodium acetate and sodium p-nitrophenate. The results are collected in table 1.

TABLE 1					
mole fraction H ₂ O ₂	acid	pH of 0•1N Na sait	рЌА	рК _{́М}	
0	p-nitrophenol	_		13.75	
0.143	acetic	6.667	4.672	9.67	
0.313	acetic	6•483	4.902	9.08	
0.337	p-nitrophenol	7.50	6.93	9.07	

The method proved quite satisfactory but the purification of the salt was tedious and, as we wished to cover the whole range of solvent composition, we decided to use the more rapid, though less precise, method of acid-base titration.

ACID-BASE TITRATION METHOD

By electrometric methods it is easy to follow the change in pH during the neutralization of an acid by a base. In the neutralization of a strong acid by a strong base there is a very sharp increase in pH at the equivalence point, consequently this point, which corresponds to the pH of the pure solvent, can be determined accurately, and the negative logarithm of the ionic product, pK_{M} , is twice the value of the pH at the equivalence point.

Solutions of perchloric acid in water and in mixtures of water and hydrogen peroxide containing up to 84 % (w/w) hydrogen peroxide were titrated with aqueous sodium hydroxide solution. The results of similar titrations in more concentrated hydrogen

peroxide solutions were difficult to interpret since the additions of small volumes of water cause marked changes in the standard potential of the glass electrode. The method adopted for concentrated solutions was to titrate a 0.001 N solution of perchloric acid with a 0.1 N solution of piperidine in the same solvent.

For mixtures containing less than 85 % (w/w) of hydrogen peroxide, titrations were carried out at 25° C with aqueous standard NaOH using a glass electrode and a saturated calomel reference electrode dipping into a Pyrex beaker containing the experimental solution. The liquid junction to the calomel electrode was made in the cylindrical channel between the ground-glass tip of the electrode and a closely fitting socket-collar. A special glass electrode reversible to hydrogen ions over the pH range 0-14 was used in the measurements made with pure water.

50 ml of a 0.01 N perchloric acid solution in the required solvent were introduced into the beaker and the e.m.f. of the cell measured. e pH of this solution equals 2. A small ume of N aqueous sodium hydroxide solun was run into the beaker from a microrette (total capacity = 1 ml), the solution Il mixed and the e.m.f. of the cell again Further additions of N NaOH asured. ution were made and the e.m.f. of the cell asured after each addition. The change pH resulting from each addition of alkali and also the pH of each intermediate solution was then calculated. A graph of pH against ml N NaOH solution added to 50 ml 0.01 N HClO₄ solution was drawn. The pH of the

solvent was read from the graph and the pK_M value of the solvent calculated. A selection of the titration curves is shown in fig. 1.

For the most concentrated peroxide mixtures it was important not to introduce water and a solution of piperidine in hydrogen peroxide was used for the titration. The titration cell which is shown in fig. 2 was made to exclude moisture. The two compartments

concenti	ration H ₂ O ₂	nKar		
%(w/w)	mole fraction	PTM		
0	0	14.0		
9.3	0.020	10.7		
23.1	0.137	9.6		
35.6	0.226	9.4	titration	
48.6	0.333	9.0	with	
60.65	0.449	9.0	aq. NaOH	

0.208

0.615

0.741

0.895

0.950

0.975

0.994

9.0

9.1

9.4

10.2

11.0

11.7

12.4

titration

with

piperidine.

TABLE	2.—рК _м	VALUES	FROM	POTENTIOMETRIC	TITRATIONS	AT	25°	С
			-					

نە _{مە}	_م مر				vol tio: bu:
0.5	0.4	0.6	O·8	1.0	we
		N₀OH	l		me
Acid-alkali titrations in H ₂ O ₂					sol
mixtu	res.	pH ag	ainst n	nl NaOH.	me
					of

water 23·10% H₂O₂ 60·65% H₂O₂

FIG. 1 H_2O

Ħ

O water; \triangle 23.10 % H₂O₂; □ 60.65 % H₂O₂.

66·1

75.1

84.4

94.2

97.3

98.6

99.7

828

11

IC

9

8

7

6

5

4

3

2

Acid-alkali titratrations

in H2O2-H2O

mixtures

A and B are mounted on aluminium stands. Tube C is tapered and compartment A is detached by means of screw D. The Cambridge glass electrode and the reference electrode which is a silver chloride electrode dipping into 3.5 N potassium chloride solution



FIG. 3.—Ionization constants of hydrogen peroxide + water mixtures pK_M against mole fraction H_2O_2

Aq. NaOH \bigcirc Piperidine \triangle acid-alkali titrations. \square salt hydrolysis.

are shown in position. The liquid junction was quickly renewed by opening tap E and allowing a few drops of solution to escape from tube C. The piperidine solution was delivered from a microbutette similar to that described by Conway.⁹ It consisted essentially of a length of Veridia tubing of uniform internal diameter 0.15 cm, so that 1 cm is equivalent to approx. 0.018 ml.

10 ml 0.001 N perchloric acid solution were introduced into the titration vessel; the glass electrode which had been previously soaked for at least 24 h in 50 % (w/w) hydrogen

830

LOGARITHMIC PHOTOMETER

peroxide solution, thoroughly rinsed with the acid solution and the cell assembled. The pH of the initial solution was 3. The microburette was filled with 0.1 N piperidine solution and the titration carried out with the minimum delay. A small amount of decomposition occurred and it was necessary to renew the liquid junction each time an addition of alkali was made. A graph of pH of the solution against scale readings was drawn and the pK_M value calculated.

The experimental results are shown in table 2 and in fig. 3. The solid line in fig. 3 shows pK_M as a function of the mole fraction hydrogen peroxide. The broken line indicates the type of curve obtained for pK_M on the assumption that the mixtures are ideal and the acidity and basicity constants are independent of the solvent.

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- ⁸ Harned and Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1950), p. 485, 478.
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