39. *Solvent Extraction Studies. Part III. The Extraction of Hydrogen Peroxide into Tri*-n-*butyl Phosphate.*

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The extraction behaviour of hydrogen peroxide (up to 6·5M-H_2O_2 in the equilibrium aqueous phase) into tri-*n*-butyl phosphate can be explained in terms of the replacement of water in the organic phase by hydrogen peroxide. The effect of the addition of an inert solvent to the organic phase has been studied. For dilute hydrogen peroxide the temperature coefficient of the extraction leads to $\Delta H = -2{\cdot}1$ kcal./mole.

HYDROGEN peroxide is extractable into basic organic solvents such as diethyl ether,[1,2,3] ethyl acetate,[3,4] *iso*butanol,[3] and pentyl alcohol.[5-9] Paulsen[10] recently gave qualitative results on the extraction into a wide range of compounds. I have used tri-*n*-butyl phosphate because it solvates many inorganic compounds[11] and water is very soluble in it.[12,13,14]

EXPERIMENTAL

Materials.—Both Analytical Reagent and laboratory grade hydrogen peroxide were used; no difference in extractive behaviour was observed. Solutions were analysed by titration with potassium permanganate solution.

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[1] Kolosovskii, *Bull. Soc. chim. France*, 1925, **37**, 372.
[2] Maass and Hatcher, *J. Amer. Chem. Soc.*, 1916, **38**, 633.
[3] Walton and Lewis, *ibid.*, 1922, **44**, 2472.
[4] Kolosovskii and Kulikov, *Ukrain. khim. Zhur.*, 1934, **9**, 37.
[5] Calvert, *Z. phys. Chem.*, 1901, **38**, 513.
[6] Joyner, *Z. anorg. Chem.*, 1912, **77**, 103.
[7] Menzel, *Z. phys. Chem.*, 1923, **105**, 402.
[8] Husain, *Z. anorg. Chem.*, 1928, **177**, 215.
[9] Livingston, *J. Amer. Chem. Soc.*, 1928, **50**, 3204.
[10] Paulsen, *Chem. and Ind.*, 1956, 1274.
[11] See, for example, Healy and McKay, *Rec. Trav. chim.*, 1956, **75**, 730.
[12] Moore, U.S.A.E.C. report AECD-3196.
[13] Alcock, Grimley, Healy, Kennedy, and McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.
[14] Tuck, *J.*, 1958, 2783.

Tri-*n*-butyl phosphate was purified as described previously [14] and stored over chromatographic alumina to prevent peroxide formation.[15] In certain experiments, the solvent was diluted with " AnalaR " carbon tetrachloride.

Procedure.—5 ml. of hydrogen peroxide solution and 5 ml. of tri-*n*-butyl phosphate were shaken in a stoppered bottle for 20 min., then centrifuged. Suitable aliquot parts were analysed. Samples of the organic phase were dissolved in *ca.* 25 ml. of aqueous acetone before titration; it was shown that direct measurement of the amount of extracted hydrogen peroxide was thus possible. Hydrogen peroxide did not decompose in any solution for which results are reported.

In investigating the effect of temperature, both phases were allowed to reach the temperature of the thermostat before mixing; after equilibration, aliquot portions were weighed and analysed, and extraction coefficients calculated on a molal basis. All other experiments were carried out at room temperature (23°).

The increase in the volume of the organic phase [16] was not significantly different from that observed on saturation with water.[14] A value of 5·35 ml. was taken for the volume of the equilibrium organic phase.

*Determination of Water in Tri-*n*-butyl Phosphate.*—The Karl Fischer volumetric determination of water is unaffected by hydrogen peroxide,[17, 18] but I found that if more is present than the sulphur dioxide in the reagent (Fischer Scientific Co.) can take up its reaction with iodine gives high results for the water concentration. Anhydrous sulphur dioxide was therefore passed through silica gel to remove traces of water vapour, and bubbled through an aliquot portion of the organic phase in the previously dried titration vessel, from which atmospheric moisture was excluded; results were then reproducible. A dead-stop end-point method was used; the Karl Fischer reagent was calibrated with " AnalaR " sodium tartrate.

RESULTS AND DISCUSSION

*Extraction into Pure Tri-*n*-butyl Phosphate.*—Table 1 gives the results (org. = organic phase; aq. = aqueous phase). The gradual decrease in the extraction coefficient, also found by Kolosovskii [1] and by Paulsen [10] for other solvents, is due to a decrease in the concentration of available solvent with increasing amounts of hydrogen peroxide in the organic phase. The constant value of $E_{H_2O_2}$ for the extraction into pentyl alcohol [5, 6, 7, 8, 9] at different hydrogen peroxide concentrations is presumably due to the hydroxylic nature of this solvent.

TABLE. 1. *Extraction of hydrogen peroxide into tri-*n*-butyl phosphate.*

H_2O_2 (M), aq.	0·605	0·835	1·46	2·53	3·44	4·22	4·44	5·43	6·41
H_2O_2 (M), org.......	0·32	0·408	0·639	0·944	1·13	1·32	1·38	1·54	1·76
$E_{H_2O_2}$	0·525	0·49	0·44	0·37	0·33	0·31	0·31	0·28	0·275

Since tri-*n*-butyl phosphate extracts water,[12, 13, 14] it seems likely that extraction of hydrogen peroxide displaces water from the organic phase. This is confirmed by the results of Karl Fischer titrations (Table 2). Within experimental limits, the sum of water and hydrogen peroxide concentrations is constant at an average of 3·49 ± 0·08 mmoles/ml. The figure for water-saturated tri-*n*-butyl phosphate, 3·45 ± 0·70M, is the mean of three determinations and three calibrations. Pure tri-*n*-butyl phosphate is 3·65M, but on allowing for the volume increase due to saturation,[14] this value is reduced to 3·43M, equal to the water concentration within experimental error.

TABLE 2. *Water content of tri-*n*-butyl phosphate solutions of hydrogen peroxide.*

H_2O (M)	3·45	3·02	2·74	2·70	2·35	2·13	2·18
H_2O_2 (M)	0	0·37	0·70	0·86	1·16	1·28	1·48
Total	3·45	3·39	3·44	3·56	3·51	3·41	3·66

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[15] Dasler and Bauer, *Ind. Eng. Chem. Anal.*, 1946, **18**, 52.

[16] Tuck, *J.*, 1957, 3202.

[17] Zimmerman, Felte, and Seifer, *Fette u. Seifen*, 1939, **46**, 446.

[18] Mitchell and Smith, " Aquametry," Interscience Publishers, Inc., New York, 1948, p. 253.

Treating the system as a competition between water and hydrogen peroxide for the organic solvent, one can write

$$\frac{K_1}{K_2} = \frac{[\mathrm{Bu_3PO_4,H_2O}][\mathrm{H_2O_2(aq)}]}{[\mathrm{Bu_3PO_4,H_2O_2}][\mathrm{H_2O(aq)}]} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where K_1 and K_2 are the respective mass-action constants for the formation of Bu_3PO_4,H_2O and Bu_3PO_4,H_2O_2. Over the concentration range studied, one can neglect the aqueous phase activity coefficients of both water and hydrogen peroxide. It will also be assumed that the activities of the species in the organic phase can be equated with the concentrations; eqn. (1) then becomes

$$K' = \frac{(\text{mole ratio } \mathrm{H_2O/H_2O_2}, \text{ organic phase})}{(\text{mole ratio } \mathrm{H_2O/H_2O_2}, \text{ aqueous phase})}$$

Table 3 shows that K' is reasonably constant, justifying the assumptions.

TABLE 3. *Mole ratios, water : hydrogen peroxide, in organic and aqueous phases.*

H_2O_2 (M), org. ...	0·32	0·41	0·64	0·94	1·13	1·38	1·54	1·76
H_2O (M),* org. ...	3·11	3·02	2·79	2·49	2·30	2·05	1·89	1·67
$H_2O : H_2O_2$, org....	9·74	7·40	4·37	2·64	2·04	1·49	1·23	0·95
$H_2O : H_2O_2$, aq. ...	91·5	66·2	38·3	21·7	15·8	12·2	9·94	8·38
K'	0·106	0·112	0·114	0·122	0·129	0·122	0·124	0·113

* By difference.

The mean value of $K' = 0{\cdot}118 \pm 0{\cdot}004$ shows that K_2 is about $8{\cdot}5K_1$, presumably because the stronger acidity of hydrogen peroxide (pK = 11·75 [19]) causes stronger complexing with the basic solvent.

Effect of Inert Solvent.—Aqueous hydrogen peroxide (3% v/v) was extracted into mixtures of tributyl phosphate and carbon tetrachloride (Table 4). Hydrogen peroxide was almost completely insoluble in carbon tetrachloride (as in benzene [2]). Comparison with the results of McKay and his co-workers [13] suggests that the extraction of hydrogen peroxide falls off more slowly than does the uptake of water with decreasing tributyl phosphate concentration. This is again presumably due to the more acidic character of hydrogen peroxide; the interaction of tri-*n*-butyl phosphate with nitric acid is virtually unaffected by non-polar solvents.[13, 14]

TABLE. 4. *Extraction of hydrogen peroxide into* Bu_3PO_4–CCl_4 *mixtures.*

Bu_3PO_4 (% v/v)	100	80	60	40	20
H_2O_2 (M), aq.	0·95	1·06	1·17	1·28	1·33
H_2O_2 (M), org.	0·45	0·33	0·21	0·10	0·029
$E_{H_2O_2}$	0·47	0·31	0·18	0·079	0·022

Effect of Temperature.—In measuring the effect of temperature on the extraction, the constant

$$K_T = \frac{\text{mole ratio, organic phase}}{\text{aq. } \mathrm{H_2O_2} \text{ concn. (molal)}}$$

was evaluated (Table 5). A decrease in $E_{H_2O_2}$ for ether with increasing temperature was reported by Walton and Lewis [3] and by Paulsen.[10] The present results give a linear plot

TABLE. 5. *Effect of temperature change on the extraction of hydrogen peroxide into tri-*n*-butyl phosphate.*

Temp.	H_2O_2 (m), aq.	$E_{H_2O_2}$	Mole ratio, org.	K_T
15·1°	0·590	0·570	0·107	0·182
24·9	0·609	0·516	0·100	0·164
35·2	0·649	0·452	0·094	0·144

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[19] Evans and Uri, *Trans. Faraday Soc.*, 1949, **45**, 224.

of log K_T against $1/T°$ K; the slope corresponds to $\Delta H = -2{\cdot}1$ kcal./mole. Similar values have been found for systems involving the extraction of chloroferric acid [20] and of molybdenum(VI) compounds.[21]

It is noteworthy that a solution of hydrogen peroxide in tri-*n*-butyl phosphate has many of the redox properties of the corresponding aqueous solution (cf. Walton and Jones [22]), and that reaction with an extract solution of chromium(VI) in this solvent [23] produces the well-known blue colour of perchromic acid; it is hoped to investigate this reaction later.

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[20] Nachtrieb and Conway, *J. Amer. Chem. Soc.*, 1948, **70**, 3547.
[21] Diamond, personal communication.
[22] Walton and Jones, *J. Amer. Chem. Soc.*, 1916, **38**, 1956.
[23] Diamond and Tuck, unpublished results.