on the cold surface. Geib[14] has proposed a mechanism for peroxide formation in which H atoms adsorbed on the cold surface react with O_2 molecules from the gas to form HO_2 free radicals which subsequently react with H atoms to give H_2O_2. Since OH is known to be present in significant concentrations,[15] the formation of condensed product from dissociated water vapor cannot be this simple; however, the mechanisms may involve reaction of adsorbed species with molecules from the gas. Smith[8] has proposed that the free radical complexes $HO\cdot O_2$ and $HO_2\cdot O_2$ might be fairly stable. Formation of these species provides a possible mechanism for retention of O_2, and their subsequent reaction with H atoms could result in the formation of H_2O_3 and H_2O_4. These same molecular species might also be expected as products in the low temperature reaction of HO_2 with OH or HO_2.

The amount of heat evolved can be estimated from the data shown in Fig. 1. Using the heat capacity 0.757 cal./g. given by Giguère and Morissette[16] for 60.1% H_2O_2 in the range 0 to 27° and applying a 28% correction for the heat capacity of the Dewar tube and thermocouple, one finds that the temperature rise from -58 to $+63°$ represents a heat evolution of 118 cal./g. From the ratio of evolved oxygen to final H_2O_2 (1:5.8) obtained from the data of Jones and Winkler,[3] the calculated heat evolved is 44 kcal. per mole of evolved oxygen. Only a small fraction of the gas appeared to be evolved below $-60°$. Within wide limits of possible error, this agrees with the amount of heat expected from the decomposition of H_2O_2 (48 kcal. per mole of evolved oxygen), and it also agrees with the amount to be expected from the decomposition of H_2O_3 or H_2O_4 if the reactions $H_2O_3 \rightarrow OH + HO_2$ and $H_2O_4 \rightarrow 2HO_2$ are assumed to be only slightly endothermal. The decomposition of $H_2O{-}O$ to form O_2 would yield only slightly less than the heat of dissociation of O_2, 116 kcal./mole, if the heat absorbed in the reaction $H_2O{-}O \rightarrow H_2O + O$ is small. Thus the observed heat associated with O_2 formation seems to favor intermediates such as H_2O_3 or H_2O_4.

Neither Robertson[17] nor Foner and Hudson[7] were able to detect HO_4 or H_2O_4 mass spectrometrically in a gas at room temperature containing HO_2 and O_2; however, this does not preclude the formation and existence of these species at lower temperatures. Below $-60°$, H_2O_3 and H_2O_4 would have low vapor pressures, perhaps too low to permit their detection in a mass spectrometer.

It should be pointed out that the conclusions from the data presented here do not support recent claims[18,19] for the existence of H_2O_4 at temperatures considerably above $-60°$.

Acknowledgments.—The author is grateful to Ralph Livingston and Henry Zeldes for many helpful discussions.

OAK RIDGE, TENNESSEE

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[14] K. H. Geib, *J. Chem. Phys.*, **4**, 391 (1936).

[15] T. M. Sanders, A. L. Schawlow, G. C. Dousmanis and C. H. Townes, *ibid.*, **22**, 245 (1945).

[16] P. A. Giguère and B. G. Morissette, *Can. J. Chem.*, **33**, 804 (1955).

[17] A. J. B. Robertson, *Chem. and Ind.*, 1485 (1954).

[18] P. M. Stadnik, *Doklady Akad. Nauk S.S.S.R.*, **87**, 445 (1952).

[19] K. E. Kruglyakova and N. M. Emanuel, *ibid.*, **83**, 593 (1952).

[CONTRIBUTION NO. 2128 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Distribution of Tripositive Arsenic between Hydrochloric Acid Solutions and β,β'-Dichlorodiethyl Ether

BY G. MYRON ARCAND[1]

RECEIVED OCTOBER 1, 1956

The distribution of tripositive arsenic between aqueous hydrochloric acid solutions and β,β'-dichlorodiethyl ether has been investigated. The hydrolysis products from the ether phases have been analyzed and the ratios of chloride to arsenic established at various aqueous hydrochloric acid concentrations. These ratios vary with the hydrochloric acid concentration which indicates that more than one chloride species of arsenic is present in both phases. Analysis of the distribution data and of solubility data taken from the literature has permitted the calculation of formation constants for the proposed species.

Introduction

This work was undertaken in an effort to establish some basis for predicting what compounds of tripositive arsenic exist in aqueous hydrochloric acid solutions. Preliminary work in this Laboratory[2] and that of Irvine and co-workers[3] have shown that tripositive arsenic can be extracted from hydrochloric acid solutions by a number of organic solvents. Of these, β,β'-dichlorodiethyl ether appeared to be most suited for the desired study, since it is easily purified, easily handled and dissolves only small amounts of hydrochloric acid and water while dissolving relatively large quantities of arsenic. Correlation of the results of this work with conductivity,[4] solubility[5,6] and electromotive force data[7] permits the prediction of the

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[1] Department of Chemistry, University of Missouri, Columbia, Missouri.

[2] Unpublished experiments by R. Deverill.

[3] J. W. Irvine, Jr., R. A. Sharp, P. Kafalas and G. O. Brink, Paper presented at the 123d National Meeting of the American Chemical Society, Los Angeles, March 15 to 19, 1953.

[4] E. W. Washburn and E. K. Strachan, THIS JOURNAL, **35**, 681 (1913).

[5] A. Seidell, "Solubility of Inorganic and Metal Compounds," Vol. I, 3d ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 108.

[6] A. B. Garrett, O. Holmes and A. Laube, THIS JOURNAL, **62**, 2024 (1940).

[7] F. Foerster and H. Pressprich, *Z. Elektrochem. angew. physik. Chem.*, **33**, 176 (1927).

TABLE I

THE DISTRIBUTION BETWEEN AQUEOUS HYDROCHLORIC ACID AND β,β'-DICHLORODIETHYL ETHER AND THE CALCULATED CHLORIDE–ARSENIC RATIO IN THE ETHER PHASE

Column II shows initial aqueous hydrochloric acid concentration; column III the calculated equilibrium aqueous hydrochloric acid concentration; column IV the initial aqueous arsenic concentration; column V the ethereal chloride concentration; column VI the ethereal arsenic concentration; column VII shows the concentration of hydrochloric acid in the ether phase in equilibrium with the corresponding concentration of aqueous hydrochloric acid shown in column III and as determined from Fig. 1. Column VIII shows the difference between columns V and VII and represents ether phase chloride bound to arsenic. Column IX shows the ratio of chloride to arsenic in the ethereal arsenic compounds.

I	II	III	IV	V	VI	VII	VIII	IX
No. of detns.	HCl_{aq} (*VF*) Initial	Equil.	$As(III)_{aq}$ (*VF*)	ΣCl_{et} (*VF*)	$As(III)_{et}$ (*VF*)	HCl_{et} (*VF*)	Cl_{et} (*VF*)	$Cl_{et}/As(III)_{et}$
5	12.3	11.8	0.1156	0.590 ± 0.004	0.1118 ± 0.0005	0.250	0.340	3.03
5	9.16	8.90	.1149	.3313 ± .0007	.1078 ± .0002	.018	.313	2.90
2	8.45	8.20	.1152	.2952 ± .0003	.1018 ± .00005	.011	.284	2.78
2	8.02	7.76	.1151	.2695 ± .0003	.0970 ± .00001	.007	.262	2.71
2	7.00	6.76	.1151	.1798 ± .0002	.0747 ± .00008	.001	.179	2.39
2	6.57	6.39	.1155	.1396 ± .0001	.0620 ± .0001	...	.140	2.25
5	5.88	5.72	.1152	.0801 ± .0003	.03944 ± .00009	...	.080	2.03

species of tripositive arsenic present, the calculation of constants for the equilibria between these species in the aqueous solution, and the calculation of distribution constants for the phase equilibria between certain of these species.

Experimental

Reagents and Equipment.—Technical grade β,β'-dichlorodiethyl ether was distilled twice at a pressure of 20 mm. of mercury. Fractions which boiled between 79 and 80° were collected.[8] Peroxides formed rapidly if distillation was attempted at atmospheric pressure. To each liter of ether was added 1×10^{-5} mole of catechol in order to prevent the formation of peroxides.[9] Arsenic forms a compound with catechol,[10] but the amount involved is insignificant. Tests with acidified potassium iodide showed that no significant quantity of peroxide formed in the ether over a period of two months.

Arsenic stock solutions were prepared by heating 28.93-g. portions of reagent grade arsenic trioxide in 12 *VF*[11] hydrochloric acid until all of the solid dissolved. When cool, the solution was transferred to a one liter volumetric flask and diluted to mark with 12 *VF* hydrochloric acid. An oily liquid, assumed to be arsenic trichloride,[12] usually separated from the solution as it was cooling, but dissolved when the mixture was diluted. The above procedure was used in order that all stock solutions would be 0.287 *VF* in arsenic trichloride.

Standard silver nitrate and potassium iodate solutions were prepared from weighed samples of reagent grade salts. Potassium thiocyanate (0.01 *VF*) was prepared by accurately diluting a 0.1 *VF* solution which had been standardized against silver nitrate. Sodium hydroxide solutions were prepared by diluting 10-ml. portions of carbonate-free 50% sodium hydroxide stock to one liter and standardizing this against analytical grade potassium acid phthalate.

Calibrated volumetric equipment was used for all analyses.

Distribution Measurements.—Preliminary qualitative distribution experiments with neutral aqueous solutions containing tripositive arsenic and either sodium chloride or sodium perchlorate showed that no significant quantity of arsenic was extracted by the ether. Similar experiments with acid solutions showed that no significant quantity of arsenic was extracted from hydrochloric acid solutions until the acid concentration was about 4 *VF* or from perchloric acid solutions at any concentration.

A 100-ml. portion of the stock solution (0.287 *VF* in arsenic trichloride and 12.3 *VF* in hydrochloric acid) was pipetted into a 250-ml. volumetric flask and diluted with hydrochloric acid and water to give the final solution having the desired concentration of hydrochloric acid and which was 0.115 *VF* in arsenic. A 100-ml. portion of this solution and 100 ml. of ether were pipetted into a 250-ml. Squibb separatory funnel which was then sealed. Mixing was obtained by rocking the funnel slowly back and forth 100 times, then the funnel was placed in a water-bath thermostated at 25 ± 0.1°. The mixing process was repeated five times over a period of three hours after which the funnel was allowed to stand in the water-bath for not less than 72 hours. The ether phase was drawn off through the stopcock; the first 5 ml. was discarded since this portion was most likely to entrap drops of the aqueous phase. About 85 ml. of the remaining ether phase was drawn into a dry glass-stoppered weighing bottle. The bottle was immediately closed to prevent escape of hydrogen chloride. Twenty-five ml. portions of the ether phase were pipetted from the bottle into three 60-ml. separatory funnels, each of which contained 10 ml. of water. The funnels were shaken vigorously, the phases separated, and the aqueous phases retained. The ether phases were washed five more times with 10-ml. portions of water. The six washings from one of the separatory funnels were combined and this solution was then analyzed for one of the desired components, *i.e.*, tripositive arsenic, chloride or hydrogen ion. The same was done with the washings from the other two separatory funnels. The tripositive arsenic was titrated with standard potassium iodate to the iodine monochloride end-point[13]; chloride was determined with standard silver nitrate by a modified Volhard method[14]; and hydrogen ion was determined by titration with standard sodium hydroxide until a *p*H of 7 was indicated on a Beckman Model F *p*H meter. The acid was determined as a check on the chloride determination, since the hydrolysis of any arsenic chloride compound yields equal quantities of chloride and hydrogen ions. The same general procedure was used to determine the distribution of hydrochloric acid between ether and aqueous solutions of the appropriate acid concentrations. In all cases, determinations were made of the various components in the aqueous solutions before equilibration with the ether.

The initial formal concentrations of hydrochloric acid ranged from 5.9 to 12.3. Experiments with aqueous solutions of lower acid concentrations were not made because of the difficulties of accurately determining the small quantities of arsenic and chloride extracted.

Data

Table I shows the data obtained from the distribution experiments described above and the calculated ratios of chloride to tripositive arsenic found in the ether phases. Aqueous equilibrium concentrations were calculated from the initial

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[8] C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 2525 (1930).

[9] R. J. Myers, D. E. Metzler, and E. H. Swift, THIS JOURNAL, **72**, 3767 (1950).

[10] A. Rosenheim, *Z. anorg. allgem. Chem.*, **200**, 173 (1931).

[11] A *volume formal* (*VF*) solution contains one gram formula weight of the particular substance stated per liter of solution. A *volume molal* (*VM*) solution contains one mole of the molecular or ionic species stated per liter of solution.

[12] L. Vanino, "Handbuch der Präparativen Chemie," Vol. 1, F. Enke, Stuttgart, 1925, p. 227.

[13] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p. 216.

[14] E. H. Swift, G. M. Arcand, E. Lutwack and D. J. Meier, *Anal. Chem.*, **22**, 306 (1950).

concentrations using appropriate corrections for phase volume changes.[8]

Calculation of Distribution and Equilibrium Constants.—Sullivan and Hindman[15] have discussed methods for calculating dissociation constants in complex ion systems. However, their methods are based on the fundamental assumption that all activity coefficients are kept constant. Because this was not done in the system under consideration here, the method of approximation described below seems more applicable.

The experimental data have been analyzed in several different ways, with one of the following assumptions having been employed in each case.

1. The species which may be present in the aqueous phase under some or all of the conditions of the experiments are $AsCl_3$, $As(OH)Cl_2$, $As(OH)_2Cl$, $As(OH)_2^+$ and H_3AsO_3; those which may be present in the ether phase are $AsCl_3$, $As(OH)Cl_2$ and $As(OH)_2Cl$.
2. The species present in both phases are $AsCl_3$, $As(OH)Cl_2$ and $As(OH)_2Cl$.
3. The species present in the aqueous phase are $AsCl_3$, $As(OH)_2Cl$, $As(OH)_2^+$ and H_3AsO_3; those present in the ether phase are $AsCl_3$ and $As(OH)_2Cl$.
4. The species present in both phases are $AsCl_3$ and $As(OH)_2Cl$.

Experiments in this Laboratory[2] indicated no change in the arsenic distribution constant when the total quantity of arsenic was varied at constant hydrochloric acid concentration, thereby apparently eliminating the possibility of the existence of polymers in the system.

Calculations based on the first assumption yield the best results. The assumption of the existence of $AsCl_3$ is reasonable, since it has been prepared by the reaction of arsenic trioxide with concentrated hydrochloric acid[16] and appeared to be present during the preparation of the arsenic stock solutions used in these experiments. The hydroxychlorides apparently have not been definitely isolated, although Prased and co-workers[17] state that they prepared $AsOCl \cdot H_2O$, but give no details of their method.

On the basis of the first assumption, the following distribution relations should apply[18]

$$[AsCl_3]_{et}/[AsCl_3]_{aq} = D_3 \qquad (1)$$

$$[As(OH)Cl_2]_{et}/[As(OH)Cl_2]_{aq} = D_2 \qquad (2)$$

$$[As(OH)_2Cl]_{et}/[As(OH)_2Cl]_{aq} = D_1 \qquad (3)$$

It has been shown that arsenious acid is not extracted significantly by ether so that the distribution constant for arsenious acid may be considered negligibly small. Therefore, if one assumed that the tripositive arsenic enters the ether phase only as un-ionized chloride species, equations (4) and (5) would be correct

$$(As(III))_{et} = [AsCl_3]_{et} + [As(OH)Cl_2]_{et} + [As(OH)_2Cl]_{et} \qquad (4)$$

$$(\Sigma Cl^-)_{et} = 3[AsCl_3]_{et} + 2[As(OH)Cl_2]_{et} + [As(OH)_2Cl]_{et} \qquad (5)$$

where $(\Sigma Cl^-)_{et}$ and $(As(III))_{et}$ represent the formal concentrations of chloride and arsenic, respectively, in the ether phase.

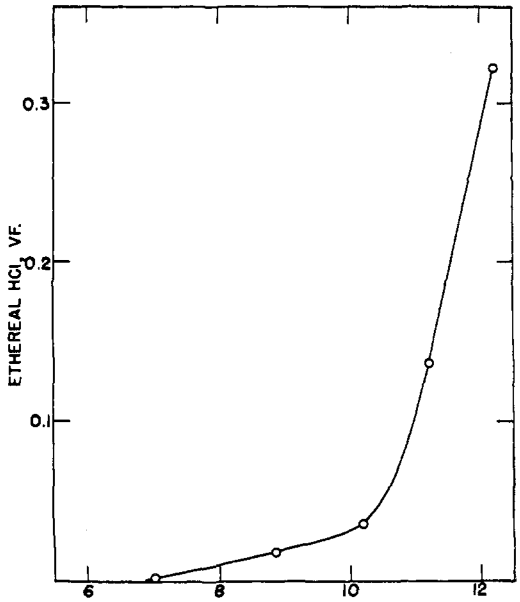

Fig. 1.—Concentration of HCl in β,β′-dichlorodiethyl ether in equilibrium with aqueous HCl.

In order to make preliminary calculations, the following assumptions were made: (1) that $AsCl_3$ is the only arsenic species present in significant quantity in the 12 *VF* aqueous hydrochloric acid phase, (2) that $AsCl_3$ and $As(OH)Cl_2$ are the predominant species in 9 *VF* hydrochloric acid, and (3) that all arsenic species (*i.e.*, $AsCl_3$, $As(OH)Cl_2$, $As(OH)_2Cl$, $As(OH)_2^+$ and H_3AsO_3) exist in significant quantities in 5.9 *VF* hydrochloric acid.

D_3 can be immediately calculated on the basis of assumption (1) since, in 12 *VF* hydrochloric acid, equation 4 reduces to

$$(As(III))_{et} = [AsCl_3]_{et} \qquad (6)$$

Combining equation 6 with equation 1 yields

$$(As(III))_{et} = D_3[AsCl_3]_{aq} \qquad (7)$$

According to assumption (2), when the aqueous hydrochloric acid concentration is 9 *VF*, equations 4 and 5 reduce to

$$(As(III))_{et} = [AsCl_3]_{et} + [As(OH)Cl_2]_{et} \qquad (8)$$

$$(\Sigma Cl^-)_{et} = 3[AsCl_3]_{et} + 2[As(OH)Cl_2]_{et} \qquad (9)$$

The reaction between $As(OH)Cl_2$ and hydrochloric acid may be represented by the equation

$$As(OH)Cl_2 + H^+Cl^- = AsCl_3 + H_2O \qquad (10)$$

so that the equilibrium expression may be written

$$[AsCl_3]_{aq}(a_{H_2O})/[As(OH)Cl_2]_{aq}(a_{\pm HCl})^2 = K_4 \qquad (11)$$

The activity of water[19] is represented by a_{H_2O} and

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[15] J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 6091 (1952).

[16] C. W. Foulk and P. G. Norton, *ibid.*, **51**, 2416 (1929).

[17] M. Prased, C. R. Kanekar and L. N. Mulay, *J. Chem. Phys.*, **19**, 1440 (1951).

[18] It seems reasonable to assume that the activity coefficients of the various uncharged chloride compounds of arsenic are approximately equal in the various aqueous solutions. Since the activities of these species appear in both numerator and denominator in all equations, the activity coefficients would tend to cancel. Therefore, concentrations are used in all expressions.

[19] M. Randall and L. E. Young, THIS JOURNAL, **50**, 989 (1928).

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF ETHEREAL ARSENIC AND CHLORIDE CONCENTRATIONS

Calculations are based on the assumption 1 above. Column II shows the calculated equilibrium concentration of hydrochloric acid in the aqueous phase; column III the aqueous tripositive arsenic concentration; columns IV and V, respectively, the observed and calculated equilibrium ethereal tripositive arsenic concentrations, and columns VII and VIII, respectively, the observed and calculated equilibrium ethereal chloride concentrations after corrections have been made for the distribution of hydrochloric acid between the two phases.

I HCl_{aq} (*VF*)	II HCl_{aq} (*VF*)	III $As(III)_i$ (*VF*)	IV $As(III)_{et\ obsd.}$ (*VF*)	V $As(III)_{et\ calcd.}$ (*VF*)	VI % Diff.	VII $Cl_{et\ obsd.}$ (*VF*)	VIII $Cl_{et\ calcd.}$ (*VF*)	IX % Diff.
12.3	11.8	0.1156	0.1118	0.1132	+1.3	0.340	0.339	−0.3
9.16	8.90	.1149	.1078	.1090	+1.1	.313	.325	+3.8
8.45	8.20	.1152	.1018	.1050	+3.1	.284	.300	+5.6
8.02	7.76	.1151	.0970	.0997	+2.8	.262	.274	+4.6
7.00	6.76	.1151	.0747	.0750	+0.4	.179	.182	+1.7
6.57	6.39	.1155	.0620	.0623	+0.5	.140	.142	+1.4
5.88	5.72	.1152	.03944	.03944	0	.080	.076	−5.0

the mean activity of H^+Cl^- as defined by Latimer[20] is represented by $(a_{\pm HCl})$. Equations 8 and 9 permit the calculation of $[AsCl_3]_{et}$ and $[As(OH)Cl_2]_{et}$. $[AsCl_3]_{aq}$ can then be calculated by using equation 1, whereupon $[As(OH)Cl_2]_{aq}$ can be found by subtracting $[AsCl_3]_{aq}$ from the total concentration of arsenic in the aqueous phase. K_4 and D_2 can then be calculated.

Equations 4 and 5 can be used directly when the aqueous phase is 5.9 *VF* in hydrochloric acid. In addition, the equations are necessary

$$As(OH)_2Cl + H^+Cl^- = As(OH)Cl_2 + H_2O \quad (12)$$

$$[As(OH)Cl_2]_{aq}(a_{H_2O})/[As(OH)_2Cl]_{aq}(a_{\pm HCl})^2 = K_3 \quad (13)$$

$$[As(OH)_2Cl]_{aq}(a_{H_2O})/[H_3AsO_3]_{aq}(a_{\pm HCl})^2 = K_2 \quad (14)$$

$$[As(OH)_2{}^+]_{aq}(a_{H_2O})/[H_3AsO_3]_{aq}(a_{\pm HCl}) = K_1 \quad (15)$$

The equilibrium constant K_1 is found by dividing Randall's[21] constant for the basic dissociation of H_3AsO_3 by the equilibrium constant for the dissociation of water.

The equilibrium constant K_2 can be calculated from the solubilities of arsenic trioxide in 1 *VF* hydrochloric acid[6] and in 1 *VF* perchloric acid[5] if the assumption is made that the difference in solubilities is due to the formation of $As(OH)_2Cl$ in the hydrochloric acid solution.

Subtracting equation 4 from equation 5 and combining the result with equation 11 yields

$$(\Sigma Cl^-)_{et} - (As(III))_{et} = (2D_3K_4(a_{\pm HCl})^2/(a_{H_2O}) + D_2)\,[As(OH)Cl_2]_{aq} \quad (16)$$

Concentrations of $AsCl_3$ and $As(OH)Cl_2$ in both phases can now be calculated.

By means of equations 14 and 15, $[As(OH)_2{}^+]_{aq}$ and $[As(OH)_2Cl]_{aq}$ can be expressed in terms of $[H_3AsO_3]_{aq}$. Thus the equation can be written

$$(As(III))_{aq} - ([AsCl_3]_{aq} + [As(OH)Cl_2]_{aq}) = \left(\frac{K_1(a_{\pm HCl})}{(a_{H_2O})} + \frac{K_2(a_{\pm HCl})^2}{(a_{H_2O})} + 1\right)[H_3AsO_3]_{aq} \quad (17)$$

Calculation of $[H_3AsO_3]_{aq}$ permits the calculation of $[As(OH)_2{}^+]_{aq}$ and $[As(OH)_2Cl]_{aq}$. Similarly, since the concentrations of $AsCl_3$ and $As(OH)Cl_2$ in the ether phase have been calculated, the remaining $As(OH)_2Cl$ may be found. With this information, D_1 and K_3 may be calculated.

Once approximate values for the constants have been found, equations 4 and 5 can be used to refine the calculations. Successive approximations yield the values for the constants

$D_1 = 0.175$ $K_1 = 0.5$
$D_2 = 2.94$ $K_2 = 0.085$
$D_3 = 55$ $K_3 = 3.4 \times 10^{-4}$
$K_4 = 6.25 \times 10^{-5}$

The constants, K_1 and K_2, were not affected by the approximations described above.

Significant concentrations of $As(OH)_2{}^+$, H_3AsO_3 and $HAsCl_4$ in the aqueous solution would change the value of D_3 by decreasing the apparent concentration of $AsCl_3$ in the aqueous phase. However, calculations show that the concentrations of $As(OH)_2{}^+$ and H_3AsO_3 are negligible in 12 *VF* hydrochloric acid. That no significant quantity of $HAsCl_4$ is formed in these solutions is suggested by two facts: the Cl/As ratio changes from 2.90 to 3.03 as the hydrochloric acid concentrations change from 9.2 to 12 *VF* and the percentage of arsenic extracted rises to about 97 when the hydrochloric acid concentration is about 10 *VF* and remains essentially constant up to 12 *VF* hydrochloric acid.

Nelson and Kraus[22] report that As(III) is adsorbed by an anion-exchange resin, indicating that $AsCl_4^-$ is probably formed at high hydrochloric acid concentrations. However, it may be that the resin adsorbs $AsCl_4^-$ strongly enough to cause a considerable shift in the equilibrium concentrations of the various species.

Formulas can be derived which express the concentrations of tripositive arsenic and chloride in the ether phase in terms of the initial concentrations of arsenic and chloride, respectively, in the aqueous phase. Values of ethereal arsenic and chloride calculated with these formulas are compared with experimental values in Table II.

Calculations based on the second assumption (*i.e.*, the species present in both phases are $AsCl_3$, $As(OH)Cl_2$ and $As(OH)_2Cl$) give values agreeing quite well with experimental values. Reasons for discarding this assumption will be shown subsequently. Calculations based on the third and fourth assumptions are less satisfactory.

Correlation with Other Data

Since calculations based on the first two assumptions given above fit the distribution data

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(20) W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1952, p. 342.

(21) M. Randall, "International Critical Tables," Vol. VII, McGraw-Hill Book Co., New York, N. Y., p. 242.

(22) F. Nelson and K. A. Kraus, THIS JOURNAL, **77**, 4508 (1955).

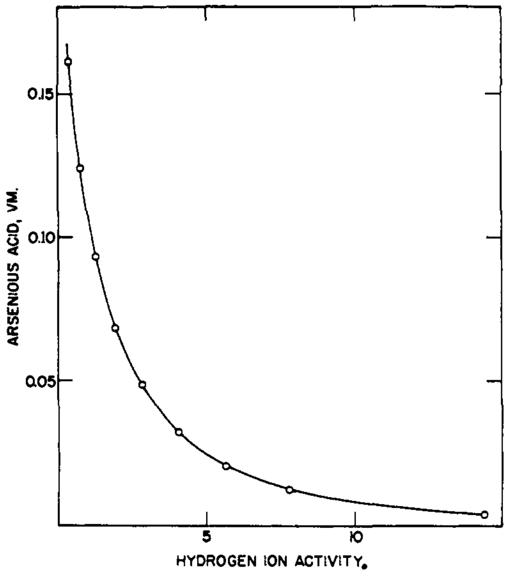

Fig. 2.—Calculated molal concentration of H_3AsO_3 in aqueous $HClO_4$.

equally well, it is desirable to find some other way to decide which of the two interpretations is the more reasonable.

Conductivity and Solubility Measurements.—One should infer from the second assumption that there is little basic dissociation of arsenious acid. Thus, the total concentration of arsenic in a perchloric acid solution saturated with arsenic trioxide should equal the concentration of arsenious acid in that solution. Since, in solutions up to 4 *VF* in acid, the activity of water is the same in hydrochloric acid[17] and perchloric acid[23] solutions of the same hydrogen ion activity, the arsenious acid concentration should be the same in hydrochloric acid and perchloric acid solutions which are saturated with arsenic trioxide. Under this assumption, the effect of dissolved arsenic trioxide on the conductivity of dilute hydrochloric acid solutions which was noted by Washburn and Strachan[4] must be caused by the formation of an un-ionized arsenic hydroxychloride rather than by the basic dissociation of arsenious acid. The decrease in conductivity would then be caused by a decrease in hydrochloric acid concentration. The equilibrium constant K_2 calculated on this basis was found to have a value of 5.6.

Knowledge of K_2, K_3 and K_4 should permit the calculation of the solubility of arsenic trioxide in hydrochloric acid. A plot of such a calculated solubility *versus* hydrochloric acid concentrations is shown in Fig. 3 (line 1). It is evident that this value for K_2 is unsatisfactory, because, at low concentrations of acid, it would control the solubility.

An attempt was made to calculate K_2 by using only the available solubility data. It was assumed that when the hydrochloric acid concentration is 0.5 *VF*, the only arsenic chloride species present in significant quantity is $As(OH)_2Cl$. This value for K_2, equal to 0.07, was used to calculate the solubility of arsenic trioxide in higher concentrations of hydrochloric acid. The results are shown in Fig. 3 (line 2) and are seen to be unsatisfactory.

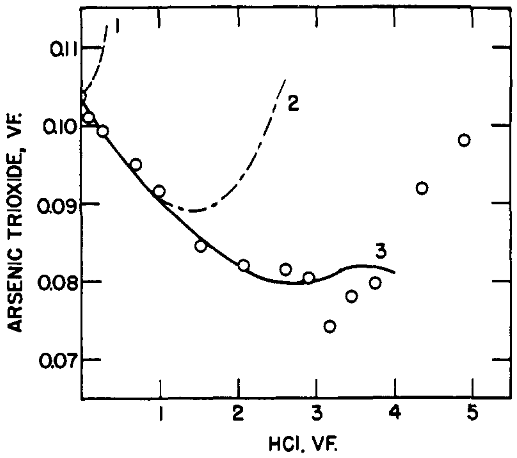

Fig. 3.—Formal solubility of As_2O_3 in aqueous HCl: O, literature solubility; 1, calculated solubility assuming presence of arsenic hydroxychlorides, but no significant amount of $As(OH)_2^+$. $K_2 = 5.6$ is calculated from conductivity data.[3] 2, solubility calculated using same assumptions as for line 1 except that $K_2 = 0.07$ is calculated from solubility data in 0.5 *VF* HCl and $HClO_4$ solutions. 3, calculated solubility assuming presence of arsenic hydroxychlorides and $As(OH)_2^+$. $K_2 = 0.085$ is calculated from solubility and conductivity data.

If one accepts the constant calculated by Randall[21] as correct, one must assume that the concentration of arsenic in a perchloric acid solution saturated with arsenic trioxide is the sum of the concentrations of H_3AsO_3 and $As(OH)_2^+$. The calculated concentrations of H_3AsO_3 for various perchloric acid concentrations from 0.5 to 5 *VF* are plotted against hydrogen ion activities in Fig. 2.

The difference between solubilities of arsenic trioxide in 1 *VF* perchloric acid and 1 *VF* hydrochloric acid was assumed to equal the concentration of $As(OH)_2Cl$ in the hydrochloric acid solution. The calculated solubilities of arsenic trioxide in hydrochloric acid are shown in Fig. 3 (line 3) where they are plotted against the formal concentration of hydrochloric acid. These values agree much more closely with the experimental values of Garrett and co-workers.[6] However, beyond 4 *VF* hydrochloric acid, the calculated solubility of arsenic trioxide drops considerably below the experimental values.

The activity of $As(OH)_2^+$ was not considered in any of the calculations made here. There is no reason to expect that the activity coefficient for this charged ion would remain constant and equal to unity throughout the range of acid activities considered. However, no data are available concerning the activity of this species.

Electromotive Force Measurements.—Foerster and Pressprich[7] found that the measured potentials for the As(III)–As(V) half-cell in hydrochloric acid were quite different from the calculated values. They used equation (18) for the half-cell reaction

$$H_3AsO_3 + H_2O = H_3AsO_4 + 2H^+ + 2e^- \quad (18)$$

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[23] Landolt-Bornstein, "Physikalisch-chemische Tabellen," Erg. B. III, 1936, p. 2144.

According to the Nernst equation

$$E = E^0 - (RT/nF)\{\ln([H_3AsO_4]/[H_3AsO_3]) - \ln[(a_{H^+})^2/(a_{H_2O})]\} \quad (19)$$

Foerster and Pressprich assumed that the only effect to be considered in the calculation of the potentials was the variation in hydrogen ion activity, since the ratio of $[H_3AsO_4]$ to $[H_3AsO_3]$ was kept equal to unity. However, the present work has shown that the concentrations of arsenious acid and therefore the potentials at various hydrochloric acid concentrations can be calculated only by applying the equilibrium constants found above. The results of such a series of calculations are shown in Table III and are compared with the experimental values found by Foerster and Pressprich. The half-cell value of −0.559 v. given by Latimer[24] was used.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED POTENTIALS

The observed half-cell potentials are those measured by Foerster and Pressprich.[7] The calculated potentials are based on the assumption 1, above.

HCl (*VF*)	E_{obsd}, v.	E_{calcd}, v.
1	−0.580	−0.559
2	− .601	− .597
4	− .641	− .643
6	− .703	− .696
8	− .808	− .756

It is seen that the calculated and observed values agree reasonably well except in 1 and 8 *VF* solutions. Since the reaction between arsenic acid and iodide in 1 *VF* hydrochloric acid is slow, the potential of that system may have been measured before equilibrium was attained, thus giving the high result. The concentration of arsenious acid in 8 *VF* hydrochloric acid is very low; a small error in its value could cause a large error in the value of the calculated potential. Such an error is quite possible in view of the uncertainty in the calculated constants and may well account for the discrepancy between the calculated and measured potentials in 8 *VF* hydrochloric acid.

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[24] W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1952, p. 115.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, AND THE DEPARTMENT OF ELECTRONICS, UNIVERSITY OF SOUTHAMPTON]

One-Equivalent Intermediates in Phthalocyanine and Porphin Oxidations Investigated by Paramagnetic Resonance

BY PHILIP GEORGE,[1a] D. J. E. INGRAM[1b] AND J. E. BENNETT[1b]

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The paramagnetic resonance absorption technique has been used to show that the two-equivalent oxidation of both metal-free phthalocyanine and $\alpha,\beta,\gamma,\delta$-tetraphenylporphin proceed *via* a one-equivalent oxidation intermediate, with properties very similar to those of the more stable intermediates formed from the Cu^{II}, Co^{II} and Al^{III} phthalocyanines. All the intermediates are paramagnetic and have a *g*-value extremely close to the free-spin value, but the line width varies from one intermediate to another. The data are in accord with a postulated structure, common to all the intermediates, in which the macrocyclic ring remains intact and the unpaired electron is situated in a π-orbital.

Introduction

Dent, Linstead and Lowe[2] first investigated the oxidation of metal phthalocyanine complexes by ceric sulfate, using suspensions in dilute sulfuric acid, and showed a two-equivalent reaction to occur giving colorless products according to equation 1.

$$(C_8H_4N_2)_4Cu + 8H_2O + 4H^+ \longrightarrow Cu^{2+} + 4C_8H_5O_2N + 4NH_4^+ + 2e^- \quad (1)$$

A reddish-purple intermediate was observed when *two equivalents* of Ce^{IV} reacted at 0° with suspensions of the metal-free phthalocyanine, metal-free tetrabenztriazaporphin and its copper complex, followed in the two latter cases by a slower further oxidation corresponding to the uptake of five oxygen atoms.[3,4] However, using the water-soluble tetrasulfonated metal phthalocyanine complexes, Cahill and Taube[5] identified the reddish-purple intermediate as a *one-equivalent* oxidation product by spectrophotometric titration with 0.5, 1.0 and 2.0 moles Ce^{IV} per mole of phthalocyanine. In the previous experiments[3,4] an excess of Ce^{IV} was always used, and the discrepancy between the two sets of results may be connected with inhomogeneous oxidation occurring in the suspensions. An identical intermediate was obtained with the Cu^{II}, Co^{II}, Zn^{II}, Al^{III} and Fe^{III} complexes, the particular metal only affecting its rate of production and its rate of disproportionation and further oxidation, as represented by equations 2, 3 and 4,

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[1] (a) John Harrison Laboratory of Chemistry, University of Pennsylvania; (b) Department of Electronics, University of Southampton, England.

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