The Hydrolysis of Tin(IV) in Sulfuric Acid

BY C. H. BRUBAKER, JR.

The hydrolysis of tin(IV) in dilute sulfuric acid solutions was studied by the technique of diluting stable acid solutions until solid, hydrous stannic oxide formed in equilibrium with the solution. When reasonable estimates of activity coefficients are taken into account the data demand that the species present in the solutions be sulfato tin(IV) sulfate, $(SnSO_4)(SO_4)$, in contrast to the Sn^{+4} ion which is indicated on the basis of concentration equilibrium considerations. The data indicate that the following takes place: $SnO_2(aq.) + 2H_2SO_4 \rightleftarrows (SnSO_4)^{++} + (SO_4)^{-} + 2H_2O$. Taking into account the best estimates of the mean activity coefficients which are available, we find, at $30°$, $K = 5 \times 10^{-2}$ and, at $18°$, $K = 2.8 \times 10^{-2}$.

In previous work[1] the complexing of tin(IV) by sulfuric acid has been examined, but final conclusions concerning the exact species present in the solutions were not possible because of a lack of information concerning the nature of the species of tin(IV) which might be present in dilute sulfuric acid solutions. Therefore this present study was undertaken in an effort to determine the nature of tin(IV) ions in dilute sulfuric acid solutions.

It appeared that it might be possible to determine the nature of the tin(IV) species present by the technique diluting stable acid solutions of tin(IV) until solid, hydrous tin(IV) oxide began to appear, allowing the suspended oxide and the solution to come to equilibrium and then analyzing the supernate for tin and acid, in order to determine the sulfuric acid dependence of the hydrolysis.

Experimental

Stock solutions of chloride free tin(IV) in perchloric and sulfuric acids were prepared as in the previous work.[1]

In order to carry out the hydrolysis, various amounts of the tin stock solution (2.059×10^{-2} M Sn in 1.921 M H_2SO_4) were placed in glass stoppered cylinders and sufficient distilled water was added to make a total volume of 50 ml. The cylinders were agitated in a constant temperature bath (at $30.0 \pm 0.2°$ and $18.0 \pm 0.2°$) until equilibrium was reached (overnight), as determined by repeated analyses. The samples were then decanted quickly through fine (No. 42) filter paper. Aliquots of the clear filtrate were taken (at $25°$) and were analyzed for tin and hydrogen ion.

It was found that the precipitates ($SnO_2 \cdot xH_2O$) prepared from solutions containing appreciable amounts of perchloric acid tended to be colloidal and the phases could not be separated completely. For this reason the hydrolysis was studied only in sulfuric acid solutions.

Similarly at $0°$ the precipitates from sulfuric acid solutions could not be completely removed from the solutions and hence analyses were carried out only on solutions which were prepared at 30 and at 18°.

All chemical analyses were performed at $25°$, in terms of volume formality. For equilibrium calculations, volume formalities were converted to weight formalities. Densities were obtained from the International Critical Tables[2] for sulfuric acid solutions and the error introduced by neglecting the effect of tin in the solutions was found small ($<1\%$) by actual density measurements in the case of the three most concentrated tin solutions.

Tin(IV) was determined spectrophotometrically at 230, 240 and 250 mμ. The sulfuric acid content of the aliquots for spectrophotometric analysis was adjusted to 1.000 and 1.000 M sulfuric acid was used as a blank.

Acidity was determined by titrating the solution against aliquots of freshly prepared sodium carbonate solution. In these determinations the further hydrolysis of tin was neglected, because sulfuric acid concentrations were of the order of 0.2–1.0 M, while tin concentrations were in the 10^{-4} M range.

Discussion

The experimental results are listed in columns 1 and 2 of Table I and the data for 30° are also represented graphically in Fig. 1. All concentrations shown are in terms of weight formalities.
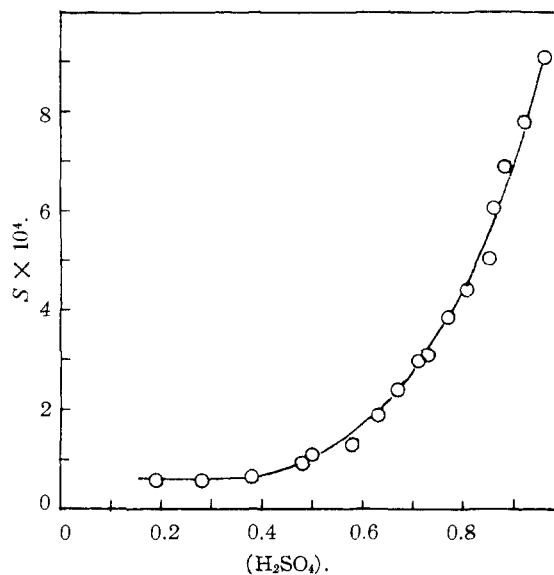

Fig. 1.

We observe that at the lowest hydrogen ion concentrations, the tin concentration does not fall to zero, but rather appears to approach a small but finite and measurable value. This suggests that this value represents the solubility of hydrous stannic oxide in water and so to find the concentration of tin(IV) ions we must subtract this limiting value (S_0) from the total tin concentration (S). The values ($S - S_0$) are tabulated in column 3, Table I.

The quantity ($S - S_0$) changes very markedly with sulfuric acid concentration and suggests, at first, a fourth-order dependence on sulfuric acid concentration. In fact, if we plot ($S - S_0$) against the fourth power of the sulfuric acid concentration, we obtain a rather good straight line. However, it seems highly improbable that there are actually hydrated stannic ions (Sn^{+4}) in such dilute acid.

Since considerable information is available on the activities of sulfuric acid solutions,[3] it should be possible to make some reasonable estimates of the

(1) C. H. Brubaker, Jr., THIS JOURNAL, 76, 4269 (1954).

(2) "International Critical Tables," 1st Ed., Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 56.

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Ch. 13, Reinhold Publ. Corp., New York, N. Y. 1949.

TABLE I

The Solubilities of Tin(IV) Oxide in Sulfuric Acid Solutions of Various Concentrations and Ionic Strengths, Mean Activity Coefficients of a 2-2 Electrolyte and of Sulfuric Acid and the Activity of Water in Sulfuric Acid Solutions

1 (H₂SO₄)	2 $S \times 10^4$	3 $(S - S_0) \times 10^4$	4 (SO₄⁻)	5 μ	6 $\gamma_\pm$	7 γ_{22}	8 γ_{22} (cor.)	9 a_{H_2O}
At 30°								
0.9605	9.08	8.50	0.201	1.483	0.124	0.074	0.103	0.958
.9221	7.77	7.19	.250	1.422	.126	.076	.106	.959
.8837	6.92	6.34	.240	1.364	.127	.077	.107	.960
.8645	6.03	5.45	.234	1.333	.128	.078	.108	.962
.8452	5.05	4.67	.229	1.303	.128	.079	.108	.963
.8068	4.40	3.82	.218	1.243	.130	.081	.110	.965
.7684	3.85	3.27	.207	1.182	.132	.083	.112	.966
.7298	3.10	2.52	.196	1.122	.134	.085	.114	.968
.7146	2.95	2.37	.192	1.099	.134	.086	.115	.969
.6723	2.39	1.81	.180	1.032	.137	.089	.118	.970
.6339	1.88	1.30	.170	0.974	.139	.092	.120	.972
.5763	1.30	0.720	.154	.884	.142	.098	.125	.968
.4995	1.09	.510	.133	.766	.147	.107	.131	.978
.4803	0.938	.358	.127	.734	.149	.100	.133	.979
.3842	.648	.068	.100	.584	.159	.126	.146	.983
.2882	.580	...	...	...	...	...	...	...
.1921	.580	...	...	...	...	...	...	...
At 18°								
0.9605	7.72	7.41	0.324	1.609	0.140	0.069	0.107	0.960
.8837	5.73	5.42	.301	1.486	.144	.073	.113	.967
.8645	4.58	4.27	.297	1.459	.144	.075	.114	.968
.8452	4.44	4.13	.388	1.421	.146	.076	.116	.969
.7684	2.88	2.57	.260	1.288	.150	.079	.120	.971
.7298	2.50	2.19	.247	1.224	.152	.082	.122	.973
.6723	1.83	1.52	.226	1.124	.156	.085	.126	.975
.5763	0.970	0.658	.192	0.960	.161	.093	.133	.979
.4995	.915	.603	.164	.828	.167	.101	.139	.982
.4803	.714	.402	.158	.796	.168	.104	.141	.983
.3842	.312	...	...	...	...	...	...	...
.2882	.312	...	...	...	...	...	...	...

activity coefficients of the species involved and thus obtain valid equilibrium constants.

When we attempt to employ activity coefficients, we soon learn that the situation is not that suggested by the graph of concentration of tin(IV) *versus* sulfuric acid concentration, but rather should be represented as

$$SnO_2(aq.) + 2H_2SO_4 = (SnSO_4)^{+2} + (SO_4)^{-2} + 2H_2O \tag{1}$$
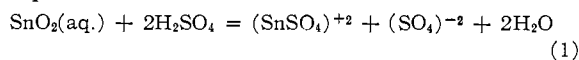
Before this conclusion was reached, a number of possible situations were examined. These included the formation of the various monomeric, partially hydrolyzed species, $Sn(OH)_3^+$, $Sn(OH)_2^{+2}$, $Sn(OH)^{+3}$ and the Sn^{+4} ion. In addition, the possibility that various partially hydrolyzed dimers, of the type

$$\begin{array}{cc} OH & + \\ | & \\ HO-Sn-O-Sn-OH \\ | & | \\ OH & OH \end{array}$$
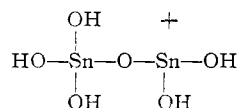
might be formed, was also considered. It is clear that none of these partially hydrolyzed species could account for the experimentally observed solubility of hydrous stannic oxide in sulfuric acid solutions, when activity coefficients are used.

But when the data are treated in accordance with the formation of the sulfato tin(IV) ion, $(SnSO_4)^{+2}$,

satisfactory agreement with the experiments is obtained.

If the situation can be represented by equation 1, then the following equilibrium constant expression is found

$$K = \frac{a_{(SnSO_4)(SO_4)} a^2_{H_2O}}{a^2_{H_2SO_4}} = \frac{(SnSO_4^{+2})(SO_4^-) \gamma^2_{22} a^2_{H_2O}}{16(H_2SO_4)^6 \gamma^6_\pm} \tag{2}$$

where γ_{22} is the mean activity coefficient of $(SnSO_4)(SO_4)$ and $\gamma_\pm$ is that of H_2SO_4. The aqueous SnO_2 is in equilibrium with solid hydrous stannic oxide, hence its activity is unity. In order to test the validity of equation 1, we must know not only the concentrations of the sulfato tin(IV) ion and sulfuric acid and the activity coefficients of these species, but we must also know the sulfate ion concentration and must correct the various activity coefficients for the presence of the other electrolytes in the solution.

To determine the sulfate ion concentration of any solution, knowing only the sulfate–bisulfate equilibrium constant and the concentration of sulfuric acid, we must know either the activity coefficients of the several species involved or at least their ratio, γ_R, defined by

$$K_{HSO_4} = \frac{(H^+)(SO_4^-)}{(HSO_4^-)} \times \frac{\gamma_{H^+}\gamma_{SO_4^-}}{\gamma_{HSO_4^-}} = \frac{(H^+)(SO_4^-)}{(HSO_4^-)} \times \gamma_R \tag{3}$$

Young and Blatz[4] and Smith[5] have calculated γ_R as a function of ionic strength at 25°. Now if we assume that γ_R does not change appreciably with temperature from 25 to 30° and 18° (the temperatures at which these experiments were carried out), we can determine appropriate concentration ratios at each sulfuric acid concentration and temperature by making use of the experimentally determined K_{HSO_4} of Young, Klotz and Singleterry.[3] Thus we calculate the sulfate ion concentrations (column 4, Table I) and the ionic strength, μ (column 5, Table I), of the sulfuric acid.

In column 6, Table I, are recorded the mean activity coefficients for pure sulfuric acid solutions of appropriate concentrations. These values were obtained from Harned and Owen.[3]

Since the experiments were carried out in moderately concentrated solutions, it appears that we might better obtain the mean activity coefficients for the sulfato tin(IV) sulfate, $(SnSO_4)(SO_4)$, from experimentally measured activity coefficients of some other 2-2 electrolyte, rather than attempt to calculate them.

We notice[3] that for a large number of divalent metal sulfates the mean activity coefficients show very little individuality and so we select the activity coefficients of zinc sulfate, of the corresponding ionic strength, to serve as the estimates of the activity coefficients of "pure" sulfato tin(IV) sulfate solutions, column 7, Table I.

Since we are treating solutions of mixed electrolytes, $(SnSO_4)(SO_4)$ and sulfuric acid, we must attempt to estimate the effects of the ions of the second electrolyte upon the activity coefficients of the first and conversely. In the case of solutions containing mixtures of strong electrolytes, we know that the following relationships exist between the activity coefficients of the individual electrolytes and those in the mixture[6]

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \qquad (4)$$

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \qquad (5)$$

Here γ_1 and γ_2 refer to the activity coefficients of the species 1 and 2 in the mixture, $\gamma_{1(0)}$ and $\gamma_{2(0)}$ to the activity coefficients of the two electrolytes alone, μ_1 and μ_2 are the ionic strengths of the species 1 and 2 and α_{12} and α_{21} are empirical constants. Further it is known that the equation

$$\log \frac{\gamma_{1(0)}}{\gamma_{2(0)}} = \mu(\alpha_{12} - \alpha_{21}) \qquad (6)$$

is obeyed for a large number of cases. Therefore, from our knowledge of the activity coefficients of sulfuric acid and our estimates of those for sulfato tin(IV) sulfate, we can determine the difference $(\alpha_{12} - \alpha_{21})$.

Since information is not available concerning the activity coefficients of any 2-2 electrolytes in sulfuric acid, we must estimate, in some way, values of the constants, α_{12} and α_{21}, which will have the difference required by equation 6 above.

Considerable information about the activity coefficients of 1-1 chlorides in hydrochloric acid is recorded[6] and appears to offer the only means we

(4) T. F. Young and L. A. Blatz, Chem. Revs., 44, 98 (1949).
(5) H. M. Smith, Ph.D. Thesis, University of Chicago, 1949.
(6) Reference 3, Ch. 14.

have for estimating the values of the constants α_{22} and $\alpha_\pm$ (where α_{22} refers to $(SnSO_4)(SO_4)$ and $\alpha_\pm$ to H_2SO_4). Let us then assume that the ratios α_{12}/α_{21} for sodium chloride in hydrochloric acid will be the same as those for the sulfato tin(IV) sulfate in sulfuric acid at the same ionic strengths. We can then determine the values of the constants from these ratios and equation 6.

In Table II are listed the values of α_{22} at 30 and at 18° which were employed. Due to the small dimensions of $\alpha_\pm$ (0.05 to 0.09) and the low ionic strengths of the sulfato tin(IV) sulfate, the correction term for the activity coefficients of the sulfuric acid is negligible, but a considerable correction will occur in the case of γ_{22}. The corrected values for γ_{22} are recorded in column 8, Table I.

TABLE II

VALUES OF THE CONSTANT α_{22} FOR SOLUTIONS OF SULFATO TIN(IV) SULFATE IN SULFURIC ACID SOLUTIONS OF VARIOUS CONCENTRATIONS

(H$_2$SO$_4$)	30° −α_{22}	18° −α_{22}	(H$_2$SO$_4$)	30° −α_{22}	18° −α_{22}
0.9605	0.098	0.118	0.7146	0.113	...
.9221	.101	...	.6723	.118	0.153
.8837	.104	.127	.6339	.119	...
.8645	.105	.126	.5763	.119	.160
.8452	.105	.129	.4995	.115	.160
.8068	.108	...	.4803	.114	.169
.7684	.111	.140	.3842	.109	.167
.7298	.115	.141			

In column 9, Table I, are listed the activities of water in sulfuric acid solutions of the appropriate concentrations.[3]

Now we are in a position to demonstrate the applicability of equation 1. If we examine equation 2, we see that a graph of

$$F = (SnSO_4)(SO_4)\gamma^2_{22}a^2_{H_2O} = (S - S_0)(SO_4)\gamma^2_{22}a^2_{H_2O}$$

plotted against

$$\frac{1}{16}a^2_{H_2SO_4} = (H_2SO_4)^6\gamma^6_\pm$$

will yield a straight line, if our analysis of the situation is indeed correct. In Fig. 2 the data from the experiments at 30° are so plotted and give an excellent straight line. From the slope of this line,
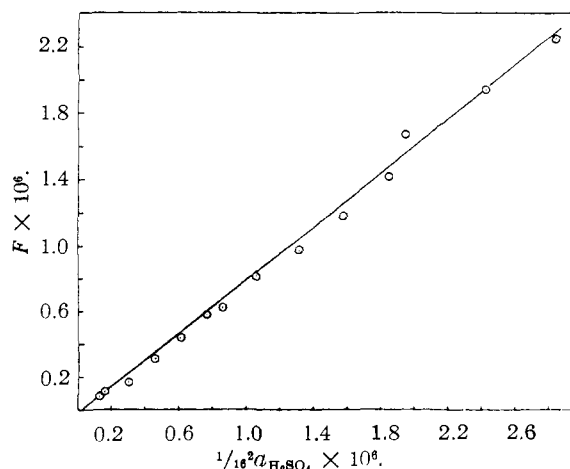

Fig. 2.

we determine the equilibrium constant to be 5.0×10^{-2}. A similar graph of the data obtained at 18° (graph not shown) gives a value of 2.8×10^{-2} for the equilibrium constant. Only two significant figures are retained because of the number of significant figures in γ_{22} and uncertainties involved in making the corrections of γ_{22}.

Conclusions

It appears then that when hydrous stannic oxide is dissolved in dilute sulfuric acid a partially complexed species, $(SnSO_4)^{++}$, is formed and that further complexing occurs only at considerably higher sulfuric acid concentrations.[1]

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Exchange of Radiocyanide Ion with Tungsten Octacyanide Complexes[1]

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Essentially no exchange of radiocyanide with $W(CN)_8^{-3}$ and $W(CN)_8^{-4}$ ions in aqueous solution of natural pH occurs in the dark at 25° even after 100 days. At 25° the corresponding respective unimolecular specific rates are $k_1 < 5.9 \times 10^{-8}$ and $k_1 < 5.3 \times 10^{-8}$ sec.$^{-1}$, and the respective bimolecular specific rates are $k_2 < 3.5 \times 10^{-7}$ and $k_2 < 3.1 \times 10^{-7}$ liter mole^{-1} sec.$^{-1}$. The rate law is not known. These exchanges are strongly light-accelerated and the rates under the illumination conditions used are approximately independent of the concentration of free cyanide ion or complex ion. These slow exchanges are consistent with Taube's postulate regarding "inert inner orbital" complexes. The effect of light on the pH of aqueous solutions of these two complex ions was investigated.

Some qualitative rate investigations and several detailed kinetic studies have been made of the isotopic exchange between free cyanide ion and metal cyanide complex ions in aqueous solutions. Previous work in this field has been reviewed by MacDiarmid and Hall[2] in their recent paper on complex cyanide–simple cyanide exchange systems.

In this paper we report our investigation of the rate of exchange of radiocyanide ion with octacyanotungstate(IV) ion and octacyanotungstate(V) ion in aqueous solution, undertaken in order to provide further information on the substitution process in octacoördinated complex ions and to give additional insight into the charge-transfer exchange of radiotungsten between these two tungsten octacyanide complex ions which we report in the succeeding paper.[3] Apparently only one octacoördinated complex, $Mo(CN)_8^{-4}$, has been investigated previously for exchange lability.[4]

Experimental

Radiocyanide Tracer.—A stock tracer solution $0.04\,f$ in NaCN labeled with C^{14} and $0.04\,f$ in NaOH was synthesized by the method of MacDiarmid and Hall[5] from C^{14}-labeled barium carbonate obtained from the Oak Ridge National Laboratory. Labeled potassium cyanide was prepared by addition of aliquots of this tracer solution to portions of reagent grade potassium cyanide solution.

Potassium Octacyanotungstate(IV) 2-Hydrate.—This compound was made from potassium enneachloroditungstate(III), $K_3W_2Cl_9$, as follows by a modification of the methods of Collenberg (*alias* Olsson).[6–8] Twenty grams

of C.P. disodium tungstate(VI) 2-hydrate and 2.2 g. of sodium carbonate were dissolved in 27 ml. of warm distilled water, heated to 65° and added at a rate of *ca.* 10 ml. per min. with swirling to 450 ml. of C.P. concd. hydrochloric acid which had been saturated with hydrogen chloride gas and heated to 65°. Resaturation of the resulting mixture with hydrogen chloride dissolved the small amount of yellow tungsten(VI) acid which had precipitated, leaving a white precipitate of sodium chloride which was filtered out. The filtrate was reduced electrolytically at a mercury cathode in a cell equipped with a graphite anode immersed in a porous cup filled with hydrochloric acid. Electrolysis with a cathode current density of 0.06 amp./sq. cm. was continued until the originally colorless solution became blue, then deep purple, after which the cathode current density was increased to 0.08 amp./sq. cm. and the temperature to 42°. At intervals 1-ml. aliquots of the catholyte were removed and titrated for W(III) with standardized potassium permanganate, electrolysis being stopped when the titer became constant. The stoichiometric amount of reagent grade potassium chloride was added to the catholyte to precipitate potassium enneachloroditungstate(III). The mixture was cooled to $-10°$ and saturated with hydrogen chloride. After 4 hours at $-10°$ the mixture was filtered and the crystals washed with ethanol and then with diethyl ether and finally sucked dry on the filter. A 48% yield of raw product, shown by permanganate titration to have a purity of 92% or less, was obtained. Other preparations were made in essentially the same way.

The crude product was converted to potassium octacyanotungstate(IV) 2-hydrate as follows. Fifty grams of the impure product was dissolved in 380 ml. of distilled water, and 158 g. of C.P. potassium cyanide was added slowly to the solution with vigorous agitation. The solution was evaporated on a steam-bath to *ca.* 80% of the original volume, a stream of nitrogen being used to facilitate evaporation and prevent air-oxidation of the enneachloroditungstate(III) ion. The precipitate which formed, mainly potassium chloride, was removed by centrifugation, and an equal volume of ethanol added to the supernatant solution, which was cooled to $-20°$ and kept there for 2 hours. The impure potassium octacyanotungstate(IV) 2-hydrate precipitate was filtered off, dissolved in distilled water, boiled for several minutes with decolorizing charcoal (Nuchar), filtered hot, and the filtrate retreated similarly with Nuchar until a clear orange-yellow color was obtained. Ethanol was added to form a saturated solution at 90°, then the flask was wrapped in a towel to allow crystallization to proceed slowly. Ultimately the mixture was cooled to $-10°$ and the crystals filtered off. This recrystallization was repeated twice, the final crop of crystals being washed with ethanol,

(1) This work was partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California.

(2) A. G. MacDiarmid and N. F. Hall, THIS JOURNAL, **76**, 4222 (1954).

(3) E. L. Goodenow and C. S. Garner, *ibid.*, **77**, 5272 (1955).

(4) A. W. Adamson, J. P. Welker and M. Volpe, *ibid.*, **72**, 4030 (1950).

(5) A. G. MacDiarmid and N. F. Hall, *ibid.*, **75**, 4850 (1953).

(6) O. Olsson, *Z. anorg. Chem.*, **88**, 49 (1914).

(7) O. Collenberg and A. Guthe, *Z. anorg. allgem. Chem.*, **134**, 317 (1924).

(8) O. Collenberg and J. Backer, *Z. Elektrochem.*, **30**, 230 (1924).