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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

An Examination of Tin(IV) Solutions in Sulfuric Acid¹

BY C. H. BRUBAKER, JR.

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Although tin(IV) is relatively insoluble in sulfuric acid solutions, spectrophotometric and electromigration studies in dilute solutions (*ca.* 10^{-3} *f* Sn(IV)) have been carried out. Examination of the apparent extinction coefficients, at 240 $m\mu$, as a function of sulfuric acid concentration and a similar examination in perchloric acid (which is assumed to be non-complexing) indicate that the following reactions take place: (1) $\text{Sn}^{+4} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Sn}(\text{SO}_4)_2$, K_1 ; (2) $\text{Sn}(\text{SO}_4)_2 + \text{H}_2\text{SO}_4 = \text{H}_2\text{Sn}(\text{SO}_4)_3$, K_2 . K for the reaction (1) was found to be 0.14 liters²/moles² and K_2 was found to be small. Electromigration studies were in agreement with the above reactions. At 1.5 *f* sulfuric acid the tin migrated to the cathode but at concentrations higher than 6 *f* H_2SO_4 it moves very slowly to the anode. Thus it appears that in 1 *f* to nearly 3 *f* sulfuric acid the tin(IV) ion is the predominant species. At higher sulfuric acid concentrations the tin (IV) sulfate is important. The trisulfato complex is present in substantial amounts only in very concentrated sulfuric acid.

In the course of an examination of the oxidation of tin(II) and reduction of tin(IV) in sulfuric acid it became necessary to obtain some information concerning the species of tin(IV) which might be present in this medium.

Ditte² has shown that stannic sulfate dihydrate ($\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$) can be prepared from approximately $1/4$ sulfuric acid solution and Weinland and Kuhl³ have prepared a series of $\text{M}_2\text{Sn}(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ from concentrated sulfuric acid solutions of tin(IV).

Domange⁴ found that chromous sulfate readily reduced tin(IV) in chloride solution, but not in sulfate, which might indicate the tin(IV) in sulfuric acid was cationic and the reaction was hampered by unfavorable coulombic effects (repulsion between Cr^{++} and the tin(IV) cation).

Spectrophotometric studies were undertaken, coupled with electromigration experiments, to determine whether further information concerning the nature of tin(IV) in sulfuric acid could be obtained.

Experimental.—Stannic hydroxide was prepared from an aqueous stannic chloride solution by precipitating the tin with ammonia solution. The stannic hydroxide thus obtained was repeatedly digested and washed with distilled water until no chloride ions could be detected in the washings. This precipitate was immediately dissolved in $1/8$ sulfuric acid; the solution was hastened by warming on a steam-bath. The solution was then evaporated on the steam-bath until $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ began to crystallize. Further crystallization was brought about by cooling. The stannic sulfate dihydrate was then dissolved in approximately 2 *f* sulfuric acid and the solution was analyzed for tin and hydrogen ion. Duplicate determinations showed that the stock solution was 0.4117 *f* in tin and 4.483 *N* in sulfuric acid.

A solution of tin(IV) in perchloric acid was prepared by dissolving the chloride-free stannic hydroxide in approximately 3 *N* perchloric acid. Analyses showed that this solution was 0.2670 *f* in tin and 3.216 in perchloric acid.

Neither of the stock solutions was stable, since after a period of several weeks they became cloudy and finally white tin(IV) oxide precipitated. However, the dilute solutions described below were prepared before the stock

solutions became turbid. The latter dilute solutions appear to be stable over the extended period of several months (at 25°).

Spectrophotometric examination of a series of tin(IV) sulfate and perchlorate solutions was carried out on a Beckman Model DU spectrophotometer, at 25° with quartz cells of path length 1.00 cm. and 0.100 cm. Since it was found that the extinction coefficients of the stannic ion and trisulfatostannate ion were large, the solutions, with varying amounts of sulfuric or perchloric acids, were prepared containing 1.647×10^{-3} *f* tin. This was accomplished by mixing appropriate quantities of the stock solutions and standardized sulfuric or perchloric acid solutions.

Electromigration studies were carried out on one-half by ten inch strips of filter paper. The paper strips were suspended horizontally with the ends dipping into beakers containing sulfuric acid of the appropriate concentration.

Carbon electrodes were placed into each beaker and a regulated potential of 50 volts was applied across the electrodes. The paper was wet with the acid and a drop of a solution of tin(IV) in the same concentration of acid was placed in the center of the paper. After a period of six to eight hours the current was stopped and the spot was developed by playing a stream of hydrogen sulfide gas over the paper. A bell jar over the apparatus prevented evaporation and drying of the paper.

In Fig. 1 are shown some typical absorption spectra for tin(IV) in sulfuric acid and in perchloric acid solutions (in the range 200 to 300 $m\mu$). The log of the "observed" extinction coefficient ($D_{\text{obs}}/C_{\text{Sn}}d$; where $D = \log I_0/I$, C_{Sn} is total tin(IV) and d is the cell path length in cm.) is plotted against wave length.

It will be seen that no clear cut maximum is observed in the region, so 240 $m\mu$, which lies on the flat portion of the curves, was selected for the calculations.

In Table I are tabulated the values of D_{obs} for 1.65×10^{-3} *f* tin in perchloric acid solutions of various concentrations. In Tables II and III are listed the data for 1.65×10^{-3} *f* tin in various sulfuric acid solutions.

TABLE I^a

THE OPTICAL DENSITY OF 1.65×10^{-3} *f* Sn(IV) IN PERCHLORIC ACID SOLUTIONS

(HClO ₄), moles/l.	D_{obsd} (25°)	(HClO ₄), moles/l.	D_{obsd} (25°)
1.496	0.242	3.168	0.250
2.139	.236	5.901	.259
2.782	.254	8.752	.258
3.006	.248		

^a Cell path = 0.100 cm.

Discussion.—Figure 2 shows e_{obs} at 240 $m\mu$ plotted against sulfuric acid concentration. The form of the first portion of this curve suggests the

(1) Presented at the 125th National Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, April 1, 1954.

(2) A. Ditte, *Compt. rend.*, **104**, 172 (1887).

(3) R. F. Weinland and H. Kuhl, *Z. anorg. Chem.*, **54**, 244 (1907).

(4) L. Domange, *Bull. soc. chim.*, **12**, 915 (1945).

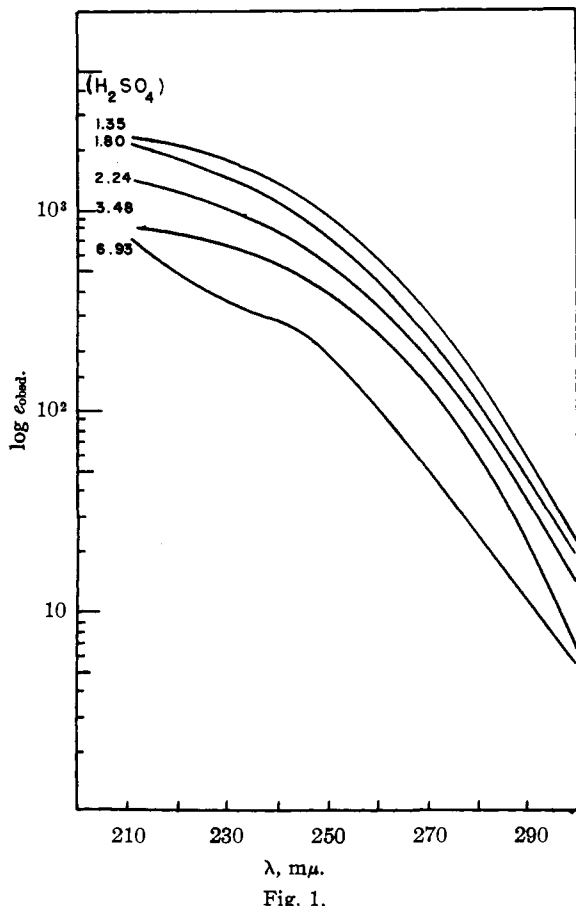


Fig. 1.

TABLE II^a

THE OPTICAL DENSITY AND VARIOUS DERIVED QUANTITIES FOR $1.65 \times 10^{-3} f$ Sn(IV) SOLUTIONS IN SULFURIC ACID OF VARIOUS CONCENTRATIONS

(SO ₄ ²⁻), moles/l.	(SO ₄ ²⁻) ²	D _{obsd} ^a (25°)	e _{obsd} ^b	$\frac{e_0 - e_{obsd}}{e_{obsd}}$ ^c
6.38	48.5	0.077	466	2.38
3.48	12.1	.107	648	1.43
3.19	10.2	.117	743	1.12
2.24	5.00	.168	1020	0.544
1.80	3.24	.220	1330	.184
1.50	2.26	.233	1410	.117
1.35	1.82	.249	1510	.042
0.910	0.82	.258	1560	...

^a For 0.100-cm. cell path at 240 mμ. ^b C_{Sn} = $1.65 \times 10^{-3} f$. ^c e₀ = 1575.

TABLE III^a

THE OPTICAL DENSITY AND VARIOUS DERIVED QUANTITIES FOR $1.65 \times 10^{-3} f$ Sn(IV) SOLUTIONS IN SULFURIC ACID OF VARIOUS CONCENTRATIONS

(H ₂ SO ₄), moles/l.	(H ₂ SO ₄) ⁻¹	D _{obsd} (25°)	1/D _{obsd}	e _{obsd}
17.30	0.0578	0.274	3.65	1660
15.4	.0651	.220	4.55	1330
14.6	.0685	.210	4.77	1270
13.9	.0722	.189	5.31	1142
13.1	.0763	.180	5.56	1090
10.4	.0961	.124	8.06	872
6.93	.144	.077	13	466

^a 0.100-cm. cell path at 240 mμ.

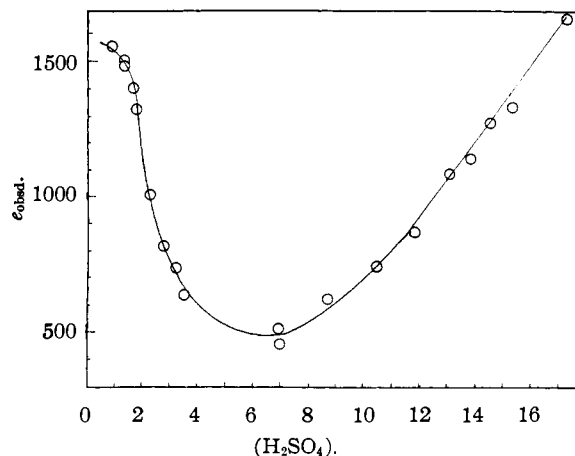
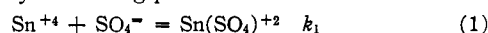
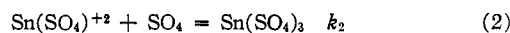


Fig. 2.

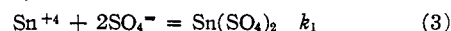
disappearance of some colored species with a second-order sulfate dependence. Since the optical density of solutions of tin(IV) in perchloric acid of various concentrations is about the same as the maximum value observed in sulfuric acid and since it does not vary appreciably from 1.5 *N* to nearly 9 *N* HClO₄, we see, at once, that the following reactions may be taking place



and



If k_1 is small, these reduce to



Now it is well known for such equilibria that

$$\frac{e_{\text{obs}} - e_0}{e_2 - e_{\text{obs}}} = \frac{(e_1 - e_0)k_1(\text{SO}_4^-) - (e_2 - e_0)k_1k_2(\text{SO}_4^-)^2}{(e_2 - e_0) + (e_2 - e_1)k_1(\text{SO}_4^-)} \quad (I)$$

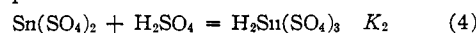
If k_1 is very small and $e_2 \ll e_0$, I becomes

$$\frac{e_0 - e_{\text{obs}}}{e_{\text{obs}}} = k_1k_2(\text{SO}_4^-)^2 = K_1(\text{SO}_4^-)^2 \quad (II)$$

where e_0 , e_1 and e_2 are the extinction coefficients of Sn⁺⁴, Sn(SO₄)⁺² and Sn(SO₄)₂, respectively, e_{obsd} is as previously defined and k_1 , k_2 and K_1 are the equilibrium constants for reactions 1, 2 and 3. $e_0 = 1575$ is obtained from the extrapolation of Fig. 2 and comparison with the perchloric acid data.

Now we plot $(e_0 - e_{\text{obs}})/e_{\text{obs}}$ against concentration of sulfate to the second power and obtain a good straight line which indicates that the above assumptions are essentially valid and that reaction 3 approximates the situation when sulfuric acid is added to stannic ion solutions in moderate amounts. K_1 is determined from the slope of this plot and is found to be 0.14 liter²/moles². Thus the ratio (Sn(SO₄)₂)/Sn⁺⁴ is 1 when the sulfate concentration is about 3 *f* and 0.1 at about 1 *f* sulfate.

The second portion of Fig. 2 suggests a first-order sulfate equilibrium such as



Since e_3 , the extinction coefficient for the sulfate complex, cannot be evaluated from the data, analysis of the type above cannot be carried out, but the first-order sulfate dependence can be demonstrated

Let

$$c^* = \text{H}_2(\text{Sn}(\text{SO}_4)_3) = K_2(\text{Sn}(\text{SO}_4)_2)(\text{H}_2\text{SO}_4)$$

Now taking the very high sulfate concentrations, where $(\text{Sn}^{+4}) \cong 0$ then

$$c'' = (C_{\text{Sn}} - c'')(\text{H}_2\text{SO}_4)K_2$$

and

$$c'' = \frac{C_{\text{Sn}}K_2(\text{SO}_4^-)}{1 + K_2(\text{SO}_4^-)} = \frac{C_{\text{Sn}}K_2(\text{H}_2\text{SO}_4)}{1 + K_2(\text{H}_2\text{SO}_4)}$$

C_{Sn} = total tin concentration

Then if $D_{\text{obsd}} = e_2 c'' d$ (i.e., if $e_3 \gg e_2$)

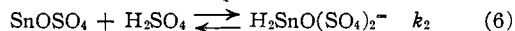
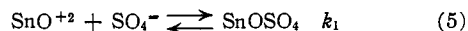
$$1/D_{\text{obsd}} = (1/e_2 C_{\text{Sn}} d)(1/K_2(\text{H}_2\text{SO}_4) + 1) \quad (\text{III})$$

Thus we plot $1/D_{\text{obsd}}$ against $1/(\text{H}_2\text{SO}_4)$ and obtain a good straight line, indicating that our reasoning was essentially correct. Then the data indicate that K_2 is quite small, since e_3 is obviously large and hence that the complex anion is present to any extent only in concentrated sulfuric acid solutions.

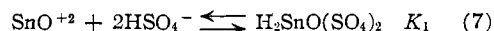
The electromigration experiments are in accord with the above conclusions. In 1.5 *f* sulfuric acid the tin migrates readily to the cathode, but in 6.0 *f* acid little migration is observed and that is toward the anode. At 3 *f* sulfuric acid some migration (as a streak rather than a spot) to the cathode is observed, which might indicate a very slow rate for reaction 3.

It is believed that all these equilibria are slow, since the spectra of freshly prepared samples were about the same as in the perchlorate solutions and slowly changed to the recorded values. Equilibrium was reached in about 24 hours. Hence all solutions were aged for one to two days before spectrophotometric examinations were undertaken.

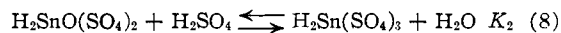
An alternative description which would also agree with the spectrophotometric data is suggested as



which are combined to give

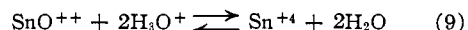


And in concentrated sulfuric acid we would have



In view of the strong tendency toward hydrolysis exhibited by tin(IV), this explanation seems more reasonable than the previous interpretation. However, if we remember that the spectrum changes very little in perchloric acid of from 1.5 to 9 *f*, this second description loses some force.

Unless k for the following



is small indeed, we should detect this reaction spectrophotometrically. Since we see no hydronium ion dependence in the spectrum, even in strongly acid solution, it seems more reasonable to assume the hydrated stannic ion is in fact the predominant species at hydronium ion concentrations above 1.5 *f*.

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EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Reaction between Platinum Chlorides and Carbon Monoxide. The Preparation and Configuration of Dichlorodicarbonylplatinum(II)¹

By J. M. LUTTON AND R. W. PARRY

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Pure dichlorodicarbonylplatinum(II) can be synthesized in good yield by the reaction between PtCl_2 and high pressure carbon monoxide at 125°. On the other hand, very poor yields of $\text{PtCl}_2(\text{CO})_2$ are obtained at all temperatures and pressures if PtCl_2 is the starting material. Pure $\text{PtCl}_2(\text{CO})_2$ loses CO irreversibly in vacuum or under nitrogen, but is stable under a CO pressure of one atmosphere. The relationship of these facts to the equilibria involved is considered. A value of 4.85 ± 0.05 Debye for the dipole moment of dichlorodicarbonylplatinum(II) in benzene solution confirms an earlier approximate value and eliminates the *trans* structure as one of the principal forms. Kurnakov's thiourea test also implies a *cis* structure for the compound, but results of the chemical test are not unequivocal. A preparation of PtCl_2 from commercial PtO_2 is described.

The unusual chlorocarbonyls of platinum were first prepared by Schutzenberger² using the reaction between platinum sponge at 250° and a rapidly flowing gaseous mixture of chlorine and carbon monoxide. The reaction, which has been studied in this and other laboratories, proceeds rapidly to give a mixture of the three known chlorocarbonyls in good yield provided active platinum sponge, such as is obtained from the thermal decomposition of ammonium chloroplatinate, is used.

A number of modifications of this procedure have been described. Phosgene gas has been used in

(1) Abstracted in part from a dissertation submitted by J. M. Lutton to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) P. Schutzenberger, *Ann. Chem. Phys.*, **15**, 100 (1868); *ibid.*, **21**, 350 (1870).

place of chlorine and carbon monoxide with relatively poor results.³ In a second modification platinum chloride has been treated with CO. Literature reports on this procedure are not consistent; an excellent modern reference book⁴ reports that PtCl_2 takes up CO more readily than does platinum sponge, yet preparative procedures involving the use of PtCl_2 have been relatively ineffective.⁵ In view of these observations the reactions between carbon monoxide and the chlorides of platinum have been reinvestigated in some detail with results as described below.

(3) F. Mylius and F. Foerster, *Ber.*, **24**, 2424 (1891).

(4) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford University Press, New York, N. Y., 1950, p. 1627.

(5) (a) W. O. Walker, Thesis, University of Chicago (1930); (b) this investigation.