Dye and Spedding,[16] involving higher terms of the electrophoretic effect than are included in the limiting law showed that these terms are by no means negligible since about half of the total deviation could be accounted for, using reasonable values for the ion-size parameter. However, to force these terms to absorb all of the deviations would require unreasonably small values for $\mathring{a}$. This is not unexpected since the same terms are neglected in the calculation of the time-of-relaxation effect, and ion-pair formation has not been taken into account.

As an alternative approximate procedure, one can assume that the deviations are entirely due to ion-pair formation and attempt to calculate association constants using the Onsager equation for the conductance of the ionic species. The limiting conductance of the ion-pair must be estimated, and it is also necessary to estimate activity coefficients with the aid of the Debye–Hückel theory. In practice, the results for these dilute solutions are not too sensitive to the latter two approximations but are very sensitive to the form of the theoretical conductance function. Such a calculation was performed for the salts studied in this research but the association "constant" A varied considerably with concentration. Typically, a ten-fold decrease in concentration from 3×10^{-3} to 3×10^{-4} N required a 100% or greater increase in A to fit the conductance data.

This once again demonstrates the inability of any single theory to cope with dilute solutions of high-charge electrolytes. One would be in a much stronger position if association constants could be measured independently; for example by the method of Cohen and Plane.[17] Unfortunately, the effect of ion-pair formation on the spectra is often too small to be useful.

Another factor which might be important is the effect of these complex ions upon the water structure. The high values for Λ^0 indicate either a small hydration tendency or an increase in fluidity of the solvent in the neighborhood of the ion due to a breakdown of hydrogen bonding. The large effect of the counter-ion on the shape of the conductance curve might be related to a cancellation of this structural effect.

It is probable that a combination of the factors mentioned is involved. If this is the case, studies involving a number of different ions of different sizes, charges and hydrophilic characteristics will be required to separate the various effects. In any event, the realm of unsymmetrical electrolyte behavior, even in dilute solutions, is not characterized by the simplicity of the univalent salts.

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[16] J. L. Dye and F. H. Spedding, THIS JOURNAL, **76**, 888 (1954).

[17] S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

A Study of the Electron Exchange Reaction between Tin(II) and Tin(IV) in Aqueous Sulfuric Acid Solutions

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The kinetics of the exchange reaction between tin(II) and tin(IV) in aqueous sulfuric acid were studied in the temperature range of 25 to 50°. Experiments were designed to determine the effects of variation in concentration of tin(II), tin(IV) $(SO_4^=)$, (H^+) and (Cl^-) ions. It was found that the reaction is first order with respect to tin(II) and tin(IV) and that the effect of increasing (H^+) is to decrease the rate of exchange, and the effect of increasing $(SO_4^=)$ is to increase the rate of exchange. An empirical equation, $R/ab = 0.674\,(H^+)^{-2} + 0.0725\,(SO_4^=)(H^+)^{-1}$, which predicts the effects of (H^+) and $(SO_4^=)$ on the rate of exchange is presented and some possible mechanisms which lead to this model are discussed. The addition of (Cl^-) to the reaction mixture in 3.00 M H_2SO_4 increases the rate by up to a factor of 100. The rate can be calculated by the equation, $R = 4.94[\mathrm{Sn(II)}][\mathrm{Sn(IV)}][Cl^-]$, above 0.5 M Cl^-, and a mechanism which leads to this model is given. Spectrophotometric examination of aqueous solutions of tin(II) in either $HClO_4$ or H_2SO_4 have been interpreted in terms of the hydrolysis of Sn^{++}. The concentration hydrolysis constant, equal to 24.5, has been evaluated. The absorption of tin(IV) solutions and tin(II)–tin(IV) solutions in 3.00 M H_2SO_4 and tin(II)–tin(IV) solutions in H_2SO_4 containing 1.00 M Cl^- (3.99 M H^+) are given. The spectra have been interpreted in terms of interaction dimers containing one atom of tin(II) and one atom of tin(IV).

Introduction

The electron exchange reaction between tin(II) and tin(IV) in hydrochloric acid has been the subject of several papers.[1,2] In both cases, the exchange reaction was found to be first order in tin(II) and tin(IV) concentrations, and an interaction dimer containing one atom of tin(II) and one atom of tin(IV) has been suggested. Our preliminary investigations indicated that the exchange was much slower in sulfuric acid than in hydrochloric acid but did proceed at a measurable rate.

We undertook the present study to try to elucidate the mechanism of the exchange reaction in sulfuric acid as part of a project in which the role of various anions as complexing agents is being studied with respect to electron transfer reactions. Our primary interest is in connection with reactions which may proceed either by direct transfer of two electrons or alternatively by the stepwise exchange of one electron at a time. We also were interested in clarification of the role of sulfate ion, in view of its effects on the tin(II)-cerium(IV) reaction.[3]

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[1] C. I. Browne, R. P. Craig and N. Davidson, THIS JOURNAL, **73**, 1946 (1951).

[2] E. G. Meyer and M. Kahn, *ibid.*, **73**, 4950 (1951).

[3] C. H. Brubaker and A. J. Court, *ibid.*, **78**, 5530 (1956).

Experimental

Materials.—Tin metal and perchloric acid were obtained from the J. T. Baker Chemical Company; lithium sulfate, lithium carbonate and oxalic acid from the Mallinckrodt Chemical Works; sulfuric and hydrochloric acids from E. I. du Pont de Nemours and Co.; and the toluene 3,4-dithiol was obtained from Matheson, Coleman and Bell. The radioactive tracer (Sn-113P), used to follow the exchange, was supplied by the Oak Ridge National Laboratory.

Tin(II) sulfate solutions were prepared indirectly by the method of Noyes and Toabe.[4] Excess tin metal was used to displace copper sulfate from solutions of cupric oxide dissolved in an excess of 3 to 5 *M* sulfuric acid. To minimize oxidation of tin(II), all preparations were carried out in an atmosphere of specially purified nitrogen.[5] The tin(II) solution was transferred to a storage flask by increasing the nitrogen pressure. A fritted glass filter facilitated removal of excess tin and copper metals. Continuous nitrogen flow allowed the tin(II) solutions to be stored for periods up to several months, without detectable oxidation.

Hydrogen trisulfatostannate(IV) monohydrate was prepared by the dissolution of tin metal in concentrated sulfuric acid at 190°. Subsequent fuming of this solution almost to dryness served to coagulate any colloidal sulfides that appeared and these were removed by filtration through a fritted glass filter after dissolution of tin(IV) sulfate in hot sulfuric acid. Fuming almost to dryness, filtering and redissolving were repeated twice. The resulting salt was hygroscopic and had the composition corresponding to hydrogen trisulfatostannate(IV) monohydrate.

Anal. Calcd. for $H_2Sn(SO_4)_3 \cdot H_2O$: Sn, 27.8; available H^+, 0.47. Found: Sn, 27.8; H^+, 0.48.

Stable solutions of tin(IV) sulfate were prepared by dissolution of 0.2 mole of $H_2Sn(SO_4)_3 \cdot H_2O$ in 1 l. of boiling H_2SO_4. These solutions were kept at the boiling point (with the periodic addition of concentrated H_2SO_4 to maintain volume) for 200–300 hr. After prolonged heating, the solutions were diluted to 10–12 *M* acid and analyzed. Further dilution resulted in solutions which were stable with respect to hydrolysis for more than 60 days.

All attempts to prepare stable solutions of tin(IV) in perchloric acid by methods similar to those used for the preparation of tin(IV) sulfate were unsuccessful. Even dissolved crystalline $H_2Sn(SO_4)_3 \cdot H_2O$ was unstable in perchloric acid.

The radioactive tin was obtained as a hydrochloric acid solution of Sn^{113}. The sample was diluted to 10 ml. with 6 *M* hydrochloric acid, 4.64 mg. of Sb^{+3} and 2.5 g. of oxalic acid were added. The solution was heated to boiling and hydrogen sulfide was bubbled into the solution until Sb_2S_3 precipitated. The solution was centrifuged and the supernatant liquid was decanted. The above procedure was repeated twice. Concentrated nitric acid was added to decompose the excess oxalic acid and the solution then was heated with concentrated sulfuric acid for 250 hr., both to remove HCl and HNO_3 and to assure identity of tracer and tin(IV) stock. It then was diluted with water to give a solution of active tin(IV) for the exchange experiments.

An aluminum absorption curve was made, and the observed range was 110 ± 2 mg./cm.², which corresponds to an electron energy of 0.37 ± 0.01 M.e.v.[6] in agreement with that expected from a K-conversion electron from the 0.39 M.e.v. gamma ray from the metastable indium daughter. A lead absorption curve was made on the same sample and a lead half-thickness of 2.77 ± 0.04 g./cm.² corresponding to a gamma energy of 0.39 ± 0.01 M.e.v. was observed. The half-life was observed to be 113 ± 2 days which is in good agreement with the value of 112 days reported in the literature.

Lithium sulfate was recrystallized and dehydrated at 200°.

Lithium perchlorate trihydrate was prepared from lithium carbonate by adding perchloric acid in a slight excess, evaporating to saturation, and cooling. The resulting solid was repeatedly crystallized from distilled water until free of acid and was dried over a quantity of the salt which had been heated in an oven at 110°.

Oxalic acid was recrystallized from distilled water, dried *in vacuo* over concentrated sulfuric acid and ground to a fine powder.

Standard NaOH solutions were prepared free of carbonate and standardized with potassium acid phthalate. Standard acids were analyzed by comparison with the sodium hydroxide.

The tin(II) concentration was determined by titration in an atmosphere of carbon dioxide with 0.07 *N* iodine solution which was standardized with As_2O_3, prior to each series of titrations, in a bicarbonate buffered medium; freshly prepared starch was used as the indicator.

The total tin concentrations were obtained by a modification of Farnsworth's method,[7] in which (H_2SO_4) was 0.21 ± 0.05 *M* and Santomerse SX (Monsanto Chemical Company) was used as the dispersing agent.

The molar ionic strength and molar concentrations of $(SO_4^=)$, (HSO_4^-) and (H^+) in the solutions were calculated from data of Smith and Maranville[8] by a method described earlier by Young and Blatz.[9] The solutions were made up from stock solutions already described.

Procedure.—The exchange studies were carried out in solutions with a molar ionic strength of 4.98 except for the series used to study very high (H^+) and $(SO_4^=)$ (in which case it was necessary to vary the ionic strength). All glassware used was carefully cleaned, dried, heated, blown out with purified nitrogen and stoppered before use. To minimize oxidation, it was necessary to keep a stream of nitrogen flowing into the reaction vessels, which were stored in a constant temperature bath. By employing a positive nitrogen pressure above the liquids, it was possible to maintain 10^{-2} *M* tin(II) solutions for periods up to 1000 hr. without detectable oxidation.

The exchange rate was measured in the following manner: after the concentrations of the species to be used had been determined, the calculated volume of sulfuric acid, the volumes of minor acids, the volumes of solutions of the lithium salts and the water were added in that order. The calculated volume of tin(IV) was added, the flasks were flushed with purified nitrogen for one hour. The calculated volume of tin(II) was added under a flow of prepurified nitrogen. At this point, the 100 ml. flasks contained approximately 96 ml. The flasks were allowed to come to thermal equilibrium for 12 hr. before the active tin(IV) sulfate was added.

The active tin(IV) (3 ml. in all cases) plus water to make 100 ml. was added, the flasks were inverted ten times to insure thorough mixing, and then were placed into the bath again and the nitrogen flow was resumed immediately. Zero time was taken as the time when one-half of the activity had drained into the flask. This final mixing procedure took less than 20 seconds. As soon as possible, after mixing, the tin(II) concentration was determined iodimetrically and the adsorption spectrum was measured. Data from runs were recorded only when the absorption spectra and tin(II) concentrations were unchanged for two half-lives.

Oxalic acid was used to precipitate stannous oxalate. The separation was effected by adding 2 ml. of reaction solution to a small beaker containing 1 g. of powdered oxalic acid and 2 ml. of saturated oxalic acid solution. To insure complete precipitation, even when tin(II) concentrations were lowered to 0.005 *M*, 1 ml. of 0.100 *M* tin(II) in 2.00 *M* hydrochloric acid was added. The solutions were stirred rapidly with a magnetic stirrer for two minutes and filtered through a stainless steel filter with a removable chimney and holding 22 mm. Whatman No. 42 paper. The rate of filtration was controlled by an aspirator connected to a micro bell-jar with a ground flange and opening for the steel funnel. The filtrate was collected in a 10 ml. volumetric flask. The beaker and precipitate were washed with two 2-ml. portions of saturated oxalic acid solution. The filtrate and washings were diluted to 10 ml. with water and mixed thoroughly. Four ml. samples of each of the filtrates plus washings were withdrawn and were mounted, for γ-counting, in new 1-dram, screw cap vials. The samples were counted 20–24 hours after separation to insure that equilibrium was established with the In^{113m}. Periodically, duplicate samples were taken to determine the sampling error. The precipitation of stannous oxalate was satisfactory for samples con-

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[4] A. A. Noyes and K. Toabe, THIS JOURNAL, **39**, 1537 (1917).

[5] F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).

[6] L. E. Glendenin, *Nucleonics*, **2**, 26 (1948).

[7] M. Farnsworth and J. Pokola, *Anal. Chem.*, **26**, 735 (1954).

[8] H. M. Smith, Ph.D. Dissertation, University of Chicago (1949), L. F. Maranville, Ph.D. Dissertation, University of Chicago (1949) and T. F. Young, *Record Chem. Progress*, **12**, 81 (1951). "The Structure of Electrolyte Solutions," W. J. Hamer, ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 35.

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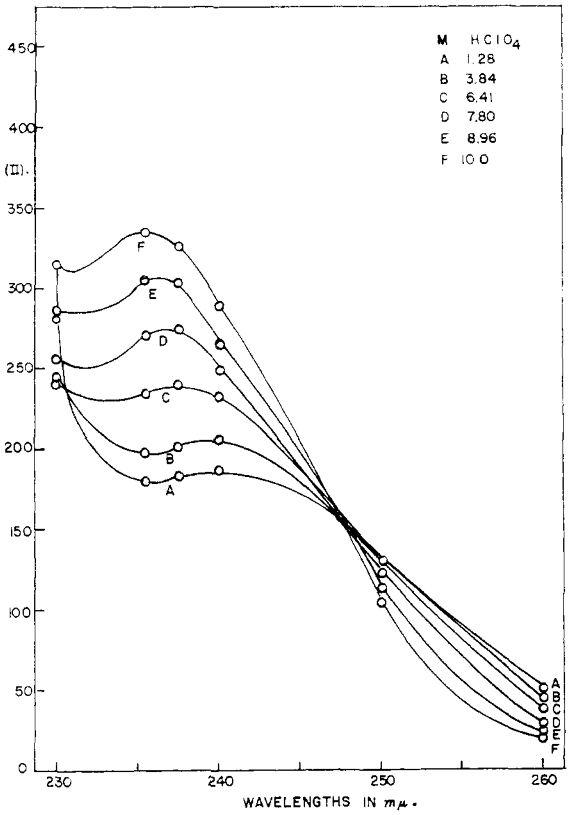

Fig. 1.—The absorbancy index of tin(II) in perchloric acid as a function of wave length.

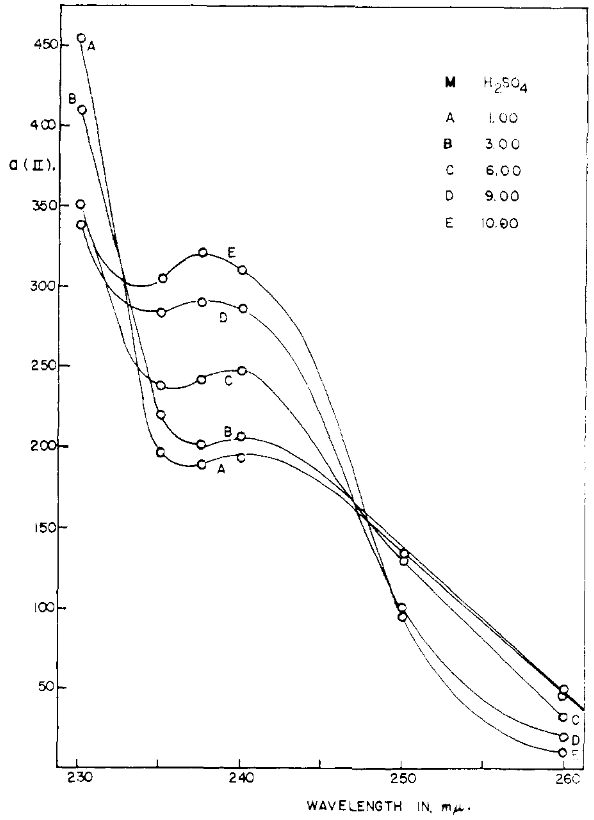

Fig. 2.—The absorbancy index of tin(II) in sulfuric acid as a function of wave length.

taining less than 0.6 *M* chloride ion. Apparent induced exchange was only 1 to 10%. Above 0.6 *M* chloride, the precipitation was kinetically hindered by the chloride and a second method of separation was utilized.

Cesium hexachlorostannate(IV), Cs_2SnCl_6, was precipitated in the high chloride samples. The exchange reaction in the sample was quenched by the addition of 2 ml. of reaction solution to 1 ml. of 0.087 *M* CsCl in 11 *M* HCl. The solution was stirred for 60 seconds and filtered, through the same apparatus used above. The filtrate was collected directly in a 1-dram, screw cap vial. The beaker and precipitate were washed with 1 ml. of concentrated hydrochloric acid. Duplicate samples gave results which agreed within expected counting precision.

Exchange half-times then were determined from graphs of log $(1 - F)$ *vs.* time (where F is the fraction exchanged), with each graph including seven to ten experimental points. Values of the exchange rates and rate constants were computed from the half-times obtained from the graphs and the concentrations of tin(II) and tin(IV). In these experiments, the apparent zero time exchange for the cesium precipitation of tin(IV), $100F$ at $t = 0$, averaged about 45%. The activities of three samples prepared from aliquots of the same active solution were the same within the counting error, indicating satisfactory reproducibility of the separation technique. For the exchange experiments, samples were counted for a minimum of 10,000 counts.

Qualitative absorption spectra were measured with a Beckman model DK-2 recording spectrophotometer. All of the quantitative spectra were measured with a line operated Beckman model DU Spectrophotometer equipped with a Photomultiplier. Matched, stoppered one centimeter quartz cells and a "blank" acid solution corresponding to each sample were used and the cells were calibrated after each series of measurements. No change in the absorbancy was observed on exposure of tin(IV) or tin(II) solutions to the ultraviolet beam in the spectrophotometer for periods up to thirty minutes. Sample cells were filled and emptied until constant absorbancies were observed. Immediately after recording the absorbancy, the concentration of the tin(II) was determined iodometrically. Samples in which more than 1% oxidation had occurred were discarded and new samples were employed.

Electromigration studies were carried out on one-half by ten inch strips of Eaton-Dikeman #652 electrophoresis paper using the apparatus described by Brubaker.[10] The apparatus was modified so that a purified nitrogen atmosphere could be maintained over the tin(II) samples to minimize oxidation.

Results and Discussion

Spectrophotometric Observations.—Absorption spectra of solutions of tin(II), 5×10^{-4} to 2×10^{-2} *M*, were found to obey Beer's law between 230 and 260 mμ. De Maine and de Maine[11] report that Beer's law is not obeyed for dilute solutions of tin(II) in 3.00-10.0 *M* (Cl^-). We find that Beer's law is obeyed, even in the presence of Cl^-, if the concentration of tin(IV) present is kept below 2% of the [Sn(II)].

In Figs. 1 and 2 are shown the spectra of solutions of tin(II) in H_2SO_4 and $HClO_4$. The absorbances for the H_2SO_4 and $HClO_4$ solutions are identical at 240-250 mμ. Thus, in that wave length region, changes may be attributed to hydrolysis and not to sulfate complexing. If

$$Sn^{++} + H_2O = SnOH^+ + H^+; \quad K_1 \qquad (1)$$

and if a_1 and a_2 are the molar absorbancy indices of $SnOH^+$ and Sn^{++}, respectively, then

$$a_{obsd} = \frac{a_1[SnOH^+] + a_2[Sn^{++}]}{[Sn(II)]} \qquad (2)$$

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[10] C. H. Brubaker, THIS JOURNAL, **76**, 4269 (1954).

[11] M. M. de Maine and P. A. D. de Maine, *J. Inorg. & Nuclear Chem.*, in press and private communication.

[Sn(II)] is the total concentration of tin(II). By combining equations 1 and 2

$$\frac{a_{\text{obsd}} - a_1}{a_2 - a_1} = \frac{a_1K_1(\text{H}^+) + a_2 - a_1[N_1(\text{H}^+) + 1]}{[a_2 - a_1][{}_1K(\text{H}^+) + 1]} \qquad (3)$$

is obtained, and by taking reciprocals, this leads to

$$\frac{a_2 - a_1}{a_{\text{obsd}} - a_1} = 1 + \frac{K_1}{(\text{H}^+)} \qquad (4)$$

At 240 mμ, $a_1 = 179$ is obtained by extrapolation of a_{obsd} *vs.* (H^+) to $(\text{H}^+) = 0$. A graph of equation 4 yields a good straight line if a_2 is taken as 320. From the slope, $K_1 = 24.5 \pm 0.1$. The pertinent data are found in Table I.

TABLE I

THE OBSERVED ABSORBANCY INDICES AND VARIOUS DERIVED QUANTITIES FOR 2.00 × 10^{-3} *M* Sn(II) IN $HClO_4$ OR H_2SO_4 SOLUTIONS AT 240 mμ

(H^+)	$a_{(\text{obsd})}$	$1/(\text{H}^+)$	$\frac{a - a_0}{[a_{\text{obsd}} - a_0]}$
1.00	185	1.000	23.5
1.40	187_5	0.714	16.6
1.60	190	.625	14.1
2.00	192	.500	10.8
3.00	199	.333	7.05
4.00	207	.250	5.05
5.00	217	.200	3.74
6.00	227	.167	2.94
7.00	238	.142	2.39
8.00	251	.125	1.96
9.00	265	.111	1.64
10.0	281	.100	1.38
11.0	298	.091	1.18

Gorman[12] has determined K_1 by e.m.f. methods and his results show that the constant depends markedly on ionic strength. If his data are extrapolated to the ionic strengths of the solutions used in this work or if his K_1 is corrected by estimating activity coefficients of Sn^{++}, $SnOH^+$ and H^+, a value of the same order of magnitude, for K_1, results.

In accord with the above ideas that $SnOH^+$ predominates in the solutions under investigation and that the only other important ionic species is Sn^{++}, electromigration studies of tin(II) solutions in $HClO_4$ and H_2SO_4, show only migration to the cathode. Some neutral $SnSO_4$ also may be present[3,13] in H_2SO_4.

If the absorbancy of $SnOH^+$ is a maximum at 240 mμ and that of Sn^{++} a maximum at shorter wave lengths, the observed minimum (230–235 mμ) would be expected and it would be expected to shift to shorter wave lengths as (H^+) is increased.

The spectra of tin(II) in sulfuric acid near 230 mμ suggest some "colored" species is formed in dilute sulfuric acid, perhaps an ion-pair such as $(SnOH^+)(HSO_4^-)$. No quantitative treatment of these observations has been found possible.

Solutions of tin(IV) in H_2SO_4, which have been prepared by boiling in concentrated H_2SO_4 for prolonged periods prior to dilution, suffer no change in absorption spectrum and exhibit no formation of hydrous tin(IV) oxide. For example solutions in 12 and 5.7 *M* H_2SO_4 have had reproducible spectra for nine months and those diluted to 3 *M* H_2SO_4 showed no change in ten weeks.

On the other hand, solutions prepared by dissolving $Sn(SO_4)_2 \cdot 2H_2O$ in 3–8 *M* H_2SO_4 undergo a slow change in absorbancy and ultimately, in 3 to 30 days, depending on (H_2SO_4), give hydrous tin(IV) oxide. These solutions have high absorbancies at 240 mμ. Furthermore it appears that the absorbancy of $SnSO_4^{++}$ is large ($a_{240} = 2.5 \times 10^3$), as is that of $H_2Sn(SO_4)_3$, but that of $Sn(SO_4)_2$ is small.[14] Thus we feel that the existence of $Sn(SO_4)_2$, as the principal species, is suggested for the solutions prepared by prolonged boiling of Sn(IV) in concentrated H_2SO_4.

The only explanation for the necessity of boiling, which we can devise, is that $Sn(SO_4)_2 \cdot 2H_2O$ is not the simple tin(IV) sulfate. Rather it may dissolve as some hydrolyzed (possibly polymerized) species which is (are) subject to further slow hydrolysis. Boiling with concentrated sulfuric acid might then be required to effect completely a slow conversion to the higher complex, $Sn(SO_4)_2$.

The absorption spectra of mixed solutions of tin(II) and tin(IV) were dependent on the history of the tin(IV) species present. The mixed solutions, in all cases, absorbed more energy than the sum of the absorptions of the individual components. The spectra were studied in 3.00 *M* H_2SO_4, except for the solutions which were 1.00 *M* in Cl^-, and these solutions were 3.99 *M* in (H^+), the (H^+) of 3.00 *M* H_2SO_4.

Continuous variation studies were carried out, by use of the stable tin(IV) stocks. In different series, various (H_2SO_4) were used and a study was also done with 1.00 *M* Cl^- present. In all cases maximum excess absorbancies appeared at a 1:1 ratio of Sn(II)/Sn(IV). Thus, as for solutions in HCl,[1,11] an interaction dimer containing one atom of tin(II) and one of tin(IV) is indicated.

Exchange Studies.—A series of experiments were designed to determine the effect of variation in concentration of tin(II), tin(IV), $(SO_4^=)$ and (H^+). These data are summarized in Tables II–V.

TABLE II

DEPENDENCE OF EXCHANGE RATE ON CONCENTRATION OF TIN(II) AND TIN(IV)

$(\text{H}^+) = 3.99$ *M*; $(SO_4^=) = 0.99$ *M*; $\mu = 4.98$

[Sn(II)] *M*	[Sn(IV)] *M*	*k*(obsd.)	*k*(I) (l./mole hr.)	*k*(II) (l./mole hr.)
0.0077_7	0.0129	0.062	0.061	0.062
.0097	.0126	.061	.061	.062
.0104	.0129	.064	.061	.062
.0129	.0129	.062	.061	.062
.0156	.0129	.060	.061	.062
.0129	$.0066_3$	.064	.061	.062
.0129	$.0086_1$	.062	.061	.062
.0129	.0106	.062	.061	.062
.0129	.0129	.064	.061	.062
.0129	.0205	.063	.061	.062

Originally we had hoped that we might be able to work with more dilute solutions, perhaps less than 1.00 *M* in acid,[10] so that the ionic strength principle might be invoked with some justification. Since it was necessary to use solutions of 4.98 molar

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[12] M. Gorman, THIS JOURNAL, **61**, 3342 (1939).

[13] H. G. Denham and W. E. King, *J. Chem. Soc.*, 1251 (1935).

[14] C. H. Brubaker, Jr., *J. Phys. Chem.*, **61**, 696 (1957).

TABLE III

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF HYDROGEN ION

$\mu = 4.98$; $(SO_4^=) = 0.99\ M$; Total (Sn) = 0.0258 M

$[H^+]$ M	$[H_2SO_4]$ M	$[HClO_4]$ M	$[Li_2SO_4]$ M	$[LiClO_4]$ M	k (obsd.)	k(I) (l./mole hr.	k(II)
3.30	2.31	0.34_5	0.34_5	...	0.082	0.083	0.084
3.60	2.61	$.20_0$	0.20_0	...	.072	.073	.072
3.99	3.00	...	...	...	.060	.062	.061
4.40	3.21	.21	...	0.57	.054	.054	.051
4.80	3.43	.38	...	0.18	.047	.047	.045
5.00	3.53	.48	...	...	.045	.044	.042

TABLE IV

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF SULFATE ION

$\mu = 4.98$; $(H^+) = 0.99\ M$; Total (Sn) = 0.0258 M

$[SO_4^=]$ M	$[H_2SO_4]$ M	$[HClO_4]$ M	$[LiClO_4]$ M	$[Li_2SO_4]$ M	k (obsd.)	(kI) (l./mole hr.)	k(II)
0.70	2.12	1.17	0.29	...	0.057	0.057	0.056
0.80	2.42	0.77	0.19	...	.058	.059	.057
0.99	3.00	...	...	...	.060	.062	.061
1.20	3.21_5	...	...	0.42_5	.065	.065	.064
1.30	3.32	...	...	$.63_0$	.066	.066	.065
1.40	3.42	...	...	$.83_0$	.066	.067	.067

TABLE V

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF HYDROGEN AND SULFATE IONS AT 25.0°; TOTAL (Sn) = 0.0258 M

$[H^+]$ M	$[SO_4^=]$ M	μ	$[H_2SO_4]$ M	$[HClO_4]$ M	$[LiClO_4]$ M	$[Li_2SO_4]$ M	k (obsd.)	k(I) (l./mole hr.)	k(II)
4.95	1.21	6.16	3.75	...	...	...	0.046	0.047	0.046
5.08	1.24	6.32	3.85	...	...	...	.043	.046	.044
5.99	1.43	7.39	4.57	...	...	...	.043	.068	.036
5.74	1.40	7.71	4.07	0.27	0.57	...	.039	.039	.038
5.42	1.73	8.00	4.12	...	...	0.42_5	.044	.045	.046
6.40	1.52	8.10	4.40	0.48_6	...	...	.033	.034	.034
6.67	1.53	8.20	4.52	0.61_5	...	...	.031	.032	.032
5.57	1.94_5	8.77	4.25	...	...	0.63_0	.045	.045	.047
5.70	2.15	9.51	4.38	...	...	0.83_0	.045	.044	.048

ionic strength, there must necessarily be doubt expressed about neglecting possible variations in activity coefficients in treating the data on the variation in concentrations of $SO_4^=$ and H^+ and later in the experiments in which hydrogen chloride is substituted for part of the sulfuric acid. Thus rates may not only reflect changes in the intended variables but may also include variations in activity coefficients. Consequently the discussion of these results remains qualitative and subject to reexamination whenever information about activity coefficients in such mixtures becomes available.

The rate of exchange, R, is defined as

$$R = k[a]^{\alpha}[b]^{\beta} \qquad (5)$$

where a is total Sn(II) and b the total Sn(IV). It was found that $\alpha = 0.99 \pm 0.04$ and $\beta = 0.99 \pm 0.01$. The constant k or R/ab can be evaluated for 3.00 M H_2SO_4 (3.99 M (H^+) and 0.99 M $(SO_4^=)$) from the above data. A value of 0.0621 ± 0.0017 liter/mole hour is obtained.

In order to evaluate the effect of (H^+) on the rate of exchange, a series of experiments were performed in which the ionic strength was maintained at 4.98 and the $(SO_4^=)$ was kept at 0.99 M. The variation of R can be shown in a log–log plot of the rate constant (R/ab) against (H^+); a slope of -1.5 ± 0.1 was observed. The variations in $(H^+)^s$ were limited by two factors: (a) the tin(IV) spectra were stable as a function if time only above 3.00 M (H^+); (b) an ionic strength of 4.98 limited the maximum (H^+) to 5.00 M.

The variation in $(SO_4^=)$ indicates that the effect of sulfate ion is very small but would correspond to an exponent of 0.25 ± 0.04 in the formulation of the rate law

$$k(\mathrm{I}) = \frac{R}{ab} = \frac{0.496[SO_4^=]^{0.25}}{[H^+]^{1.5}} \qquad (6)$$

Due to the insolubility of tin(IV) in perchloric acid, it was impossible to diminish the sulfate ion concentration below 0.70 M at constant ionic strength and constant (H^+). Constant ionic strength limited the maximum $(SO_4^=)$ to 1.40 M. In order to study the effect of higher (H^+) and $(SO_4^=)$ than was allowed at $\mu = 4.98$, a series of measurements were made in which the ionic strength was allowed to vary (Table V). The value $k_{\mathrm{obsd.}}$ is the apparent rate constant calculated from the observed half-life and k(I) has been evaluated from equation 6.

It can be seen that, with the exponents chosen, equation 6 predicts the experimental rates rather well. The exponents obtained, in this mathematical expression for the rate constant, suggest that the exchange is due to several equilibria or steps. The equation

$$R/ab = k(\mathrm{II}) = 0.674(H^+)^{-2} + 0.0725(SO_4^=)(H^+)^{-1} \qquad (7)$$

also predicts the experimental R/ab well. The k(II) are tabulated in the tables for comparison with k(obsd.) and k(I). Alternative equations were sought, but no others with integral exponents were found to agree with experiment.

Equation 7 suggests two paths for exchange in sulfuric acid solutions. In the first, two hydrolysis steps are required to arrive at the exchanging species, and in the second, one hydrolysis step and one sulfate complexing step. If the predominant species are actually $SnOH^+$ and $Sn(SO_4)_2$, then exchanging species must be entities such as $SnO(SO_4)_2^= + SnOH^+$ or $Sn(OH)_2SO_4 + SnOHSO_4^-$ and $SnOH(SO_4)_2^- + SnOHSO_4^-$.

In the absence of more information concerning the formation of such species, more detailed interpretations probably should not be attempted. It is interesting to note that reasonably satisfying, symmetrical, bridged interaction dimers, formed from the above pairs of species, can be written.

The rates of exchange have been studied at three different temperatures, for solutions containing 2.58×10^{-2} M total tin in 3.00 M H_2SO_4 (Table VI). The graphs of $\ln(1 - F)$ *vs.* t gave the anticipated linear relationship at 25.0 and 37.8°. At 49.7° the absorption spectra remained constant for 50-60 hr., followed by an increase in the absorbancy as a function of time. At 400 hr. a visible precipitate of unknown composition (but presumably hydrous tin(IV) oxide) appeared in the reaction flasks. The McKay plots were not linear, but the tail of the curve is linear and suggests that two processes are taking place at different rates. Graphical subtraction of the linear tail of the McKay plot (extrapolated to zero time) from the original curve results in a straight line. Perhaps it is fortuitous that resolution of the curves results in a straight line, but it suggests that two different sets of species are involved in the electron exchange and that equilibrium between these species is kinetically slow. Although an Arrhenius plot of these data may be meaningless due to the lack of linearity of the McKay plot, it is of interest that the exchange rate determined from the first part of the curve (0.750) gives a linear Arrhenius plot, when combined with the data from the other two temperatures. The slope, E_a, equals 19.0 kcal./mole.

TABLE VI

DEPENDENCE OF EXCHANGE RATE ON TEMPERATURE

$\mu = 4.98$; 3.00 M H_2SO_4; $(H^+) = 3.99$ M $(SO_4^=) = 0.99$ M; $C_{Sn} = 0.0258$ M

Temp., °C.	k (l./mole hr.)
25.0	0.062
37.8	0.211
49.5	1.38 (net); 0.750 (original); 0.084 (tail)

The Effect of Chloride Ion on the Exchange.—Acceleration of the Sn(II)–Sn(IV) exchange in sulfuric acid was observed, when chloride was added to the system (Tables VII, VIII and IX). In solutions containing less than 0.5 M Cl^-, the exchange was not first order in tin(II) or tin(IV) and the orders depend on (Cl^-).

TABLE VII

ACCELERATION OF EXCHANGE BY CHLORIDE ION

$\mu = 4.98$; $(H^+) = 3.99$ M; Total (Sn) = 0.0258 M

$[Cl^-]$ M	$[H_2SO_4]$ M	[HCl] M	[LiCl] M	k (obsd.) (l./mole hr.)
0.015	2.98	0.015	...	0.0632
.030	2.97	.030	...	.0809
.060	2.94	.060	...	.1162
.0075	2.92	$.077_5$	...	.154
$.103_3$	2.90	$.103_3$	...	.215
.120	2.88	.120	...	.298
.129	2.87	.129	...	.325
.150	2.85	.185	...	.472
$.193_7$	2.81	$.193_7$	...	.691
.200	2.80	.200	...	1.058
$.258_2$	2.74	$.258_2$	...	1.078
.300	2.73	.260	0.40_0	1.283
$.516_3$	2.70	.416	$.10_0$	2.59
.600	2.68	.460	$.14_0$	3.00
.900	2.46	.720	$.18_0$	4.62
1.20	2.28	.960	$.24_0$	5.72

TABLE VIII

ACCELERATION OF EXCHANGE RATE BY CHLORIDE ION WITH VARIATION IN TOTAL TIN CONCENTRATION

$\mu = 4.98$; $(H^+) = 3.98$ M

[Sn(II) M	[Sn(IV)] M	$[Cl^-]$ M	k (obsd.) (l./mole hr.)
0.0128	0.0100	0.129	0.245
.0128	.0129	.129	.325
$.0096_0$	.0129	.129	.405
.0055	.0134	.200	1.98
.0085	.134	.200	1.46
$.0125_0$	.0134	.200	1.05_8
.0195	.0134	.200	0.69_8

TABLE IX

DEPENDENCE OF THE EXCHANGE RATE ON CONCENTRATION OF TIN(II) AND TIN(IV)

$(H^+) = 3.99$ M; $(Cl^-) = 1.00 M$

[Sn(II)] M	[Sn(IV)] M	k (obsd.) (l./mole hr.)
0.0048_7	0.0131_5	4.34
$.0088_5$	$.0131_5$	4.38
.0129	.0129	4.58
.0171	.0133	4.39
.0126	.0053	4.56
.0126	.0093	4.40
.0126	.0178	4.42

Above 0.5 M Cl^-, the exchange is of order 1.00 ± 0.03 in chloride, while it is about $^3/_2$ order in chloride below 0.5 M. With 1.00 M Cl^-, the order in Sn(II) is 1.00 ± 0.02 and 0.99 ± 0.04 in Sn(IV). Thus, for solutions more than 0.5 M in Cl^-, one can write

$$R = 4.94[\mathrm{Sn(II)}][\mathrm{Sn(IV)}][\mathrm{Cl}^-] \qquad (8)$$

where R is mole liters^{-1} hours^{-1}.

If one considers that $SnCl_6^=$ is the predominant species of tin(IV)[15] above 0.5 M Cl^- and that $SnCl_3^-$ is the principal tin(II) species,[16] then the expression indicates that exchange is between $SnCl_4^=$ and $SnCl_6^=$ which forms $Sn_2Cl_{10}^{-4}$. This forma-

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[15] L. Smith, *Z. anorg. Chem.*, **219**, 39 (1934).

[16] C. E. Vanderzee and D. E. Rhodes, THIS JOURNAL, **74**, 3552 (1952).

tion of the interaction dimer is in accord with our spectrophotometric data and the findings of previous workers.[1,2]

TABLE X

DEPENDENCE OF EXCHANGE RATE ON TEMPERATURE

$\mu = 4.98$; $(H^+) = 3.99\ M$; $(Cl^-) = 1.00\ M$

Temp., °C.	k (l./mole hr.)
25.0	4.58
37.8	19.3
49.7	88.5 (net)

The effect of temperature on the rate of exchange in 1.00 M Cl^- also was studied at three different temperatures (Table X). Once again, non-linear McKay plots were observed at 49.7°. The original curve is non-linear for the first 140 minutes. Beyond that time a straight line is obtained. Graphical subtraction of the extrapolated straight line results in another straight line, which suggests once again that the higher temperature has accelerated the hydrolysis of the Sn(IV) and the hydrolyzed species is (are) either extremely slow to exchange or possibly does (do) not exchange. The log of the rate, calculated from the slope of the net straight line, when combined with the data from the other temperatures was plotted against the reciprocal of the absolute temperature and the resulting Arrhenius plot is linear with $E_a = 22.6$ kcal./mole.

[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, MALLINCKRODT CHEMICAL WORKS, ST. LOUIS, MISSOURI]

Nickel(II) Complexes of N,N'-Disubstituted Dithiooxamides[1]

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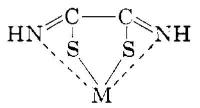
N,N'-Dimethyl- (I), N,N'-dibenzyl- (II), N,N'-dioctadecyl- (III), N,N'-bis-(2-hydroxyethyl)- (IV), N,N'-bis-(2-acetoxyethyl)- (V) and N,N'-bis-(3-dimethylaminopropyl)-dithiooxamide (VI) formed intensely colored nickel complexes (VII–XII), respectively. N,N'-Dimethyldithiooxamidonickel(II) (VII) is a low polymer whose size and terminal structure are dependent on both the manner of preparation and purification. VII is crystalline and paramagnetic. N,N'-Bis-(2-hydroxyethyl)-dithiooxamidonickel(II) (X) was acetylated, but the product (XIV) contains only half the number of acetyl groups of N,N'-bis-(2-acetoxyethyl)-dithiooxamidonickel(II) (XI) prepared directly from V. The reaction of I with trisethylenediaminenickel(II) ion gave a complex product (XIII) differing from VII. Certain primary alkylamines were found to react with I, and in the case of trisethylenediaminenickel(II) ion, such reaction may have occurred during the formation of XIII.

Introduction

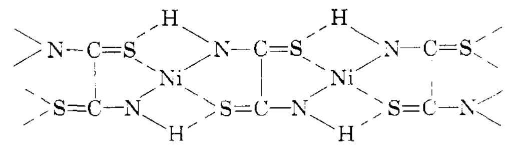
Dithiooxamide (rubeanic acid) has a long record of use as a reagent for the detection[2] and determination[3] of many metals, including nickel. Very little information has been published, however, concerning the structures and properties of dithiooxamidonickel(II) complexes, and until this year nothing had been reported on the structures and properties of N,N'-disubstituted dithiooxamidonickel(II) complexes.

Rây and Rây first proposed a structure (A) for dithiooxamidometal complexes in which "M" represents copper, cobalt or nickel.[4] This structure is of historical interest primarily, as today it must be regarded as improbable for steric reasons.



A

The nickel complex was found to be nearly diamagnetic.[5] Jensen then suggested that dithiooxamidonickel(II) was a polymer by analogy to the diamagnetic, tetracoördinate, nickel mercaptides, which were known to be polymers.[6] Recently, a study of the infrared absorption bands of dithiooxamidonickel(II) led Barceló to conclude that this complex had the polymeric structure B.[7]



B

Results and Discussion

Formation and Structure of N,N'-Disubstituted Dithiooxamidonickel(II) Complexes.—With all of the dithiooxamide derivatives examined, reaction with a nickel salt occurred instantaneously on admixture of the two starting materials in aqueous alcoholic solution at room temperature.

All of the complexes observed in this work were from dithiooxamides that were monosubstituted at both amido nitrogens. A completely substituted dithiooxamide, tetraethyldithiooxamide, that contains no amido hydrogens, did not react with nickel(II) ion in aqueous alcoholic solution.

N,N'-Dibenzyldithiooxamide (II), N,N'-dioctadecyldithiooxamide (III), N,N'-bis-(2-hydroxyethyl)-dithiooxamide (IV), N,N'-bis-(2-acetoxyethyl)-dithiooxamide (V) and N,N'-bis-(3-dimethylaminopropyl)-dithiooxamide (VI) formed nickel

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[1] Presented in part at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 18, 1959.

[2] F. Feigl, "Spot Tests," Vol. I, 4th Ed., translated by R. E. Oesper, Elsevier Publishing Co., New York, N. Y., 1954, pp. 83, 139, 145.

[3] (a) J. M. Pheline and R. Castro, *Congr. groupe avance method. anal. spectrograph produits met. Paris*, **8**, 47, 177 (1947); (b) I. V. Tananaev and S. Y. Levitman, *Zhur. Anal. Khim.*, **4**, 212 (1949); (c) S. V. Vaeck, *Anal. Chim. Acta*, **10**, 48 (1954); (d) F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., New York, N. Y., 1948, p. 148.

[4] P. Rây and R. M. Rây, *J. Indian Chem. Soc.*, **3**, 118 (1926).

[5] P. Rây and H. Bhar, *ibid.*, **5**, 497 (1928).

[6] R. A. Jensen, *Z. anorg. Chem.*, **252**, 227 (1944).

[7] J. Barceló, *Spectrochim. Acta*, **10**, 245 (1958).