[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY OF AGRICULTURE AND APPLIED SCIENCE]

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

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The kinetics of the reaction between tin(II) and cerium(IV) in aqueous sulfuric acid was studied in the temperature range from 0 to 25°. Three types of reaction were observed corresponding to (1) low sulfate ion and tin(IV) concentration, (2) high sulfate ion and tin(IV) concentrations and (3) the presence of colloidal tin(IV) in the solutions. Only the first type seems subject to interpretation and appears to represent the stepwise oxidation of tin(II) by the tris-sulfatocerate(IV) ion.

We have selected the reaction between tin(II) and cerium(IV) in sulfuric acid solutions for study for several reasons. Our primary interest has been in connection with oxidations which may proceed either by direct transfer of several electrons from reducing to oxidizing agent or alternatively by a stepwise loss of one electron at a time. We have also been intrigued by the possibility of finding evidence for the existence of tin(III) as an intermediate during oxidations of tin(II) or reductions of tin(IV).[2,3]

In hydrochloric acid the reaction between tin(II) and cerium(IV) is fast,[3] but other reactions in this medium, such as the tin(II)–uranium(VI) reaction[4] and the reduction of iron(III) by tin(II)[2,5–7] have been found slow enough that the rates could be measured. These reactions appear to go stepwise and in the second case the existence of a tin(III) intermediate has indeed been postulated,[2] although the over-all mechanism appears to be a matter of interpretation.[8,9]

Experimental

Equipment and Reagents.—Reaction rates were determined by using a Beckman Model DU spectrophotometer. The solutions were kept in 1 cm. spectrophotometer cells throughout the course of the reaction and the temperature of the cell housing was controlled to ±0.2° over the temperature range 0–25°.

The source of each reagent and method of determination of its concentration was as follows: ammonium hexanitratocerate(IV), obtainable from the G. F. Smith Chemical Company, was recrystallized, converted to the hydroxide then dissolved in concentrated sulfuric acid according to the method of Smith and Fly[10] and the resulting solution was diluted with distilled water and standardized with iron(II) in the presence of phosphoric acid using barium diphenylamine sulfonate as an indicator. Solutions of cerium(III) were obtained by reduction of cerium(IV) solutions with sulfur dioxide and after oxidation with sodium bismuthate, cerium concentrations were determined as before. Tin(II) solutions were prepared by the method of Noyes and Toabe[11] in that copper was displaced from sulfuric acid solution by metallic tin; aliquots of these solutions were analyzed by the dithiol method[12] using Santomerse 30m as surfactant. Lithium sulfate was recrystallized, dried until the anhydrous form was obtained and weighed directly. Tin(IV) sulfate was prepared by reaction of the metal with concentrated sulfuric acid at 190° and was recrystallized several times from the concentrated acid; tin(IV) oxide was obtained by ignition of the sulfate for 12 hours at 500°. Reagent grade sulfuric and perchloric acids were standardized volumetrically.

In general, particular pains were taken to exclude air from all solutions which were to be used in the rate studies, although no different results were obtained when the reactions were allowed to take place in solutions which were saturated with air (just before mixing the reactants). The solutions were prepared with air-free distilled water and were stored under nitrogen. The spectrophotometer cells in which the reactions were carried out, were capped and made reasonably air-tight with stopcock lubricant around the caps.

Spectrophotometric Determination of the Rate of Reaction.—At 315 mμ, absorbancies of tin(II) and (IV) in sulfuric acid are negligible; extinction coefficients of cerium(IV) and (III) are $\epsilon_4 = 5.58 \times 10^3$ and $\epsilon_3 = 2.7 \times 10^2$,[13] respectively, in sulfuric acid concentrations from 1 to 3 M. Thus the rate of reaction can be followed by absorbancy measurements upon the solution, by making suitable correction for cerium(III) present.

Solutions of tin(II) and cerium(IV) were mixed in the spectrophotometric cells. Generally, 1 ml. of tin(II) was forced into 2 ml. of cerium(IV); zero time was taken as the time mixing began; absorbancies were recorded for about 5 min. and then at $t_\infty = 50$ min. Whenever cerium(IV) > 2 tin(II) at $t = 0$, concentrations of both reactants were obtainable from the corrected optical densities. Because initial tin(II) concentrations were only determined from cerium(IV) absorbancies, at t_∞, and determinations of total tin, then if cerium(IV) < 2 tin(II) at $t = 0$, at $t = 5$ min. more standard cerium(IV) was added such that, at t_∞, cerium(IV) > 2 tin(II) = 0. In this way tin(II) concentrations were calculable from the absorbancy data.

The numerical values of k which are presented in this paper were determined graphically. The number of readings taken per experiment ranged from 15 to 25 with an average of 20 for all experiments reported.

Sulfate Ion, Bisulfate Ion, Hydrogen Ion and Ionic Strength Dependence.—Since the reaction rate was most easily measured at 0°, a study of the effect of the concentration of these ions and the ionic strength was performed at this temperature. Raman spectral data (leading to activity coefficient ratios) are available for sulfuric acid solutions at 25°.[14] For the purposes of this study, concentrations of the various ions were estimated in the following manner. Young, Klotz and Singleterry[15] values of the thermodynamic dissociation constants for bisulfate ion were used and it was assumed that (1) the molal activity coefficient ratio, $\gamma_{H^+} \cdot \gamma_{SO_4^=}/\gamma_{HSO_4^-}$, is essentially constant over the temperature range 0–25°, (2) the correspondence (as obtained by these approximations at 0°) of the molal dissociation constant of

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[1] Abstracted from a thesis submitted by Anita Jeanne Court to the School of Advanced Graduate Studies, Michigan State University, in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

[2] J. Weiss, *J. Chem. Soc.*, 309 (1944).

[3] A. E. Remick, THIS JOURNAL, **69**, 94 (1947).

[4] R. L. Moore, *ibid.*, **77**, 1504 (1955).

[5] A. A. Noyes, *Z. physik. Chem.*, **16**, 546 (1895).

[6] W. F. Timofeew, G. E. Muchin and W. G. Gurewitsch, *ibid.*, **115**, 161 (1925).

[7] F. R. Duke and R. C. Pinkerton, THIS JOURNAL, **73**, 3045 (1951).

[8] J. Gorin, *ibid.*, **58**, 1787 (1936).

[9] R. A. Robinson and N. H. Law, *Trans. Faraday Soc.*, **31**, 899 (1935).

[10] G. F. Smith and W. H. Fly, *Anal. Chem.*, **21**, 1233 (1949).

[11] A. A. Noyes and K. Toabe, THIS JOURNAL, **61**, 3342 (1939).

[12] W. Dupraw, private communication; *cf.* M. Farnsworth and J. Pekola, *Anal. Chem.*, **26**, 735 (1954).

[13] A. I. Medalia and B. J. Byrne, *ibid.*, **23**, 453 (1951).

[14] H. M. Smith, Ph.D. Dissertation, University of Chicago, 1949.

[15] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Ch. 14, Reinhold Publ. Corp., New York, N. Y., 1949.

bisulfate ion to the ionic strength is not altered by the presence of perchloric acid, lithium sulfate or cerium and tin species in solution and (3) both perchloric acid and lithium sulfate are essentially completely ionized. Molar concentrations of the various species were then calculated from molalities and known or measured densities. Ionic strengths recorded in the tables of results are actual ionic strengths computed from those molal concentrations.

Results

Most of the experiments were carried out at 0° with freshly prepared tin(II) and tin(IV) solutions and under such conditions that the oxidation of tin(II) by cerium(IV) followed a second-order rate law [first order in tin(II) and first order in cerium(IV)]. Throughout a range of $[Ce(IV)]_0/[Sn(II)]_0$ from 6.72 to 1.34 the average value of the second-order rate constant was 19.8 l./mole-sec. $[Ce(IV)]_0$ and $[Sn(II)]_0$ are the initial concentrations of the two reactants. The initial cerium(IV) concentrations ranged from 4.09×10^{-4} *M* to 1.44×10^{-4} *M* and the stoichiometric sulfuric acid concentration was 1–3 *M*. The results are collected in Table I and a typical run is shown graphically in Fig. 1.

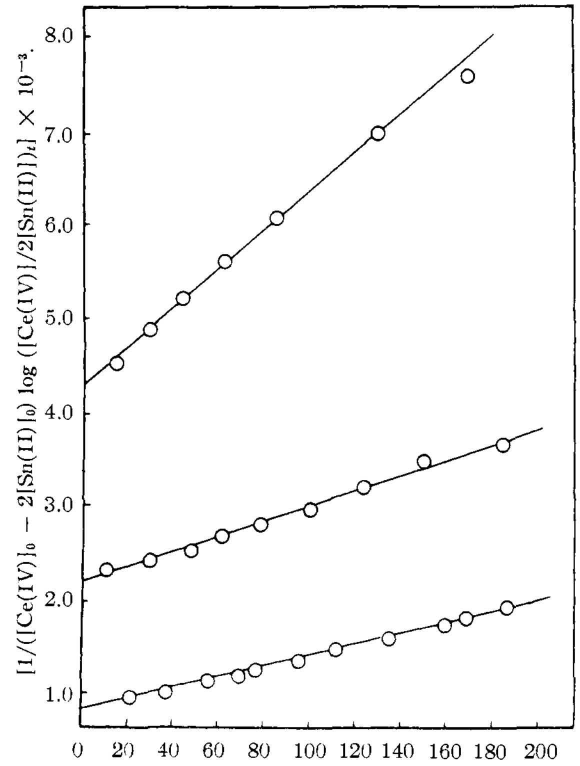

Fig. 1.—Kinetic treatment of "normal" second-order rates at 20° (upper curve), 10° (middle curve) and 0° (lower curve).

In the presence of added initial cerium(III), the rate constant was 18.3 l./mole sec. These results also appear in Table I. When tin(IV) is present to the extent that a suspension (concentrations greater than 5.9×10^{-4}) was visible in the reaction mixture, the average value of *k* was 17.8 l./mole sec. Similarly in the presence of an externally prepared tin(IV) oxide slurry, the average value of *k* was 21.2 l./mole sec.

If, however, a solution of tin(II) sulfate was aged, or exposed to air (by bubbling air through it for one to three hours), so that tin(IV) was formed in the presence of tin(II), and then was added to the reaction mixture, two successive phenomena were observed. At first, accelerated second-order rates were encountered (values of *k* were 30, 70 and even 100 l./mole sec.). These rates remained second order throughout the course of the reaction. No data are shown, since results were not reproducible, but examples are shown graphically in Fig. 2. Later, as the age of the tin(II) solutions increased, hence as more tin(IV) formed in the presence of tin(II), the rate became first order in tin(II) and independent of cerium(IV) concentration. The data are not tabulated, but examples are shown graphically in Fig. 3.

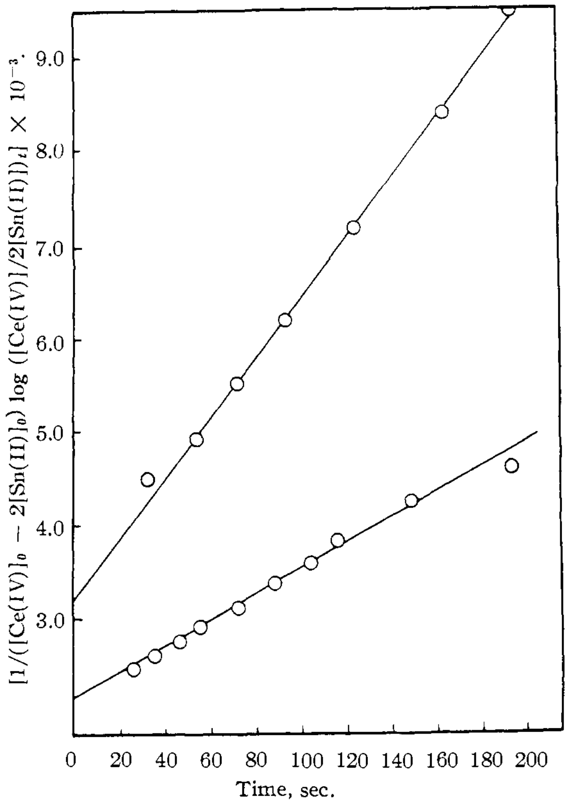

Fig. 2.—Kinetic treatment of accelerated second-order rates at two ionic strengths: upper curve, $\mu = 5.33$; lower curve, $\mu = 1.96$.

Had the small amount of iron(III) present ($10^{-3} \times [Ce(IV)]_0$) been responsible for the above phenomena, we should also observe some such effects upon placing additional iron(III) in the reaction mixtures; however, even when the iron concentration was increased to $0.1[Ce(IV)]_0$, no change in rate or order of the reaction was observed. The aged tin solutions were examined for the possible presence of copper or peroxides, but the dithizone test indicated no copper, and no peroxides could be detected by several of the usual tests for peroxide. Thus it seems that such species could not be responsible for the observed phenomena.

In practically all cases the orders of the reactions did not change (*i.e.*, second order, accelerated

TABLE I

SUMMARY OF SECOND-ORDER REACTION RATES AT 0°

No. of expt.	μ	$[H^+]$, *M*	$[HSO_4^-]$, *M*	$[SO_4^=]$, *M*	Other ions present, *M*	k_{av}, l./mole sec.
5	2.008	1.515	0.584	0.465		19.8 ± 2.4
12	2.005	1.488	.580	.453		
8	1.963	1.454	.556	.449		
8	1.879	1.367	.599	.384		
1	2.577	1.915	.656	.581		18.3
4	5.33	3.705	1.308	1.167		18.7 ± 4.2
6	5.33	2.321	0.917	1.335	Li^+, 1.268	23.5 ± 3.7
12	5.33	1.884	.774	1.406	Li^+, 1.705	26.0 ± 5.5
1	4.057	3.516	.568	0.418	ClO_4^-, 2.112	19.8
1	3.264	2.752	.573	.413	ClO_4^-, 1.353	15.4
9	2.965	2.444	.602	.428	ClO_4^-, 0.986	23.7 ± 4.3
9	2.573	2.307	.346	.223	ClO_4^-, 1.593	20.3 ± 1.4
16	2.483	1.974	.600	.431	ClO_4^-, 0.483	17.1 ± 3.1
12	2.305	0.776	.373	.631	Li^+, 0.859	23.1 ± 1.5
9	2.138	1.010	.463	.543	Li^+, 0.538	20.2 ± 1.1
13	1.326	1.077	.342	.227	ClO_4^-, 0.280	19.6 ± 2.1
10	2.024	1.477	.585	.454	Ce(III), 5.8×10^{-4}	18.3 ± 3.0
2	1.960	1.455	.562	.447	Ce(III), 5.8×10^{-4}	
3	2.577	1.915	.656	.581	$Sn(SO_4)_2$ slurry	20.4 ± 4.6
1	5.34	3.705	1.308	1.167	$Sn(SO_4)_2$ slurry	17.8
2	5.34	3.705	1.308	1.167	SnO_2 slurry	21.2 ± 0.7

second order or first order) during their course. There does not appear to be any quantitative correlation between the initial concentration of tin(IV) and either the acceleration of second-order rates or the magnitude of the first-order rates. Since the acceleration or change of order did not take place in the presence of externally prepared slurries of either tin(IV) sulfate or tin(IV) oxide, we assume that ordinary wall-catalysis is not responsible.

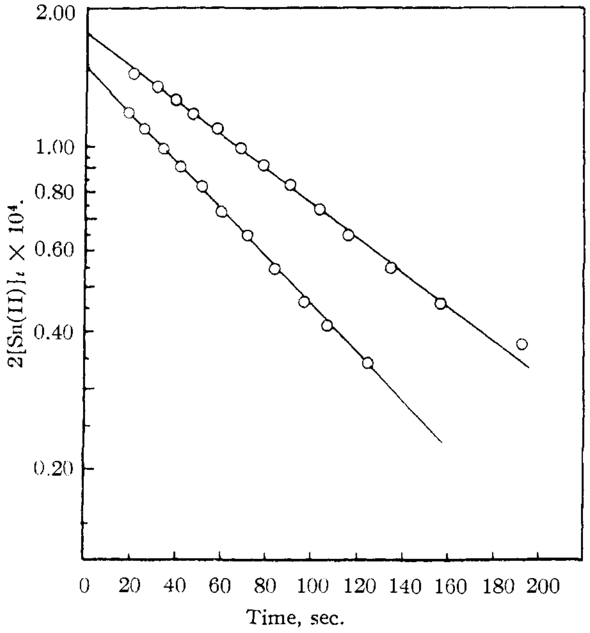

Fig. 3.—Kinetic treatment of rates first-order in tin(II) at 0° and two ionic strengths: upper curve, μ = 5.33; lower curve, μ = 1.83.

The "normal" second-order rates are independent of ionic strength, hydrogen, bisulfate and sulfate ion concentrations (Table I). Accelerated second-order rates do depend on the ionic strength of the solutions.[16]

We have not been able to correlate those rates which are first order in tin with ionic strength, hydrogen, bisulfate or sulfate ion concentrations. They may depend in a very complex manner on these quantities and the age, history and concentration of the tin solutions.

Reactions following both second-order and first-order rate laws were studied as a function of temperature, but only in the case of the "normal" second-order reactions could any correlation of rate and temperature be made (Table II).

TABLE II

RATE CONSTANTS FOR THE OXIDATION OF TIN(II) BY CERIUM(IV) AT VARIOUS TEMPERATURES ("NORMAL" SECOND-ORDER PROCESS)

No. of expt.	Temp., °C.	k_{av}, l./mole sec.
33	0	19.8 ± 2.4
4	5	26.0 ± 1.5
12	10	28.6 ± 4.2
10	15	56.3 ± 4.0
9	20	53.3 ± 2.0
3	25	62.9 ± 10.7

In the case of the second-order reactions, a graph of log *k versus* $1/T$ gives an experimental activation energy of 7.6 kcal. The *k* obtained at 0, 5, 20, 25° lie on a good straight line, but those from measurements at 10 and 15° lie off the Arrhenius plot.

Deviations reported for the rate constants are average deviations.

Discussion

Only the "normal" second-order reactions, those without large excesses of tin(IV), *i.e.*, carried out in freshly prepared tin(II) solutions, are readily subject to interpretation.

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[16] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," 1st Ed., Ch. VIII, McGraw-Hill Book Co., New York, N. Y., 1941.

From an examination of the work of Hardwick and Robertson,[17] we feel safe in assuming that, in all solutions we have used, the major species of cerium(IV) is the trissulfatocerate(IV) ion, $Ce(SO_4)_3^=$. Although, at present, equilibrium constants cannot be determined, a critical examination of the data of Denham and King[18] indicates that no higher tin(II) complexes than $SnSO_4$ are found in sulfuric acid solutions. Then we assume that the major (and reacting) species of tin(II) is the ion-pair (or complex), $SnSO_4$, thus the rate of the reaction may be moderately slow, compared to a reaction involving Sn^{++} and $Ce(So_4)_3^=$. If these are indeed the reacting species, it is not unreasonable to expect the rate to be independent of ionic strength,[16] although predictions at these high ionic strengths are not strictly justified.

The following mechanism is consistent with the "normal" second-order reaction which occurs at moderate sulfate ion concentrations

$$SnSO_4 + Ce(SO_4)_3^= \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{tin intermediate} \quad (1)$$

$$\text{tin intermediate} + Ce(SO_4)_3^= \xrightarrow{k_2} SnSO_4^{++} + 2Ce(SO_4)_2^- \quad (2)$$

If the first of these reactions is the rate-determining step and the steady-state approximation is made for the tin intermediate, and if k_{-1} is small, then the rate expression is obtained

$$\frac{-\mathrm{d}[Ce(SO_4)_3^=]}{\mathrm{d}t} = 2k_1[SnSO_4][Ce(CO_4)_3^=] \quad (3)$$

which is in agreement with the experimentally observed rate law.

The products shown for equation 2 are based on information available in the literature,[19,20] but there are no data which clearly establish the nature of the products of reaction 1. Equally probable are products such as $SnSO_4^+ + Ce(SO_4)_2^- + SO_4^=$ or a tin–cerium complex [*e.g.*, $SnCe(SO_4)_x^{6-2x}$]. As we have indicated in the introduction, we are not without precedent in postulating tin(III) as an intermediate.

We have obtained no experimental evidence concerning the nature or properties of the intermediate, aside from its reactivity. Visible and ultraviolet spectrophotometry give no evidence of an intermediate interaction complex [$SnCe(SO_4)_x^{6-2x}$] or a tin(III) species. That adding excess cerium(III) produces a negligible effect on the rate may mean that no sulfatocerate(III) is formed in reaction 1 or simply that k_{-1} is very small.

We cannot postulate a mechanism for the "accelerated" second-order reactions from the information found in the experimental data and can only point out that the observed second-order rate is suggestive of stepwise oxidation of tin(II).

Likewise the only statement that can be made concerning the first-order reactions is that the experimental evidence seems to indicate that the rate-determining step must be the adsorption of the tin(II) on some internally formed, colloidal, tin(IV) species.

Conclusions

It then appears that, in the absence of tin(IV) colloids, the oxidation of tin(II) by cerium(IV) in 1–3M sulfuric acid solutions proceeds along a two step path. The experimental evidence is compatible with the possibility that tin(III) exists as an intermediate; however, the data do not exclude alternatives such as tin–cerium sulfate complexes (*e.g.*, the $SnCe(SO_4)_x^{6-2x}$, which we have discussed). Of course, such a tin–cerium intermediate may contain either tin(III) and cerium(III) or tin(II) and cerium(IV).

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[17] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818, 828 (1951).

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

[19] F. H. Spedding and S. Jaffe, THIS JOURNAL, **76**, 884 (1954).

[20] C. H. Brubaker, Jr., *ibid.*, **77**, 2671 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Measurement of Diffusion Currents at Cylindrical Electrodes Using a Current Integrator

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The measurement of charge transferred during an increment of time shortly after the beginning of electrolysis has been found to provide an accurate method for studying diffusion currents at solid microelectrodes. By the use of short times of electrolysis, convection processes are avoided. Results obtained are in agreement with theory.

The use of solid electrodes for voltammetry at constant potential is often complicated by the contribution of convection processes to the mass transfer process. Mathematical treatments of diffusion currents at several shapes of stationary electrodes have been developed.[1] With plane or cylindrical electrodes, diffusion currents decrease with increasing time and no steady state should be observed. Limiting currents at cylindrical electrodes were observed by Laitinen and Kolthoff,[2] but convection apparently was involved. If convective processes are to be avoided, currents must be measured as functions of time at short times after the start of electrolysis. Such measurements

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[1] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chap. 3.

[2] H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).