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Kinetics of the Oxidation of Tin(II) by Cobalt(III) in Aqueous Perchlorate Solutions

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The rate law for the oxidation of tin(II) by cobalt(III) in perchlorate acid solutions is given by $-d[Co(III)]/dt = k'\cdot[Co(III)][Sn(II)]$, where $k' = k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$. The activation parameters associated with k_{-1} and k_{-2} are $\Delta H_{-1}^* = 13.2 \pm 0.3$ kcal/mol, $\Delta S_{-1}^* = 5.2 \pm 1$ cal/(mol deg), $\Delta H_{-2}^* = 17.4 \pm 0.8$ kcal/mol, and $\Delta S_{-2}^* = 17 \pm 3$ cal/(mol deg).

Introduction

Alternate mechanisms, involving either a sequence of one-electron steps or a single, two-electron step, are possible for the oxidation of Sn(II). Therefore, the reactions of Sn(II) with one-electron oxidants such as Co(III) are of mechanistic interest. Many[1-7] of the previous studies involving the reaction of Sn(II) with a variety of oxidants were carried out in hydrochloric or sulfuric acid solutions in order to prevent formation of insoluble stannic oxide. These complexing acids often affect the reaction rate and may even have an effect on the stoichiometry. Complex formation and its problems may be avoided by using perchloric acid as the solvent. Although the oxidation of Sn(II) in perchloric acid eventually produces colloidal stannic oxide, the rate of oxide formation is slow[8] compared to the rate of oxidation of Sn(II). As a result, oxide formation does not interfere with rate measurements made in perchloric acid solution.

Experimental Section

Materials. Solutions of tin(II) perchlorate were prepared, stored, and handled as described previously.[9] Most of the rate runs were made using solutions of cobalt(III) perchlorate prepared by the electrolytic oxidation of cobalt(II) perchlorate solutions. The electrolysis was carried out in a two-compartment cell employing a platinum gauze anode through which a current of 0.5 A was passed for 6–7 hr. During the electrolysis, the cell contents were stirred and were maintained at 0–5° with an ice bath. A few runs were made using Co(III) solutions prepared by a slight modification of the method of Hofmann-Bang and Wulff.[10] In this method, Co(II) is oxidized by hydrogen peroxide in the presence of potassium bicarbonate to yield solutions of tris(carbonato)cobaltate(III) ion. Acidification of the solutions produces solutions of the aquo ion. Solutions of iron(III) perchlorate were prepared from G. F. Smith iron(III) perchlorate which had been recrystallized three times. Lithium perchlorate was prepared by neutralizing the carbonate with perchloric acid. The salt was recrystallized twice from water before being used to prepare stock solutions.

Analyses. Stock cobalt(III) perchlorate solutions were analyzed for Co(III) by delivering an aliquot of the deaerated solution into a known excess of iron(II) sulfate solution followed by back-titration of the Fe(II) left after the Co(III)–Fe(II) reaction was complete. The Co(III) content of solutions used in kinetic experiments was determined spectrophotometrically at 250 nm. Total cobalt concentrations of stock solutions were determined spectrophotometrically[11] after reduction of the Co(III) with sodium sulfite. Cobalt(II) concentrations were determined from the difference in total cobalt and Co(III) concentrations.

Table I. Apparent Second-Order Rate Constants at Different Reactant Concentrations[a]

10^4[Co(III)]$_0$, *M*	10^4[Sn(II)]$_0$, *M*	$10^{-3}k'$, M^{-1} sec^{-1}	10^4[Co(III)]$_0$, *M*	10^4[Sn(II)]$_0$, *M*	$10^{-3}k'$, M^{-1} sec^{-1}
21.3	10.4	16.0	2.83	2.04	14.2
14.5	10.4	16.1	6.15	5.20	15.9
9.56	10.4	15.6[b]	14.2	18.0	15.3
5.74	10.4	15.7	14.0	31.0	14.4
1.25	10.4	15.3			

[a] Conditions: 20°, 1.0 *M* $HClO_4$, $\mu = 2.0$ ($LiClO_4$). [b] Co(III) prepared by bicarbonate method.

The Sn(II) content of the tin(II) perchlorate solutions was either determined iodometrically[12] or determined by addition of an aliquot to a known excess of vanadium(V) perchlorate solution followed by titration of the excess vanadium(V) with Fe(II) in 6 *M* sulfuric acid. In a few stoichiometry experiments Sn(II) was determined spectrophotometrically at 252.5 nm.

The acid concentration of metal ion solutions was calculated from a knowledge of the metal ion concentration and the total perchlorate concentration as determined by passage of an aliquot through a cation-exchange resin and titration of the hydrogen ion in the eluent.

Rate Measurements. The rate of the reaction was followed by measuring the decrease of the absorbance of Co(III) at either 402 nm or 604 nm as a function of time using a Durrum-Gibson D-110 stopped-flow spectrophotometer. Apparent second-order rate constants were calculated from the absorbance *vs.* time data.

Calculations. Apparent second-order rate constants and activation parameters were calculated using a nonlinear least-squares computer program.

Induction Experiments. Attempts were made to induce the slow[13] reaction between Sn(II) and Fe(III) by the addition of Co(III). In a typical experiment 0.034 mequiv of Co(III) was added to a stirred solution containing 0.359 mequiv of Sn(II) and 0.105 mequiv of Fe(III). In other experiments, the order of addition was Fe(III)–Co(III)–Sn(II). The reaction medium was 1.2–2.9 *M* $HClO_4$ at 22–24°. The amount of Fe(III) consumed was determined spectrophotometrically at 310 nm.

Results

Stoichiometry. The expected stoichiometry is given by

$$Sn(II) + 2Co(III) \rightarrow Sn(IV) + 2Co(II) \qquad (1)$$

The stoichiometry was checked by mixing Sn(II) and Co(III) in mole ratios ranging from 10:1 to 1:10, allowing the reaction to take place, and determining the amount of excess reactant left after the reaction was complete. Agreement between the

Table II. Effect of Hydrogen Ion and Temperature on the Apparent Rate Constant at $\mu = 2.0$ ($LiClO_4$)

Temp, °C	[HCl-O$_4$], *M*	$10^{-3}k'$, M^{-1} sec^{-1}	Temp, °C	[HCl-O$_4$], *M*	$10^{-3}k'$, M^{-1} sec^{-1}
2.0	0.30	14.1	20.0	0.25	100
	1.00	3.12		0.50	41.2
	1.75	1.65		1.00	15.9
10.0	0.30	27.6		1.50	10.2
	0.50	13.3		2.00	6.80
	1.00	6.25	27.0	0.50	66.4
	1.75	3.33		0.75	39.9
	1.90	3.03		1.00	27.0
				1.50	16.9
				1.90	12.4

Table III. Ionic Strength Effect[a]

μ, *M*	0.50	0.71	1.25	2.02	2.91	3.69
$10^{-3}k'$, M^{-1} sec^{-1}	32.8	35.4	37.3	41.1	39.8	43.4

[a] Conditions: 20°, $[HClO_4] = 0.50\ M$, $[Sn(II)]_0 = 5.15 \times 10^{-4}\ M$, $[Co(III)]_0 = (4.8\text{–}6.5) \times 10^{-3}\ M$, $LiClO_4$ medium.

amount expected based on eq 1 and the amount found was usually ±1% or better.

Metal Ion Dependence. At constant hydrogen ion concentrations, the Sn(II)–Co(III) reaction obeys the rate law

$$-d[Co(III)]/dt = k'[Sn(II)][Co(III)] \qquad (2)$$

where k' is the apparent second-order rate constant. Table I summarizes values of k' calculated from runs in which the initial reactant concentrations were varied. Experiments in which the initial concentration of Co(II) was as much as 500 times greater than the initial Co(III) concentration indicated that Co(II) had no effect on the rate. Tin(IV) when present initially at concentrations about 0.6 that of the initial Co(III) concentration also had no effect on the rate. Rate constants obtained from runs made at 604 nm were in excellent agreement with those obtained from runs which were made at 402 nm, the wavelength used for most of the runs.

Hydrogen Ion and Temperature Dependence. The effects of hydrogen ion and temperature on k' are summarized in Table II.

Ionic Strength Effect. The effect of ionic strength on k' was studied in a series of runs in which the ionic strength was varied from 0.50 to 3.69 *M*. The results are summarized in Table III.

Induction Experiments. When Co(III) is added to stirred solutions containing Sn(II) and Fe(III), some of the Fe(III) is consumed. The Co(III)–Sn(II) reaction apparently induces the slow Sn(II)–Fe(III) reaction. Induction factors, defined as moles of Fe(III) consumed per moles of Co(III) added, ranged from 0.3 to 0.6 depending upon the order of mixing of reagents and the acidity of the medium.

Interpretation and Discussion

The form of the rate law requires that the rate-determining step involve one Co(III) and one Sn(II). Because the overall stoichiometry and the stoichiometry of the rate-determining step differ, the reaction cannot occur in a single step and must produce reactive intermediates. Indeed the induced reduction of Fe(III) indicates the presence of reducing intermediates. The most likely intermediates are Sn(III) produced in an initial one-electron step or Co(I) produced in an initial two-electron step. The lack of product inhibition by either Co(II) or Sn(IV) prevents identification of the intermediate.

The nature of the Co(III) species present in aqueous, acid solutions has been the subject of some controversy. Dimerization has been suggested[13-15] to account for some of the behavior of Co(III) in aqueous solutions. Estimated values for the hydrolysis constant range from 0.22[16] to $<3 \times 10^{-3}$.[17] Davies and Warnqvist[18] have summarized the arguments regarding the nature of the Co(III) species present in solution. They estimated an upper limit of 250–500 for the dimerization constant at 25° in 0.05–0.5 *M* acid. They also estimated a best value of 2×10^{-3} for the hydrolysis constant at 25° and 1 *M* ionic strength and concluded that the predominant Co(III) species present in 1.0 *M* acid at 25° is Co^{3+}. Based on their estimates, we have assumed that the predominant Co(III) species present in our solutions is Co^{3+}. Under the conditions used in this study, the hydrolysis of Sn^{2+} is negligible.

The rate law (eq 2) can be rewritten in terms of the principal metal ion species Co^{3+} and Sn^{2+} to give

$$-d[Co(III)]/dt = k''[Co^{3+}][Sn^{2+}] \qquad (3)$$

where $k'' = k'(1 + K_h/[H^+])$ and K_h is the hydrolysis constant for Co^{3+}.

In order to specify the reaction pathways and the composition of the activated complexes formed in the rate-determining step, a rate law which includes the hydrogen ion dependence is needed. The data in Table II indicate that the hydrogen ion dependence is predominantly an inverse first-order dependence with some contribution from a minor term. Therefore, the most important net activation process[19] is

$$Sn^{3+} + Co^{3+} + H_2O \rightarrow [\ *]^{4+} + H^+ \qquad (4)$$

The minor term in the rate law may correspond to a second net activation process

$$Sn^{2+} + Co^{3+} + H_2O \rightarrow [\ *]^{3+} + 2H^+ \qquad (5)$$

which occurs consecutively or parallel with the process of eq 3 and gives rise to a $k_{-2}[H^+]^{-2}$ term in the rate law. Accordingly, the acid dependence may be represented by eq 6 or 7. The appropriate plots for both functions are reasonably linear.

$$k'' = k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2} \quad \text{(parallel paths)} \qquad (6)$$

$$1/k'' = 1/k_{-1}[H^+]^{-1} + 1/k_{-2}[H^+]^{-2} \quad \text{(consecutive paths)} \qquad (7)$$

Alternatively, the minor term may be a medium effect for which the acid dependence has the form

$$k'' = k_{-1}[H^+]^{-1}e^{\beta H} \qquad (8)$$

Table IV. Activation Parameters for the Sn(II)–Co(III) Reaction

Function	ΔH_{-1}^*, kcal/mol	ΔS_{-1}^*, cal/(mol deg)	ΔH_{-2}^*, kcal/mol	ΔS_{-2}^*, cal/(mol deg)	$10^2\beta$	$10^2\alpha$[a]	K_h	Weighted variance × 10^3
Eq 6	13.2 ± 0.3[b]	5.2 ± 1	17.4 ± 0.8	17 ± 3				4.4
Eq 6	13.2 ± 0.3	5.2 ± 1	17.4 ± 0.8	17 ± 3			0.002	4.4
Eq 6	13.1 ± 0.3	4.7 ± 1	18.2 ± 0.8	20 ± 3			0.030	4.4
Eq 6	12.3 ± 0.3	1.9 ± 1	20.7 ± 0.5	30 ± 2			0.22	4.7
Eq 7	14.3 ± 0.5	10.1 ± 2	12.2 ± 0.1	5 ± 4				8.8
Eq 8	13.2[c]	5.2[c]			9.4 ± 3.5	3.8 ± 3.3		41.7
Eq 8	13.7 ± 0.4	6.9 ± 1			15.5[c]	0.0[c]		38.4

[a] α is the temperature coefficient of β. [b] The uncertainties are standard deviations calculated by the least-squares program. [c] Treated as a fixed parameter.

Table V. Comparison of Observed and Calculated Values of k'

Temp, °C	[HCl-O_4], M	$10^{-3}k'$-(obsd)	$10^{-3}k'$(calcd)		
			Eq 5[a]	Eq 6[b]	Eq 7[c]
2.0	0.30	14.1	13.4	13.1	9.16
	1.00	3.12	3.02	3.21	3.06
	1.75	1.64	1.62	1.53	1.97
10.0	0.30	29.3	29.6	27.8	19.1
	0.50	13.3	14.9	15.6	11.8
	1.00	6.25	6.36	6.70	6.39
	1.75	3.33	3.37	3.16	4.10
	1.90	3.03	3.07	2.82	3.86
20	0.25	100	100	82.7	53.9
	0.50	41.2	37.2	37.6	28.0
	1.00	15.4	15.4	15.9	15.1
	1.50	10.1	9.52	9.19	10.9
	2.00	6.84	6.88	6.08	8.84
27	0.50	66.4	68.6	67.1	49.6
	0.75	39.8	39.8	40.8	34.4
	1.00	27.0	27.7	28.1	26.8
	1.50	16.9	17.0	16.1	19.3
	1.90	12.4	12.9	11.4	16.2

[a] Based on values from line 1, Table IV. [b] Based on values from line 5, Table IV. [c] Based on values from line 6, Table IV.

Table VI. Thermodynamic Quantities of Activation

Net activation process	ΔH^*, kcal/mol	ΔS^*, cal/(mol deg)	S^*(complex), cal/(mol deg)	Ref
$Sn^{2+} + Co^{3+} + H_2O \rightarrow [\ *]^{4+} + H^+$	13.2	5.2	−58	This work
$Sn^{2+} + VO_2{}^+ + H^+ \rightarrow [\ *]^{4+}$	6.0	−39.5	−60	9
$Sn^{2+} + 2VO_2{}^+ \rightarrow [\ *]^{4+}$	3.9	−29.5	−55	9
$Fe^{2+} + Co^{3+} + H_2O \rightarrow [\ *]^{4+} + H^+$	18.8	16.0	−66	20
$Cr^{2+} + Co^{3+} + H_2O \rightarrow [\ *]^{4+} + H^+$	12.7	1.7	−70	21
$Mn^{2+} + Co^{3+} + H_2O \rightarrow [\ *]^{4+} + H^+$	16.1	6.0	−67	22
$Sn^{2+} + Co^{3+} + H_2O \rightarrow [\ *]^{3+} + 2H^+$	17.4	16.7	−46	This work
$UO_2{}^+ + V^{3+} + H_2O \rightarrow [\ *]^{3+} + 2H^+$	22.1	12.9	−52	23
$NpO_2{}^+ + U^{4+} + 2H_2O \rightarrow [\ *]^{3+} + 2H^+$	32.2	26.2	−41	24
$VO_2{}^+ + V^{3+} + H_2O \rightarrow [\ *]^{3+} + H^+$	16.5	7.1	−47	25

The data in Table II were used to calculate values for the activation parameters associated with k_{-1} and k_{-2}. The calculations were made using a least-squares program which simultaneously uses the acid and temperature dependences to calculate the values of the activation parameters which best reproduce the observed value of k'. The calculations were carried out for each of the interpretations of the minor term in the rate law. The effect of various assumptions regarding the magnitude of the hydrolysis constant, K_h, was also examined. The results of the calculations are summarized in Table IV.

It is apparent from the data in Table IV that replacing the k_{-2} term in the rate law with a Harned term gives a distinctly poorer fit of the data. Except for the highest reported[16] value of K_h, inclusion of a hydrolysis correction has essentially no effect on the quality of the fit or the value of the activation parameters for the major term in the rate law. The parallel path function reproduces the experimental data somewhat better than the consecutive path function. A comparison of observed and calculated values of k' for the three functions is shown in Table V.

The parallel-path function gives calculated values which agree within ±6% of the observed values for k' for 16 of the 18 data points; whereas the consecutive-path function reproduces the experimental data within ±6% for 8 of the 18 points. Although the consecutive pathway cannot be excluded unequivocally, the slightly better fit to the parallel path function and the greater frequency of occurrence of parallel paths suggest that the minor term in the rate law probably corresponds to a parallel path with an inverse second-order hydrogen ion dependence as shown in eq 6.

Table VI compares activation parameters obtained for the Sn(II)–Co(III) reaction with those of some other reactions in which activated complexes of 4+ and 3+ charges are formed.

Although the value of S^*(complex) for the activated complex of 4+ charge falls on the upper end of the range of values reported[26] for complexes of charge 4+, it agrees very well with the entropies of the 4+ complexes formed in the Sn(II)–V(V) reaction. The entropy of the 3+ complex is about average for complexes of that charge.

In summary, the oxidation of Sn^{2+} by Co^{3+} takes place by a multistep mechanism which produces a reactive intermediate, most likely Sn(III). The most important activated complexes, $[SnCoOH^*]^{4+}$ and $[SnCo(OH)_2{}^*]^{3+}$ are produced from Co^{3+}, Sn^{2+}, and H_2O by parallel pathways.

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