Table VIII compares the formation and dissociation rate constants of ammonia and some aminocarboxylates with nickel(II). A second glycine coordinates faster than the first but a second IDA is slower to coordinate than the first. The difference in electrostatic attraction accounts in part for this behavior but there also is a difference in lability of some of the coordinated water. Thus, the ammonia substitution for water is faster with $NiNH_3(H_2O)_5^{2+}$ than it is for $Ni(gly)(H_2O)_4^+$ than it is for $NiIDA(H_2O)_3^0$. The increased value of $k_d^{NiL_2}$ compared to k_d^{NiL} may also be largely an electrostatic effect.

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The Kinetics of the Oxidation of Tin(II) by Vanadium(V) in Aqueous Perchlorate Solutions

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In perchlorate solutions Sn(II) and V(V) react to produce Sn(IV) and V(IV). The rate of the reaction is given by: $-d[V(V)]/dt = k_3'[Sn(II)][V(V)]^2 + k_2'[Sn(III)][V(V)]$ where $k_2' = k_{21}[H^+]$ and $k_3' = k_{30} + k_{31}[H^+]$ or $k_{30}e^{\beta[H^+]}$. The activation parameters associated with k_{21} and k_{30} are: $\Delta H^* = 6.0 \pm 0.2$ kcal/mol, $\Delta S^* = 39.2 \pm 0.8$ cal/mol deg, $\Delta H^* = 3.9 \pm 0.3$ kcal/mol, $\Delta S^* = -29.5 \pm 1.1$ cal/mol deg. Some plausible mechanisms for the reaction are considered.

Introduction

Because the oxidation of Sn(II) may involve either a single, two-electron step or successive one-electron steps, the oxidation of Sn(II) is of mechanistic interest. In order to prevent the formation of colloidal stannic oxide, hydrochloric and sulfuric acids have been used[2-5] as solvents in previous studies. The use of these complexing solvents makes difficult unambiguous interpretation of the results. The problem of complex formation can be avoided by the use of perchlorate solutions. We have found[6] that the formation of stannic oxide is slow compared to the rate of oxidation of Sn(II) and that rate studies can be carried out in perchloric acid.

In hydrochloric acid the reaction between excess Sn(II) and V(V) produces both V(III) and V(IV) and the rate is reported[7] to be too fast to measure by conventional techniques. In contrast, the reaction in perchloric acid is slow and V(IV) is the only vanadium product.

Experimental Section

Materials.—Tin(II) perchlorate was prepared by the reaction of excess tin metal with copper(II) perchlorate dissolved in perchloric acid under conditions which allowed the isolation and recrystallization of the Sn(II) compound. In a typical preparation 12 g of tin was allowed to react overnight with *ca.* 14 g of the hydrated copper salt dissolved in 32 ml of 9 *M* $HClO_4$. The reaction mixture was then filtered through a glass frit and 50 ml of concentrated $HClO_4$ was added to the filtrate. Cooling the acid solution in an ice-salt bath yielded *ca.* 8 g of crystalline product. The crystals were recrystallized from 25 ml of warm, 65°, concentrated $HClO_4$. Apparently the reaction conditions are critical. Shortly after combining the reactants, in a preparation in which the quantities of reactants were doubled, the reaction mixture began to evolve fumes and became sufficiently hot to char the laboratory bench. All preparations of tin(II) perchlorate should be carried out with adequate safety precautions.

Stock solutions of tin(II) perchlorate were prepared by dissolving the solid in concentrated $HClO_4$ and diluting to an appropriate volume with water. All operations involving Sn(II) were carried out in an argon atmosphere.

Vanadium(V) perchlorate solutions were prepared by dissolving vanadium pentoxide in perchloric acid. The oxide was prepared by ignition of ammonium metavanadate at 400°.

Potassium trioxalatocobalt(III) was prepared according to published[8] methods.

Lithium and sodium perchlorates were prepared by neutralizing the metal carbonate with perchloric acid. The salt was recrystallized twice from water.

Analyses.—The Sn(II) content of the tin(II) perchlorate solutions was determined by treating an aliquot of the solution with a known excess of cerium(IV) sulfate and back-titration of the excess Ce(IV) with Fe(II) after the Sn(II)–Ce(IV) reaction was complete. The acid concentration of the Sn(II) solutions was calculated from a knowledge of the Sn(II) concentration and the total perchlorate concentration determined by passage of an aliquot through a cation-exchange resin and titration of the hydrogen ion in the eluent.

Vanadium(V) was determined by titration with Fe(II) in 6 *M* sulfuric acid.[9] The acid concentration of the vanadium(V) solutions was taken as the difference between the amount of acid initially added and the amount consumed by the reaction of vanadium pentoxide and perchloric acid.

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Vanadium(IV) was determined spectrophotometrically.

Rate Runs.—The apparatus and procedures used to measure the reaction rates was essentially the same as described by Newton and Baker.[10] The rate of the reaction was followed by measuring either the V(V) absorbance at 320–360 nm or the V(IV) absorbance at 760 nm as a function of time. In most runs the reaction was followed to 85–90% completion.

Calculations.—A computer program which utilizes the differential form of the rate law[11] was used to calculate apparent rate constants from the absorbance *vs.* time data. Values of activation parameters were calculated by the use of a nonlinear least-squares computer program.

Results

Stoichiometry.—When V(V) is present in a twofold or greater molar excess, V(III) cannot be a final product of the V(V)–Sn(II) reaction because any V(III) produced would react rapidly[12] with the excess V(V). The results of stoichiometry experiments with V(V) present in small excess confirmed that 2 mol of V(V) is consumed per mole of Sn(II) In chloride solutions large excesses of Sn(II) react with V(V) to produce V(III) as the major vanadium product. The stoichiometry was studied with Sn(II) in excess by spectrophotometrically determining the amount of V(IV) produced. If V(III) were produced, the observed absorbance at 7600 Å should be less than that calculated assuming V(V) to be the only vanadium product. The results are summarized in Table I. The data in Table I indicate that even where Sn(II) is present in a tenfold molar excess the stoichiometry is represented by

$$\mathrm{Sn(II)} + 2\mathrm{V(V)} \longrightarrow \mathrm{Sn(IV)} + 2\,\mathrm{V(IV)} \qquad (1)$$

TABLE I

RESULTS OF THE STOICHIOMETRY STUDY IN EXCESS TIN(II)[a]

$[\mathrm{Sn(II)}]_0$, mmol	$[\mathrm{V(V)}]_0$, mmol	mmol of V(IV) produced/mmol of V(V) added
0.166	0.144	1.00
1.140	0.110	1.01
1.740	0.110	0.89
1.910	0.110	0.91

[a] Conditions: 25°, 1.00 *M* $HClO_4$, 60-ml volume.

Metal Ion Dependence.—The data in Table II clearly indicate that the rate of the Sn(II)–V(V) reaction does not obey the usual second-order rate law. At the higher vanadium concentrations the data fit eq 2 reasonably well. However, in a large excess of

$$\frac{-\mathrm{d}[\mathrm{V(V)}]}{\mathrm{d}t} = k_3[\mathrm{V(V)}]^2[\mathrm{Sn(II)}] \qquad (2)$$

Sn(II) at low vanadium concentrations the data fit eq 3 fairly well and fit eq 2 very poorly. Such behavior

$$\frac{-\mathrm{d}[\mathrm{V(V)}]}{\mathrm{d}t} = k_2[\mathrm{V(V)}][\mathrm{Sn(II)}] \qquad (3)$$

suggests that all of the data should fit the two-term rate law

$$\frac{-\mathrm{d}[\mathrm{V(V)}]}{\mathrm{d}t} = k_3'[\mathrm{V(V)}]^2[\mathrm{Sn(II)}] + k_2'[\mathrm{V(V)}][\mathrm{Sn(II)}] \qquad (4)$$

Support for the third- plus second-order rate law is given by the fact that a plot of (initial rate)/$[\mathrm{V(V)}]_0$ *vs.* $[\mathrm{V(V)}]_0$ at a constant $[\mathrm{Sn(II)}]_0$ is linear. Calculation of k_2' and k_3' from the intercept and slope gives values of 0.44 M^{-1} sec^{-1} for k_2 and 2900 M^{-2} sec^{-1} for k_3. Additional support is given in Table II by the nearly constant value obtained for k_3', the third-order constant corrected for the second-order term.

Either term of the rate law can be made to predominate by adjustment of the reactant concentrations. Although both constants could not be determined simultaneously, good estimates of k_2' and k_3' could be obtained from runs in which one of the terms can be neglected. For example, runs 12–14 of Table II give an estimate of 0.60 M^{-1} sec^{-1} for k_2'. Since this value of k_2' is not corrected for k_3', it must be larger than the true value of k_2'. Calculation of k_3' for runs 1–3 fixing k_2' at 0.60 M^{-1} sec^{-1} gives a value of 2900 M^{-2} sec^{-1} for k_3'. Since the estimate used for k_2' was too large, the value obtained for k_3' must be too small and the true value must lie between 3200 and 2900 M^{-2} sec^{-1}. Calculation of k_2' for runs 12–14 fixing k_3' in the range 3200–2900 M^{-2} sec^{-1} gives a value of 0.46 M^{-1} sec^{-1} for k_2'. The values calculated for k_3' in Table II were obtained by fixing k_2' at 0.46 M^{-1} sec^{-1}.

TABLE II

APPARENT RATE CONSTANTS AT VARIOUS INITIAL REACTANT CONCENTRATIONS[a]

Run	$[\mathrm{V(V)}]_0$, M	$10^3[\mathrm{Sn(II)}]_0$, M	k_2, M^{-1} sec^{-1}	$10^{-3}k_3$,[b] M^{-2} sec^{-1}	$10^{-3}k_3'$,[c] M^{-2} sec^{-1}
1	5.59	1.08	13.5	3.19	3.09
2	5.59	0.868	14.6	3.17	3.07
3	5.59	0.434	16.0	3.13	3.05
4	2.80	0.434	7.40	3.09	2.90
5	2.80	0.217	7.94	3.06	2.88
6	2.80	0.108	8.02	3.05	2.88
7	1.32	0.514	3.14	3.47	2.96
8	1.32	0.257	3.74	3.44	3.03
9	0.992	0.770	2.06	3.58	2.89
10	0.661	0.514	1.64	4.11	2.98
11	0.272	0.634	0.96	6.04	3.18
12	0.105	1.28	0.60	11.9	2.87
13	0.079	1.03	0.60	14.6	3.42
14	0.079	0.513	0.60	12.6	3.08

[a] Conditions: 20°, 1.0 *M* $HClO_4$, μ = 2.0 ($LiClO_4$). [b] No correction made for second-order term. [c] Two-term rate law, with k_2' fixed at 0.46 M^{-1} sec^{-c}.

Runs in which the reaction products, Sn(IV) and V(V), were present initially at concentrations 2–10 times higher than the concentration of the limiting reagent indicate that the products have no effect on the rate. Rate constants obtained for runs in which V(IV) appearance was followed were in excellent agreement with those obtained for runs in which V(V) disappearance was monitored.

Hydrogen Ion and Temperature Dependence.—The effect of hydrogen ion and temperature on the apparent second- and third-order rate constants was determined. In general, the acid dependence of k_2' and k_3' was determined from runs in which the contribution of the term of interest accounted for nearly all of the rate.

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(10) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

(11) We are indebted to Drs. T. W. Newton and R. H. Moore of the Los Alamos Scientific Laboratory for making this program available.

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Refined values of k_2' and k_3' were calculated as described above. The formation of colloidal tin(IV) oxide restricted the range of acidity and temperature that could be studied. The results are summarized in Table III.

TABLE III

THE EFFECT OF HYDROGEN ION AND TEMPERATURE ON THE APPARENT RATE CONSTANTS AT μ = 2.0 ($LiClO_4$)

Temp, °C	[$HClO_4$], M	k_2', M^{-1} sec^{-1}	k_3', M^{-2} sec^{-1}
10	0.50	0.17	2190
	1.00	0.37	2250
	1.50	0.46	2410
	2.00	0.58	2470
20	0.50	0.25	2680
	1.00	0.46	2900
	1.50	0.72	3020
	2.00	0.91	3130
30	0.50	0.33	3600
	1.25	0.89	
	1.50	1.01	3880
	1.75	1.24	
	2.00	1.29	4040

Ionic Strength and Medium Effect.—The effect of ionic strength on the values of k_2' and k_3' was studied in a series of runs in which μ was varied from 0.50 to 3.00 M. The results are summarized in Table IV. Substitution of $NaClO_4$ for $LiClO_4$ did not change the values of k_2' and k_3' significantly.

TABLE IV

IONIC STRENGTH EFFECT[a]

μ, M	0.50	1.50	2.00	3.00
k_2', M^{-1} sec^{-1}	0.11	. . .	0.24	0.35
k_3', M^{-2} sec^{-1}	867	1980	2760	4910

[a] Conditions: 20°, [$HClO_4$] = 0.50 M, $LiClO_4$ medium.

Chloride Effect.—The effect of chloride ion on the rate of the reaction was determined with chloride ion concentrations in the range 1.5×10^{-3} to 1.5×10^{-2} M and metal ion concentrations 1.7×10^{-3} M. The addition of chloride markedly increases both rate constants. Metal ion dependences carried out at a constant chloride concentration give constant values of k_2' but varying values of k_3' indicating some departure from the rate law of eq 4.

Induction Experiments.—The induced reduction of $K_3Co(C_2O_4)_3$ has been used to detect the presence of Sn(III).[13] Attempts to detect Sn(III) as a possible reactive intermediate were made by allowing Sn(II) and V(V) to react in presence of the Co(III) complex. Experiments were performed with the initial Sn(II) and Co(III) concentrations 1×10^{-3} M and with the initial V(V) concentration either 6×10^{-3} M (k_3' predominant) or 6×10^{-5} M (k_2' predominant). In either case no consumption of Co(III) complex, other than that due to aquation, could be detected. Vanadium(III), another possible intermediate, does not react with the Co(III) complex. The results of the induction experiments suggest either that Sn(III) is not an intermediate or that the Co(III) complex cannot compete with V(V) for it.

Interpretation and Discussion

The data in Table III show that the value of k_2' is much more dependent on hydrogen ion concentration than is the value of k_3'. A plot of k_2' *vs.* [H^+] is linear with an intercept very near zero. The acid dependence of k_2' can be represented by eq 5, where k_{20} is very small. A plot of k_3' *vs.* [H^+] is also linear with the slope equal to about 10% of the value of the intercept. The minor term may be interpreted as a minor path, eq 6, or a medium effect, eq 7.

$$k_2' = k_{21}[H^+] + k_{20} \tag{5}$$

$$k_2' = k_{31}[H^+] + k_{30} \tag{6}$$

$$k_3' = k_{30}e^{\beta[H^+]} \tag{7}$$

It is of interest to use the data in Table III to calculate values for the activation parameters associated with the rate constants. The calculations were made using a least-squares program in which the hydrogen ion and temperature data were used simultaneously to find values of the activation parameters which best reproduce the experimental data. The results of the calculations are shown in Tables V and VI.

TABLE V

ACTIVATION PARAMETERS FOR k_{20} AND k_{21}

ΔH_{20}*, kcal/mol	ΔS_{20}*, cal/mol deg	ΔH_{21}*, kcal/mol	ΔS_{21}*, cal/mol deg	Weighted variance × 10^3
-7.20 ± 16[a]	-91.8 ± 55	6.42 ± 0.5	-38.2 ± 1.5	5.45
. . .	. . .	6.01 ± 0.2	-39.2 ± 0.8	5.46

[a] The uncertainties are standard deviations calculated by the least-squares program.

The large uncertainties in the activation parameters corresponding to k_{20} and the fact that omission of this term has little effect on either the quality of the fit or the values of ΔH_{21}* and ΔS_{21}* indicate that the hydrogen ion dependence of k_2' is adequately described by

$$k_2' = k_{21}[H^+] \tag{8}$$

The data in Table VI show that the minor term in the hydrogen ion dependence of k_3' can be explained equally well by a medium effect or a zero-order hydrogen ion term.

Table VII compares activation parameters[9,14-19] obtained for the Sn(II)–V(V) reaction with those for some other reactions in which activated complexes of charge +4 are formed. Newton and Rabideau[20] have pointed out the correlation between S*(complex) and the charge on the activated complex. Although the values of S*(complex) for the activated complexes for

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TABLE VI

ACTIVATION PARAMETERS FOR k_{30} AND k_{31}

ΔH_{30}*, kcal/mol	ΔS_{30}*, cal/mol deg	ΔH_{31}*, kcal/mol	ΔS_{31}*, cal/mol deg	β	α[b]	Weighted variance × 10^3
3.87 ± 0.4[a]	−28.6 ± 1.2	2.07 ± 2.7	−40.4 ± 9.2			1.75
3.91 ± 0.3	−29.5 ± 1.1	...	...	0.12 ± 04	0.01 ± 0.0001	1.74

[a] The uncertainties are standard deviations calculated by the least-squares program. [b] α is the temperature coefficient of the Harned term.

TABLE VII

THERMODYNAMIC QUANTITIES OF ACTIVATION

Net activation process	ΔH*, kcal/mol	ΔS*, cal/mol deg	ΔS* (complex), cal/mol deg	Ref
$VO_2^+ + Sn^{2+} + H^+ \rightarrow [*]^{4+}$	6.0	−39.5	−60	This work
$2VO_2^+ + Sn^{2+} \rightarrow [*]^{4+}$	3.9	−29.5	−55	This work
$VO_2^+ + Fe^{2+} + H^+ \rightarrow [*]^{4+}$	1.5	−37	−70	9
$NpO_2^+ + Fe^{2+} + H^+ \rightarrow [*]^{4+}$	8.6	−38	−69	14
$Fe^{2+} + Fe^{3+} + H_2O \rightarrow [*]^{4+} + H^+$	19.4	+9	−70	15
$Cr^{2+} + Cr^{3+} + H_2O \rightarrow [*]^{4+} + H^+$	22	−2	−79	16
$Fe^{2+} + Co^{3+} + H_2O \rightarrow [*]^{4+} + H^+$	19	16	−66	17
$V^{3+} + VO^{2+} + H_2O \rightarrow [*]^{4+} + H^+$	20	−3	−77	18
$V^{2+} + VO^{2+} \rightarrow [*]^{4+}$	12	−76	−65	19

the Sn(II)–V(V) reaction are somewhat lower than the average for complexes of charge +4, they fall within the range −50 to −88 compiled[21] for complexes of charge +4.

Although rate laws give information regarding the compositions of the most important activated complexes formed in the course of the reaction, they give little information about the details of the reaction mechanism. A valid mechanism for a reaction must be in accord with the experimental observations. Therefore, it is of interest to examine plausible mechanisms to determine whether they are in accord with the experimental data.

Noncomplementary reactions, such as the Sn(II)–V(V) reaction, often involve a reactive intermediate. Plausible reactive intermediates are V(III), produced in an initial two-electron change, or Sn(III), produced by an initial one-electron change. A mechanism in which V(III) is a reactive intermediate is

$$\mathrm{Sn(II)} + \mathrm{V(V)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Sn(IV)} + \mathrm{V(III)}$$

$$\mathrm{V(III)} + \mathrm{V(V)} \xrightarrow{k_2} 2\mathrm{V(IV)}$$

Assuming steady-state behavior for V(III) leads to the rate law

$$\frac{-\mathrm{d}[\mathrm{V(V)}]}{\mathrm{d}t} = \frac{2k_1k_2[\mathrm{Sn(II)}][\mathrm{V(V)}]^2}{k_{-1}[\mathrm{Sn(IV)}] + k_2[\mathrm{V(V)}]} \qquad (9)$$

The rate law for the proposed mechanism indicates that Sn(IV) should inhibit the rate and that at high V(V) concentrations the rate law should approach overall second-order behavior. The experimental facts are that the products have little or no effect and that at high V(V) concentrations nearly clean third-order behavior is observed. Therefore, the proposed mechanism cannot be the only path by which reactants are converted to products. Similar arguments can be brought to bear against a single-path mechanism involving Sn(III) as an intermediate. Since −d[V(V)]/dt = d[V(IV)]/dt, the formation of long-lived intermediates is ruled out.

The form of the rate law requires that the reactants be converted to products *via* two parallel paths. The most important activated complexes[22] are formed by the net activation processes

$$VO_2^+ + Sn^{2+} + H^+ \longrightarrow [VO_2HSn^*]^{4+} \qquad (10)$$

$$2VO_2^+ + Sn^{2+} \longrightarrow [(VO_2)_2Sn^*]^{4+} \qquad (11)$$

Because the stoichiometry of eq 10 and the overall reaction stoichiometry are different, the second-order path must involve an intermediate. Both V(III) and Sn(III) are plausible intermediates. Deviations from 2:1 stoichiometry at high Sn(II) concentrations suggest production of V(III) and lend some support to the speculation of V(III) as an intermediate in the second-order path.

Although kinetic data do not allow one to determine how the activated complex [$(VO_2)_2Sn^*$] is formed, one can postulate two possible routes for its formation. One such route is the reaction of V(V) with a V(V)–Sn(II) species formed in a rapid preequilibrium. If formation of the V(V)–Sn(II) "complex" is important, one might expect a decrease in k_{obsd} at very high Sn(II) concentrations. Runs made with $[\mathrm{Sn(II)}]_0$ as high as 0.08 *M* do not show any decrease in k_{obsd}, perhaps because the second-order term strongly predominates under these conditions.

The third-order term could also be accounted for by the reaction of Sn(II) with V(V) "dimer." Cobble and LaSalle[23] stated that VO_2^+ is the only important V(V) species present if the acid concentration is 0.10 *M* or greater and we can find no spectrophotometric evidence for existence of the dimer. However, the possible existence of a highly reactive V(V) dimer has been considered as a possible explanation for the second-order vanadium(V) dependence in the V(IV)–V(V) exchange[24] and in the V(V) oxidation of $Ta_6Br_{12}^{2+}$.[25]

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