be conducted with extreme caution. Unless experimental conditions in the two cases are identical, such subsidiary reactions may occur on parts of the surface which are not operative in the catalysis." Our picture of a catalyst surface which must be defined with the help of *all* effective parameters both external and internal, gives a clear understanding of this perturbation. At the same time, the induced heterogeneity of our model of a catalyst surface in an intermediate state of dynamic equilibrium gives fresh information on the nature of the active centers. The existence of active centers depends on the postulate that *all the sites* may not be active *all the time*. In the past, various efforts have been made to identify the centers with points, holes, edges, steps, planes, etc., with the idea that only a *fraction of the sites* is active *all the time*. These attempts now appear futile: the postulate may also be fulfilled if *all the sites* are active only *part of the time*. This dynamic picture of the active centers is a direct consequence of our model of a catalyst surface.

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The Oxidation of Stannate(II) Ion by Some Cobalt(III) Complexes[1]

BY RICHARD C. PINKERTON AND FREDERICK R. DUKE

The oxidation of stannate(II) ion by hexammine- and hydroxypentamminecobalt(III) ions was found to be zero-order in the cobalt(III) concentration. Upon standing in strongly basic solution, however, the hydroxypentamminecobalt(III) was found capable of participating in a rate-determining reaction. For the hexammine complex, the reaction was found first-order in hydroxide concentration and near half-order in stannate(II) concentration. It is proposed that stannate(II) ion exists in solution chiefly as a dimer, and that some active form of the monomer is responsible for the reduction. Of a number of anions tested for catalytic effect, cyanide and thiosulfate were found to accelerate the reaction. However, the hexacyanocobaltate(III) ion cannot be reduced by stannate(II) ion. Cyanide is also the only one of the pseudohalides tried which will replace ammonia in the cobalt(III) complexes at a rate appreciable enough to influence the reduction.

Introduction

The reactions of complex cobalt(III) ions with stannate(II) ion are of interest for several reasons. First, much information can be obtained concerning the effect of certain anions on the rates of oxidation-reduction reactions. It has been shown previously that the accelerating effect of halides on the ferric-stannous reaction is correlated with the oxidizability of the halide used.[2] It is possible that in such reactions, the anion should be closely bound to the oxidizing agent in the activated complex in order for it to be effective. Unlike ferric ion, cobalt undergoes complexing reactions which are, as a rule, much slower than its reductions. For reductions of the type which are accelerated by anions, the activated complex would be in equilibrium only with the cobalt(III) complexes already containing the proper number of anions. If these ideas are correct, the reductions of cobalt(III) offer the possibility of finding out the geometric requirements of the activated complex.

In this paper, however, we shall be more concerned with the reaction of stannate(II) ion. Surrounding cobalt(III) with ammonia molecules has the effect of insulating it from attack by this reducing agent. In fact, Lewis and Coryell[3] have already pointed out that the activation energy for the exchange reaction between hexamminecobalt(III) and hexamminecobalt(II) is much higher than that expected from the charge repulsion alone. In our case, it turns out that the reductions of hexamminecobalt(III) and hydroxypentamminecobalt(III) depend not at all on the cobalt concentrations, and the rate-determining steps are concerned only with stannate(II) ion. Since we have little information about the behavior of basic solutions of metal ions, the kinetic behavior of stannate(II) ion is of additional interest.

Before describing the experiments and their results, we should say that the experimental error present is higher than that ordinarily expected in kinetics investigations because of the difficulty of duplicating results when working with strongly basic solutions. We have tried to find out only the orders of the reaction with respect to the several reactants, and little significance is to be attached to the absolute magnitudes of the constants reported.

Experimental Part

Materials.—The hexamminecobalt(III) chloride used was prepared as described in reference 4. The solid salt was purified by twice recrystallizing from water. Solutions were made by dissolving the salt in concentrated ammonium hydroxide, since fairly high amounts of ammonia had to be present in the runs and this was a convenient way of adding it. The solutions were analyzed for cobalt by electrolytic deposition on platinum. The stannate(II) solution was prepared by dissolving about 50 g. of $SnCl_2 \cdot 2H_2O$ in 100 ml. of water in a 500-ml. volumetric flask. To the milky suspension of the hydrolyzed salt was then added 150 ml. of concd. ammonium hydroxide followed by 250 ml. of 5 M sodium hydroxide solution. After standing a few days, all remaining suspended matter settled out and metallic tin was deposited until equilibrium was reached. The solution prepared in this manner was found to be reasonably stable and easily duplicated. It was standardized on the day of each series of runs by titration with standard ceric sulfate. An approximately 5 M solution of sodium hydroxide was

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[1] This work was performed in the Ames Laboratory of the AEC.

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

[3] W. B. Lewis and C. D. Coryell, BNL-C-8, "Isotopic Exchange Reactions and Chemical Kinetics," 1948, pp. 131-143.

[4] W. C. Fernelius, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., New York, N. Y., 1946.

made and standardized against potassium hydrogen phthalate. Solutions of 5 *M* concentration of various salts such as sodium chloride, sodium nitrate and sodium perchlorate were made simply by dissolving the correct weighed amounts in water.

Procedure.—For the general rate run, the reaction mixture was made up as follows: Known volumes of a solution of the particular cobalt(III) complex, concd. ammonium hydroxide, 5 *M* sodium hydroxide, 5 *M* salt solution (added to maintain constant ionic strength), distilled water and sometimes 2 *M* sodium sulfite solution were mixed together and brought to 25 ± 0.2° in a water-bath. The total volume was kept between 10 and 12 ml. in order to fit in the cuvette of a Coleman Model 14 Spectrophotometer. The reaction was then started by adding a small known volume of approximately 0.3 *N* $NaHSnO_2$ solution. The spectra of the various cobalt(III) complexes and their reduction products were originally examined using a Cary Recording Spectrophotometer. It was found that the cobalt(III) ammines had little absorption in the red region, while the blue reduction products absorbed strongly around 630 mμ. This was the wave length used for all analyses. The optical density of the reaction mixture against a solution of the cobalt(III) complex at its original concentration was determined at ten intervals ranging from 50 to 200 seconds. Between measurements the cuvette was immersed in the water-bath. The final extinction of each run was found several minutes after no further change was apparent, and was taken as a measure of the molar extinction of the product.

In the first runs made with the hexamminecobalt(III) ion it was impossible to reproduce the results because of an induction period of varying length during which there was no apparent reaction. This was found to be due to the presence of dissolved oxygen in the strongly basic solutions, which would be capable of reoxidizing the hexamminecobalt(II) ion back to its original state. Because of the impracticality of sweeping out oxygen from a strongly basic, ammoniacal solution the following modification was devised: To the original mixture, one ml. of 2 *M* sodium sulfite solution was added and the stoppered test-tube was allowed to stand overnight. When the run was made, the proper volume of stannate(II) solution was added from a fast-flowing graduated pipet, the contents of the tube were poured rapidly into a cuvette, and the top of the solution was covered with a half cm. of white mineral oil. Even with these precautions, reproducibility was poor at low tin concentrations. Hence all reaction mixtures contained an excess of stannate(II).

A serious drawback encountered with all systems was that the permitted variations in concentrations of base, ammonia and stannate(II) were small because of the narrow regions of stability of the cobalt(II) complexes and of stannate(II) itself.

The Reduction of the Hexamminecobalt(III) Ion and the Behavior of Stannate(II) Ion.—It was first found that the rate was independent of cobalt concentration. At high stannate(II) concentrations, a simple plot of optical density *vs.* time gave straight lines. A variation of initial cobalt concentration also did not affect the rate of production of the cobalt(II) ammine.

The behavior upon variation of hydroxide concentration was next investigated. The results are listed in Table I. To maintain constant ionic strength 5 *M* sodium nitrate solution was used. In basic solution, nitrate will not oxidize stannate(II). In the earlier investigations with the pentammine complex, sodium chloride, perchlorate and sulfate were all used to control ionic strength, with substantially the same results. Reproducibility is more difficult with the pentammine complex, however. The quantity *R* reported in the table was found by plotting the extinctions *E* *vs.* the time in minutes and then dividing the slope by the final extinction, E_{max}. The result was then multiplied by a factor of 10^2 to obtain *R*. The concentrations of hydroxide are not simply those due to sodium hydroxide solution added because there was a large contribution from base in the stannate(II) solution used. In this solution, it was figured that three hydroxide ions were consumed by each stannous ion present in the original mixture. Thus in order to obtain the base concentration of the stannate (II) solution, three times the molarity of the stannate(II) ion was subtracted from the known molarity of the sodium hydroxide in this solution. If this assumption were incorrect, that is; if the equilibrium constant for a reaction of the type

$$HSnO_2^- + OH^- \rightleftarrows SnO_2^{=} + H_2O$$

were at all significant, a marked drift would appear in the values $R/[OH^-]$ reported. The results show that the reaction is first order in hydroxide. but that there is no large amount of tin in the form of $SnO_2^{=}$ even in solutions of 2 *M* base. This suggests that stannous acid might not be dibasic.

TABLE I

THE EFFECT OF VARYING HYDROXIDE CONCENTRATION[a]

$[OH^-]$	$R = E/E_{max.}$ per min. × 10^2	$R/[OH^-]$	Dev. from av., %
0.561	1.89	3.37	+1.5
.913	2.94	3.22	−3.0
1.45	4.58	3.35	+0.9
1.89	6.33	3.34	+ .6
2.33	7.77	3.32	.0
	Av.	3.32	

$[Co(NH_3)_6^{+++}] = 0.00351$ $[NH_4OH] = 6.8$

$[Sn(II)] = 0.0156$ $[Na_2SO_3] = 0.18$

[a] All concentrations are in moles/liter.

A series of runs was also made in which chloride ion in varying concentrations was added. The concentration of base was kept constant and the ionic strength again maintained by adding sodium nitrate. The purpose was to determine whether or not chloride ion accelerated the reaction. The results (not reported here) showed no effect even for solutions well over one molar in chloride. The addition of bromide or iodide to reacting solutions showed little effect. It is to be noted that the halides will not displace ammonia from the hexamminecobalt(III) ion under these conditions.

Although it was at first assumed that the dependence on stannate(II) concentration would be first order, the situation was more complicated. It was not possible to get consistent results except in a medium range of tin(II) concentrations (see Table II). For low values, there was still serious interference from dissolved oxygen. For high values, a precipitate sometimes formed, making optical analyses difficult. Because of the precipitation the final extinctions varied somewhat. It was assumed that they should all be equal, and a single value of E_{max} was used for the series in making the calculations. The quantity S_0 is the initial slope of a plot of $\log_{10} (2b - x)$ *vs.* (t) in minutes, where $2b$ refers to the extinction which would be obtained if an amount of hexamminecobalt(III) ion equivalent to the number of moles of stannate(II) initially added were completely reduced in the volume of solution used. That is, (*b*) is the initial concentration of tin in terms of extinction units. The quantity (*x*) is the extinction found at time (*t*). The results are listed in Table II. In addition to the erratic fluctuations due to poor reproducibility, there is an over-all decrease by an approximate factor of two as the tin is increased tenfold.

TABLE II

THE EFFECT OF VARYING STANNATE(II) CONCENTRATION

$[\mathrm{Sn(II)}]_0 = B$	$-S_0 \times 10^3$	$-BS_0 \times 10^5$ (exptl.)	$-BS_0 \times 10^5$ (calcd.)	Dev., %
0.00975	4.08	3.98	4.29	− 7.2
.0104	4.85	5.09	4.53	+12.4
.0195	3.50	6.83	7.47	− 8.6
.0208	3.62	7.53	7.83	− 3.8
.0390	3.30	12.87	12.37	+ 4.0
.0416	2.88	11.98	12.96	− 7.6
.0623	2.92	18.20	17.20	+ 5.8
.0975	2.10	20.48	22.74	− 9.9
.1039	2.61	27.12	23.74	+14.3

$[\mathrm{Co(NH_3)^{+++}}] = 0.00307$ $[\mathrm{OH^-}] = 1.62$
$[\mathrm{NH_4OH}] = 4.8$ $[\mathrm{Na_2SO_3}] = 0.17$

The results may be explained by assuming that stannate(II) ion, whose formula we take to be $\mathrm{HSnO_2^-}$, can dimerize. We shall write down the simple equilibrium

$$2\mathrm{HSnO_2^-} \rightleftarrows \mathrm{Sn_2O_3^{=}} + \mathrm{H_2O}$$

If we let B equal the total tin in moles/liter, the concentration of monomer is given by

$$m = [\mathrm{HSnO_2^-}] = (\sqrt{1 + 8BK} - 1)/4K \quad (1)$$

where K is the equilibrium constant for the dimerization reaction. To simplify the equations for the kinetics we shall let (m) stand for the concentration of monomer $\mathrm{HSnO_2^-}$ and (c) stand for the concentration of hydroxide ion. Then the rate expression is

$$\mathrm{d}X/\mathrm{d}t = 2kcm \quad (2)$$

Here X will stand for the molar concentration of cobalt(II) complex ion formed. Then

$$\frac{1}{2B - X}\frac{\mathrm{d}(2B - X)}{\mathrm{d}t} = \frac{-2kcm}{2B - X} \quad (3)$$

$$\left[\frac{\mathrm{d}\ln(2B - X)}{\mathrm{d}t}\right]_0 = \left[\frac{\mathrm{d}\ln(2b - x)}{\mathrm{d}t}\right]_0 = \frac{-kcm_0}{B} = 2.303S_0 \quad (4)$$

Subscript 0's refer to initial concentrations. As before, B and X refer to molar concentrations, while (b) and (x) are in extinction units. From (1) and (4) the following expression may be obtained

$$-BS_0 = (\sqrt{1 + 8BK} - 1)\,kc/4 \times 2.303\,K \quad (5)$$

Using any two values of S_0 and B from Table II, we may get from equation (5) a rough value of $K = 17$. The expression is not very sensitive to the value of K, and only one significant figure should be set down. However, K is large enough to show appreciable dimerization if we assume it to be the cause of the observed order.

If $-BS_0$ from Table II is plotted *vs.* $(\sqrt{1 + 8\,Bk} - 1)$ the slope will be equal to $kc/4 \times 2.303\,K$ (Fig. 1). The value of the slope is 8.3×10^{-5}, which gives a value of (k) equal to 8.0×10^{-3} min.$^{-1}$ $[\mathrm{OH^-}]^{-1}$.

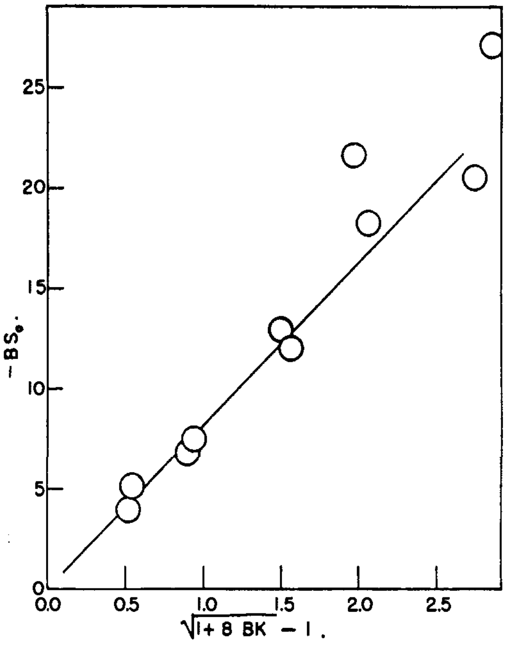

Fig. 1.—Graph for the evaluation of the rate constant *k*.

From the values of (k) and K found, the quantity $-BS_0$ was calculated for each run and compared with the experimental value in Table II. Some of the deviations are as much as 14% but with the correction for K they are no longer systematic.

The rates were not changed appreciably by varying the ammonia concentration, and variations in surface area did not affect the results.

The Reduction of the Hydroxypentamminecobalt(III) Ion.—The preparation of solutions of the aquopentamminecobalt(III) sulfate and perchlorate was carried out along the lines of the procedure described by Booth for the bromopentamminecobalt(III) bromide.[5] The pentammine sulfate and perchlorate were found to be very soluble and were therefore used as prepared in solution. In the rate runs, no attempt was made to deoxygenate with sulfite. Because of the instability of the hydroxypentamminecobalt(III) ion in basic solutions the runs were started as soon as the cobalt complex was added. As before, the rates were found to be independent of the cobalt concentration. It was not possible to obtain verification of the order in hydroxide concentration.

Of more interest is the change in the kinetic behavior when a basic solution is allowed to act on the pentammine complex. If allowed to stand more than 24 hours, the brown hydroxide is completely precipitated from the solution. But long before this occurs, and before any appreciable change can be detected spectroscopically, the rate of reduction is increased. This is illustrated in Fig. 2. The lower curve is the one usually obtained, the cobalt being added last to start the reaction. The upper curve shows the effect of one hour standing on the hydroxypentammine. Two things are apparent: The cobalt is now

[5] H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

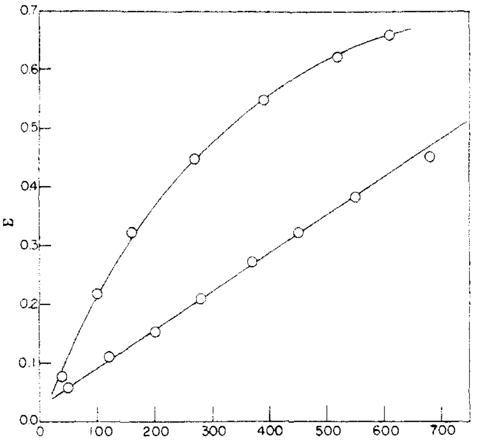

Fig. 2.—The effect of base on the rate of reduction of the pentammine complex: upper curve, the complex was permitted to stand one hour in basic solution prior to reduction; lower curve, stannate(II) was added immediately to start the reduction.

capable of participating in a rate-determining reaction, since the new order is closer to one than zero. Further, this reaction must involve ordinary stannate(II) since the over-all rate is increased. That is, the new reaction does not depend on the formation of some active form of tin(II) as apparently was the case before. We suggest as an explanation that OH^- ions can "catalyze" the reduction of cobalt when present in the complex, but that more than one is necessary. It is to be remembered that in the ferric–stannous reaction, two hydroxide ions were found necessary,[6] and in the halide-catalyzed case, three were needed in the activated complex.[1]

A comparison of the reduction products in the hexammine and pentammine complexes showed that the absorption spectra were almost identical. However, if after a partial reduction a solution of the hexammine was vigorously shaken in air, the original orange color was restored. If very small amounts of dilute hydrogen peroxide were added to the solution of the reduced pentammine complex, the original color was produced. In spite of the similarity of the spectra of the reduction products, it was concluded that the cobalt(II) forms were still different. Probably the nuclear structures of the hexammine and pentammine complexes are not disturbed by the reduction.

Other Results

It was found that cyanide ion in very small amounts acts as an effective catalyst for the reduction of either of the above complexes. No other anion of the group Cl^-, Br^-, OH^- and CNS^- was found to do this except OH^- in the sense described above. Cyanide ion is the only one of this group capable of rapid replacement of ammonia in the hexamminecobalt(III) ion. An exact kinetic treatment was not attempted because of the complexity. In small traces, cyanide led to the usual blue reduction products. In larger quantities, green, brown and red products were formed. The latter color was presumably due to cyanocobaltate(II) ion. However, when large amounts of cyanide were added, no reduction occurred. Stannate(II) will not reduce hexacyanocobaltate(III) ion.

Of a number of other common anions, thiosulfate ion was also found to catalyze these reactions. Thiosulfate will not replace ammonia and its action is apparently of a different type.

trans-Dichloro-bis-ethylenediamminecobalt(III) chloride was prepared[3] and its basic solution was reduced by stannate(II) to a blue product. The rate observed was not noticeably faster than the other cases reported. Apparently the presence of two chloride ions in the complex (or more probably two hydroxide ions under these conditions) is insufficient for the rapid reaction.

In general, we may conclude that certain of the anions classed as oxidizable are capable of catalyzing the reduction of cobalt(III) complexes by stannate(II) ion, but that they must be attached to the cobalt to be effective. In the absence of catalysts, some high energy form of tin(II) appears necessary for the reduction. It is also probable that the predominant form of tin(II) in basic solutions is not $HSnO_2^-$, and that stannous acid may not be dibasic.

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(6) M. H. Gorin, THIS JOURNAL, **58**, 1787 (1936).