shown to remain essentially constant during the polymerization. The kinetics are interpreted on the basis that the zero-order dependence of polymerization in emulsion on monomer content is not due to a difference in mechanism from solution polymerization but is limited by the solubility of the styrene in the water phase, within which the polymerization takes place.

Polymerization of styrene emulsified by potassium dehydroabietate or mixed hydro-dehydroabietate gave a somewhat lower-molecular-weight polymer and a slightly slower rate of reaction than emulsification by soaps of high-molecular-weight fatty acid.

Addition of dodecyl mercaptan to the polymerization greatly reduced the molecular weight of the polymer formed, as well as the induction period before polymerization started, but had little effect on the rate of reaction.

URBANA, ILLINOIS RECEIVED JUNE 18, 1945

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

The Polarographic Reduction of Some Cobaltammines and Related Compounds

BY J. B. WILLIS, J. A. FRIEND AND D. P. MELLOR

Although the polarographic reduction of complex metal ions has already been studied to some extent both in theory and in practice,[1a] attention has hitherto been almost entirely confined to complexes in which the coördination sphere of the metal ion contains only one kind of molecule or ion, as in such complexes as $[Co(NH_3)_6]^{+++}$ and $[Fe(CN)_6]^{---}$. Ions such as $[Co(NH_3)_5NO_2]^{++}$, for instance, do not seem to have been studied. One reason for this is that in previous investigations the complex ions have as a rule been formed by the addition of a simple metal salt to a large excess of the coördinating substance, which also acts as supporting electrolyte; no attempt has been made to isolate the substance actually undergoing reduction.

The purpose of the present investigation was to study the reduction of complex ions formed from the hexammine cobaltic ion by progressive substitution of the ammonia molecules by other groups. Complexes with ethylenediamine were also studied. Among the ammines, the nitro-substituted compounds were selected for intensive study because these compounds have been well studied from the point of view of physicochemical properties, and because almost a complete series from $[Co(NH_3)_6]^{+++}$ to $[Co(NO_2)_6]^{---}$ is known, the only missing member being $[Co(NH_3)(NO_2)_5]^{--}$.

Some chloro- and aquo-substituted complexes also were studied.

Theory

Since it was desired to prevent the complexes from undergoing alteration when dissolved, a supporting electrolyte was required which would not tend to coördinate with the metal ion. Normal potassium nitrate was first tried, since the nitrate ion shows great reluctance to coördinate, but maxima were obtained which were very difficult to suppress. Normal potassium sulfate, 0.1 N potassium sulfate and 0.1 N sodium acetate were used and found satisfactory for different sections of the work. As far as maxima were concerned the ammonia complexes caused much less trouble than complexes containing ethylenediamine. Maxima obtained with the former could be suppressed easily by methyl red, whereas those obtained with the latter often did not respond to this treatment.

That the cobaltammines preserve their identity in aqueous solution is shown by the following: (a) Conductivity measurements have been satisfactorily and reproducibly carried out on them. (b) Each substance gives a characteristic and reproducible polarogram which does not change after the solution has stood for some time. The determination of the number of electrons involved in the polarographic reduction was carried out by the application of the Ilkovič equation.[2] The diffusion coefficient of the ion undergoing reduction was calculated from its equivalent conductivity at infinite dilution as described by Kolthoff and Lingane.[1b]

Experimental

A manual instrument, similar to that previously described,[3] was used.

All measurements were made at 25°; air was displaced from solutions by purified nitrogen. The half-wave potentials ($E_{1/2}$) are relative to the saturated calomel electrode, and are considered to be in error by not more than approximately ±10 mv. They are corrected for the potential drop across the polarographic cell. Methyl red was used as a maximum suppressor, because by experience it was found that, unlike gelatin and methyl cellulose, it does not cause a shift in the half-wave potential.

The substances used were mainly the chlorides of the complex cations, and sodium or ammonium salts of complex anions. They were prepared according to the standard methods of Jörgensen and Werner,[4] and were checked for purity by gentle ignition with a few drops of concentrated sulfuric acid and weighing as anhydrous cobalt sulfate.

The solutions were 0.001 M with respect to the ion

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(1) (a) Kolthoff and Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1941, p. 161; (b) Kolthoff and Lingane *ibid.*, p. 44.

(2) Ilkovič, *Coll. Czech. Chem. Comm.*, **6**, 498 (1934).

(3) Willis, THIS JOURNAL, **66**, 1067 (1944).

(4) Jörgensen, *J. prakt. Chem.*, **39**, 8 (1889); *Z. anorg. allgem. Chem.*, **17**, 455 (1898), etc.; Werner, *Ber.*, **39**, 2678 (1906); *ibid.*, **45**, 121 (1912), etc. For a full list of references, see Weinland, "Komplexverbindungen," Ferd. Enke, Stuttgart, 1924.

studied. They were made up in the cold and used immediately after preparation in order to avoid any possibility of decomposition.

Results

In every compound studied except the hexanitrocobaltate and chloropentammine cobaltic ions, which are discussed below, two steps were obtained. The height of the second step was very close to twice that of the first, which suggests that a one-electron reduction is followed by a two-electron reduction. This is confirmed by the application of the Ilkovič equation, the results of which are shown in Table I, where $n = i_d/605\ CD^{1/2}m^{2/3}t^{1/6}$, the symbols having the usual significance.

TABLE I

APPLICATION OF ILKOVIČ EQUATION TO COMPLEXES

The literature references are to conductivity data

Ion undergoing reduction	n	
	1st Step	2nd Step
$[Co(NH_3)_6]^{+++}$[5]	0.95	1.97
$[Co(NH_3)_5(NO_2)]^{++}$[5]	0.93	1.92
cis-$[Co(NH_3)_4(NO_2)_2]^{+}$[6]	1.06	2.09
trans-$[Co(NH_3)_4(NO_2)_2]^{+}$[6]	0.96	1.97
$[Co(NH_3)_2(NO_2)_4]^{-}$[5]	.96	2.04
$[Co(NH_3)_5Cl]^{++}$[6]	..	1.99
$[Co(NH_3)_5(H_2O)]^{+++}$[7]	.95	2.14

In Table II are shown the half-wave potentials of the ammonia complexes in N potassium sulfate.

TABLE II

HALF-WAVE POTENTIALS OF AMMINES IN N POTASSIUM SULFATE

Ion undergoing reduction	$E_{1/2}$, v.	
	1st Step	2nd Step
$[Co(NH_3)_6]^{+++}$	−0.437	−1.279
$[Co(NH_3)_5NO_2]^{++}$	− .264	−1.288
$[Co(NH_3)_5ONO]^{++}$	− .263	−1.279
cis-$[Co(NH_3)_4(NO_2)_2]^{+}$	− .043	−1.283
trans-$[Co(NH_3)_4(NO_2)_2]^{+}$	− .207	−1.281
$[Co(NH_3)_3(NO_2)_3]$	− .026	−1.277
$[Co(NH_3)_2(NO_2)_4]^{-}$	− .070[a]	−1.276
$[Co(NO_2)_6]^{---}$	....	−1.425
$[Co(NH_3)_5Cl]^{++}$	...	−1.275
$[Co(NH_3)_5OH]^{++}$	− .473	−1.279
cis-$[Co(NH_3)_4Cl_2]^{+}$	− .415	−1.279
trans-$[Co(NH_3)_4Cl_2]^{+}$	− .415	−1.281
$[Co(NH_3)_3(H_2O)_3]^{+++}$	− .249	−1.274[a]
$[Co(NH_3)_5H_2O]^{+++}$	− .474	−1.274
$[Co(H_2O)_6]^{++}$	...	−1.428

[a] Maximum, suppressed with 0.005% methyl red.

In Table III the half-wave potentials of representative compounds of several series in various supporting electrolytes are tabulated. Only the second step is shown here.

Discussion

From the tables it may be seen that the reduction of each compound, with the exceptions already noted, takes place in two stages, the first at a potential which varies from compound to compound, the second at a potential constant within the limits of experimental accuracy for all the compounds studied. The most probable explanation seems to be this: the original ion takes up one electron in the first reduction step and is thereby converted to a Co^{II} complex, *e. g.*, $[Co(NH_3)_5NO_2]^{++}$ would be reduced to $[Co(NH_3)_5NO_2]^{+}$. It is well known that the ammines of Co^{II} are extremely unstable, and are immediately hydrolyzed by water, so that the above ion would be instantly decomposed to give $Co(H_2O)_6^{++}$. The net reaction at the first step is thus considered to be the total disruption of the original complex with reduction to free Co^{++} ion. At the second step the reaction is the same for all the complexes, *viz.*, $Co^{++} \rightarrow Co$, so that $E_{1/2}$ for this step is the same in every case.

TABLE III

VARIATION OF HALF-WAVE POTENTIAL OF THE SECOND STEP WITH SUPPORTING ELECTROLYTE

Ion undergoing reduction	$E_{1/2}$, v.		
	N K_2SO_4	0.1 N K_2SO_4	0.1 N NaOAc
$[Co(NH_3)_6]^{+++}$	−1.279	−1.20	−1.215
trans-$[Co(NH_3)_4Cl_2]^{++}$	−1.281	−1.16	−1.19
$[Co\ en_3]^{+++}$	−1.27	−1.20	−1.20
$[Co(NH_3)_2\ en_2]^{+++}$	−1.29	−1.19	−1.21
trans-$[Co\ en_2Cl_2]^{+}$	......	−1.18	−1.18
cis-$[Co\ en_2(NO_2)_2]^{+}$	−1.28	−1.20	−1.17
$Co(H_2O)_6^{++}$	−1.428	−1.208	−1.190
$[Co(NO_2)_6]^{---}$	−1.425[a]	−1.248[a]	−1.209

[a] In N and 0.1 N Na_2SO_4, respectively.

It was thought at first, from the results obtained in N K_2SO_4, that the reduction of the complexes could not take place through the intermediate formation of free Co^{++}, as the values of $E_{1/2}$ for the complexes were all about −1.28 v., and cobaltous sulfate was reduced at −1.428 v. However, in 0.1 N K_2SO_4 the latter was reduced at −1.208 v., and the $E_{1/2}$ values of the second step of the complexes were all within a few mv. of this value. Furthermore, the second steps of ethylenediamine complexes showed this same $E_{1/2}$, indicating that the same ion was being reduced as in the ammine complexes. It is clear therefore that the reduction of all the Co^{III} complexes in 0.1 N K_2SO_4 solution takes place *via* the hydrated Co^{++} ion. The anomalous behavior in N K_2SO_4 remains to be explained.

A possible solution to the difficulty was found in an abstract of papers by Fedoroff and Demassieux.[8] These authors carried out polarographic and conductometric studies of solutions of the double sulfates $K_2SO_4 \cdot MSO_4 \cdot 6H_2O$ (M = Co, Cu, Cd, Fe, Ni, Zn, Mg, Mn). They found that in solutions of concentration 10^{-4} *M* or less, the salts exist as K^{+}, M^{++} and SO_4^{--} ions. In more concentrated solutions, complex ions such as $[M(SO_4)_2]^{--}$ exist as well as undissociated MSO_4

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(5) Werner and Miolati, *Z. physik. Chem.*, **14**, 511 (1894).

(6) Lorenz and Posen, *Z. anorg. allgem. Chem.*, **96**, 81 (1916).

(7) Werner and Miolati, *Z. physik. Chem.*, **21**, 237 (1896).

(8) Fedoroff and Demassieux, *Ann. chim.*, **16**, 154, 216 (1941).

and K_2SO_4 molecules. It is clear, therefore, that the SO_4^{--} ion does tend to coördinate with Co^{++} and it seems very probable that this is the explanation of the difference in behavior between the more concentrated solutions (10^{-3} *M* $CoSO_4$ in *N* K_2SO_4) and the more dilute ones (10^{-3} *M* $CoSO_4$ in 0.1 *N* K_2SO_4). In the more dilute solutions, the reduction will approximate more closely to that of simple $Co(H_2O)_6^{++}$ ions.

A possible reduction scheme would then be

$$[CoA_{6-n}X_n]^{(3-n)} + 6H_2O + e \longrightarrow Co(H_2O)_6^{++} + (6-n)A + nX^-$$
$$Co(H_2O)_6^{++} + 2e \longrightarrow Co + 6H_2O \quad (n^-)$$

To test these conclusions, experiments were carried out using 0.1 *N* sodium acetate as supporting electrolyte. Under these conditions simple Co^{++} salts and ammonia complexes gave satisfactory waves. Unfortunately ethylenediamine complexes gave waves with maxima which could not be suppressed by methyl red. The values of $E_{1/2}$ recorded for ethylenediamine complexes are those obtained by neglecting the maxima and calculating the half-wave potential accordingly. It is realized that this practice is open to question and that the values of $E_{1/2}$ are not strictly correct, but these considerations do not affect the general nature of the result. From Table III it is seen that all compounds studied gave steps with $E_{1/2}$ practically constant at −1.19 v., the value for the simple $Co(H_2O)_6^{++}$ ion. This confirms the conclusion previously reached that all cobaltic complexes are reduced by way of the cobaltous ion, except where the supporting electrolyte interferes by forming complex ions. The case of sodium hexanitrocobaltate, which is exceptional, is discussed below.

It is assumed that the second step of the polarographic reduction of complexes in potassium sulfate solution takes place before the reduced ion can be sulfated. In solutions of $CoSO_4$, the Co^{++} ion is sulfated, and therefore behaves abnormally, in concentrated solutions. Apparently the sulfating of the intermediate ions in *N* K_2SO_4 is not as complete as in the case of cobalt sulfate in this electrolyte.

Adsorption of Nitro Complexes on Charcoal

Some interesting correlations may be made between the above conclusions and measurements of the adsorption of the nitro-cobaltammines on charcoal. Shilov and Nekrassov[9] found that these compounds were adsorbed and decomposed, being reduced to the $Co(NH_3)_2^{++}$ ion in the process.

If it was assumed that the least stable ammines showed the highest adsorption, the ammines could be arranged in order of stability.

Since the first step in the polarographic reduction of these complexes corresponds to the disruption of the complex ions, its half-wave potential may be regarded as a measure of the stability of the ion. The ions which require more energy for disruption will have more negative half-wave potentials. Making allowance for the fact that the adsorption work was carried out in aqueous solution and the polarographic measurements in *N* potassium sulfate, it will be seen that a fair correspondence exists between the two sets of results.

TABLE IV

STABILITY OF COMPLEXES BY POLAROGRAPHIC AND ADSORPTION MEASUREMENTS

	$E_{1/2}$, v.	Adsorption on charcoal
$[Co(NH_3)_6]^{+++}$	−0.437	61.9
$[Co(NH_3)_5(NO_2)]^{++}$	− .264	54.2
trans-$[Co(NH_3)_4(NO_2)_2]^+$	− .207	53.1
$[Co(NH_3)_2(NO_2)_4]^-$	− .070	72.1
cis-$[Co(NH_3)_4(NO_2)_2]^+$	− .043	70.6
$[Co(NH_3)_3(NO_2)_3]$	− .026	75.3

The nitropentammine ion requires a high overvoltage for reduction, as is shown by the gradual nature of its first step, and this accounts for the fact that polarographic measurements class it as more stable than the *trans*-dinitro-tetrammine ion, in contradiction to adsorption measurements. As expected the *trans*-dinitrotetrammine compound is shown by both methods to be more stable than the *cis*-form. The reverse appears to be the case in ammoniacal[10] and sodium nitrite solutions.

Notes on Individual Complexes

Nitrito-pentammine cobaltic ion gave the same polarogram as the nitro complex, although the solutions of the two complexes were perceptibly different in color.

In the case of the chloropentammine cobaltic ion, only the second step could be obtained. The first stage of the process presumably takes place at a potential too positive to be recorded polarographically.

The *cis*- and *trans*-dichlorotetrammines are unstable in solution and rapidly pass to the ion $[Co(NH_3)_4(H_2O)Cl]^{++}$ (presumably *trans*-) with the result that both compounds give the same polarogram, the first step being very drawn-out.

Sodium hexanitrocobaltate appears to be reduced in a similar way to $Co(H_2O)_6^{++}$ ion, in *N* sodium sulfate and in 0.1 *M* sodium acetate. In 0.1 *N* sodium sulfate its behavior is intermediate between that of cobaltous sulfate and cobaltic complexes. Apparently, the first stage of the reduction takes place at a positive potential, as the diffusion current is abnormally large. On standing, solutions of this salt in *N* sodium sulfate show waves which seem to be due to the decomposition of the $[Co(NO_2)_6]^{---}$ ion, yielding nitrous and nitric acids, which are then reduced. In sodium acetate, only one step, at −1.209 v., is found.

Acknowledgments.—The authors wish to thank Dr. B. Breyer for much helpful discussion

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[9] Shilov and Nekrassov, *Z. physik. Chem.*, **118**, 79 (1925).

[10] Lamb and Larson, THIS JOURNAL, **42**, 2024 (1920).

and advice. This work was carried out under the Masson Memorial Scholarship awarded to one of them (J. B. W.) by the Australian Chemical Institute.

Summary

1. The polarographic reduction of a number of complexes of cobalt (III) with ammonia and ethylenediamine have been studied in *N* and 0.1 *N* potassium sulfate and in 0.1 *N* sodium acetate.

2. In all cases reduction takes place in two stages, the first involving one, and the second, two, electrons. The half-wave potential of the first step varies from compound to compound, but that of the second is the same for all compounds. It is considered probable that the first step corresponds to the reduction and disruption of the complex ion to form $Co(H_2O)_6^{++}$; the second step corresponding to the reduction of $Co(H_2O)_6^{++}$ to cobalt.

3. A correlation is made between the mechanism of reduction proposed and the decomposition processes of the nitro-cobaltammines when adsorbed on charcoal. The relative stabilities of the compounds as shown by the two methods are in fair agreement.

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[CONTRIBUTION FROM THE COATES LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Characterization of Silicic Acid–Celite Mixtures for Chromatography

BY ARTHUR L. LEROSEN

In order to use chromatography most effectively, it is necessary to select the best adsorbent for a given purpose. This requires a thorough knowledge of the properties of the materials used.

Several methods have been devised for standardizing adsorbents: the use of dye mixtures by Brockmann and Schodder[1]; the calorimetric method of Müller[2]; the use of V_t (threshold volume) by H. Weil-Malherbe[3]; and the method suggested by the present author.[4]

It is the purpose of this paper to show that the terms suggested by the author permit a good characterization of adsorbents. For this study the system silicic acid–Celite was selected. The terms evaluated are: S, V_c, R,[5] and T_{50}.[6,7]

These terms can be made more specific by certain notations: the solvent, etc., may be specified: V_c^{benzene}, T_{50}^{benzene}, $R_{p\text{-nitroaniline}}^{\text{benzene}}$. Unless otherwise noted R refers only to the lower edge of a zone, however in some studies it is useful to determine R for both top and bottom edges of a zone, R_t and R_b.

In this work a change has been made from the larger (20 × 200 mm.) chromatographic tube previously used to the smaller 9 (inside diameter) × 130 mm. tube. All tests were standardized on a column of adsorbent 75 ± 2 mm. long. The smaller tube requires less adsorbent and is more convenient than the larger one.

Several kinds of silicic acid were tested and the results are given in Table I. The pre-washing

TABLE I

THE CHROMATOGRAPHIC CHARACTERISTICS OF SEVERAL SILICIC ACID SAMPLES

Adsorbent brand	S	T_5	V_c	$R_{p\text{-nitroaniline}}^{\text{benzene}}$ Un-treated	Pre-washed[a]
Merck Reagent (Approx. H_2SiO_3)	1.54	121	9.8	0.22	0.031
J. T. Baker, C. P.	1.42	10.5	90.0	0.59	0.520
Central Scientific Company, Tech.	1.65	148.0	6.8	0.85	...

[a] See Table II.

TABLE II

THE CHARACTERISTICS OF SILICIC ACID (MERCK)–CELITE MIXTURES[a]

Silicic acid fraction in mixture Wt.	Vol.	S	T_{50}	V_c	$R_{p\text{-nitroaniline}}^{\text{benzene}}$ Un-treated	Pre-washed[b]
1.00	1.00	1.54	121	9.8	0.22	0.031
0.90	0.83	1.51	69	18.9	.26	.034
.80	.69	1.49	54	22.6	.30	.038
.67	.52	1.45	24	52.0	.34	.050
.50	.36	1.41	12	88.0	.48	.096
.20	.12	1.31	7	165.0	.68	.245
.00	.00	1.24	4	326.0	1.00	1.000

[a] Celite (No. 535) is manufactured by the Johns-Manville Co., 22 E. 40th St., New York 16, N. Y.

[b] These columns were pre-washed with 3.3 ml. of acetone, 3.3 ml. dry ether, and 6.6 ml. petroleum ether (b. p. 60–70°) to remove moisture. (The removal of moisture is indicated by the presence of droplets of water in the washings from the column. The water was identified positively.)

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[1] H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941).

[2] P. B. Müller, *Helv. Chim. Acta*, **26**, 1945 (1943); **27**, 404, 443 (1944); *Verhandl. Ver. Schweiz. Physiol.*, **21**, 29 (1942).

[3] H. Weil-Malherbe, *J. Chem. Soc.*, 303 (1943).

[4] A. L. LeRosen, THIS JOURNAL, **64**, 1905 (1942).

[5] The terms were defined as follows (ref. 4):

S = length of adsorbent column containing one unit volume of solvent/length of unfilled tube required to contain the same volume of solvent.

V_c = rate of flow of the developing solvent through the column when a state of constant flow has been reached (mm./min.).

R = rate of movement of the adsorbate zone (mm./min.)/rate of flow of the developing solvent (V_c).

[6] Suggestion by the author, mentioned first by L. Zechmeister and A. Polgár, THIS JOURNAL, **66**, 137 (1944), footnote 10.

[7] T_{50} is defined for used with a 9 mm. dia. tube in place of the 20 mm. dia. tube of ref. 6.

T_{50} = the time in seconds required for a solvent to penetrate 50 mm. into an initially dry 9 × 75 ± 2 mm. column under a vacuum given by the water pump. This term is defined for a specific column due to the lack of sufficient data for columns of other sizes.