TABLE III

EFFECT OF TYPE OF ADDED SALT UPON Pu^{+3}–Pu^{+4} FORMAL POTENTIALS AT CONSTANT IONIC STRENGTH AND 25°

(H^+), moles/l.	($NaClO_4$), moles/l.	($LiClO_4$), moles/l.	$E^{0\prime}$, volts
2.000	0.000	0.000	−0.9826
0.500	.000	1.500	− .9797
.500	1.500	0.000	− .9791
.200	0.000	1.800	− .9771
.200	1.800	0.000	− .9768
.100	0.000	1.900	− .9719
.100	1.900	0.000	− .9728

the substitution of sodium ions for lithium ions in these solutions of constant ionic strength.

It might have been predicted from the treatment of Robinson and Stokes[12] that the above activity coefficient ratio would be significantly altered in the solution of mixed electrolytes since the osmotic coefficients and the hydration numbers of sodium perchlorate and lithium perchlorate are appreciably different. However, it appears that this difference is not observed experimentally in view of the small changes noted in the formal potentials of the Pu^{+3}–Pu^{+4} couple.

LOS ALAMOS, NEW MEXICO

[12] R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Butterworths Publications, Ltd., London, 1955, p. 443.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Composition and Formation of Cobalt Complexes with 1-Nitroso-2-naphthol

BY I. M. KOLTHOFF AND EINAR JACOBSEN

RECEIVED MARCH 7, 1957

Controversial statements are found in the literature on the composition and the mode of formation of the complex which precipitates upon addition of a solution of 1-nitroso-2-naphthol (HR) to a cobalt(II) solution in an acetate buffer. The precipitate is soluble in benzene and acetonitrile (AN). From its polarographic properties in AN, from amperometric titrations in water and AN, and from gravimetric studies it was concluded that the complex has the formula Co(III) $R_3 \cdot H_2R'$, $H_2R\cdot$ being the semiquinone obtained by a one-electron reduction of HR. $H_2R\cdot$ is unstable in a vacuum at 110°. $H_2R\cdot$ is soluble in 40% acetic acid; the precipitate obtained from this medium has the composition Co(III)R_3. It is proposed that Co(II)R_2 is the first reaction product which, in acid medium, decomposes rapidly according to the equation: $2Co(II)R_2 \rightarrow Co(III)R_3 + H_2R\cdot + Co(II)$. A precipitate of Co(II)R_2 is obtained from neutral and slightly alkaline aqueous medium. When dissolved in AN which contains acid, the reaction products of the disproportionation are found in the solution. The polarographic properties of some other metal–HR complexes have been determined.

Ilinsky and v. Knorre[1] reported in 1885 that upon addition of excess cobalt(II) to a neutral aqueous solution of the sodium salt of 1-nitroso-2-naphthol (designated in this paper as HR) a brown-red precipitate is formed. By addition of acid to the mixture and heating, the precipitate is transformed to a purple-red compound. The purple complex is also obtained when the precipitation is carried out in acid medium. The percentage of cobalt in the complexes was determined and the formulas CoR_2 and CoR_3 for the brown-red and purple-red complexes were suggested.

During this century HR has been recommended by a number of investigators for the determination of cobalt. The precipitate has been reported to be of variable composition, and for this reason is ignited to and weighed as Co_3O_4 or the oxide is reduced with hydrogen to the metal.[2,3]

Mayer and Feigl[4] suggest that divalent cobalt is partly oxidized by the reagent to the trivalent state and claim that the precipitate formed by addition of HR to an acid solution of divalent cobalt is not a pure compound but contains both divalent and trivalent cobalt. In order to obtain all cobalt in the trivalent form they first convert cobalt(II) into cobaltic hydroxide by addition of hydrogen peroxide and sodium hydroxide. The hydroxide is dissolved by heating in a fairly concentrated solution of acetic acid to yield a complex trivalent cobalt acetate. After dilution the cobalt(III) is precipitated with the reagent and the precipitate weighed as $CoR_3 \cdot 2H_2O$. It is not realized by these authors that on heating of a cobalt(III) solution in aqueous acetic acid reduction to cobalt(II) occurs.

Kolthoff and Langer[5] titrated divalent cobalt in acetate buffer amperometrically with HR. The ratio of cobalt to HR in the purple-red precipitate was found to be 1:4 and they suggested the formula $CoR_2 \cdot 2HR$.

In a discussion of these results Feigl[6] suggested that HR reacts with cobalt(II) salts to form an inner complex containing trivalent cobalt. He suggests that the precipitate is composed of the trivalent cobalt complex with one molecule of coördinated reagent. No experimental evidence however was presented and no simple reaction mechanism would account for this suggestion.

From the above review it is evident that the composition of the red cobalt complex and its mode of formation are not yet clear. In the present paper experiments are described which establish the composition of the red precipitate and the reactions leading to its formation.

It was observed that some of the metal complexes with HR, which are precipitated from aqueous medium, are soluble in benzene and acetonitrile (designated in this paper as AN). In AN as solvent or in mixtures of AN with benzene well-de-

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[1] M. Ilinski and G. von Knorre, *Ber.*, **18**, 699 (1885).

[2] P. Slawik, *Chem. Z.*, **38**, 514 (1914); *C. A.*, **8**, 2541 (1914).

[3] H. Willard and D. Hall, THIS JOURNAL, **44**, 2219 (1922).

[4] C. Mayer and F. Feigl, *Z. Anal. Chem.*, **90**, 15 (1932).

[5] I. M. Kolthoff and A. Langer, THIS JOURNAL, **62**, 3172 (1940).

[6] F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, New York, N. Y., 1949, pp. 252–262; *Anal. Chem.*, **21**, 1298 (1949).

fined polarographic waves of the metal complexes were obtained. A polarographic study of the cobalt complexes indicated that cobalt is present in the trivalent form. Evidence is presented that cobalt(II) reacts in an acetate buffer or in other acid medium with RH to form $Co(II)R_2$ which rapidly is transformed into $Co(III)R_3$ and $H_2R{\cdot}H_2R{\cdot}$ having properties of a semiquinone. In dilute acetic acid medium $H_2R{\cdot}$ precipitates quantitatively with the red compound, which has the overall composition $CoR_3{\cdot}H_2R{\cdot}$. At higher concentrations of acetic acid the semiquinone is soluble and the precipitate is composed of CoR_3. This interpretation was supported by gravimetric and amperometric experiments.

Experimental

Materials Used.—C.P. chemicals were used unless otherwise stated. Standard solutions of HR were prepared and standardized as recommended by Kolthoff and Langer.[5] Unless otherwise stated, 0.1 *M* sodium perchlorate prepared from the anhydrous salt served as supporting electrolyte in AN as solvent.

Technique.—The conventional type of dropping mercury electrode and of electrolysis cell were used. Current–voltage curves were recorded with a Sargent Recording Polarograph Model XXI. Oxygen was eliminated from the solutions by bubbling pure nitrogen through the cell for 10 min. and passing it over the solution during the electrolysis. Further details on the polarographic technique in AN are found in a recent paper.[7]

Results

Polarography.—Irreproducible and poorly defined current–voltage curves of the reagent and its metal complexes in AN were obtained in acid-free solutions of sodium perchlorate. By addition of acetic acid or perchloric acid well-defined and reproducible polarograms were observed.

Current–voltage curves of 10^{-3} *M* HR in AN of different acidity are plotted in Fig. 1. The diffusion current was found not to be affected by concentration and kind of acid present and to be proportional to concentration of HR, the value of $i_{d/c}$ being equal to 16.0 μa./mmole HR/liter. By assuming a reasonable value for the diffusion coefficient of HR, it was inferred that its reduction involves four electrons. This corresponds to a reduction of the nitroso group to the amine. The half-wave potential is shifted to more positive values with increasing concentration of acetic acid, while the stronger acid perchloric in 0.1 *M* solution has a much greater effect than 1.5 *M* acetic acid. Identical waves were obtained when the reagent was extracted with benzene from aqueous acetic acid solution and the benzene solution diluted with AN which contained the appropriate amount of acid and salt.

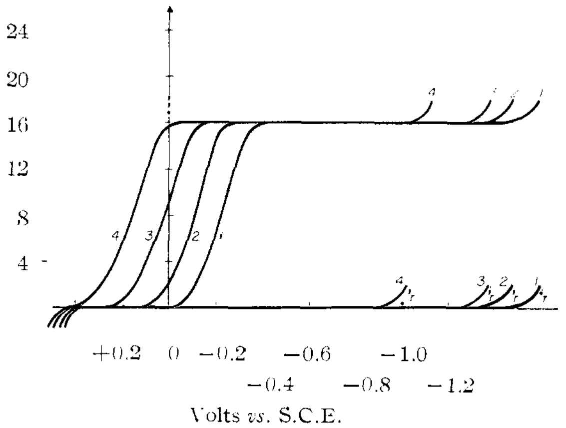

Fig. 1.—Current-voltage curves of 10^{-3} *M* HR in 0.1 *M* sodium perchlorate in acetonitrile: (1) 0.1 *M*; (2) 0.5 *M*; (3) 1.5 *M* in acetic acid; (4) 0.1 *M* in perchloric acid.

Complexes of various metals with HR were prepared by adding a known volume of the reagent in 60% acetic acid to aqueous 0.2 *M* sodium acetate solutions containing an excess (50 to 100%) of the metal salts. The precipitates formed were extracted with benzene and an aliquot part of the extract diluted with AN, which was 0.5 *M* in acetic acid and 0.1 *M* in sodium perchlorate, shortly before recording the polarograms. Current–voltage curves of the metal complexes are plotted in Fig. 2. Diffusion currents and $E_{1/2}$ values are reported in Table I.

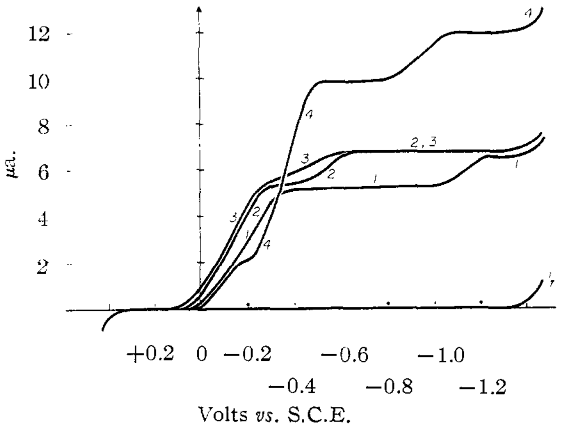

Fig. 2.—Current-voltage curves of various metal complexes with HR in AN (0.5 *M* in acetic acid and 0.1 *M* in $NaClO_4$): 1) 2×10^{-4} *M* $Fe(II)R_2$; (2) 2×10^{-4} *M* $Ni(II)R_2$; (3) 2×10^{-4} *M* $Cu(II)R_2$; (4) 2×10^{-4} *M* $Co(III)R_3.R$.

Solutions of the metal complexes also were prepared by mixing together equivalent amounts of the metal perchlorates and the reagent in acetonitrile which was 0.5 *M* in acetic acid. Current–voltage curves of these solutions were identical with those in Fig. 2 and the i_d values were proportional to the concentration of the respective complexes.

The polarograms of copper(II), nickel(II) and the iron(II) complexes exhibit two waves. The first wave corresponds to reduction of the reagent in the complex, the second wave to reduction of the metal ion to amalgam. The half-wave potentials of the second wave of the nickel and ferrous iron complexes are practically identical with the observed $E_{1/2}$ value of the corresponding metal/perchlorates in the same medium (Table I). The $E_{1/2}$ value of the second wave of the copper complex is close to that of copper(I) to copper amalgam. The copper(II) in the complex is held firmly and cannot be reduced until all the reagent is reduced. Apparently, the reduced reagent also

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[7] I. M. Kolthoff and J. F. Coetzee, This Journal, **79**, 870 (1957).

TABLE I

DIFFUSION CURRENTS AND $E_{1/2}$ VALUES OF 2×10^{-4} M METAL COMPLEXES WITH HR IN ACETONITRILE

Complex	Color	i_{d1}	i_{d2}	Ratio i_{d2}/i_{d1}	$E_{1/2}$ 2nd wave	$E_{1/2}$ of $Me(ClO_4)_2$	
NiR_2	Brown	5.30	1.30	1:4.1	−0.54	Ni(II)-Ni(0)	−0.55
FeR_2	Green	5.20	1.30	1:4.0	−1.12	Fe(II)-Fe(0)	−1.11
CuR_2	Brown	5.40	1.35	1:4.0	−0.42	Cu(I)-Cu(0)	−0.40
$CoR_3.R\cdot$	Purple-red	9.85	1.96	1:5.0	−0.93	Co(II)-Co(0)	−0.68

stabilizes the copper(II). Considering that the reduction of one molecule of reagent involves 4 electrons and that of one metal(II) 2 electrons, the ratio i_{d_2}/i_{d_1} should be 1:4 for MR_2. As seen from Table I, this ratio is found experimentally.

The polarogram of the cobalt complex differs from the others. The half-wave potential of the second wave was found to be 0.25 volt more negative than the $E_{1/2}$ for reduction of uncomplexed cobalt(II) ions in the same medium. This difference might be attributed to complex formation of cobalt with the reduced reagent. If the complex had the composition $CoR_2 \cdot 2HR$, the ratio of i_{d_2}/i_{d_1} should be 1:8, while the ratio should be 3:16 or 1:5.33 if the formula were $CoR_3 \cdot HR$. Actually, a ratio of 1:5.00 was found, which corresponds to a formula $Co(III)R_3 \cdot R\cdot$, in which $R\cdot$ is the semiquinone of HR, which would require 3 electrons per molecule for its reduction. From Fig. 2 it is seen that the reagent wave of the cobalt complex is composed of two waves, the first wave being about 2 μa., and the second wave 7.9 μa. According to the formula $Co(III)R_3 \cdot R\cdot$ the ratio of the waves should be 1:5.0, which is actually found.

In order to get further information on the formation and composition of the cobalt complex several amperometric titrations and gravimetric determinations have been carried out.

The Amperometric Titrations.—Cobalt(II) chloride in 0.2 M aqueous acetate buffer was titrated amperometrically with HR dissolved in 60% acetic acid. The diffusion current of the reagent was measured at an applied potential of −0.6 volt *vs.* S.C.E. The titration curve is plotted in Fig. 3 curve 1. In agreement with Kolthoff and Langer[5] the ratio Co:R in the precipitate at the end-point was found to be exactly 1:4.00. When the titration was carried out in 40% acetic acid, a current passed immediately upon addition of reagent, this current increased linearly with the volume of reagent added until the end-point. After the end-point the increase in current became much greater (curve 2, Fig. 3). Again, the end-point was found at a ratio of Co:R of 1:4.00.

Several titrations were carried out by first precipitating the cobalt as cobaltic hydroxide and dissolving the precipitate in hot acetic acid solution according to Mayer and Feigl's[4] procedure for preparation of the trivalent cobalt acetate. In agreement with Kolthoff and Langer[5] the results were found somewhat variable; in several titrations the ratio Co:R in the precipitate at the end-point varied between 1:3.70 and 1:3.90, indicating that most of the cobalt(III) was reduced to the divalent form upon dissolution in 40% acetic acid. A typical titration curve is plotted in Fig. 3, curve 3.

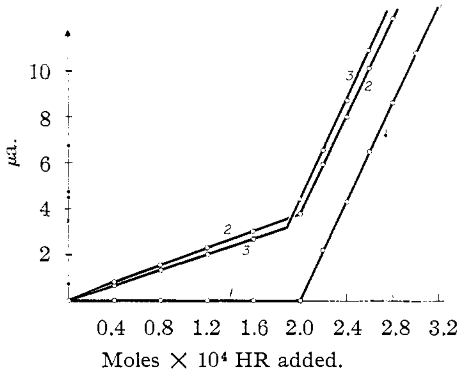

Fig. 3.—Amperometric titration of cobalt with 0.1 M HR in 60% acetic acid at −0.60 volt: (1) 5×10^{-5} M cobalt(II) in 50 ml. of acetate buffer; (2) in 50 ml. of 40% acetic acid; (3) 5×10^{-5} M "cobalt(III)" in 50 ml. of 35% acetic acid.

Amperometric titrations of the reagent with cobalt(II) perchlorate were carried out in AN which was 1 M in acetic acid and 0.1 M in sodium perchlorate. The titrations were carried out at −0.16 volt at which potential the free reagent yields a diffusion current, and the reagent in the complex a very small current only (compare Figs. 1 and 2). A typical titration line is given in Fig. 4. The end-point corresponded again to a ratio of Co:HR of 1:4.00

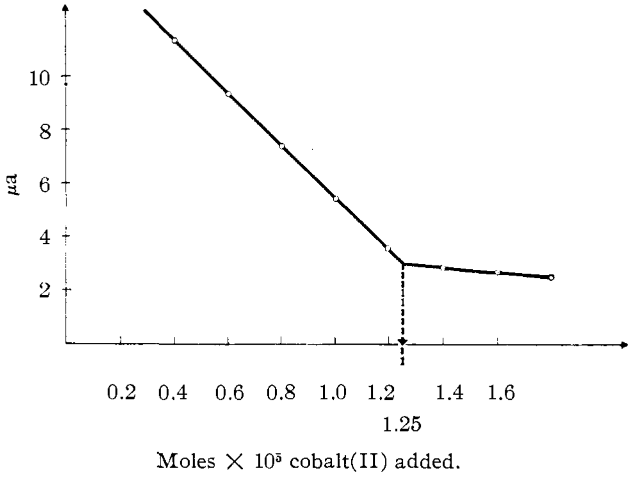

Fig. 4.—Titration of 5×10^{-5} M HR in 50 ml. of acetonitrile which was 1.0 M in acetic acid with 10^{-2} M $Co(ClO_4)_2$ in acetonitrile. Measured at −0.16 volt *vs.* S.C.E.

Gravimetric Determinations.—Several gravimetric determinations were carried out in which cobalt(II) in acetate buffer was partially precipitated with a 0.1 *M* solution of HR. One hundred per cent. excess of cobalt was present in all experiments. The precipitate was filtered, washed with distilled water, and dried in a vacuum oven at 110°. The weight of the precipitate decreased with time of heating. The results of two experiments are reported in Table II.

TABLE II

WEIGHT OF THE COBALT COMPLEX UPON DRYING IN VACUUM OVEN AT 110°, USING 8 ML. 0.1 *M* HR AND EXCESS COBALT (II)

Medium	Heating time, hr.	Wt. of ppt. in g. a	b
Acetate buffer	2	0.1366	0.1370
Acetate buffer	4	.1350	.1352
Acetate buffer	6	.1340	.1341
Acetate buffer	8	.1325	.1323
40% acetic acid	2	.1226	.1228
40% acetic acid	4	.1222	.1223
40% acetic acid	6	.1223	.1222

If the composition of the complex were $CoR_2 \cdot 2HR$, the weight of the precipitate should be 0.1499 g. assuming quantitative precipitation of HR. If 4 moles of the reagent react with 1 mole cobalt(II) to give a complex of the form $CoR_3 \cdot 2H_2O$, the weight of the complex should be 0.1223 g. As seen from Table II the final weight of the precipitate was between these two values.

The precipitation also was carried out in 40% acetic acid as solvent. The precipitate was filtered and washed with 40% acetic acid. The weight of the precipitate became constant after heating for 4 hr. and corresponded to the theoretical value of 0.1223 g. for the complex $CoR_3 \cdot 2H_2O$ suggested by Myaer and Feigl.[4]

The dried precipitates dissolved easily in benzene. Such solutions were diluted with AN which was 0.5 *M* in acetic acid and 0.1 *M* in sodium perchlorate, and current-voltage curves were run. Some results are plotted in Fig. 5. The precipitate obtained from the acetate buffer and dried at room temperature gave the same polarogram (curve 1, Fig. 5) as the complex which was formed in AN (Fig. 2). However, on drying, the first wave of the reagent wave decreased markedly. The decrease of the height of the total reagent wave corresponded to the decrease of the prewave. The ratio i_{d_2}/i_{d_1} decreased from 1:4.99 (air-dried) to 1:4.33 after 8 hr. drying at 110°.

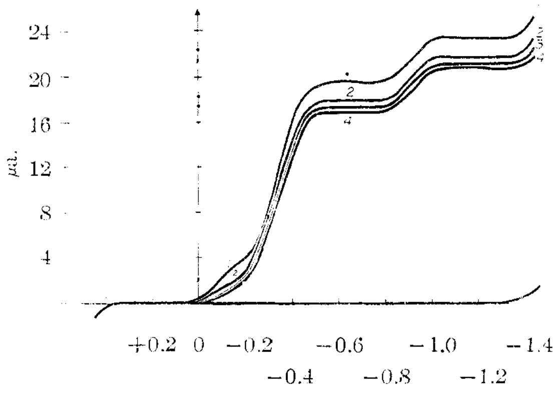

Fig. 5.—Current-voltage curves of 4 × 10^{-4} *M* Co-complex in acetonitrile which was 0.1 *M* in $NaClO_4$ and 0.5 *M* in acetic acid: (1) precipitate dried at room temperature; (2) dried 2 hr.; (3) 4 hr.; (4) 8 hr.

The current-voltage curve of the dried complex prepared in 40% acetic acid is plotted in Fig. 6, curve 2. This polarogram does not exhibit a prewave. The ratio i_{d_2}/i_{d_1} was found to be 1:4.02, indicating that the composition of the complex corresponds to $Co(III)R_3$. After precipitation in 40% acetic acid the filtrate was shaken out with benzene and the extract diluted with AN. The polarogram of this solution is plotted in curve 3 of Fig. 6. The height of this wave was 3.8 μa. while the height of the reagent wave in $Co(III)R_3$ was 15.9 μa. (curve 2). The sum of the two is 19.7 μa. and exactly equal to the total height of the total reagent wave in the complex prepared in dilute acetate buffer (curve 1). This agreement, combined with the fact that the wave in curve 3 occurs in the same potential region as the prewave in curve 1, allows the conclusion that the prewave is given by the species which is soluble in 40% acetic acid. This was confirmed by preparing a complex from dilute acetate buffer and extracting it with hot 40% acetic acid. The resulting complex now gave a polarogram identical with that in curve 2 (Fig. 6) instead of that in curve 1, while the soluble species after extraction gave a wave identical with curve 3.

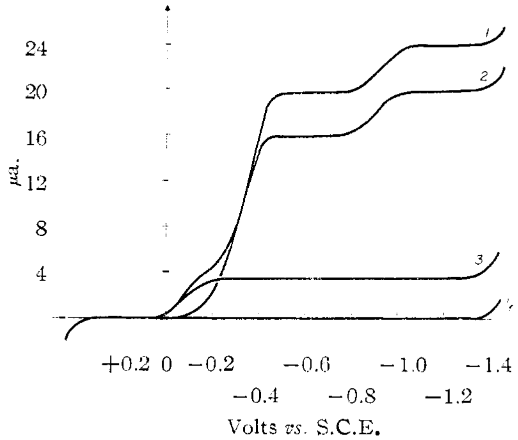

Fig. 6.—(1) Current-voltage curves of 4 × 10^{-4} *M* Co-complex in acetonitrile; (0.5 *M* in acetic acid and 0.1 *M* in sodium perchlorate); (2) of 4 × 10^{-4} *M* complex, prepared in 40% acetic acid; (3) of extract of the 40% acetic acid filtrate.

Composition and Formation of Cobalt Complexes with HR.—On the basis of the experimental results presented in the previous section it is possible to present the equations of formation and the composition of cobalt complexes with HR. The precipitate obtained from an acetate buffer is evidently not a pure compound and contains some "coprecipitated reagent." This "coprecipitated reagent" is soluble in warm 40% acetic acid. After extraction of the precipitate with 40% acetic acid its formula is $Co(III)R_3$. This compound is obtained directly when the precipitation is carried out in 40% acetic acid as was indicated by the results of polarographic and gravimetric experiments and amperometric titrations.

The precipitate obtained from dilute acetate buffer contains cobalt and reagent in the molecular ratio 1:4.00. After extraction with 40% acetic acid this ratio becomes 1:3.00 (Co(III)R_3). The extracted reagent requires only 3 electrons per molecule in its reduction, while HR requires 4 electrons. This is strong evidence that the extra molecule of reagent is a free radical, denoted as $H_2R\cdot$, which is an intermediate and stable product formed in the reduction of HR

$$\mathrm{HR} + \mathrm{H}^+ + e^- \longrightarrow \mathrm{H_2R}\cdot$$

It is not plausible to assume that the precipitate in dilute acetate buffer is formed by the sequence of reactions

$$\mathrm{Co(II)} + \mathrm{HR} \longrightarrow \mathrm{Co(III)} + \mathrm{H_2R}\cdot \qquad (1)$$

$$\mathrm{Co(III)} + 3\mathrm{HR} \longrightarrow \mathrm{Co(III)R_3} + 3\mathrm{H}^+ \qquad (2)$$

$$\mathrm{Co(III)R_3} + \mathrm{H_2R}\cdot \longrightarrow \mathrm{CoR_3{\cdot}H_2R}\cdot \qquad (3)$$

In amperometric titrations of cobalt(II) with the reagent in acetate buffer and in the reverse titration it was found that at any stage of the titration before and after the end-point the over-all composition of the precipitate corresponded to 1:4.00. In 40% acetic acid the reaction ratio in both types of titration also was at any stage 1:4.00, although the precipitate had the composition Co(III)R_3. Finally, from the identical polarographic behavior in AN of the precipitate formed from dilute acetate buffer and of the reaction product obtained by mixing cobalt(II) and HR in AN, and also from amperometric titrations in AN it appears impossible that the formation of the final reaction product occurs by the sequence of reactions 1 and 2. It is postulated that this sequence of reactions accounts for the observed results

$$\mathrm{Co(II)} + 2\mathrm{HR} \longrightarrow \mathrm{Co(II)R_2} + 2\mathrm{H}^+ \qquad (4)$$

$$2\mathrm{Co(II)R_2} \longrightarrow \mathrm{Co(III)R_3} + \mathrm{H_2R}\cdot + \mathrm{Co(II)} \qquad (5)$$

The cobalt(II) complex formed according to eq. 4 is transformed rapidly in acid medium. In dilute acetate buffer $H_2R\cdot$ is insoluble and coprecipitates with Co(III)R_3. In 40% acetic acid $H_2R\cdot$ is soluble and only Co(III)R_3 precipitates. In AN both Co(III)R_3 and $H_2R\cdot$ are soluble.

As stated by Ilinski and v. Knorre[1] and confirmed in this Laboratory Co(II)R_2 precipitates on mixing cobalt(II) with the sodium salt of the reagent in neutral or slightly alkaline medium. When such a precipitate is dissolved in AN containing acetic acid, it should disproportionate according to eq. 5. Qualitatively the polarogram should be and is found similar to that of curve 1 in Fig. 6. The ratio of the prewave to that of the total reagent wave minus the prewave was found 1:4, as required by eq. 5. The ratio of i_{d2} (cobalt wave, in this case Co(III) and Co(II)) to i_{d1} (total reagent wave) should be 1:3.00. Actually in several experiments a ratio of 1:2.97 ± 0.03 was found, in excellent agreement with the postulated interpretation.

The gravimetric data (Table II) and Fig. 5 indicate that coprecipitated $H_2R\cdot$ can be volatilized more or less completely in a vacuum oven at 110°. The reason why Mayer and Feigl[4] could obtain such good results is not because they first oxidized cobalt from the divalent to trivalent state, but because they carried out the precipitation in fairly concentrated acetic acid medium in which $H_2R\cdot$ is soluble.

Acknowledgment.—Appreciation is expressed to the Graduate School of the University of Minnesota for a grant in support of this research.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, WESTVACO CHLOR-ALKALI DIVISION, FOOD MACHINERY AND CHEMICAL CORPORATION]

The Synthesis of Tetrakis-(dichloromethylphosphine)-nickel from Methyldichlorophosphine and Nickel[1a]

BY LOUIS D. QUIN[1b]

RECEIVED FEBRUARY 23, 1957

The reaction of bulk nickel with methyldichlorophosphine was found to proceed readily to give high yields of tetrakis-(dichloromethylphosphine)-nickel. This represents the first synthesis of this type of compound by the direct reaction of nickel and a trivalent phosphorus compound. A small amount of a black unidentified solid adhering to the residual nickel is also formed. Similar conditions were not effective for causing phosphorus trichloride or phenyldichlorophosphine to react with nickel. The properties of tetrakis-(dichloromethylphosphine)-nickel were in general similar to those of related compounds.

Several compounds of the type $Ni(PY_3)_4$ have been prepared in recent years by the reaction of nickel tetracarbonyl[2-5] or other $Ni(PY_3)_4$ compounds[2,3] with trivalent phosphorus compounds. Their preparation by the direct reaction of nickel with phosphorus compounds has not yet been successful, although evidence of a reaction has been obtained with phosphorus trichloride.[2] Phosphorus trifluoride showed no reaction with nickel.[3,6] We now wish to report the facile synthesis of the new compound tetrakis-(dichloromethylphosphine)-nickel, $Ni(CH_3PCl_2)_4$ (I), by the reaction of methyldichlorophosphine and elemental nickel.

The reaction has been affected by several tech-

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(1) (a) Portions of this paper report work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C. (b) Department of Chemistry, Duke University, Durham, N. C.

(2) J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

(3) G. Wilkinson, THIS JOURNAL, **73**, 5501 (1951).

(4) G. Wilkinson, *Z. Naturforsch.*, **9b**, 446 (1954).

(5) L. Malatesta and A. Sacco, *Ann. chim.*, **44**, 134 (1954).

(6) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).