various builders, and with sodium or potassium chloride and other soaps.

More of the silicious silicates than of the metasilicate or phosphates is required to "salt in" liquid crystalline middle soap or to "salt out" liquid crystalline neat soap. The silicious silicates have less effect than the phosphates on the transition temperature from crystalline to liquid crystalline soap systems.

PHILADELPHIA, PENNA. RECEIVED SEPTEMBER 9, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Oxidation of +4 Vanadium

BY JAMES J. LINGANE AND LOUIS MEITES, JR.

The fact that +4 vanadium in 1 *N* sodium or potassium hydroxide produces a well developed anodic wave, representing oxidation to the +5 state, was recently reported.[1] The present paper presents the results of a systematic study of various factors on the oxidation of +4 vanadium at the dropping electrode.

Experimental

Polarograms were recorded with a Sargent-Heyrovsky Model XI Polarograph calibrated according to the usual techniques.[2] Diffusion current constants were measured with a manual instrument incorporating a calibrated Leeds and Northrup Type HS galvanometer.

An H-cell[3] provided with a saturated calomel electrode whose potential was periodically checked against other reference electrodes was used. The dropping electrode assembly included a vertical stand-tube connected to a mercury reservoir and to an automatic *m*-measuring device.[4]

Since alkaline solutions of +4 vanadium are rapidly oxidized by air, we employed both hydrogen and sulfite ion to remove oxygen from the solutions. A stock solution of +4 vanadium was prepared by reduction with sulfur dioxide of a suspension in 10 *M* sulfuric acid of a sample of specially purified ammonium metavanadate whose preparation we have previously described.[5] The completely reduced solution was freed from sulfur dioxide by prolonged boiling and sweeping out with carbon dioxide. It was then cooled, filtered and diluted to volume. Other chemicals were reagent grade and were not further purified.

A water thermostat was used to maintain a temperature of 25.00 ± 0.01°. A Beckman glass electrode *p*H meter was used for all *p*H measurements.

Data and Discussion

Seven determinations of the half-wave potential of the anodic wave of +4 vanadium in 1 *N* sodium hydroxide containing 0.08 *M* sodium sulfite (curves I, Fig. 1) led to a mean value of −0.432 ± 0.004 v. *versus* the saturated calomel electrode. These measurements were made from large-scale plots of $E_{\text{d.e.}}$ against log $(i/i_d - i)$, and their mean is in good agreement with a previous measurement.[1]

Table I presents data on the diffusion current constant, $i_d/Cm^{2/3}t^{1/6}$, of this wave. The supporting electrolyte was protected by both purified hydrogen and sulfite, and the acidic vanadyl solution was saturated with sulfur dioxide to prevent local oxidation on addition to the alkaline supporting electrolyte. The measurements were made at −0.20 v. *versus* the saturated calomel electrode. Diffusion currents have been corrected for the residual current. No gelatin or other maximum suppressor was present. The diffusion current is not appreciably changed by varying the sodium hydroxide concentration between 0.3 and 3 *N*.

TABLE I

DIFFUSION CURRENT CONSTANT OF +4 VANADIUM IN 1 *N* SODIUM HYDROXIDE–0.08 *M* SODIUM SULFITE

$m^{2/3}t^{1/6} = 2.425$ mg.$^{2/3}$ sec.$^{-1/2}$

+4 Vanadium, millimolar	i_d microamp.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
0.1900	−0.677	−1.465
.346	−1.240	−1.466
.374	−1.334	−1.469
.548	−1.940	−1.463
.667	−2.378	−1.468
.719	−2.540	−1.464
.880	−3.131	−1.467
.966	−3.44	−1.468
1.038	−3.67	−1.462
1.190	−4.24	−1.468
1.245	−4.45	−1.469
1.338	−4.75	−1.464
1.480	−5.29	−1.469
1.619	−5.74	−1.462
		Mean −1.466 ± 0.002

Curves II of Fig. 1 demonstrate the deleterious effect of gelatin on the polarograms of +4 vanadium in 1 *N* sodium hydroxide–0.08 *M* sodium sulfite. The half-wave potential in the presence of 0.01% gelatin is −0.35 v., or 0.08 v. more positive than in the absence of gelatin. Although careful measurements have shown that the diffusion cur-

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[1] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

[3] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[4] J. J. Lingane, *ibid.*, **16**, 329 (1944).

[5] J. J. Lingane and L. Meites, Jr., THIS JOURNAL, **68**, 2443 (1946)

rent constant at −0.20 v. is not altered by the presence of 0.01% gelatin, the considerable shortening of the plateau resulting from the positive shift of the half-wave potential makes the use of gelatin undesirable.

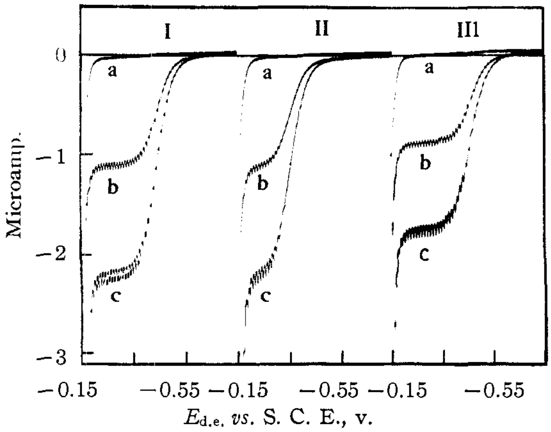

Fig. 1.—(I) Polarograms of (a) 0, (b) 0.45 and (c) 0.88 millimolar +4 vanadium in 1 *M* sodium hydroxide, 0.08 *M* sodium sulfite. (II) Same as I with 0.01% gelatin. (III) Same as I with 1 *M* sodium carbonate.

As the concentration of sodium hydroxide is decreased below about 0.25 *N* in the presence of 0.08 *M* sodium sulfite, the wave divides into two waves of nearly equal height, the first of which is rather poorly developed due to the small separation of the waves, while the second is distorted by a rounded minimum. Typical of this behavior is the polarogram in Fig. 2, which was recorded with 0.88 millimolar +4 vanadium in 0.030 *M* sodium hydroxide and 0.08 *M* sodium sulfite. Both waves are seen by their slopes to be irreversible, in contrast to the apparent reversibility of the wave in 1 *N* alkali.[1] The most probable explanation of the doublet wave is the existence of two vanadium species in sluggish equilibrium. Crow[6] has presented evidence that alkaline solutions of +4 vanadium contain both $V_4O_9^{--}$ and $V_2O_5^{--}$.

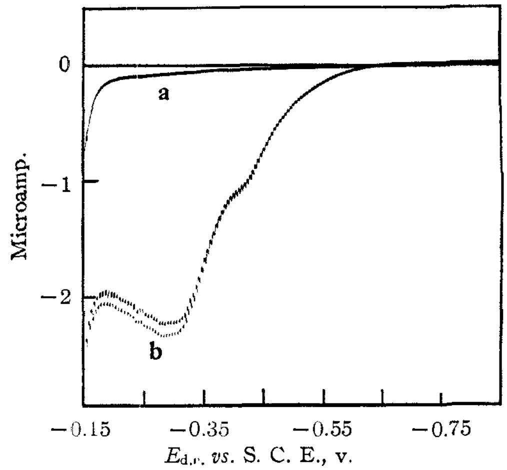

Fig. 2.—Polarograms of (a) 0 and (b) 0.88 millimolar +4 vanadium in 0.030 *M* sodium hydroxide and 0.08 *M* sodium sulfite.

In 2.00 *M* sodium hydroxide the half-wave potential of the single wave is −0.438 v., in 1.00 *M* sodium hydroxide the half-wave potential is 0.432 v. and in 0.50 and 0.25 *M* sodium hydroxide the half-wave potentials are −0.426 and −0.419 v., respectively.

In 0.122 *M* sodium hydroxide the half-wave potential of the first wave is −0.50 v. and that of the second is −0.40 v.; in 0.061 *M* sodium hydroxide the half-wave potentials are −0.49 and −0.39 v., and in 0.030 *M* sodium hydroxide they are −0.47 and −0.36 v.

In carbonate buffers of *p*H smaller than that corresponding to 0.03 *M* sodium hydroxide, the anodic wave is normal and there is no sign of the doublet wave observed in very dilute sodium hydroxide. As the *p*H of the carbonate solutions is decreased, the half-wave potential becomes increasingly more positive: in 0.5 *M* sodium carbonate −0.5 *M* potassium bicarbonate (*p*H 9.4) the

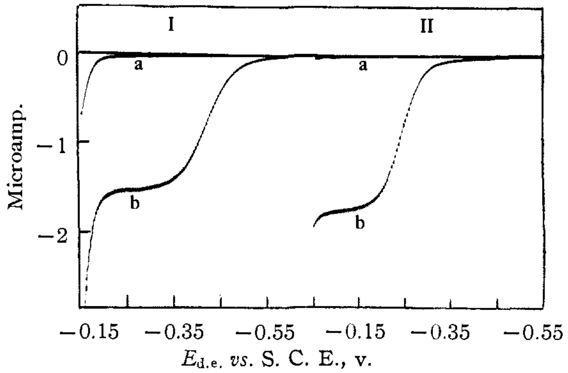

Fig. 3.—Polarograms of (a) 0 and (b) 0.88 millimolar +4 vanadium in (I) 1 *M* sodium hydroxide and 0.08 *M* sodium sulfite, and (II) 0.5 *M* sodium carbonate, 0.5 *M* potassium bicarbonate and 0.08 *M* sodium sulfite, *p*H 9.4.

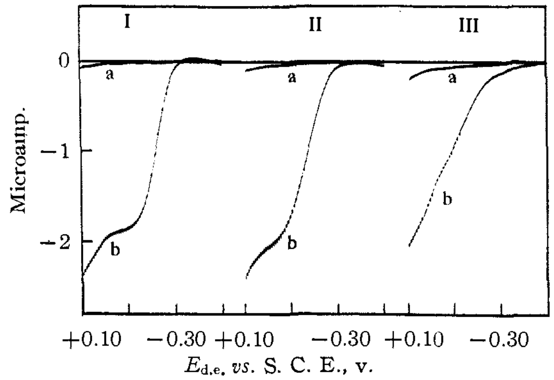

Fig. 4.—Polarograms of (a) 0 and (b) 0.88 millimolar +4 vanadium in (I) 1 *M*, (II) 0.5 *M* and (III) 0.1 *M* potassium bicarbonate saturated with carbon dioxide. *p*H values were, respectively, 7.6, 7.2 and 6.7.

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[6] J. K. Crow, *J. Chem. Soc.*, **30**, 454 (1876).

half-wave potential is -0.342 v., in 1 *M* potassium bicarbonate saturated with carbon dioxide (*p*H 7.6) it is -0.22 v., and in 0.5 and 0.1 *M* potassium bicarbonate saturated with carbon dioxide (*p*H 7.2 and 6.7) the half-wave potentials are -0.16 and -0.09 v., respectively. Polarograms of $+4$ vanadium in these media are shown in Figs. 3 and 4. Figure 5, made with solutions of $+4$ vanadium in acetic acid–sodium acetate buffers, shows that the shift of the half-wave potential to more positive values with decreasing *p*H continues until the wave has almost disappeared at *p*H 4.7.

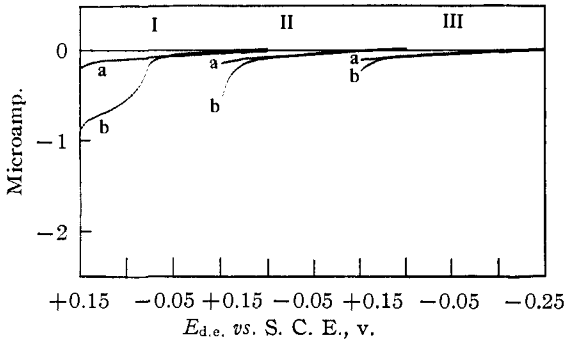

Fig. 5.—Polarograms of (a) 0 and (b) 0.88 millimolar $+4$ vanadium in acetic acid–sodium acetate buffers, *p*H (I) 6.1, (II) 5.5 and (III) 4.7.

Even though the wave in an 0.5 *M* potassium bicarbonate–saturated carbon dioxide buffer *p*H 7.2 (curves II, Fig. 4) is not well-defined, the diffusion current constant, measured with the manual instrument at $+0.04$ v. *versus* the saturated calomel electrode, was found to be reproducible and equal to -1.41 ± 0.01 over a range of $+4$ vanadium concentrations from 0.17 to 1.62 millimolar. The wave in this medium has been applied to the rapid determination of vanadium in steels and other ferro-alloys.[7]

Addition of 1 *M* sodium carbonate to the sodium hydroxide–sodium sulfite supporting electrolyte (curves III, Fig. 1) decreases the diffusion current constant from -1.466 to -1.17, although the half-wave potential remains constant at -0.44 v. Although ammonium vanadylcarbonate is completely dissociated in dilute solution in pure water,[8] the large decrease in the diffusion current constant in the presence of a large excess of sodium carbonate must be attributed to the formation of a vanadylcarbonate ion having a considerably smaller diffusion coefficient than the vanadite ion. The observed behavior agrees with that expected in the presence of a weak complex in rapid equilibrium with the predominating form.

Curves I of Fig. 6 show the effect of 1 *M* potassium thiocyanate on the anodic wave of $+4$ vanadium. The small anodic wave in the residual current curve is undoubtedly due to the presence of some impurity in the potassium thiocyanate used. In this medium the half-wave potential shifts to a value which cannot be measured precisely, but which appears to be close to -0.30 v., and consequently there is no opportunity for the development of the plateau before the dissolution of the electrode mercury begins. This indication of a fairly strong thiocyanate complex of $+4$ vanadium is in accord with the investigation of Koppel and Goldman.[9] These authors prepared the solid salts $(NH_4)_2VO(SCN)_4 \cdot 5H_2O$ and $K_2VO(SCN)_4 \cdot 5H_2O$, but did not study their behaviors in solution. The polarographic evidence indicates that a vanadyl thiocyanate complex exists in aqueous solution, and from the shift in the half-wave potential we calculate the approximate value 10^{-2} for its dissociation constant.

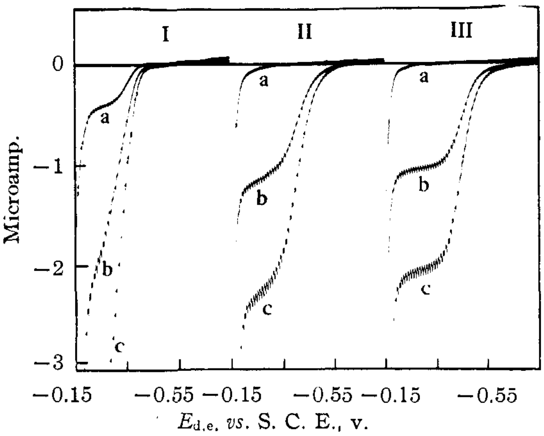

Fig. 6.—Polarograms of (a) 0, (b) 0.45 and (c) 0.88 millimolar $+4$ vanadium in 1 *M* sodium hydroxide, 0.08 *M* sodium sulfite and (I) 1 *M* potassium thiocyanate, (II) 1 *M* potassium chloride and (III) 1 *M* potassium fluoride.

Curves II of Fig. 6 are polarograms of $+4$ vanadium in 1 *N* sodium hydroxide–0.08 *M* sodium sulfite–1 *M* potassium chloride. The half-wave potential in this medium (-0.39 v.) is 0.04 v. more positive than in the absence of chloride, which points to the formation of a chloride complex, possibly $VOCl_4^{--}$.

In 1 *N* sodium hydroxide–0.08 *M* sodium sulfite–1 *M* potassium fluoride (curves III, Fig. 6) the half-wave potential is -0.44 v., and thus virtually identical with that observed in the absence of fluoride. This indication that no fluoride complex of $+4$ vanadium is formed is in agreement with the fact that the alkali vanadylfluorides prepared by Petersen[10] displayed none of the character of true complexes. The diffusion current of the excellently-defined wave in this medium has been found to be -1.46 ± 0.01, and thus the same as in the absence of fluoride.

Solutions of $+4$ vanadium in 1 *N* sodium hydroxide–0.08 *M* sodium sulfite–1 *M* sodium tar-

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(7) L. Meites, Jr., Ph.D. Thesis, Harvard University, 1947.

(8) I. Koppel, R. Goldmann and A. Kaufmann, *Z. anorg. Chem.*, **45**, 319 (1905).

(9) I. Koppel and R. Goldman, *ibid.*, **36**, 281 (1903).

(10) E. Petersen, *J. prakt. Chem.*, [2] **40**, 193 (1889).

trate (curves I, Fig. 7) give an anodic wave at −0.38 v., whose poorly developed diffusion current plateau indicates that the oxidation is partly rate-controlled. Barbieri[11] has reported the preparation of several alkali vanadyltartrates having the type formula $M_2(VO)(C_4H_2O_6)\cdot 2H_2O$, in which the VO^{++} ion replaces the two hydrogens of the hydroxyl groups. The complex was found to be very stable toward alkalies, and electrolysis showed the vanadium to be in the anion.

We find that, on the basis of its polarographic behavior, the vandyltartrate ion is not much more stable than the $V_4O_9^=$ and $V_2O_5^=$ ions which appear[6,9] to be the ionic state of +4 vanadium in tartrate-free alkaline solutions, but that the complex dissociates only slowly, so that the anodic limiting current is controlled to some extent by the rate of dissociation of the complex rather than entirely by the rate of diffusion of the ion up to the electrode surface.

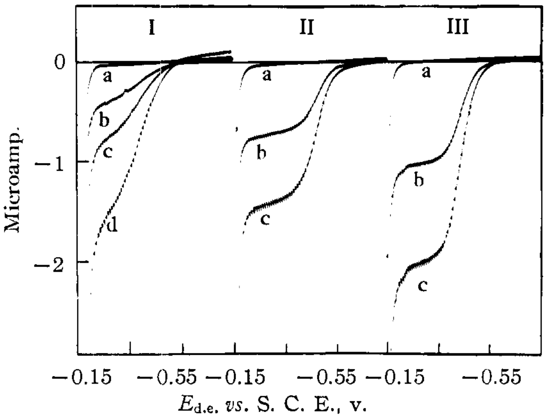

Fig. 7.—Polarograms of (a) 0, (b) 0.45 and (c) 0.88 millimolar +4 vanadium in 1 *M* sodium hydroxide, 0.08 *M* sodium sulfite and (I) 1 *M* sodium tartrate, (II) 1 *M* sodium citrate and (III) saturated potassium oxalate.

Curves II of Fig. 7 are polarograms of +4 vanadium in 1 *N* sodium hydroxide–0.08 *M* sodium sulfite–1 *M* sodium citrate. Since the citrate ion does not possess the >C(OH)—C(OH)< group found in the tartrate ion, it is to be expected that a vanadylcitrate complex will be less stable than the tartrate complex. The smallness of the diffusion current constant in the presence of 1 *M* sodium citrate (−1.10 ± 0.02) indicates that a citrate complex is present in the strongly alkaline solution, but the fact that the half-wave potential is virtually the same as in the absence of citrate ion shows that the complex is weak.

In 1 *M* sodium hydroxide–0.08 *M* sodium sulfite–saturated potassium oxalate (curves III, Fig. 7) the half-wave potential is −0.43 v., indicating that no oxalate complex of +4 vanadium exists under these conditions. The diffusion current constant of +4 vanadium in this alkaline oxalate medium is −1.36 ± 0.02, only slightly less than in the absence of oxalate ion, which confirms the conclusion that an oxalate complex is not formed.

In the formation of complexes between metal ions and tartrate or citrate ions the hydroxyl groups play an important role, and especially in alkaline media there is conclusive evidence that the hydrogen of the hydroxyl group is replaced by a bond to the metal ion. As a general rule the adjacent hydroxyl groups in tartrate ion lead to the formation of more stable complexes than the lone hydroxyl group in citrate ion, and the absence of hydroxyl groups in oxalate ion renders oxalate complexes the least stable of the three.

Saturating the standard sodium hydroxide–sodium sulfite supporting electrolyte with sodium phosphate produces a positive shift of the half-wave potential to −0.37 v. (curves I, Fig. 8), indicating the formation of a phosphate complex. Although Berzelius[12] reported the preparation of vanadyl phosphate, no previous information has been published bearing on the existence of a vanadyl–phosphate complex.

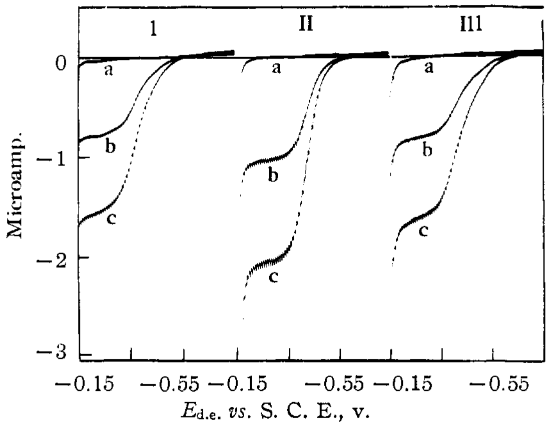

Fig. 8.—Polarograms of (a) 0, (b) 0.45 and (c) 0.88 millimolar +4 vanadium in 1 *M* sodium hydroxide, 0.08 *M* sodium sulfite and (I) saturated sodium phosphate, (II) saturated sodium pyrophosphate and (III) 1 *M* sodium tetraborate.

The wave in 1 *N* sodium hydroxide–0.08 *M* sodium sulfite saturated with sodium pyrophosphate is normal in all respects and indistinguishable from that obtained in the absence of pyrophosphate (curves II, Fig. 8).

Addition of 1 *M* sodium tetraborate to the standard supporting electrolyte (curves III, Fig. 8) causes no shift in the half-wave potential, but the diffusion current constant decreases to −1.22. The decreased diffusion current constant, coupled with the greater wave slope as compared to 1 *N* sodium hydroxide alone, suggests the formation of a vanadylborate complex.

Summary

1. The polarographic oxidation of +4 vana-

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(11) G. A. Barbieri, *Atti accad. Lincei*, **23**, II, 47 (1914).

(12) L. Gmelin and K. Kraut, "Handbuch der anorganischen Chemie," 3, ii, 125, Heidelberg (1908).

dium has been studied in 1 *N* sodium hydroxide solutions containing many different added anions, and information is presented on the ionic states of the vanadium in these solutions.

2. In solutions of sodium hydroxide less concentrated than about 0.25 *N*, +4 vanadium yields a double anodic wave which is ascribed to oxidation of the two ions $V_2O_5^{--}$ and $V_4O_9^{--}$ present in approximately equal quantities.

3. Anodic waves for the oxidation of +4 vanadium to the +5 state are obtained at all *p*H values greater than about 4.7, and the characteristics of the waves in acetate and bicarbonate buffers of varying *p*H have been studied.

CAMBRIDGE 38, MASSACHUSETTS

RECEIVED JANUARY 6, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

The Oxygen-carrying Synthetic Chelate Compounds. VII. Preparation[1]

BY R. H. BAILES[2] AND M. CALVIN

In previous papers of this series[3] a number of physical measurements on a selected group of chelate compounds in certain special states, were described. It is the purpose of the present paper not only to give the methods of preparation of these compounds in all of their forms, but to describe all of those which were prepared for the examination of their oxygen carrying properties, and sufficiently well characterized to be certain of their structure.[4]

I. Cobalt Chelates Prepared from Salicylaldehyde and Its Derivatives and with Diamines of the Type of Ethylenediamine[5]

(1) **Cobalt Di-(salicylal)-ethylenediimine.**—Pfeiffer[6] reported the preparation of the red crystalline compound and stated that it slowly turned brown on standing exposed to air. He apparently did no further work with this compound. Tsumaki[7] took up the problem and announced that the darkening was due to a reversible oxidation. He recrystallized the red crystals (obtained from aqueous alcohol) from benzene and from chloroform. From benzene he obtained red brown needles which were slowly oxygenated in air and would, when heated to 100°, return to their original color and weight. From chloroform he obtained shining dark-red prisms which contained one solvated chloroform molecule. By heating the dark-red prisms to 100° they changed to a red-brown powder which would absorb oxygen much more rapidly than the needle-like crystals. They would become black after a day and reach a constant weight. The black powder would lose its oxygen easily when heated in a stream of carbon dioxide and return to its original color and weight. This black compound contained one mole of oxygen to three moles of cobalt.

At this point we took up the problem. We very soon found that this chelate could be prepared readily in a well-defined crystal form which was inactive toward oxygen, of which the following method furnishes a yield of 86%.

Five hundred and seventy-six grams of salicylaldehyde and 203 g. of 68.6% ethylenediamine were dissolved in 6.5 liters of 95% ethanol placed in a 12-liter flask fitted with a stopcock. They react together to give the Schiff base which precipitates but will dissolve when warmed to about 60°; five hundred and seventy-six grams of cobaltous acetate tetrahydrate was dissolved in 3 liters of water and heated to 60°. The cobaltous acetate solution was then rapidly poured, with shaking, into the alcohol solution of the Schiff base. The flask was then closed with a stopper fitted with a stopcock and connected to the aspirator. When the boiling alcohol had swept all the air from the flask the stopcock was closed. At first a brown gelatinous product forms which rapidly changes to large red crystals provided the flask is kept warm. After cooling the crystals were filtered or centrifuged, washed with water and then dried in a vacuum desiccator. These large red crystals do not absorb oxygen. If the entire preparation is done at room temperature the product is a brown gelatinous material which is partially active to oxygen. If the brown gelatinous product is not filtered but is allowed to remain in the flask away from air it slowly changes to large dark red, almost black, crystals, the change being complete in about ten days depending upon the quantity and the room temperature.

Analysis of red-black crystals. Calcd.: C, 59.10; H, 4.30; N, 8.63; Co, 18.14. Found: C, 59.09, 59.23; H, 4.35, 4.06; N, 8.62; Co, 18.15, 17.91.

If methyl alcohol is substituted for ethyl in the above preparation, identical products are obtained.

The red crystals are insoluble in water, ether, carbon tetrachloride, triethylamine, slightly soluble in di-isopropylamine, ethanol, benzene, chloroform, acetone, *n*-propyl alcohol, isoamyl alcohol, methylene dichloride, soluble in piperidine, *n*-butylamine, aniline and pyridine.

It was found possible to crystallize the red inactive crystals from pyridine in absence of air. This was done by heating them to boiling under reflux in a good hood with 13 ml. of pyridine for each gram of chelate. When cooled an almost quantitative yield of fine bright red crystals is obtained which are monopyridinate. When heated for one and one-half hours at 170° at a pressure not greater than 2 mm. they lose 19.7% in weight while the calculated value for one pyridine is 19.55%. The color changes from bright red to brown.

Analysis of $CoC_{16}H_{14}N_2O_2 \cdot 1C_5H_5N$. Calcd.: C, 62.4; H, 4.74; N, 10.39; Co, 14.6. Found: C, 62.29, 62.18; H, 4.66, 4.62; N, 10.3, 10.1; Co, 15.0, 15.6.

This brown powder obtained by removal of the pyridine

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[1] The work herein reported was done in part under contract OEM sr-276 between the National Defense Research Committee and the University of California during the period February 1941 to April 1944.

[2] Present address: Department of Chemistry, Boston University, Boston, Massachusetts.

[3] I through V, THIS JOURNAL, **68**, Nov. (1946); VI, *ibid.*, **68**, Dec. (1946).

[4] A further group of 119 compounds were also prepared but their characterization was incomplete. The list of these compounds together with the observations that were made of their behavior may be obtained upon request from the Library Photo Service, University of California, Berkeley (Photostat, $1.50; Microfilm, $1.00).

[5] Nitrogen analyses were performed by the micro-Dumas technique. Carbon and hydrogen analyses were obtained by the micro-Liebig method. Cobalt values were calculated from the residues of the Liebig combustions and are frequently in error due to sublimation of the compound being burned. Occasionally a sample would explode so that no cobalt residue would be obtained.

[6] P. Pfeiffer, *Ann.*, **503**, 84 (1933).

[7] Tsumaki, *Bull. Chem. Soc. Japan*, **13**, 247 (1938).