number of hours and the requisite amount of ether was then distilled into B. After freezing the ether in liquid air, the unit was evacuated and sealed at K and L. On inverting the apparatus the bromide was dissolved and an iron weight, sealed in glass (S), broke the inseal (N). The solution on coming in contact with the sodium amalgam first acquired the yellow color of the free radical and finally the reddish-orange color of the sodium derivative. The curve for the absorption spectrum of sodium triphenylmethyl, which is presented in this paper, was obtained for a 0.0011 molar solution of triphenylmethyl in contact with a 10% sodium amalgam containing 0.025 mole of sodium. The curve that was obtained shortly after the color of the sodium derivative appeared in the solution showed the presence not only of the metal derivative, but also of the free radical (detected by the band at about 3000 mm.$^{-1}$). The curve as presented was obtained after the system had been shaken until it reached equilibrium.

Sulfur dioxide solutions of triphenylmethyl were prepared in two ways: first, by the reaction in that solvent of a known amount of triphenylbromomethane and silver; and, second, by the use of a known amount of crystalline triphenylmethyl, previously prepared. The identical absorption curve was obtained by either method.

Other investigators have reported that triphenylmethyl in sulfur dioxide does not react with oxygen. This observation has been corroborated. When the sulfur dioxide was evaporated and pure ether added, the absorption spectrum, typical of the ether solution, was obtained and from this ether solution the peroxide was obtained. The yellow residue obtained upon evaporation of the sulfur dioxide was only partially soluble in ether and even after boiling the mixture the residue retained the odor of sulfur dioxide, showing that a complex of free radical and sulfur dioxide was formed that is quite stable at ordinary temperatures.[18]

The temperature of the air-bath which was used for the low temperature spectral work was ascertained with a calibrated copper–constantan thermocouple and potentiometer. The apparatus and procedure for obtaining the quantitative absorption spectra has been described.[19]

Summary

1. Curves are presented for the quantitative absorption spectrum of each: ether solutions of triphenylmethyl and of the sodium derivative of triphenylmethyl, and sulfur dioxide solutions of triphenylbromomethane and of triphenylmethyl.

2. The data indicate that triphenylmethyl exists in a quinonoid modification in solution in ether and in sulfur dioxide.

3. When dissolved in sulfur dioxide, triphenylmethyl is in equilibrium with the triphenylmethyl cation and an electron, with solvation, of course, of the ions.

ANN ARBOR, MICHIGAN RECEIVED JULY 2, 1935

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(18) Schlenk and Weickel have described an addition compound from tribiphenylmethyl and sulfur dioxide [*Ann.*, **372**, 11 (1909)].

(19) Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RHODE ISLAND STATE COLLEGE]

The Hexammine Cobaltic Compounds in the Gravimetric Determination of Vanadium[1]

BY W. GEORGE PARKS AND H. J. PREBLUDA

M. Parks[2] in the development of a gravimetric method for the determination of vanadium, found that the addition of hexammine cobaltic ion to a neutral solution of the metavanadate results in an apricot colored precipitate which when ignited gives a mixture of oxides represented by $2CoO\cdot 3V_2O_5$. Addition of the $Co(NH_3)_6^{+++}$ ion to an alkaline solution results in the precipitation of an orange colored precipitate which on ignition yields a mixture of oxides represented by $4CoO\cdot 3V_2O_5$. The metavanadate ion in a solution acidified with acetic acid and ammonium acetate (*p*H 5.1) gives a yellow precipitate which on ignition yields a mixture of oxides represented by $2CoO\cdot 9V_2O_5$. In this acid medium the metavanadate may be separated quantitatively from phosphate, arsenate, ferric, cupric and calcium ions. It cannot be separated from tungstate, molybdate or lead ions.

Parks assumed that hexammine cobaltimetavanadate $Co(NH_3)_6(VO_3)_3$ was formed in a neutral solution, hexammine cobaltipyrovanadate $[Co(NH_3)_6]_4(V_2O_7)_3$ in a basic solution and hexammine cobaltideuterohexavanadate $[Co(NH_3)_6]_4(V_6O_{17})_3$ in an acid solution because these formulas were the only possibilities consistent with the data obtained from the ignited oxides.

This investigation was undertaken to establish the definite composition of these compounds by chemical analysis.

Preparation of Materials

Ammonium Metavanadate Solution.—A sample of C. P. NH_4VO_3, furnished by the Vanadium Corporation of America, was recrystallized three times from distilled

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(1) This paper is from a thesis submitted by H. J. Prebluda to the Faculty of Rhode Island State College in partial fulfilment of the requirements for the degree of Master of Science.

(2) M. Parks, "Dissertation," Columbia University, 1930.

water. To avoid decomposition the solution was not heated above 45°. The final product was pure white. A solution was made up containing 5.1457 g. of NH_4VO_3 per liter (0.1 g. of V_2O_5 per 25 cc.).

Hexammine Cobaltichloride Solution.—The best grade of C. P. salt was recrystallized three times from distilled water. A solution was made up containing 20 g. of the salt per liter. This reagent was preserved in a bottle covered with dark paper since exposure to light will cause decomposition.

Sodium Hydroxide Solution.—Approximately 0.1 *N* sodium hydroxide was prepared according to standard methods[3] and standardized against Bureau of Standards potassium acid phthalate. The solution was preserved in a waxed bottle fitted with an all glass carbon dioxide guarded buret. An approximately 0.1 *N* hydrochloric acid solution was prepared and standardized against the sodium hydroxide.

Ceric Sulfate Solution.—Approximately 0.1 *M* ceric sulfate was prepared by dissolving ceric ammonium sulfate in 1 *M* sulfuric acid. The solution was standardized according to the method of Willard and Young[4] using the ferrous complex of *o*-phenanthroline as indicator.

Ferrous Sulfate Solution.—Approximately 0.01 *M* ferrous sulfate solution in 1 *M* sulfuric acid was standardized against the ceric sulfate immediately before use as recommended by Walden, Hammett and Edmonds.[5]

Mercury.—Redistilled mercury was further purified by the method of Hulett.[6]

Solutions of Acids and Bases.—C. P. solutions of hydrochloric acid, ammonium hydroxide, and acetic acid were used and diluted to the desired concentrations.

Experimental Procedure

The neutral, basic, and acid precipitates were prepared according to the methods given by Parks.[2] The precipitates were washed and dried at 110°.

Ammonia determinations were made on samples of each of the precipitates using a modified Kjeldahl method. The apparatus was tested by running a blank determination using a known quantity of the purified hexammine cobaltichloride. The results checked with the theoretical ammonia content to within 0.03%. The samples of the precipitates to be analyzed were weighed in a very small beaker and dropped into a Kjeldahl flask containing 100 cc. of concentrated sodium hydroxide. Standard hydrochloric acid was used in the receiver and the excess was determined by titration with standard sodium hydroxide using methyl orange as indicator. The results are given in Table I.

The neutral, basic and acid precipitates dissolve in dilute hydrochloric acid. This was the starting point for any cobalt determination. It was difficult to proceed because if the solution was made basic at any time precipitation would take place. Cobalt could not be precipitated in this acid solution. An attempt was made to find a complex ion of either cobalt or vanadium in an acid medium which would permit separation of the cobalt or vanadium. A series of weak inorganic and organic acids was tried with negative results.

Since vanadium cannot be deposited by electrolysis in this acid solution,[7] these precipitates were dissolved in 6 *N* hydrochloric acid and electrolyzed using a mercury cathode. A current of 0.4 of an ampere per sq. dm. was employed until the solution gave no test for cobalt using ammonium sulfide. The mercury was slowly stirred during the electrolysis. The amalgam was then set aside for several days and dilute hydrochloric acid was added to dissolve the cobalt. The hydrochloric acid solution, after removing the mercury, was then made basic with ammonium hydroxide and electrolyzed according to the method given by Scott[8] using a platinum gauze cathode and a current density of 0.5 ampere per sq. dm. The results were low in all cases. It is believed that all of the cobalt cannot be removed from the amalgam once formed, so the method was abandoned.

If the ammonia in these compounds is removed, or the form of the vanadium changed, the solution can be made basic without reprecipitating the salt. Consequently, samples of the precipitates were ignited to the oxides and then dissolved in 12 *N* hydrochloric acid, producing a clear greenish-blue solution. This was diluted and neutralized with ammonium hydroxide which precipitated the vanadium leaving a pink solution of cobalt. The precipitate gave a positive test for vanadium with hydrogen peroxide.[9] The filtrate was then electrolyzed as previously described.[8] This method of analysis proved fairly satisfactory and the results are given in Table I.

In order to make the results more conclusive, all constituents in each compound were determined in the following manner. Duplicate samples of each precipitate after being washed and dried were analyzed for ammonia as previously described. The residue remaining in the flask was filtered off, dissolved in hydrochloric acid and made basic with ammonium hydroxide. This solution was analyzed for cobalt.[8] The solution remaining from this determination was acidified and the vanadium determined by the method of Walden, Hammett and Edmonds.[5]

Results and Discussion

In Table I we give a comparison of the experimentally determined value for each constituent and the theoretical value calculated from the proposed formula for the neutral, basic and acid precipitate obtained when the metavanadate ion reacts with hexammine cobaltic ion. The results given under determination number 1 were obtained by taking a separate sample of each compound for each constituent whereas the results under determination number 2 were obtained by the complete analysis of each sample taken.

It will be noted that in most cases the individual values agree within the experimental error. The

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[3] Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., Vol. II, 1929, pp. 77–78.

[4] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[5] Walden, Hammett and Edmonds, *ibid.*, **56**, 57 (1934).

[6] Hulett, *Phys. Rev.*, **21**, 388 (1905); **33**, 307 (1911).

[7] Groves and Russell, *J. Chem. Soc.*, 2805 (1931); Irvin and Russell, *ibid.*, 891 (1932); also E. F. Smith, "Electro-analysis," Blakiston's Sons and Company, Philadelphia, Pa., 5th ed., p. 267.

[8] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1925, Vol. I, p. 170.

[9] Meyer and Pawletta, *Z. anal. Chem.*, **69**, 15 (1926).

TABLE I

SUMMARY OF RESULTS

	Co, %			NH_3, %			V, %		
$Co(NH_3)_6(VO_3)_3$ (neutral)									
Calcd.	12.88			22.31			33.37		
Detn. 1	12.50	13.22	12.90	22.34	22.31	22.34			
Average	12.87 ± 0.25			22.33 ± 0.01					
Detn. 2	12.87	12.84	12.86	22.29	22.29	22.31	33.33	33.35	33.33
Average	12.86 ± 0.01			22.30 ± 0.01			33.34 ± 0.01		
$[Co(NH_3)_6]_4(V_2O_7)_3$ (basic)									
Calcd.	18.33			31.78			23.77		
Detn. 1	18.65	18.24	18.12	31.79	31.79	31.81			
Average	18.34 ± 0.21			31.80 ± 0.01					
Detn. 2	18.29	18.29	18.32	31.75	31.75	31.77	23.77	23.76	23.70
Average	18.30 ± 0.01			31.76 ± 0.01			23.74 ± 0.03		
$[Co(NH_3)_6]_4(V_6O_{17})_3$ (acid)									
Calcd.	9.91			17.20			38.57		
Detn. 1	9.96	9.92	9.93	17.28	17.24	17.25			
Average	9.94 ± 0.02			17.26 ± 0.02					
Detn. 2	9.88	9.93	9.89	17.19	17.19	17.17	38.55	38.56	38.55
Average	9.90 ± 0.02			17.18 ± 0.01			38.55 ± 0.00		

average value obtained for the percentage of ammonia and cobalt in these compounds agrees with the calculated to approximately 0.1% except in the case of the acid precipitate. This error is due, no doubt, to the difficulty of drying this precipitate without decomposition. On long drying at 110° the edges of the precipitate become dark. This darkened portion was removed as well as possible before the samples were taken for analysis. It should be pointed out that the variation in the individual values for cobalt is rather large. However, calculations on the basis of other possible formulas from the ratio of ignited oxides show that the formulas assigned are correct. The agreement between the experimental and theoretical values for the percentage of vanadium is also approximately 0.1%. The data obtained are satisfactory for definitely establishing the formulas of the precipitates.

Summary

The following compounds first reported in the literature by M. Parks[2] from theoretical considerations are shown by chemical analysis to be correct: $Co(NH_3)_6(VO_3)_3$, $[Co(NH_3)_6]_4(V_2O_7)_3$, $[Co(NH_3)_6]_4(V_6O_{17})_3$. The color of these compounds is apricot, orange and yellow, respectively. They are produced when $Co(NH_3)_6{}^{+++}$ is added to a neutral, basic and acid solution of metavanadate ion. The compounds are named according to the nomenclature recommended by Mellor.[10] The precipitate formed in acid solution will give a quantitative separation of vanadium from phosphate, arsenate, ferric, cupric and calcium ions.[2] Vanadium cannot be separated from tungstate, molybdate or lead ions by this method.

KINGSTON, RHODE ISLAND RECEIVED MAY 13, 1935

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(10) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, 1929, Vol. IX, p. 758.