indicate that the acid concentration should not be below 0.1 N in the case of bromoosmate and 0.5 N in the case of chloroosmate.

At the foot of the table are shown the average deviations of the values of the equivalent weights obtained with the two salts. In spite of the fact that the percentage deviation in the values of the corresponding atomic weights of osmium is multiplied by about four in the case of bromoosmate and 2.5 in the case of chloroosmate, it is interesting to note how closely the two averages agree with that reported by Gilchrist.

TABLE I

THE DETERMINATION OF THE EQUIVALENT WEIGHTS OF POTASSIUM BROMOOSMATE AND POTASSIUM CHLOROOSMATE

Salt used	Detns.	Acid used and its concn., N	Average equiv. wt. by titrn.	Av. diff. between equiv. wt. found and Gilchrist's value, %
K_2OsBr_6	3	0.02–0.05 HBr	752.7	+0.45
K_2OsBr_6	8	0.13–0.25 HBr	749.1	− .03
K_2OsBr_6	2	0.60–0.95 HBr	749.8	+ .07
K_2OsCl_6	4	0.10–0.40 HCl	484.4	+ .39
K_2OsCl_6	8	0.50–0.80 HCl	482.6	+ .02

Average deviation last 10 results with K_2OsBr_6 = 0.10%
Average deviation last 8 results with K_2OsCl_6 = 0.10%
Average atomic weight of osmium by K_2OsBr_6 = 191.5
Average atomic weight of osmium by K_2OsCl_6 = 191.7
Gilchrist's value of atomic weight of osmium = 191.55

Since considerable difficulty due to hydrolysis was experienced when solutions of the osmium salts were heated to remove the last traces of oxygen, several solutions of the bromoosmate were treated in the apparatus shown in Fig. 2, and titrated in the same manner as the dichromate solutions. It was found that the concentration of the hydrobromic acid in the flask during boiling could be as low as 2 N without decomposition of the osmium salt taking place. Six 20.00-cc. portions of bromoosmate ranging in normality from 0.01333 to 0.01335 were titrated with 0.01187 N chromous sulfate and the maximum difference between the titrated value of the normality and that based on the amount of salt in the solution was less than 0.2%.

Summary

Apparatus and procedure are described for storing and handling chromous sulfate solutions, for standardizing these solutions with potassium ferricyanide and potassium dichromate, and for determining the osmium in potassium bromoosmate and potassium chloroosmate by potentiometric titration.

Solutions stored as described remained constant in titer for a month. Standardizations of chromous sulfate by the two methods agreed within 0.1% and the error in the osmium determinations was less than 0.2%.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 27, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Preparation of Potassium Molybdo- and Molybdicyanides[1]

BY HOBART H. WILLARD AND R. C. THIELKE

In attempting to prepare potassium molybdocyanide, $K_4Mo(CN)_8{\cdot}2H_2O$, the methods previously used were found to give very poor yields. This investigation was undertaken to find a more satisfactory method for preparing this compound. The methods of Rosenheim and co-workers,[2] Chilesotti,[3] later used by Bucknall and Wardlaw,[4] were found to be unsatisfactory. The method of Jakob and Turbiewicz[5] was not tried because it seemed to offer difficulties. Sand and Burger[6] reported that ammonium thiocyanate and molybdate when dissolved in dilute hydrochloric acid and reduced electrolytically gave a product which could be extracted by ether and which was precipitated by pyridine from the dry ethereal solution. The oil after separation from ether solidified to a dark solid which melted at 189°. This reaction was modified to prepare potassium molybdocyanide.

---

[1] From a dissertation by R. C. Thielke presented to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935.

[2] Rosenheim and Koss, *Z. anorg. Chem.*, **49**, 148 (1906); Rosenheim, *ibid.*, **54**, 97 (1907).

[3] Chilesotti, *Gazz. chim. ital.*, **34**, ii, 493 (1904).

[4] Bucknall and Wardlaw, *J. Chem. Soc.*, 2981 (1927).

[5] Jakob and Turbiewicz, *Roczniki Chem.*, **11**, 569 (1931).

[6] Sand and Burger, *Ber.*, **38**, 3384 (1905).

Experimental

Preliminary experiments showed that molybdic oxide dissolved in 8 *N* hydrochloric acid was not completely reduced by shaking with mercury for several hours. However, the octocyanide could be obtained with a 50% yield from the reduced molybdenum solution by following a procedure similar to that of Sand and Burger.[6]

Electrolytic reduction was finally adopted as the most convenient and rapid method. The cathode consisted of a hollow lead tube 0.5 cm. in diameter and of 126 ml. capacity. A graphite rod in a porous cup served as the anode. The anolyte was a 15% hydrochloric acid solution. A current of 5–10 amperes was used and the cathode was water cooled. Ten per cent. solutions of molybdic oxide in 8 *N* hydrochloric acid were used for most of the reductions. Carbon dioxide was bubbled through the solution to maintain an inert atmosphere. It was found that when trivalent molybdenum chloride was added to thiocyanate a green solution was produced instead of the characteristic blood-red thiocyanate complex, and that none of the molybdenum complex was extracted by ether. When the reduction was stopped at an apparent valence of four, as found by removing samples from time to time and titrating with permanganate, the blood-red complex was obtained when the molybdenum chloride was added to thiocyanate, and two-thirds of it could be extracted by ether. If a sample was completely reduced to the trivalent form, treated with the theoretical quantity of molybdic oxide to oxidize the molybdenum to the quadrivalent state, then treated with thiocyanate and extracted with ether, it was found that roughly one-tenth of the complex was extracted. These experiments explain the low yields obtained in the preparation of the octocyanide when this procedure was used with trivalent or quadrivalent molybdenum.

Preliminary experiments showed that a pyridine molybdenum thiocyanate complex could be precipitated from the thiocyanate solution by making it slightly alkaline with ammonia after the addition of pyridine. With trivalent molybdenum the aqueous solution contained about two-thirds of the molybdenum. The pyridine complex could not be successfully converted into the octocyanide. Quadrivalent molybdenum, however, was nearly quantitatively precipitated. A representative run contained only 0.03 g. of Mo in the aqueous solution. With this as a basis many experiments were performed to determine the best procedure for converting the complex to the octocyanide, separation of the complex cyanide from the reaction products and the final purification of the compound.

The following procedure has been found to be best and gives a 70–75% yield of potassium molybdocyanide based on the molybdic oxide used. Fifteen grams of pure molybdic oxide or an equivalent amount of the 85% material is dissolved in 150 ml. of warm 8 *N* hydrochloric acid. The solution is electrolytically reduced to trivalent molybdenum in the apparatus described and is then treated with 7.5 g. of molybdic oxide dissolved in 75 ml. of 8 *N* hydrochloric acid. The green solution assumes a reddish color at this stage. The mixture is added to a concentrated solution of 95 g. of ammonium thiocyanate. Sixty grams of pyridine is added and the solution is then made slightly alkaline with ammonia. These operations are best carried out in the absence of oxygen. Saturating the solutions with carbon dioxide has been found to work very well. A black oil is formed during the neutralization. After cooling in ice the black tar is separated from the aqueous solution by decantation and washed. The black tar is added slowly to a hot saturated solution of ten molecular proportions of potassium cyanide. The reaction mixture is concentrated until crystallization starts, is cooled in ice and filtered. The mother liquor is further concentrated and the double cyanide precipitated by adding alcohol with rapid swirling. The impure product is dissolved in a little water, heated with charcoal, filtered, concentrated and again precipitated with alcohol. The golden yellow crystals are then quite pure but still contain traces of thiocyanate. This may be removed by another crystallization. The yield of $K_4Mo(CN)_8 \cdot 2H_2O$ is about 55 g.

It was noticed that in some cases the crystals of the octocyanide were golden yellow and in other cases they were a bright yellow. Analyses of both showed them to be identical. Both were titrated to molybdicyanide with standard permanganate with the following result.

Yellow, % Mo	19.51	
Golden yellow, % Mo	19.56	Calcd. 19.35

A sample of each was decomposed with concentrated sulfuric acid by evaporation to fumes, diluted, reduced to the trivalent sulfate in a Jones reductor and titrated with standard permanganate.

Yellow, % Mo	19.51
Golden yellow, % Mo	19.97

Preparation of Potassium Molybdicyanide

The method given in the literature for the preparation of potassium molybdicyanide, $K_3Mo(CN)_8$, is very troublesome. It consists in oxidizing the molybdocyanide in acid solution with permanganate, precipitating in the dark gelatinous silver molybdicyanide and converting this into the potassium salt by treatment with potassium chloride. It is extremely difficult to obtain a pure solution because of the instability of the silver salt.

A quantitative yield of potassium molybdicyanide in solution is obtained by the following procedure. The molybdocyanide is oxidized in a slightly acid solution with permanganate until the purple tint is faintly perceptible, then two-thirds of an equivalent amount of permanganate is added in excess. Upon making the solution slightly alkaline with potassium hydroxide, the excess permanganate oxidizes the manganous ion and is itself reduced to manganese dioxide which is removed by filtration through asbestos. In order to make the resulting molybdicyanide solution more stable, it should again be slightly acidified. Even then, however, the solution is quite unstable. A solution which was prepared by the above method, stored in a brown bottle and kept from strong light was found to be decomposed to the extent of 20% after ten days. The preparation of the crystalline salt was not attempted.

Summary

1. Quantitative studies showed that the trivalent and quadrivalent molybdenum thiocyanate

complexes were only partially extracted by ether, resulting in a poor yield of molybdocyanide.

2. A quadrivalent molybdenum pyridine thiocyanate is almost completely precipitated in ammoniacal solution. By treatment of this with potassium cyanide a 70–75% yield of $K_4Mo(CN)_8 \cdot 2H_2O$ was obtained.

3. Quantitative yields of potassium molybdicyanide in solution were obtained by oxidizing potassium molybdocyanide with permanganate in acid solution and removing the manganese by oxidation to dioxide with permanganate after making the solution alkaline.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 28, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Studies on Hydrazine: Heats of Solution of Hydrazonium Salts at 25°. II

BY E. C. GILBERT AND V. C. BUSHNELL

The heat of solution of a number of hydrazonium salts has recently been reported from this Laboratory.[1] To complete the series the heats of solution of hydrazonium dibromide (anhydrous), hydrazonium sulfate, and hydrazonium dibromide (hydrated) have now been determined. That of the sulfate has also been determined by Bach[2] at a lower temperature.

Experimental

Apparatus.—The calorimeter was the same as previously used and the procedure was unchanged. It was again checked by measuring the heat of solution of sodium chloride.

Materials.—The salts were prepared from the free base and acids and purified by repeated crystallization. The anhydrous bromide was prepared from the hydrate by drying over phosphorus pentoxide. The preparation of the hydrate with exactly two molecules of water is somewhat difficult. It is very soluble in water and addition of nonaqueous solvents like alcohol removes one equivalent of acid, precipitating the monobromide. This peculiarity likewise precludes washing the crystals with anything but water. Forced drying practically always results in a slight loss either of water or hydrobromic acid. The samples used were analyzed both for hydrazine and for bromide. The preparation of the hydrated bromide used indicated by such analysis the presence of 0.2% of the monobromide. Samples of different origin were used in different runs and the heat quantities showed good agreement among themselves.

Results and Calculations

The results are shown in Table I. Specific heats for the bromide solutions were taken from the work of Cobb and Gilbert.[3] The specific heat of solutions of the sulfate is not found in the literature, hence it has been determined over a limited concentration range by the same method (3) and is given in Table II. From the values of the total molal heat of solution ΔH in Column 4 of Table I,

TABLE I

HEATS OF SOLUTION AT 25° (IN 15° CAL.)

The molality of the dibromide is expressed in every case as moles of anhydrous salt in 1000 g. of water in the resulting solution.

Molality Initial m_1	Final m_2	Heat absorbed per mole of salt dissolved	Total molal heat of solution m_2
	Hydrazonium Sulfate		
0.00	0.0576	8132	8132
.00	.0579	8134	8134
.00	.0567	8171	8171
	Hydrazonium Dibromide Dihydrate		
0.00	0.1327	11106	11106
.00	.1322	11130	11130
	Hydrazonium Dibromide, Anhydrous		
0.00	0.1314	4862	4862
.00	.1326	4866	4866
.00	.1874	4840	4840
.1314	.2455	4718	4794
.1874	.2768	4686	4790
.1326	.3181	4671	4755
.2455	.4566	4493	4655
.3181	.5111	4336	4600
.4556	.6641	4164	4502
.6641	.8387	3882	4372

TABLE II

SPECIFIC HEAT OF AQUEOUS HYDRAZONIUM SULFATE AT 25°

Molality	Sp. ht. in 15° cal. per g.
0.00	0.9979
.0476	.9930
.0795	.9889
.0856	.9891
.1058	.9852

---

(1) Gilbert and Cobb, THIS JOURNAL, **57**, 39 (1935).

(2) R. Bach, *Z. physik. Chem.*, **9**, 241 (1892).

(3) Cobb and Gilbert, THIS JOURNAL, **57**, 35 (1935).