King and Dismukes[12] applied to the separation of the chromic thiocyanate complexes. A 10^{-2} M solution of $K_2RuCl_5 \cdot H_2O$ in 1.00 M trifluoroacetic acid was equilibrated by heating at 64°, diluted twofold, and passed onto an ion-exchange column of Dowex-50 in the hydrogen ion form. On the basis of the ease of elution with acid they tentatively assigned formulas to three species: Ru^{+3}, $RuCl^{+2}$ and $RuCl_2^+$. Comparison with the present results may be made by means of the molar absorptivities. The spectrum of the species which they postulated to be Ru^{+3} resembles that of Ru^{+3} in Fig. 1 much more closely than it does Wehner and Hindman's Ru(III). In the wave length range covered (260 to 420 mμ) their molar absorptivities lie higher than ours by as much as a factor of three but approach ours at the two extreme wave lengths. The maximum percentage deviation occurs near 300 mμ.

Rehn and Wilson's molar absorptivities for their $RuCl^{+2}$ lie above ours at all wave lengths but approach ours closely around 340 mμ. They found a maximum at 308 mμ with a molar absorptivity of 804 compared to 315 mμ and 677, respectively, for our curve. At 260 mμ their curve was twofold higher than ours. Their curve for $RuCl_2^+$ agrees well with ours for the 0.05 M $HClO_4$ solution except that theirs shows no shoulder around 350 mμ. The spectrum which they assigned to $RuCl_3$ or $RuCl_4^-$ does not at all agree with that of the neutral species in Fig. 2.

Application of the Method to Other Systems.—The present method should be useful in establishing formulas of species in other systems. It is necessary that the species not change appreciably during the course of the measurements, except for hydrolysis. Undoubtedly the necessary experiments could be performed much more rapidly than was the case in the present work, but highly labile systems cannot be studied by this method. Anions can be studied using anion-exchange resins, as shown by preliminary measurements. Everest and Salmon[4] have already determined the charge per atom in pentagermanate ion.

The reliability of the charge per species determination for large and highly charged ions has not yet been established. As long as the variation in activity coefficients in the aqueous phase on dilution is not too great the method should be satisfactory. It should be interesting to investigate the behavior of such species as polymolybdates.

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BERKELEY, CALIFORNIA

[12] E. L. King and E. B. Dismukes, THIS JOURNAL, **74**, 1674 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY]

Interaction of Osmium with 1,2,3-Benzotriazole[1]

BY RAY F. WILSON AND LAWRENCE J. BAYE

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Methods for the synthesis of some 1,2,3-benzotriazole coördination compounds of certain metals and of certain halides of osmium in high yield and in high purity are reported.

During the course of this study on the interaction of 1,2,3-benzotriazole with osmium, we have had occasion to prepare several 1,2,3-benzotriazole coordination compounds of osmium. In previous papers, the interaction of palladium with 1,2,3-benzotriazole has been reported.[2]

It was the purpose of this investigation to ascertain the possibility of obtaining reproducible and accurate stoichiometric results in the interaction of osmium with 1,2,3-benzotriazole.

Experimental

Materials.—The osmium stock solution was prepared by dissolving 5.0054 g. of osmium tetroxide, obtained from A. D. Mackey, Inc., in 250 ml. of 0.1 M sodium hydroxide and diluting the resulting solution to 1 liter with distilled water.

A 1.5% stock solution of 1,2,3-benzotriazole was prepared by dissolving recrystallized reagent in distilled water.

Absolute alcohol was used to reduce the tetroxide of osmium presumably to the plus 3 oxidation state; allylalcohol also may be used for the same purpose.

All other materials were reagent grade chemicals. All precipitates were filtered using medium or fine porosity, sintered-glass crucibles.

Analyses.—The osmium content in the compounds reported was determined using an inert hydrogen atmosphere according to modifications of the Gilchrist–Wichers procedure.[3] Carbon, nitrogen, hydrogen, halogen and other metals were determined using conventional methods of analyses. It was observed in the determination of carbon and hydrogen contents in osmium coördination compounds that these compounds had to be mixed first with potassium chlorate and combusted at a temperature of about 1000° instead of the usual 700°.

Preparation of $Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]$.—To an erlenmeyer flask which contained 5 ml. of ethyl alcohol were added 20 ml. of stock osmium tetroxide solution. The color of the system changed to a faint pink over a period of 30 seconds. This color change is apparently characteristic of some lower oxidation state of osmium or of the osmite ion. To the pink solution was added 10 ml. of 1.5% 1,2,3-benzotriazole solution and the color changed from faint pink to a deep red. The mixture was digested for about 2 hours and then upon setting for 2 hours, the red crystals were salted out using excess sodium nitrate crystals. A faint red color always is left in the flask after such a separation. The crystals, in fine porosity, sintered-glass crucibles, were washed free of sodium nitrate and 1,2,3-benzotriazole with several portions of a hot water–ethyl alcohol mixture. The precipitates were dried in an oven at 105° for three hours to constant weight. Because of the apparent non-quantitative results of the precipitation method, gravimetric precision and accuracy were not studied for this compound. *Anal.* Calcd. for $Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]$: C, 35.16; H, 2.95; N, 20.51; Na, 8.41; Os, 23.20. Found: C, 35.01; H, 2.95; N, 20.32; Na, 8.30; Os, 23.23. The above de-

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[1] This work was supported by a grant from The Robert A. Welch Foundation.

[2] R. F. Wilson and L. E. Wilson, THIS JOURNAL, **77**, 6204 (1955); **78**, 2370 (1956); *Anal. Chem.*, **28**, 93 (1956).

[3] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffmann, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 338-383.

scribed reactions appear to follow the path given below in which RH is used instead of $\mathrm{C_6H_4NHN_2}$ to represent the formula of 1,2,3-benzotriazole.

$$\mathrm{OsO_4 \xrightarrow{\text{ethyl alcohol, NaOH}} OsO_3^-}$$

$$\mathrm{OsO_3^{=} + 4RH + 2H_2O \longrightarrow [OsO_3(RH)_4(H_2O)_2]^-}$$

$$\mathrm{3Na^+ + [OsO_3(RH)_4(H_2O)_2]^{=} \longrightarrow}$$

$$\mathrm{Na_3[OsO_3(RH)_4(H_2O)_2] \overset{\text{when dried above } 130^\circ}{\rightleftarrows} Na_3[OsO_3(RH)_4] + 2H_2O}$$

Preparation of $\mathrm{Ba_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2}$.—The red solution was obtained as in the foregoing preparation and to it was added barium acetate. A brick red precipitate was formed immediately; 3 *M* acetic acid was added to dissolve any barium hydroxide which might have formed, and the hydrogen ion concentration was suppressed sufficiently to prevent the formation of the yellow precipitate, $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$, by the addition of a large excess of barium acetate. The brick red precipitate was washed with several portions of hot distilled water and dried at 105° for about 2.5 hours. The red color was retained at this temperature. Three 10-ml. aliquots of osmium stock solution gave the following weights of precipitates: 188.2, 188.0, 188.4 mg. *Anal.* Calcd. for $\mathrm{Ba_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2}$: C, 30.13; H, 2.53; N, 17.57; OS, 19.88; Ba, 21.53. Found: C, 30.04; H, 2.50; N, 17.57; Os, 19.80; Ba, 21.64. The reaction probably proceeds as

$$\mathrm{3Ba^{++} + 2[OsO_3(RH)_4(H_2O)_2]^- \longrightarrow}$$

$$\mathrm{Ba_3[OsO_3(RH)_4(H_2O)_2]_2] \overset{\text{when dried above } 130^\circ}{\rightleftarrows} Ba_3[OsO_3(RH)_4]_2 + 2H_2O}$$

Preparation of $\mathrm{Pb_3[OsO_3(C_6H_4NHN_2)_4]_2}$.—Three 10-ml. aliquots of osmium tetroxide stock solution were used to prepare three portions of the red sodium salt described above. The *p*H of the solution was adjusted to between 6.0 to 6.5 with acetic acid and sodium acetate to protect the system against the formation of lead hydroxide. A 2% lead acetate solution was introduced into the system, giving a voluminous yellow precipitate. The precipitate was digested for 2 hours on a steam-bath during which time the precipitate developed into a beautiful crystalline form which remained yellow in color. After allowing the crystals to set for 2 hours, the supernatant liquid was quite clear and the precipitate appeared well formed. The precipitates were filtered through medium porosity sintered-glass crucibles and dried at 115° in an oven. The weights of the precipitates were as follows: 202.1, 201.8, 201.7 mg. *Anal.* Calcd. for $\mathrm{Pb_3[OsO_3(C_6H_4NHN_2)_4]_2}$: C, 28.19; H, 1.97; N, 16.39; Os, 18.54; Pb, 30.30. Found: C, 28.62; H, 2.14; N, 16.30; Os, 18.55; Pb, 30.25. The reaction probably proceeds as

$$\mathrm{3H^+ + [OsO_3(RH)_4(H_2O_2]^{\equiv} \xrightarrow[\mathit{p}H\ \sim 6.0]{\text{HAc, NaAc}} Os(OH)_3(RH)_3 + RH + 2H_2O}$$

$$\mathrm{3Pb^{++} + 2Os(OH)_3(RH)_3 + 2RH \longrightarrow Pb_3[OsO_3(RH)_4]_2 + 6H^+}$$

Preparation of $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$.—Fifteen 10-ml. portions of the alkaline-ethyl alcohol osmium stock solution were treated with 1,2,3-benzotriazole, in 1 molar acid medium, to give the roseo complex, as discussed above. Each of the aliquots regardless of the acid with which it was treated produced yellow precipitates. Each of the precipitates was filtered through medium porosity sintered-glass crucibles and washed with hot water. The precipitates were dried at 110° for about 2 hours to obtain constant weight. The weights of the precipitates were as follows: From acetic acid: 117.8, 118.2, 118.3 mg. From hydrochloric acid: 118.2, 118.0, 117.6 mg. From hydrobromic acid: 117.9, 117.8, 117.9 mg. From nitric acid: 118.1, 118.1, 118.1 mg. *Anal.* Calcd. for $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$: C, 36.12; H, 3.03; N, 21.06; Os, 31.77. Found: C, 35.90; H, 3.07; N, 21.12; Os, 31.92. The reaction seems to proceed as

$$\mathrm{[OsO_3(RH)_4(H_2O)_2]^- + 3H^+ \longrightarrow Os(OH)_3(RH)_3 + RH + 2H_2O}$$

Preparation of $\mathrm{Ag_2[OsO_2CH(C_6H_4NHN_2)_3]}$.—Three 10-ml. aliquots of the stock osmium tetroxide solutions were made to undergo the reaction which produces the $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$ compound quantitatively. The precipitates were obtained on sintered-glass crucibles and their weights recorded. Then 5% sodium hydroxide was poured over the yellow solids causing them to dissolve and be transferred to the bottom of a benzotriazole-free suction flask. The red solutions were then treated with 6 *N* nitric acid to reduce the concentration of base to about neutrality. There resulted a yellow turbid mass of $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$ in the flasks. To these turbid suspensions were added an excess amount of 1.5% silver nitrate solution. A beautiful amber red precipitate which was quite granular settled out of the solution. After about 15 minutes, the supernatant liquid became clear and the precipitates were filtered in medium porosity, sintered-glass crucibles, washed with very dilute hot nitric acid and then with hot water and heated at 105° for about one hour to constant weight. The following weights were obtained for the indicated amount of $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$: 160.8, 161.0, 159.0 mg. of $\mathrm{Ag_2[OsO_2OH(C_6H_4NHN_2)_3]}$ were obtained from 118.0, 118.2, 117.9 mg. of $\mathrm{Os(OH)_3(C_6H_4NHN_2)_3}$. *Anal.* Calcd. for $\mathrm{Ag_2[OSO_2OH(C_6H_4NHN_2)_3]}$: C, 26.61; H, 1.99; N, 15.52; Os, 23.63; Ag, 26.56. Found: C, 26.42; H, 1.89; N, 15.72; Os, 23.50; Ag, 26.58. The reaction appears to proceed as

$$\mathrm{2Ag^+ + Os(OH)_3(RH)_3 \longrightarrow Ag_2[OsO_3H(RH)_3] + 2H^+}$$

Preparation of $\mathrm{Zn[OsO_2OH(C_6H_4NHN_2)_4]}$.—Three 10-ml. aliquots of stock osmium tetroxide solution were treated in such a manner as to produce the sodium osmium benzotriazole hydrate complex as described previously. To each of the rose complex systems was added acetic acid and then sodium acetate. To the buffered solutions were added an excess amount of a 2% zinc chloride solution. There resulted a bright yellow precipitate. The precipitates were digested for 1.5 hours on a steam-bath and filtered in medium porosity sintered-glass crucibles. The precipitates were washed with hot dilute acetic acid and finally with three portions of hot water. The precipitates were dried to constant weight in an oven at 115° for 2 hours. The following weights of precipitates were obtained from the three aliquot portions: 154.0, 154.2, 153.9 mg. *Anal.* Calcd. for $\mathrm{Zn[OsO_2OH(C_6H_4NHN_2)_4]}$: C, 36.90; H, 2.71; N, 21.52; Os, 24.35; Zn, 8.37. Found: C, 36.81; H, 2.90; N, 21.32; Os, 24.40; Zn, 8.29. The reaction probably proceeds as

$$\mathrm{Zn^{++} + Os(OH)_3(RH)_3 + RH \longrightarrow Zn[OsO_2OH(RH)_4] + 2H^+}$$

Preparation of $\mathrm{K_3[OsO_3(C_6H_4NHN_2)_4]}$.—A 30-ml. aliquots of the sodium osmium–benzotriazole hydrate complex was prepared in the usual manner and the *p*H of the system was adjusted to about 6 or less using dilute nitric acid and observing the disappearance of the red color as the neutrality point. Then 20% potassium hydroxide was introduced quickly into the system which produced a very deep red solution somewhat different from the red obtained from the previously described sodium hydroxide 1,2,3-benzotriazole system. The compound was coagulated by digesting the mixture on a steam-bath down to a small volume. The crystals then begin to separate as shiny plates, wine-red in color. Quantitative precipitation of the crystals could not be obtained even when large quantities of potassium hydroxide, potassium nitrate or 1,2,3-benzotriazole were added. The deep red colored precipitate was collected in a fine porosity sintered-glass crucible and washed several times with hot water and was dried at 105° to constant weight. *Anal.* Calcd. for $\mathrm{K_3[OsO_3(C_6H_4NHN_2)_4]}$: C, 34.65; H, 2.42; N, 20.20; Os, 23.08; K, 14.10. Found: C, 34.90; H, 2.32; N, 20.02; Os, 22.90; K, 14.25. The reaction probably follows the path

$$\mathrm{3K^+ + Os(OH)_3(RH)_3 + RH \longrightarrow K_3[OsO_3(RH)_4] + 3H^+}$$

Preparation of $\mathrm{Ca_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2}$.—Three aliquots of the sodium osmium–benzotriazole hydrate compound were prepared in the usual manner and the solutions were treated with excess calcium hydroxide, giving a brick red colored precipitate. The precipitates were digested 1.5 hours in a water-bath at 90°, and after letting the precipitate resettle out leaving a clear supernatant liquid, the precipitates were washed thrice with a hot solution consisting of about 1% acetic acid and 5% calcium acetate and then four times with hot water. The brick red precipitates were dried in an oven at 105° to constant weight. The weights of the three precipitates were: 157.5, 157.0, 157.2 mg. *Anal.* Calcd. for $Ca_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2$: C, 35.55; H, 2.98; N, 20.73; Os, 23.46; Ca, 7.41. Found: C, 35.60; H, 2.90; N, 20.68; Os, 23.40; Ca, 7.43. The reaction seems to follow the path

$$3Ca^{++} + 2[OsO_3(RH)_4(H_2O)_2]^{\equiv} \longrightarrow Ca_3[OsO_3(RH)_4(H_2O)_2]_2$$

Preparation of $OsCl_3(C_6H_4NHN_2)_3$.—Three 10-ml. aliquots of the stock osmium tetroxide solution were made to undergo the reaction which produces the sodium osmium–1,2,3-benzotriazole hydrate complex. To these mixtures were added 12 *N* hydrochloric acid and sodium chloride in large excess. At room temperature no reaction was observed, but as the temperature of the mixture was raised, the yellow color of $Os(OH)_3(C_6H_4NHN_2)_3$ gradually changed over to a light green color and the solid retained this color on heating at 105° for 5 hours. The green precipitates were filtered in medium porosity sintered-glass crucibles and washed with hot water several times. The precipitates were dried in an oven at 110° to constant weight. The weights of the green colored precipitates were: 128.6, 128.2, 128.0 mg. *Anal.* Calcd. for $OsCl_3(C_6H_4NHN_2)_3$: C, 33.01; H, 2.31; N, 19.25; Os, 29.04; Cl, 16.39. Found: C, 32.89; H, 2.14; N, 18.97; Os, 29.13; Cl, 16.48. The reaction appears to follow the path

$$Os(OH)_3(RH)_3 + 3HCl \xrightarrow[\text{Concn. HCl}]{\text{NaCl}} OsCl_3(RH)_3 + 3H_2O$$

Preparation of $OsBr_3(C_6H_4NHN_2)_3$.—Three 10-ml. aliquots of the stock osmium tetroxide solution were made to undergo the reaction which produces the sodium osmium–1,2,3-benzotriazole hydrate complex. To these mixtures was added 4 *N* hydrobromic acid in large excess. At room temperature no reaction was observed but at about 100° a purple precipitate forms and retains its color during 4 hours of intensive digesting in the presence of excess sodium bromide. The purple precipitates were filtered in fine porosity sintered-glass crucibles and washed with dilute (1:25) hydrobromic acid solution and next with hot water. The precipitates were dried at 110° in an oven for 2 hours, to constant weight. Some of the green precipitate which was observed to form before the formation of the purple precipitate was recovered in another reaction flask but the amount which could be recovered was very small. The weights of the purple compounds were: 155.0, 154.8, 154.6 mg. *Anal.* Calcd. for $OsBr_3(C_6H_4NHN_2)_3$: C, 27.39; H, 1.92; N, 15.97; Br, 30.37; Os, 24.10. Found: C, 27.14; H, 1.84; N, 15.85; Br, 30.52; Os, 24.08. The reaction appears to follow the path

$$Os(OH)_3(RH)_3 + 3HBr \xrightarrow[\text{4 } N \text{ HBr}]{\text{NaBr}} OsBr_3(RH)_3 + 3H_2O$$

Discussion

From weight relationships and elemental analyses, it appears that an ethyl alcohol solution of osmium tetroxide in basic medium reacts with 1,2,3-benzotriazole to form a complex ion with composition $[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]^{\equiv}$. Optimum conditions for the preparation of coördination compounds of the osmium benzotriazole complex ion with ions of sodium, potassium, calcium, barium, zinc and lead were found. The osmium benzotriazole complex ion reacted with all common acids at room temperature to produce a substance of composition $Os(OH)_3(C_6H_4NHN_2)_3$. Also, the chemical reactions between 1,2,3-benzotriazole and osmium seem to indicate that an ionic species of $Os(OH)_3$ or of H_3OsO_3 probably exist in solution; in either case osmium would be expected to exhibit an oxidation state of +3.

Since osmium is in the same group of elements as cobalt and chromium and since these elements form red aquo-ammine salts, it seems that osmium might behave similarly with 1,2,3-benzotriazole serving as coördinating agent as ammonia does in hexamminecobalt(III) and hexamminechromium(III) while the other ions or groups perform their usual function. For example, the color of the bromide and chloride coördination compounds of osmium are analogous to the corresponding bromides and chlorides of cobalt and chromium, *i.e.*, purple and green, respectively. A green solution was obtained from the osmium–1,2,3-benzotriazole system when iodide was used but attempts at isolation of the compound were all without success.

When $Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]$ was heated above 130°, the red colored compound lost reversibly its two molecules of water to form the green colored precipitate $Na_3[OsO_3(C_6H_4NHN_2)_4]$. The brick red colored precipitates $Ca_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2$ and $Ba_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]_2$ both turned a dull brownish-red when heated above 120 and 130°, respectively.

The bromine and chloride compounds formed in the interaction of osmium with 1,2,3-benzotriazole were soluble in bases but were insoluble in acidic or neutral media. The solubility of these compounds in basic media is in conformity with a general rule governing the formation of complex ions, *viz.*, in order of decreasing coördination stability CN^-, SCN^-, F^-, OH^-, Cl^-, Br^-, I^-. Thus, it can be seen readily that OH^- should form its complex in preference to Cl^-. Similarly, it was noted that at room temperature the chloride precipitate was not affected by the presence of bromide or iodide ions. It was also interesting to note that the green bromide compound had the same elemental analysis as the purple one, both corresponding to the formula $OsBr_3(C_6H_4NHN_2)_3$. This seems to point to the existence, under prescribed conditions, of two isomeric forms of $OsBr_3(C_6H_4NHN_2)_3$. As yet, it has not been possible to carry out magnetic susceptibility study of these compounds; however, the investigation of the stereochemistry of these compounds will be pursued further.

HOUSTON 4, TEXAS