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

Pentammineiridium(0)[1]

BY GEORGE W. WATT AND PEGGY I. MAYFIELD

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The reduction of bromopentammineiridium(III) bromide with potassium in liquid ammonia at its boiling point results in complete removal of bromine and the formation of ammonia-insoluble pentammineiridium(0). Thermal decomposition of this product produces only ammonia and iridium; the latter is effective as a catalyst for the hydrogenation of olefins. The reaction between bromopentammineiridium(III) bromide and potassium amide in liquid ammonia yields iridium(III) amide 1-ammonate.

In an earlier report from these laboratories, evidence for the existence of an unstable ammine of platinum in the zero oxidation state was presented.[2] The present paper is concerned with data relative to an analogous but much more stable compound of iridium.

The reduction of bromopentammineiridium(III) bromide with potassium in liquid ammonia at −33.5° requires exactly three gram-atoms of potassium per mole of the bromide; water-insoluble gases are not evolved during the course of the reaction, and elimination of bromide ion is complete. The ammonia-insoluble reduction product consists of a pale yellow and apparently crystalline solid which is devoid of activity as a catalyst for the interaction of potassium and ammonia or for the hydrogenation of allyl alcohol. Thermal decomposition of the reduction product occurs at 92–93°; the decomposition products include *only* ammonia and iridium in an average mole ratio of 4.3/1. The iridium so produced exhibits an activity as a hydrogenation catalyst that is comparable to that of other Group VIII metals.

The primary reduction reaction may be represented as

$$[\mathrm{Ir(NH_3)_5Br}]^{2+} + 2\mathrm{Br}^- + 3\mathrm{K}^+ + 3e^- \longrightarrow [\mathrm{Ir(NH_3)_5}]^0 + 3\mathrm{KBr}$$

The bromopentammineiridium(III) ion is undoubtedly an octahedral complex of the d^2sp^3 type. Complete removal of bromine from the starting material results in a +3 ion, $[\mathrm{Ir(NH_3)_5}]^{3+}$, which differs from the initial cationic component only in that one 6p orbital is not utilized. In the reduction of the $[\mathrm{Ir(NH_3)_5}]^{3+}$ ion, two of the three available electrons must therefore be added to the available 6p orbital and one to the 7s orbital thus leading to a neutral species which may be expected to exhibit an appreciable stability.[3] This, however, does not account for the fact that this ammine is more stable than the corresponding platinum compound[2] unless the stability of the former is enhanced owing to dimerization, in which case the ammine of iridium should be diamagnetic. Magnetic susceptibility measurements have indeed shown that the product in question is diamagnetic, but this result is still not finally conclusive.[4]

In order to show that reactions involving potassium amide are not responsible for the observed product, the action of this base upon bromopentammineiridium(III) bromide was studied, and evidence for the following reactions was obtained

$$[\mathrm{Ir(NH_3)_5Br}]\mathrm{Br_2} + 3\mathrm{KNH_2} \longrightarrow \mathrm{Ir(NH_2)_3{\cdot}NH_3} + 3\mathrm{KBr} + 4\mathrm{NH_3}$$

$$\mathrm{Ir(NH_2)_3{\cdot}NH_3} + 3\mathrm{KNH_2} \longrightarrow \mathrm{K_3Ir(NH_2)_6} + \mathrm{NH_3}$$

Although the latter product was not isolated, exactly three moles of potassium amide react with one mole of the lemon-yellow iridium(III) amide to form a red-brown ammonia solution.[5]

Experimental

Materials.—With the exception noted below, all materials employed in this work were reagent grade chemicals.

Since efforts to prepare bromopentammineiridium(III) bromide by the method of Palmaer[6] were unsuccessful, the following procedure was devised. An aqueous solution containing 3.0 g. of iridium(III) chloride was evaporated just to dryness, treated with 20 ml. of 48% hydrobromic acid solution and again evaporated just to dryness. Treatment of the residue with 15 ml. of hydrobromic acid followed by evaporation was repeated eight times; the final evaporation was discontinued at a volume of 5 ml. This solution was neutralized with 26% aqueous ammonia, then poured into 600 ml. of this reagent. Ammonia gas was bubbled through the resulting solution while it was evaporated to dryness and thereafter heated for 2 hours on a steam-bath. The mass of dull yellow crystals thus formed was heated nearly to boiling with 2 l. of 26% aqueous ammonia, filtered while hot, and the filtrate was evaporated to a volume of 100 ml. Addition of 3 ml. of hydrobromic acid resulted in precipitation of pale yellow crystals which were filtered, washed with dilute hydrobromic acid, finally with ethyl alcohol, and dried at 110°. The yield was 60%. X-Ray diffraction data for this product are given in Table I.

Anal. Calcd. for $[\mathrm{Ir(NH_3)_5Br}]\mathrm{Br_2}$: Ir, 37.3; $^2/_3$Br, 30.9. Found: Ir,[7] 37.1; $^2/_3$Br, 30.3.

The Solubility of Bromopentammineiridium(III) Bromide in Liquid Ammonia at −33.5°.—An excess of the bromide was equilibrated with liquid ammonia at −33.5° for several hours, and an 11.8-ml. sample of the saturated solution was removed, the solvent was evaporated, and the residual solid analyzed for iridium. The total iridium found was 0.0381 g., or 0.1022 g. of $[\mathrm{Ir(NH_3)_5Br}]\mathrm{Br_2}$; this corresponds to a solubility of 0.9 g. of the bromide/100 ml. of solution. That the composition of the solid phase in equilibrium with the saturated solution was that corresponding to the formula $[\mathrm{Ir(NH_3)_5Br}]\mathrm{Br_2}$ was confirmed by analysis for iridium (Found: Ir, 37.9. Calcd.: Ir, 37.3) and by the fact that a sample gave an X-ray diffraction pattern identical with that of the starting material.

The Reduction of Bromopentammineiridium(III) Bromide with Potassium.—In a typical experiment, 0.83 g. of

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[1] This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

[2] G. W. Watt, M. T. Walling, Jr., and P. I. Mayfield, THIS JOURNAL, **76**, 6175 (1954).

[3] L. Pauling, *Contrib. étude structure mol., Vol. commen. Victor Henri*, **1**, 1947–1948; *C. A.*, **43**, 2830 (1949).

[4] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., p. 114.

[5] Evidence for the occurrence of at least two other reactions between bromopentammineiridium(III) bromide and potassium amide has been obtained by means of potentiometric titrations (G. W. Watt, G. R. Choppin and J. L. Hall, unpublished work). These data will be published elsewhere.

[6] W. Palmaer, *Z. anorg. Chem.*, **10**, 320 (1895).

[7] Iridium was determined by a spectrophotometric method; see G. H. Ayres and Q. Quick, *Anal. Chem.*, **22**, 1403 (1950).

TABLE I

X-RAY DIFFRACTION DATA FOR BROMPENTAMMINEIRIDIUM (III) BROMIDE[a]

d, Å.	I/I_1	d, Å.	I/I_1
6.04	0.92	2.81	0.26
5.47	.16	2.73	.40
4.96	.11	2.50	.22
4.31	.14	2.38	.17
4.13	.51	2.26	.13
3.67	1.00	2.14	.46
3.43	0.32	2.06	.34
3.25	.14	1.96	.37
3.12	.17	1.87	.10
3.01	.35	1.71	.10[b]

[a] These data were obtained using $CuK\alpha$ radiation, a Ni filter, a tube voltage of 30 kv. and a filament current of 15 ma. [b] Less intense lines not indexed.

the bromide dissolved and suspended in 15 ml. of anhydrous liquid ammonia at its boiling point was reduced with 0.25 g. of potassium added as a solid. The potassium reacted rapidly without gas evolution until the final piece was added, whereupon the characteristic blue color of alkali metal solution persisted without further evidence of reaction for 1 hr.[8] The solution was removed by filtration and the pale yellow solid product was washed with liquid ammonia until the first evidence of peptization was observed.

Analysis of the solid residue remaining after evaporation of the combined supernatant solution and washings gave the following results: Ir, 4.0 mg. (presumably lost to the filtrate owing to peptization); K, 0.21 g.; Br, 0.35 g. (calcd. 0.38 g.).

The weight of the ammonia-insoluble reduction product was 0.436 g., or a yield of 99.6% in terms of $Ir(NH_3)_5$ based on $[Ir(NH_3)_5Br]Br_2$ used.

Anal. Calcd. for $Ir(NH_3)_5$: Ir, 69.5. Found: Ir, 70.0.

This product reacts vigorously upon exposure to the atmosphere and with all common aqueous media to form residues that are insoluble in all reagents except hot concentrated nitric acid. This product failed to give a satisfactory X-ray diffraction pattern.

A 0.141-g. sample of the solid reduction product was transferred (without exposure to the atmosphere) to a Vycor bulb which was then attached to a Toepler pump and evacuated at room temperature. The bulb was heated slowly by means of an electric furnace. At 92–93° the yellow solid decomposed to a black solid and ammonia gas. The temperature was increased to 110° and held at this temperature until all of the ammonia (46.1 cc.) was pumped off. The ammonia was absorbed in water and the absence of hydrogen and nitrogen was shown by the fact that there was no residual water-insoluble gas. The temperature was then raised slowly to *ca.* 300° whereupon traces of a white crystalline solid sublimed into the top of the bulb.[9] Further elevation of the temperature to 875° produced no further change except for the liberation of negligible quantities of gaseous ammonia. The weight of the residual black solid was 0.1060 g. as compared with a value of 0.1061 g. calculated on the assumption that the solid is elemental iridium. The ratio of moles NH_3/gram-atom of Ir calculated on the basis of the above data is 4.2; somewhat higher ratios were found in other experiments. Attempts to analyze the black solid for iridium were complicated by difficulties encountered in getting the samples into solution; values found, however, ranged from 93–99% Ir. An X-ray diffraction pattern showed the presence of iridium and traces of potassium bromide[9] (Table II).

TABLE II

X-RAY DIFFRACTION DATA FOR PRODUCT FROM THERMAL DECOMPOSITION OF AMMONIA-INSOLUBLE REDUCTION PRODUCT

Product		Iridium[a]		Potassium bromide[a]	
d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1
3.75[b]	0.04[c]				
3.29	0.04			3.29	1.00
2.22	1.00	2.20	1.00		
1.93	0.43	1.91	0.50		
1.36	.40	1.35	.28	1.34[d]	0.07
1.16	.60	1.15	.36	1.16[d]	.03
1.11	.17	1.10	.08	1.10[d]	.03
0.96[b,e]	.08				
.88	.05	0.88	.08		
.86	.05	0.86	.08		

[a] Data from A.S.T.M. Index of X-Ray Diffraction Patterns. [b] Unidentified. [c] Less intense lines not indexed. [d] In view of the low intensity of the line corresponding to d = 3.29 Å., it is doubtful that these are attributable to KBr. [e] Since this line was found on all patterns for iridium samples and is not otherwise identified, it is believed to be a previously unindexed component of the iridium diffraction pattern.

Data on the magnetic susceptibility of a sample of the ammonia-insoluble reduction product were obtained through the courtesy of Prof. H. B. Jonassen of Tulane University who reported that the compound is diamagnetic.

Catalytic Acitivity of Iridium.—Using methods previously described,[10] a sample of $[Ir(NH_3)_5]_2$ showed no activity as a catalyst for the hydrogenation of allyl alcohol. However,

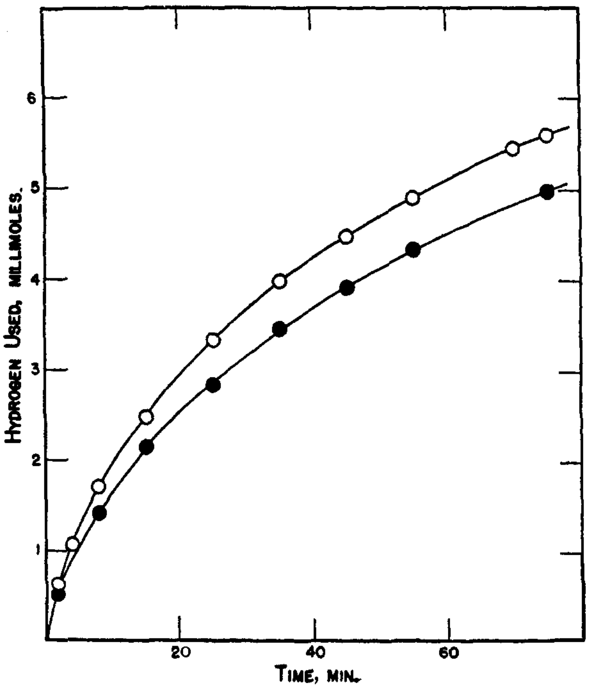

Fig. 1.—Hydrogenation of allyl alcohol over iridium: ○, 0.93 g. of Ir from decomposition of $Ir(NH_3)_5$; ●, same except that catalyst was washed with ethanol.

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[8] In independent experiments, a reaction ratio of three gram-atoms of potassium/mole of the bromide was established by direct titration using the first permanent blue color as the end-point indicator. For example, a solution and suspension of 3.14 millimoles of the bromide in liquid ammonia was titrated with 7.4 *M* potassium solution. The end-point was observed after addition of 12.0 ml. of potassium solution (calcd. 12.6 ml.).

[9] An aqueous solution of this solid gave positive qualitative tests for ammonium and bromide ions, and the solid gave an X-ray diffraction pattern identical with that listed in the A.S.T.M. Index of X-ray diffraction patterns for ammonium bromide. The presence of this salt as a trace impurity is not surprising since its complete removal by washing with liquid ammonia was precluded by peptization of the ammonia-insoluble reduction product. For the same reason, the less soluble by-product potassium bromide may also be present in detectable quantity (see Table II).

[10] G. W. Watt, W. F. Roper and S. G. Parker, THIS JOURNAL, **73**, 5791 (1951).

elemental iridium formed by decomposition of the pentammine at temperatures not greater than 110° catalyzed the hydrogenation of allyl alcohol at the rate shown in Fig. 1. In these experiments, the hydrogenation of 14.6 millimoles of allyl alcohol in 10 ml. of ethanol was catalyzed by 93 mg. of iridium at 30°, a hydrogen pressure of 2 atm., and an agitation rate of 930 r.p.m. By a modification of the method of Brunauer, Emmett and Teller[11] the surface area of the iridium catalyst was found to be 36 m.^{2}/g.

The Action of Potassium Amide upon Bromopentammineiridium(III) Bromide.—In a typical experiment, 1.13 g. of the bromide dissolved and suspended in 20 ml. of liquid ammonia at −33.5° was treated with the potassium amide equivalent to 0.26 g. of potassium in 35 ml. of liquid ammonia. The reaction was rapid and proceeded without liberation of insoluble gases. The pale yellow solution was removed and the dull yellow solid product was washed 6 times with 20-ml. portions of ammonia. Analysis of the combined supernatant solution and washings gave the following results: Ir, 19 mg.; Br, 0.48 g. (calcd. 0.52 g.).

Anal. Calcd. for $Ir(NH_2)_3 \cdot NH_3$: Ir, 74.9. Found: Ir, 74.6.

This product, which failed to give a satisfactory X-ray diffraction pattern, reacts upon exposure to the atmosphere, reacts with water, and is soluble in hot concentrated nitric acid.

A 0.140-g. sample of the solid reaction product was transferred without exposure to the atmosphere to a Pyrex bulb which was then attached to a Toepler pump and evacuated at room temperature; the bulb was then heated slowly by means of an electric furnace. At 115–120° the yellow solid decomposed to form gaseous ammonia and nitrogen, and a black solid. The temperature was increased to 350° and held at this temperature until gas evolution was complete. The weight loss attributable to gas evolution amounted to 0.035 g. or 25.0% of the sample. The weight of the black solid was 0.1053 g. as compared with 0.1049 g. calculated on the assumption that the black solid is elemental iridium; an X-ray diffraction pattern showed only the lines characteristic of iridium.

In independent experiments, iridium(III) amide prepared as described above, was titrated with potassium amide solution. Addition of exactly three moles of KNH_2/mole of $Ir(NH_2)_3$ resulted in complete dissolution of the precipitate and the formation of an intensely brown colored solution.

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[11] H. E. Ries, R. A. Van Nordstrand and W. E. Kreger, THIS JOURNAL, **69**, 35 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Spectrophotometric Investigation of the Equilibria Existing in Acidic Solutions of Chromium(VI)[1-3]

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Acidic solutions of chromium(VI) are observed to exhibit significant deviations from Beer's law. Measurements of the optical density of chromium(VI) solutions at the wave lengths 370, 380, 390 and 400 mμ enable one to determine the values of the equilibrium quotients for the reactions: $2HCrO_4^- \rightleftarrows Cr_2O_7^= + H_2O$; $H_2CrO_4 \rightleftarrows H^+ + HCrO_4^-$; $HCr_2O_7^- \rightleftarrows H^+ + Cr_2O_7^=$. At 25° in perchloric acid–lithium perchlorate media of unit ionic strength, the values of the equilibrium quotients for these reactions are $K_d = 98$, $K_{11} = 1.21$ and $K_{22} = 0.85$, respectively. The values of the dimerization quotient, K_d, have been determined as a function of the ionic strength; an extrapolation to zero ionic strength yields the value $K_d^0 = 35.5$.

The equilibria existing in aqueous acidic solutions of chromium(VI) have been studied by a number of investigators.[4] The glass electrode study of the acidity of chromium(VI) solutions by Neuss and Rieman[4] has given the values 3.20 × 10^{-7} and 43 for the equilibrium constants of the two reactions

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^= \qquad (1)$$

$$2HCrO_4^- \rightleftarrows Cr_2O_7^= + H_2O \qquad (2)$$

In the present work, a spectrophotometric investigation, attention has been confined to solutions in which the hydrogen ion concentration is greater than approximately 10^{-3} *M*. In such media, $CrO_4^=$ is not an important species. The relative importance of the species $HCrO_4^-$ and $Cr_2O_7^=$ depends upon the total concentration of chromium(VI), and, therefore, at wave lengths where the extinction coefficients of $HCrO_4^-$ and $Cr_2O_7^=$ (calculated on the gram-atom/liter concentration basis) are not equal, Beer's law is not obeyed by acidic chromium(VI) solutions.[5] The wave length region in which spectral data provided the most accurate information regarding dimerization was chosen after examining light absorption data obtained over a wide range of wave lengths. Such data obtained at 25°, which are presented in Fig. 1, suggest that the deviations from Beer's law in the region of 400 mμ are of a large enough magnitude to elucidate the dimerization equilibrium.

In order to account for the observed spectral changes with changes of the concentration of chromium(VI) and hydrogen ion, it is necessary to assume that the species $Cr_2O_7^=$, $HCr_2O_7^-$, $HCrO_4^-$ and H_2CrO_4 exist in the concentration ranges which have been studied: 10^{-3} to 1.0 *M* hydrogen ion and 4 × 10^{-5} to 0.013 gram-atom of chromium(VI) per liter. (The upper limit of the chromium(VI) concentration was determined by the maximum value of the optical density which could be determined. While higher concentrations of chromium(VI) would favor the formation of dimeric species, and therefore might be desirable from the point of view of establishing the value of the equilibrium quotient for reaction 2, possible adverse effects would also be introduced. These are the possibility of higher polychromates being present in more concentrated solutions and the uncertainty in the medium effect caused by the presence of ions of multiple charge at appreciable concentrations.)

The various symbols and definitions which are used in this paper are presented in Table I. In the

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(1) This work has been supported in part by the United States Atomic Energy Commission.

(2) Presented at the 124th Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

(3) From the Ph.D. thesis of James Y.-P. Tong, University of Wisconsin, 1953.

(4) J. D. Neuss and W. Rieman, THIS JOURNAL, **56**, 2238 (1934); references to earlier work are presented in this paper.

(5) The failure of acidic solutions of chromium(VI) to obey Beer's law also has been observed by J. A. Campbell and R. A. Howald, unpublished work.