THE POTENTIOMETRIC DETERMINATION OF IRIDIUM

BY SHO-CHOW WOO AND DON M. YOST

Introduction

In connection with a study of the reduction potential of the chloroiridous–iridic acids[1] it was necessary to develop good volumetric methods for the determination of the concentrations of the metal in its higher state of oxidation. In addition to this it was necessary to prepare solutions of chloroiridous and chloroiridic acids free from other elements of the platinum group and from the baser metals. Owing to the incomplete knowledge of the chemistry of the platinum group elements and the high cost of the iridium itself, both problems presented especial difficulties. In this paper are described a new method and a modified method for the volumetric determination of iridium, and incidentally the procedures used for the preparation of pure solutions of chloroiridous and chloroiridic acids.

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Preparation of the Materials

Ammonium Hexachloroiridate.—Fairly pure metallic iridium in a finely divided state was first digested for three hours with a hot mixture of hydrochloric and nitric acids. This treatment removes any organic matter and the base metals as well as some of the platinum, the iridium not being much attacked. The residual metal was next intimately mixed with three times its weight of pure sodium chloride, and the mixture was heated to 650° for one hour in a quartz tube through which was passed a stream of chlorine. All of the platinum metals were converted by this procedure into the double chlorides. The mixture of the chlorides was dissolved in a small volume of dilute hydrochloric acid and the resulting solution was saturated with chlorine and then heated on a water-bath. This treatment resulted in the oxidation of the iridous to the iridic chloride and in the decomposition by heat of any quadrivalent palladium compounds.

To remove the palladium and rhodium, the solution of the chlorides was saturated with ammonium chloride and then cooled in an ice-bath. The precipitate (which contains the iridium) was filtered off and redissolved, and the solution was again precipitated as before. This procedure was repeated several times and yielded a product free from palladium and rhodium.

The resulting ammonium hexachloroiridate was next heated with concentrated nitric acid, fresh acid being added from time to time. To the residue in the flask was added concentrated perchloric acid, and the mixture was boiled until the greater part of the acid had been driven off; then more acid was added and the treatment repeated. Continued application of this procedure caused the complete volatilization of osmium and ruthenium as the tetroxides, leaving the iridium free from all platinum metals except platinum.

The residue was heated nearly to dryness and dissolved in a small amount of water.

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[1] Sho-Chow Woo, THIS JOURNAL, **53**, 469 (1931).

To the solution was added an excess of sodium bicarbonate solution and bromine water, and the resulting mixture was boiled.   This caused the precipitation of iridic hydroxide, but not that of platinum.   The precipitate was redissolved in hydrochloric acid and subjected again to the bicarbonate precipitation.   This treatment was repeated several times.   The final product, iridium hydroxide, was dissolved in hydrobromic acid and, after treatment with nitric and hydrochloric acids to convert the bromides to chlorides, the solution was saturated with ammonium chloride and cooled, and the resulting precipitate of ammonium hexachloroiridate was filtered off.   In order to make sure that no sodium salts were present, the ammonium chloride precipitation was repeated several times.   The resulting ammonium chloroiridate was washed with ice-cold water and then dried over concentrated sulfuric acid in a vacuum desiccator.

After each separation procedure a portion of the iridium-containing mixture was tested for the element being removed, using the dimethylglyoxime[2] test for palladium and the methods of Noyes and Bray[3] for the other elements.   These tests show the presence of 0.3 mg. or less of the elements tested for.   The procedures for the removal of osmium and ruthenium give a very complete separation, and the test for palladium is quite sensitive.   Therefore the only contaminating elements present to the extent of 0.3% or less are rhodium and platinum, since the purification was always carried out until the tests for the contaminating elements were negative.

Chloroiridic and Chloroiridous Acids.—The ammonium chloroiridate was digested for ten hours with aqua regia upon a water-bath until all of the ammonia had been destroyed, and the nitric acid was then destroyed by repeated digestion with hot concentrated hydrochloric acid.   The resulting solution consists principally of a mixture of chloroiridic acid and hydrochloric acid.   For use in the electromotive force measurements a portion of this solution was reduced to chloroiridous acid with pure redistilled alcohol, using the procedure described by Delépine.[4]   The small quantity of metallic iridium which separated was removed by filtering the solution through a hardened filter after the alcohol had been driven off by heating, and the solution was finally evaporated to dryness in a vacuum desiccator.   The residue was dissolved in dilute hydrochloric acid of known strength.

Hydrochloric Acid and Other Analytical Reagents.—The best obtainable hydrochloric acid was redistilled and diluted with redistilled conductivity water.   The other analytical reagents used were of c. p. grade.

The Methods of Analysis Studied

The iodometric method of analysis that has been described by Delépine[4] was first tested.   In this method a hydrochloric acid solution of the chloroiridate is reduced to the chloroiridite by potassium iodide, and the liberated iodine is titrated with thiosulfate with starch as an indicator.   In this form the method was not accurate since the color of the solution obscured the end-point; but it was found to give very satisfactory results when benzene was used to determine the point at which all of the iodine had been reduced. The titrations were carried out in 0.1 to 0.2 N hydrochloric acid solutions in a volumetric flask whose volume was such that the benzene layer rose

[2] Wunder and Thuringer, Z. anal. Chem., **52,** 101–104, 660–664 (1913); H. B. Wellman, THIS JOURNAL, **52,** 985 (1930).

[3] Noyes and Bray, "Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, **1929,** pp. 39, 117, 118.

[4] Delépine, Ann. chim., **7,** 277 (1917).

into the neck when the last portions of thiosulfate were added. This procedure facilitated the determination of the end-point, especially when the narrow column of benzene was observed against a white background.

In the second method studied, titanous chloride was used for the estimation of quadrivalent iridium. This standardized reagent was added to a hydrochloric acid solution, and the end-point was determined electrometrically. During the initial stages of the titration the potential reaches a steady value after a short time, and at the end-point it changes abruptly from 0.65 to 0.4 volt. Some time, however, is required for the electromotive force to become constant near the end-point, and the stage at which the sharp change occurs may be considered to be the end-point only in case the titanous chloride is added very slowly. The addition of sodium chloride to solutions of chloroiridic acid free from other salts was found to increase the sharpness of the end-point. The initial concentration of the hydrochloric acid in the solutions titrated was from 0.1 to 0.2 N, and the total initial volume was 50 cc. The amounts of sodium chloride added to the titration mixtures varied from 2 to 3 g. The other half-cell consisted of a saturated calomel electrode.

For comparison the iridium in the ammonium salt and in the solutions was determined by the well-known gravimetric method of igniting the salt in a current of hydrogen. With the small amounts of material used extreme care was necessary to avoid the small accidental losses that usually accompany this method of analysis. The determinations differed by less than 1% in all cases, usually by not more than 0.5%.

An attempt was also made to determine iridium by precipitating it with strychnine sulfate, but the precipitation was found to be incomplete.

Results of the Test Analyses

In Tables I, II and III are presented, the results of analytical experiments in which the above-described methods were used. The iridium solutions were measured by weighing them in a pipet designed for the

TABLE I

CONSISTENCY OF THE RESULTS BY THE IODOMETRIC METHOD AND COMPARISON WITH THOSE BY THE TITANOUS CHLORIDE TITRATION

| No. | H_2IrCl_6 soln., g. | Solution used, cc. | | Iridium per gram of solution, mg. |
		$Na_2S_2O_3$	$TiCl_3$	
1	2.0483	7.57	..	4.44
2	3.2762	12.10	..	4.44
3	2.5943	9.56	..	4.43
4	10.3615	14.05	..	1.630
5	10.4763	14.23	..	1.634
6	8.1114	11.00	..	1.630
7	9.4657	...	8.03	1.629
8	10.4119	...	8.87	1.635
9	11.2136	...	9.55	1.634

TABLE II

COMPARISON OF THE IODOMETRIC AND GRAVIMETRIC METHODS

| Expt. | Milligrams taken | | Milligrams of iridium found | |
	$(NH_4)_2IrCl_6$	Iridium	Iodometric	Gravimetric
1	37.4	16.3	16.3	..
2	47.5	20.8	20.7	..
3	68.3	29.8	29.7	..
4	68.3	29.8	29.8	..
5	81.3	35.5	..	35.6

TABLE III

IODOMETRIC, TITANOMETRIC AND GRAVIMETRIC RESULTS COMPARED WITH THE CALCULATED IRIDIUM CONTENT OF AMMONIUM CHLOROIRIDATE

| Method | $(NH_4)_2IrCl_6$ soln., g. | Milligrams of iridium per gram of solution | |
		Found	Present[a]
Iodometric	7.3742	2.758	
Iodometric	6.8145	2.763	
		Mean 2.761	2.766
Titanous chloride	9.6965	2.755	
Titanous chloride	8.7137	2.755	
Titanous chloride	9.0680	2.755	
		Mean 2.755	2.766
Gravimetric	15.9696	2.786	
	15.3795	2.766	
		Mean 2.776	2.766

[a] As calculated from the amount of $(NH_4)_2IrCl_6$ known to be present per gram of solution.

purpose. The thiosulfate used was 0.00623 N. The titanous chloride used was 0.00994 N for the experiments of Table I and 0.009285 N for those of Table III.

It is seen from the tables that the two volumetric methods yield concordant results, the maximum deviation from the mean being about 0.3%. Moreover, the amount of iridium in the salt $(NH_4)_2IrCl_6$ as determined volumetrically and gravimetrically is, within a few tenths of one per cent., the same as that calculated from the formula.[5]

Summary

The results (given in Tables I–III) show that the new titanometric method of determining iridium gives results in agreement with those given by the earlier iodometric method, which was refined by using benzene to

[5] This tendency to form non-hydrated chloro salts is not found with some other platinum metals. The results of Howe [THIS JOURNAL, 49, 2381 (1927)] and of Crowell and Yost [ibid., 50, 374 (1928)] emphasized this for the case of ruthenium, and at the same time clarified an important question in the chemistry of coördination compounds. Werner, "Neuere Anschaungen auf dem Gebiete der anorganischen Chemie," Vieweg und Sohn, Braunschweig, 1909, 2d. ed., p. 292.

detect the liberated iodine.   Both these methods gave results in agreement with the gravimetrically determined amounts of iridium present in the solutions.   They show, moreover, that the iridium content of crystalline ammonium hexachloroiridate as determined volumetrically and gravimetrically is the same, within a fraction of one per cent., as that calculated from the formula $(NH_4)_2IrCl_6$.

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ACIDITY IN NON-AQUEOUS SOLVENTS. CONDUCTIMETRIC AND ELECTROMETRIC TITRATIONS OF ACIDS AND BASES IN BENZENE

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I.   Introduction

When we consider the remarkable successes which the theory of Arrhenius achieved in correlating such diverse properties of aqueous solutions as (a) conductivity, (b) osmotic properties, (c) acid and base catalysis, (d) hydrogen electrode potentials, and (e) indicator effects, it is quite natural that the degree of acidity should have been taken as synonymous with the concentration of hydrogen ions behaving osmotically as solute particles independent of the acid ionogen.   In other words, it has been tacitly assumed that on passing from one solvent to another the purely thermodynamic properties like (b) and (d) will run parallel to properties like (a) and (c) which depend only indirectly upon thermodynamic relations.   On this view the acidity of an acid dissolved in benzene should at best be very small, since its degree of dissociation as judged by conductivity is very minute.

The experimental work of Hantzsch,[1] of Brönsted,[2] and of Hall and Conant,[3] is primarily responsible for demonstrating that this assumed

[1] (a) Hantzsch, Z. Electrochem., 29, 230 (1923).   Hammett, THIS JOURNAL, 50, 2666 (1928), gives complete references of Hantzsch's work up to 1928 and presents the salient features.   Later papers of importance are (b) Hantzsch and Voigt, Ber., 62, 975 (1929); (c) Hantzsch and Buroway, ibid., 63, 1180 (1930).

[2] Brönsted, (a) Z. physik. Chem., 108, 217 (1924), with Kai Pedersen, (b) Rec. trav. chim., 42, 718 (1923) (definition of acids and bases).   Similar views were presented independently by Lowry, Trans. Faraday Soc., 20, 58 (1924); Chemistry Industry, 42, 43 (1923); (c) J. Phys. Chem., 30, 777 (1926); (d) THIS JOURNAL, 49, 2554 (1927), with E. A. Guggenheim (catalysis by undissociated molecules); (e) Ber., 61 2049 (1928) (indicators in benzene); (f) Z. physik. Chem., 143, 301 (1929) (acidity and ion potentials); (g) Chem. Rev., 5, 284 (1928) (review of subject).

[3] (a) Hall and Conant, THIS JOURNAL, 49, 3047, 3062 (1927);   (b) Hall and Werner, ibid., 50, 2367 (1928);   (c) Hall, J. Chem. Ed., 7, 782 (1930);   (d) THIS JOURNAL, 52, 5115 (1930).