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

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XIII. THE DETERMINATION OF MERCUROUS MERCURY

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Introduction

Few of the volumetric oxidation or reduction methods for mercurous mercury afford a separate estimation of it in the presence of mercuric ion. Among the procedures which accomplish this may be mentioned (1) its reduction by potassium iodide to mercury, followed by addition of excess standard iodine solution, and determination of the excess iodine with thiosulfate;[1] (2) its precipitation as mercurous oxalate by excess standard oxalate, the excess oxalate in the filtrate being determined with permanganate;[2] (3) its oxidation with excess standard permanganate, followed by addition of excess standard ferrous sulfate and back titration with permanganate;[3] (4) its precipitation by excess standard sodium chloride solution, followed by filtration, precipitation of the mercuric salt with hydrogen sulfide, filtration, removal of hydrogen sulfide by boiling and titration of the excess sodium chloride with standard mercurous nitrate, using diphenylcarbazide as indicator[4]—obviously a tedious process; (5) its titration in strong hydrochloric acid solution with potassium iodate, using chloroform as indicator.[5] This last method appears to be the one most widely used.

The present paper is a study of the oxidizing action of ceric sulfate on mercurous ion and describes a volumetric procedure for mercurous mercury, applicable in the presence of large amounts of mercuric salts.

Experimental

Mercurous sulfate was made by adding slowly a solution of mercurous perchlorate to dilute sulfuric acid. The precipitate was thoroughly washed, then suspended in 0.1 *M* sulfuric acid. This mixture, after being stirred for five to six hours, was filtered. The mercurous sulfate solution thus obtained was standardized gravimetrically by precipitating the mercurous mercury as chloride and drying the precipitate to constant weight over phosphorus pentoxide. The results of three experiments gave 0.0295, 0.0295 and 0.0296 g. of mercury per 100 cc. The filtrate from the mercurous chloride gave no test for mercury when made ammoniacal and treated with hydrogen sulfide and solid ammonium chloride.

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[1] Hempel, *Ann.*, **110**, 176 (1859).

[2] Peters, *Z. anorg. Chem.*, **24**, 402 (1900).

[3] Randall, *Am. J. Sci.*, [4] **23**, 137 (1907).

[4] Oddo, *Gazz. chim. ital.*, **39**, I, 666 (1909).

[5] Jamieson, *Am. J. Sci.*, **33**, 349 (1912).

The ceric sulfate solution was part of a large supply made by the method described by the authors[6] from high grade ceric oxide and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate.[7] The ferrous sulfate solution was standardized electrometrically against standard ceric sulfate.[7]

Measured portions of the standard mercurous sulfate were taken, diluted with water, sulfuric acid (sp. gr. 1.5) and 0.09611 *N* ceric sulfate to a definite volume, heated to boiling and held just below the boiling point over a small flame for the time indicated. The solutions were then cooled to 30–35° and titrated electrometrically with standard ferrous sulfate. The results of a number of experiments are indicated in Table I.

TABLE I

THE OXIDATION OF MERCUROUS MERCURY WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, (sp. gr. 1.5) before ox., cc.	Time at b. p., min.	Vol. during ox., cc.	0.09611 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	Hg_2^{++} taken, g.	Hg_2^{++} found, g.
1	10	15	200	25	1.47	0.0295	0.0295
2	10	30	200	25	1.48	.0295	.0297
3	30	15	200	25	?	.0295	?
4	50	30	200	25	1.48	.0295	.0297
5	10	30	300	25	1.48	.0295	.0297
6	50	30	300	25	1.47	.0295	.0295
7	10	30	200	15	?	.0295	?
8	10	60	200	15	1.46	.0295	.0293
9	50	60	200	15	?	.0295	?
10	10	15	200	50	1.48	.0295	.0297
11	50	15	200	50	?	.0295	?
12[a]	10	30	200	25	1.47	.0295	.0295
13[b]	10	30	200	25	1.50	.0295	.0301
14	10	15	200	25	0.73	.0148	.0147
15[c]	50	15	200	25	0.75	.0148	.0150
16[c]	10	30	200	25	2.20	.0443	.0442
17	10	30	200	50	2.20	.0443	.0442
18	15	30	300	50	2.94	.0590	.0590
19	20	30	400	50	?	.0885	?
20	20	60	400	50	4.42	.0885	.0887
21[d]	10	30	200	50	1.49	.0295	.0297
22[d]	20	60	400	50	4.43	.0885	.0889

[a] 5 cc. of $HClO_4$ (70%) present. [b] 5 cc. of HNO_3 (sp. gr. 1.42) present.
[c] End-point poor. [d] 0.3 g. of Hg^{++} present.

In Expts. 17, 18, 20, 21 and 22 blank corrections of 0.07, 0.10, 0.17, 0.15 and 0.21 cc., respectively, have been applied to the volume of 0.1 *N* ceric sulfate used for the oxidation. If more than 30–35 mg. of mercurous mercury is present in a sample, it is always necessary to run a blank determination, using the same quantities of reagents and the same procedure

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[6] Willard and Young, THIS JOURNAL, **51**, 149 (1929).

[7] Willard and Young, *ibid.*, **50**, 1322 (1928); see also Furman, *ibid.*, **50**, 755 (1928).

as for the unknown. An amount of mercuric sulfate, free from mercurous ion, approximately equal to that in the unknown should be added to the blank before heating. Mercuric ion in considerable amount tends to cause a slight decomposition of ceric sulfate in hot solution.

The experiments in Table I show that mercurous ion is quantitatively oxidized to mercuric ion provided that a large excess of ceric salt is used, that the acidity of the solution is not too great and that the oxidizing agent is allowed to act in hot solution for thirty to sixty minutes. A moderate amount of perchloric acid causes no interference but nitric acid produces a slight effect. A large amount of mercuric ion does not interfere if a blank correction is made for its slight action on ceric sulfate in hot solution.

Summary

An accurate method has been developed for mercurous mercury, based upon its oxidation in hot sulfuric acid solution by excess ceric sulfate and titration of the excess electrometrically with standard ferrous sulfate. Mercuric ion in large amount does not interfere.

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[Contribution from the Kent Chemical Laboratory of the University of Chicago]

PHOTOCHEMICAL STUDIES. XI. THE QUANTUM EFFICIENCY OF OZONE FORMATION IN THE FLUORITE REGION

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The photochemistry of the range of wave lengths below those transmitted by quartz has received scant attention. The difficulty of obtaining monochromatic radiation of sufficient intensity to produce measurable chemical effects in this region of the spectrum is great. In a recent article the photochemical decomposition of ammonia was studied in the fluorite region.[1] By a comparison of the rate of ozone formation with the rate of decomposition of ammonia under the influence of those wave lengths transmitted by fluorite but not by quartz, it was possible to calculate the quantum efficiency of the latter reaction by making the following assumptions: (1) that the photochemical decomposition of ammonia is represented by the equation $2NH_3 = N_2 + 3H_2$; (2) that the absorption of ammonia is identical with that of oxygen in this range of wave lengths; (3) that two molecules of ozone are formed per quantum of radiation absorbed by oxygen. With these assumptions it was possible to show that the average quantum efficiency of ammonia decomposition is about 0.7 for the approximate spectral region 150mμ to 190mμ.

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[1] Kassel and Noyes, This Journal, 49, 2495 (1927).