[CONTRIBUTION FROM THE INSTITUTE OF ANALYTICAL CHEMISTRY OF CHARLES UNIVERSITY]

Volumetric Determinations in Strongly Alkaline Solutions. III. The Titration of Thallium and Cerium with Hypobromite

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In the preceding communications of this series,[1,2] the results of titrations with ferricyanide were given. In the present paper new titrations with hypobromite are described. This reagent has already been used for the determination of ammonia, ammonium salts and urea,[3] for the determination of arsenites,[4] iodides,[5] thiocyanates,[6] and thiosulfates.[5,7]

Applying the potentiometric control, we have repeated the mentioned determinations[8] and also tried the possibility of the titration of yet other reduction–oxidation systems. Efforts to bring about a direct oxidation of plumbous, ferrous and chromic salts were without success. However, cerous salts could be titrated in a way analogous to that which has been described for the use of ferricyanide.[9] Such a titration with hypobromite proceeds very slowly and is not very satisfactory, while that of thallous salts (in the form of sulfate, carbonate, chloride or nitrate) is quick and complete. As thallous salts, especially the carbonate and sulfate, are easily prepared in a pure and well-defined state, they can be recommended as starting substances for the standardization of hypobromite solutions; thallous carbonate has already been employed as an acidimetric standard.[10]

A second reason for the advisability of thallous salts as starting substances for the direct standardization of solutions of alkali hypobromites is the fact that the accuracy of the determination is not so much dependent upon the basicity of the solution as in the case of arsenite solutions, which would otherwise be most suitable.

Materials and Apparatus

Solution of Sodium Hypobromite (in Some Cases the Potassium Salt).—About 0.05 *M* sodium hypobromite [potassium hypobromite] was prepared as follows. To an aqueous solution of *ca.* 0.5 *M* sodium [potassium] hydroxide of usual purity, which is cooled by freezing mixture of salt and ice to −4°, is added chemically pure bromine (8 g. per liter). The solution is well mixed and then left in the freezing mixture for two hours in the dark. After twelve more hours its titer was determined. The solution which has a yellow to greenish-yellow color was always stored in a bottle of dark hard glass in a cool place. Even hypobromite solutions, which were prepared with the utmost care, contain bromide and bromate ions (and sometimes perhaps also traces of bromite). For the direct titration in alkaline solutions only the hypobromite content is of significance. The standardization is made with arsenite or thallous salt as described below. The total oxidizing capacity of the solution (equal content of $BrO^- + BrO_3^-$) is determined, if desired, best by introducing the hypobromite solution in a solution of potassium iodide, which has been acidified with sulfuric acid; the titration then is carried out with thiosulfate. The solutions of hypobromite are not very stable; it is therefore advisable to check their titer before and after each series of experiments. For instance, the titer of a solution *ca.* 0.05 *M* sodium hypobromite and *ca.* 0.5 *M* sodium hydroxide was unchanged for a month; after three months it fell 16.7% and after six months 30.2%.

Solution of Arsenite (0.05 *M*).—It was prepared from chemically pure arsenic trioxide by the usual method.[11]

Thallous Salts and their Solutions.—For their preparation were used anhydrous, chemically pure thallous salts, which had been dried at 100° to constant weight, *viz.*, thallous sulfate (Tl_2SO_4) and thallous carbonate (Tl_2CO_3). To prepare a 0.025 *M* standard solution, 5.860 g. of thallous carbonate or 6.311 g. of thallous sulfate was weighed out exactly, then dissolved by warming and after cooling made up to 500 cc. Such a solution is very stable and does not change its titer even after many months. The other solutions were furthermore controlled by titrating with exactly standardized potassium ferricyanide.[1]

For the determination of cerium, a solution of cerous chloride, free from other earths, had been prepared; its titer was determined with 0.1 *M* ferricyanide solution.[9]

All other salts and reagents used were of average purity.

The apparatus and the calibrated vessels were the same as described in the previous communication.[1] In cases where oxidation by atmospheric oxygen did not interfere, the solution was stirred by an electrical stirrer without passing any carbon dioxide. The titration vessels were of hard glass throughout.

Titration of Thallium

The titrations were carried out as follows. To 25 cc. of the 0.025 *M* solution of thallous sulfate were first added

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(1) O. Tomíček and F. Freiberger, THIS JOURNAL, **57**, 801 (1935).

(2) O. Tomíček and J. Kalný, *ibid.*, **57**, 1209 (1935).

(3) P. Artmann and A. Skrabal, *Z. anal. Chem.*, **46**, 5 (1907).

(4) I. M. Kolthoff and A. Laue, *ibid.*, **73**, 177 (1928).

(5) H. H. Willard and F. Fenwick, THIS JOURNAL, **45**, 631 (1923).

(6) J. Golse, *Bull. Soc. Pharmacol.*, **66**, 139 (1928), and **67**, 226 (1929).

(7) I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1931, 2d ed., p. 311.

(8) The results of these experiments will be given elsewhere later.

(9) O. Tomíček, *Rec. trav. chim.*, **46**, 410 (1925).

(10) R. Hac and K. Kámen, *Coll. Czechoslovak Chem. Comm.*, **4**, 145 (1932).

(11) I. M. Kolthoff, "Die Massanalyse," II, Verlag Julius Springer, Berlin, 1931, 2d ed., p. 379.

various quantities of sodium or potassium hydroxide. Then the solution was titrated sometimes in an atmosphere of carbon dioxide and sometimes open to the air with *ca.* 0.05 M sodium hypobromite solution, which had been standardized with arsenite simultaneously under the same conditions.

It was found unnecessary to work in an atmosphere of carbon dioxide. The liquid, which at the beginning remained clear even after the addition of sodium hydroxide, became turbid at once after the first drops of the hypobromite were added, forming a precipitate of thallium hydroxide. If the solution is stirred vigorously, this precipitate does not at all delay the quick attainment of a stable potential, and thus does not interfere with the exact course of the titration. A few results of many experiments are compiled in the following tables. It may be seen that the most suitable alkalinity is that when the reaction liquid at the end of titration is 1.5 to 2 M sodium hydroxide. Under these conditions, the inflection potential lies at +0.05 volt against the saturated calomel electrode. The drop in potential is considerable and well recognizable, and a stable potential is quickly attained also in the neighborhood of the equivalent point. With increasing concentration of hydroxide, this jump in potential is somewhat smaller. It is advisable to clean the indicating platinum electrode before each titration by washing with hydrochloric acid and burning in the flame. The course of a titration may be seen from Fig. 1.

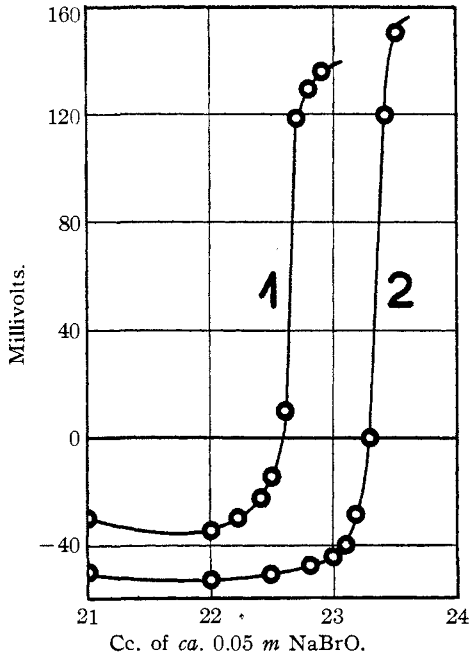

Fig. 1.—The titration curves of thallous salts by hypobromite: Curve 1, the titration of thallous carbonate in 3 M NaOH. Curve 2, the titration of thallous sulfate in 2.5 M NaOH.

TABLE I

TITRATION OF 25.00 CC. 0.025 M Tl_2CO_3 AND 0.025 M Tl_2SO_4

Basicity of titration, M		*Ca.* 0.05 M NaBrO for 25.00 cc. of		
Beginning	End	0.05 M Na_3AsO_3	0.025 M Tl_2CO_3	
0.5	0.5	30.15	29.73	29.73
1.0	0.8	30.20	29.90	29.90
2.0	1.5	30.05	30.07	30.07
3.0	2.5	29.95	30.07	30.07
4.0	3.5	29.80	30.07	30.07
			0.025 M Tl_2SO_4	
0.5	0.5	23.15	22.95	22.95
1.0	0.8	23.25	22.95	22.93
2.0	1.5	23.05	22.95	22.95
3.0	2.5	22.95	22.95	22.95
4.0	3.5	22.75	22.95	23.00

TABLE II

TITRATION OF VARIOUS QUANTITIES OF 0.025 M Tl_2SO_4

0.025 M Tl_2SO_4, cc.	Basicity of titration, M		*Ca.* 0.05 M NaBrO, cc.		
	Beginning	End	Calcd.	Used	
5.00	2.0	1.9	3.73	3.75	3.73
10.00	2.0	1.8	7.45	7.43	7.45
20.00	2.0	1.65	14.90	14.85	14.90
50.00	2.0	1.5	37.25	37.20	37.30

The following experiments show that thallous nitrate also may be titrated in the same way: 0.2358 and 0.4510 g. of thallous carbonate were treated with a few drops of dilute nitric acid until the evolution of carbon dioxide ceased; the resulting solution was diluted with water and then treated as in the preceding experiments. It was found that the presence of nitrate ions did not interfere at all. The amount of *ca.* 0.05 M sodium hypobromite spent was as follows: 14.95 cc. (calcd. 15.00 cc.) and 28.75 cc. (calcd. 28.70 cc.).

Also the reverse titration of hypobromite with a solution of thallous salts is possible, but is of less importance due to the readiness with which it is oxidized by air. It is of no particular interest to study the interference of easily oxidizable cations as the main purpose of these investigations was to prove that thallous salts are very suitable for the standardization of hypobromite solutions.

For the standardization of *ca.* 0.025 M hypobromite solution a thallium salt is therefore quite suitable, in accordance with the equations

$$Tl_2CO_3 + 2NaBrO + 2NaOH + 2H_2O = 2Tl(OH)_3 + 2NaBr + Na_2CO_3$$

$$Tl^+ + BrO^- + OH^- + H_2O = Tl(OH)_3 + Br^-$$

Either 0.025 M solution of thallous sulfate or carbonate may be used in the standardization, or 0.25-g. portion of salt may be weighed out, dissolved in about 20 cc. of water, with warming if necessary. The cool solution is then diluted with concd. sodium or potassium hydroxide in such amount that the final solution (50–75 cc.) is 2–3 M in base. This solution is titrated with the unknown hypobromite to the maximum of inflection, according to the procedure already described.

Determination of Cerium

Preliminary experiments to titrate cerous salts with hypobromite in a solution which had been made alkaline with sodium or potassium hydroxide gave no satisfactory results. However, a cerous salt solution (either the chloride or sulfate) to which so much potassium carbonate had been added that it contained 20 to 30% of potassium carbonate at the end of the titration could be titrated with hypobromite, if the atmospheric oxygen was removed from the solution by passing carbon dioxide or nitrogen (free from oxygen) through it. The reaction liquid remains clear and becomes yellow in color after the addition of hypobromite. Yet the attainment of stable potentials is extremely slow and could not be accelerated by changes of temperature or any addition of catalyzers. It is, therefore, of advantage to obtain an idea as to the position of the maximum by a preliminary titration. For the proper titration almost the whole amount of necessary hypobromite is added at once and only the remaining few tenths cc. are used to accomplish the titration. On the whole the procedure is the same as has been described[9] for the much quicker and thereby much more satisfactory titration of cerous salts with ferricyanide. The inflection potential under the given conditions is 0.10 volt against the saturated calomel electrode.

Experiments.—20.00 cc. of *ca.* 0.1 *M* cerous chloride solution required for a titration 19.13 and 19.13 cc. of 0.1 *M* ferricyanide. The same quantity of cerous chloride required 19.20, 19.13, 19.04 and 19.09 cc. of the 0.05 *M* solution of hypobromite.

Summary

1. A new and simple titration of thallous salts with hypobromite has been described. It is very suitable for the standardization of hypobromite solutions by using thallous carbonate or sulfate as standard.

2. Also cerous salts can be titrated with hypobromite in 20 to 30% solution of potassium carbonate from which the atmospheric oxygen has been removed. However, the titration with ferricyanide is to be preferred.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

Photochemical Investigations. II. The Photochemical Decomposition of Ethylene Iodide in Solutions of Carbon Tetrachloride[1]

BY ROBERT E. DERIGHT AND EDWIN O. WIIG

The thermal decomposition of ethylene iodide in solutions of carbon tetrachloride was found by Polissar[2] to consist of two parts, the ordinary and that catalyzed by iodine. Arnold and Kistiakowsky[3] found similar reactions to occur in the gas phase. The iodine photosensitized decomposition in solutions of carbon tetrachloride was found by Schumacher and Wiig[4] to be a chain reaction propagated by iodine atoms. It was thought that an investigation of the decomposition brought about by light absorbed by the ethylene iodide itself might give some insight into the mechanism of the decomposition and the manner in which the iodine is split off the ethylene iodide.

Experimental Details

Preparation and Purification of Materials.—The carbon tetrachloride was purified by the method used by Polissar.[2] Only the middle fraction from the last distillation was retained. The ethylene iodide was prepared from pure ethylene and iodine[5] and purified by recrystallization from dry ether. Attempts to prepare ethylene iodide by bubbling ethylene into concentrated solutions of iodine in carbon tetrachloride gave negligible yields. Uranyl sulfate and oxalic acid were purified in the manner described by Leighton and Forbes.[6]

The decomposition of ethylene iodide was followed by titrating the liberated iodine with *N*/200 solutions of sodium thiosulfate and of iodine. The relative strength of these solutions was checked frequently, the normality of the iodine being determined by titration against potassium permanganate solutions, the titer of which against sodium oxalate remained constant over long periods.

Apparatus and Procedure.—The reaction cell was cylindrically shaped with optically plane windows. The cell, made from fused quartz with fused seams, was 40 mm. in diameter and 35 mm. in length and was filled with 37 cc. of solution by means of a 12-mm. tube located near the rear window. In the experiments with the uranyl sulfate–oxalic acid solutions a stirrer was inserted through this tube. This cell was immersed in a thermostat, provided with a fused quartz window, in which the temperature of the water was regulated to ±0.03°.

The light source was a vertical Uviarc quartz mercury vapor lamp operated on 120 volt d. c. The lamp was rigidly mounted and the voltage carefully controlled so that the intensity was constant over long periods. A large crystalline quartz monochromator (f:1.9) with collimator and exit slits of 1.50 and 1.05 mm., respectively, was adjusted with the aid of a Beck fluorescent spectroscope to give the maximum intensity of light of the wave length desired. In all experiments, except those used to evaluate

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[1] Presented at the New York meeting of the American Chemical Society, April, 1935.

[2] Polissar, THIS JOURNAL, **52**, 956 (1930).

[3] Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

[4] Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

[5] Semenoff, Jahresberichte über die Fortschritte der Chemie, 1864, p. 483.

[6] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).