[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

An Electrometric Study of the Reaction between Chromate and Indium Ions

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The addition of a chromate to a solution of an indium salt results in the formation of a yellow precipitate which for a time was tentatively assumed to be indium chromate. Stubbs[2] first studied this precipitation in detail, but did not arrive at a definite conclusion regarding the chemical nature of the precipitate.

Experimental

A solution of indium chloride was prepared by dissolving 99.9% pure indium[3] in a minimum amount of concentrated hydrochloric acid and diluting to the desired volume. Twenty ml. of 0.00957 *M* indium chloride was titrated against 0.1002 *M* potassium chromate. As the reaction proceeded, the change in *p*H was followed by means of a Beckmann *p*H-meter. Three series of titrations, consisting of three runs each, were conducted at 10, 25 and 40°. In each of these series, no significant discrepancies between individual runs were observed. For purposes of comparison, indium chloride was also titrated against 0.1003 *M* sodium hydroxide.

The precipitate was brought into solution by means of dilute sulfuric acid; indium hydroxide was precipitated from this solution by ammonium hydroxide, filtered off, redissolved in sulfuric acid and reprecipitated by ammonium hydroxide, the second filtrate being added to the first. The combined filtrates were analyzed for chromate. After the yellow color had been removed in the manner just described, the white precipitate of indium hydroxide was ignited to the oxide; the latter was determined gravimetrically.

Studies of precipitation under various conditions, to determine the presence of adsorption, were made, and are described in the following section.

Results and Discussion

Twenty ml. of 0.00957 *M* indium chloride, containing some free hydrochloric acid, at a *p*H of 0.80, was titrated with 0.1002 *M* potassium chromate having a *p*H of 8.5. The *p*H changes during the titration are given by the curve shown in Fig. I. The curve shows two points of inflection: (1) at 32.6 ml. and a *p*H of 3.4; (2) at 38.5 ml. and a *p*H of 4.8. Precipitation started in the region of the first point of inflection and terminated at the second. The first point is readily seen to be that at which neutralization of the free hydrochloric acid present originally is practically complete, and at which the chromate becomes available for the precipitation of the indium salt.

The quantity of potassium chromate reacting in the range between the two points of inflection equals 0.00059 mole; the amount of indium available for reaction is 0.000191 mole. The titration ratio is therefore $CrO_4^{=}/In^{+++} = 3.1/1$. If indium chromate were precipitated, the titration ratio would be 1.5/1; this possibility is therefore eliminated. A ratio of 3.0/1 would be obtained in the precipitation of indium acid chromate, indium dichromate, or indium hydroxide according to the reaction

$$In^{+++} + 3CrO_4^{=} + 3H_2O \longrightarrow In(OH)_3 + 3HCrO_4^{-}$$

or a mixture or basic salt formed by these compounds. Qualitative analysis of the precipitate is used to differentiate between these alternatives.

The possibility of precipitation of either the acid chromate or the dichromate is ruled out by the low chromium content of the precipitate. The composition of the latter is seen from Table I, in which the second column gives the amount of chromate actually available for precipitation after account has been taken of the quantity needed to neutralize the acid corresponding to the original *p*H. The results of the electrometric and quantitative analyses, together with the fact that the precipitation takes place over exactly the same *p*H interval whether the titration is carried out with a chromate or a hydroxide, are sufficient grounds for believing that indium hydroxide is precipitated when chromate and indic ions are mixed.

The $CrO_4^{=}/In^{+++}$ reaction ratio for the precipitation of $In(OH)_3$ is 3.0/1, as shown by the equation given above. The ratio found experimentally is 3.1/1. An excess of 0.1 mole of chromate to 1.0 mole of indium used is therefore unaccounted for. This observation, added to the fact that the analysis of the precipitate (Table I) gives values of chromate of about 0.12 mole to 1.0 mole of indium used, indicate that the excess chromate is adsorbed on the indium hydroxide, giving this precipitate properties which have led previous investigators to the belief that it contained a chromate of indium.

The samples of precipitate for the analyses given in Table I were taken after more than three equivalents of chromate had been added to the indium ion solution. The analyses show that the

TABLE I

ANALYSIS OF PRECIPITATE

Sample taken after second point of inflection

K_2CrO_4 total ml.	K_2CrO_4 available for pptn., ml.	*p*H initial	*p*H final	Indium in ppt., moles × 10^4	Chromate in ppt. moles × 10^4
38.68	10.68	0.85	4.90	1.91	0.23
39.09	9.09	.83	4.91	1.90	.21
42.79	6.79	.75	5.60	1.91	.23
44.17	8.17	.75	5.75	1.91	.24
48.58	18.58	.83	6.02	1.91	.25
49.82	23.82	.88	6.08	1.91	.25

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[1] From a thesis submitted to the Graduate School of Arts & Science of New York University in partial fulfillment of the requirements for the Master of Science degree, under the supervision of Professor William F. Ehret.

[2] Stubbs, THIS JOURNAL, **66**, 498 (1944).

[3] From the Indium Corporation of America, Utica, New York.

indium was recovered completely and that the amount of chromate present was small and variable, the average ratio of $CrO_4^{=}/In^{+++}$ being about 0.12. Results similar to the above were obtained when precipitates that came down shortly after the first point of inflection were examined. Here, also, the molar ratio of chromate used in the precipitation to indium was slightly greater than 3:1, and the ratio of $CrO_4^{=}/In^{+++}$ in the precipitate averaged 0.12. This indicates that the product at the start of precipitation is of the same nature as that finally obtained.

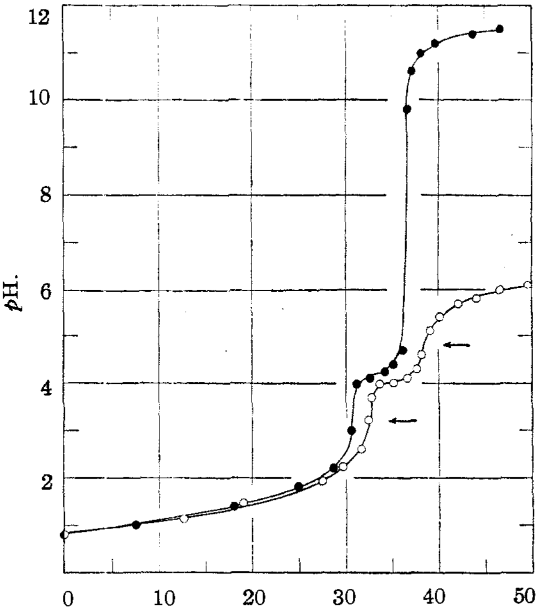

Fig. 1.—Titration of 0.01 *M* $InCl_3$ with: ⊙, 0.1 *M* K_2CrO_4; ●, 0.1 *M* NaOH; at 25°. Arrows indicate beginning and end of precipitation.

The results of experiments designed to show a connection between the chromate content of precipitates and chromate sorption by indium hydroxide were as follows: (a) Two precipitates, each from one of the standard titrations, were digested in 20 ml. of water at 25° for one week. In one case the yellow coloration of the precipitate was markedly diminished, and in the other a pure white residue was observed. Three standard precipitates were digested, as above, for 2, 4 and 6 days, respectively, and they retained, after these periods, 0.15, 0.14 and 0.09 × 10^{-4} mole of chromate. (b) A quantity of freshly precipitated indium hydroxide, equivalent in amount to that in a standard precipitate, when digested for two days in 20 ml. of 0.1 *M* potassium chromate, at *p*H 5.2 and 25°, and then washed, contained 0.02 × 10^{-4} mole of chromate. The relatively small quantity of chromate taken up by indium hydroxide when thus exposed may be attributed to the fact that this was solely a surface phenomenon, *i. e.*, adsorption, whereas the sorption during the precipitation of indium hydroxide by potassium chromate involves occlusion as well, since in this case the sorption occurs while the reaction is in progress. (c) It is well-known that the amount of a substance that is sorbed generally decreases with temperature. This was shown to hold true for the reaction under investigation. As may be seen from Fig. 2, titration curves were obtained at 10 and 40° under conditions which were otherwise kept as similar as possible, particularly in reference to the speed of addition of the reagent and the amount of stirring. The quantitative analysis of the precipitates obtained at these two temperatures points to the existence of sorption, as the excess chromate diminished noticeably from 10 to 40°. Thus at 10° there was 0.19 × 10^{-4} mole of chromate in the precipitate from 20 ml. of 0.00957 *M* indium solution, whereas at 40° there was only 0.14 × 10^{-4}. In passing it may be noted that if the curve for the titration at 25° were drawn in Fig. 2, it would at all points be intermediate between the curves for 10 and 40°.

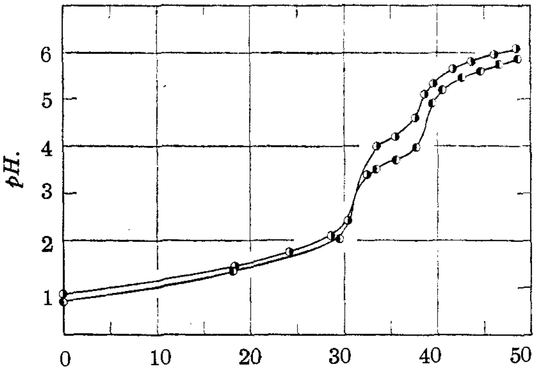

Fig. 2.—Effect of temperature on titration of 0.01 *M* $InCl_3$ with 0.1 *M* K_2CrO_4: ◑, 10°; ◐, 40°.

Microscopic examination showed no essential difference between the white crystals of indium hydroxide and the yellow ones obtained upon precipitation with potassium chromate. Well-defined crystals could not be recognized. Both groups of crystals were isotropic.

Acknowledgment.—The appreciation of the author is due to Dr. William F. Ehret for valuable advice and guidance.

Summary

The precipitate obtained upon addition of potassium chromate to a solution of indium chloride was investigated by electrometric titrations and by quantitative analyses. The ratio of the actual reacting substances at complete precipitation was found to average 3.1 moles of chromate ion to 1 mole of indium; the amount of chromium in the precipitate averaged 0.12 mole to 1 mole of indium. This led to the conclusion that the precipitate consists of indium hydroxide and that no indium chromate is precipitated. The chromium salt found in the precipitate is present in an adsorbed or occluded form, this conclusion being supported by sorption studies in which it was demonstrated that the final chromate content of the precipitate is dependent upon the conditions under which it is formed and washed.

NEW YORK, N. Y. RECEIVED AUGUST 20, 1946