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

The Action of Phenolphthalein on Insoluble Hydroxides

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The subject of the following investigation was suggested by the observation that ceric hydroxide precipitated from a $K_2Ce(SO_4)_3$ solution turns brown when spotted with phenolphthalein (private communication from F. Feigl). By extending the test to other commoner hydroxides, a series of reactions were found that do not seem to have been described hitherto.

Kolthoff, however, points out[1] as an example of the so called activated adsorption, that a lanthanum hydroxide precipitate is colored blue by thymolphthalein, although the hydroxide is not sufficiently soluble in water to make it alkaline toward this indicator. On the other hand, thymolphthalein and phenolphthalein are adsorbed by aluminum hydroxide in their nonactivated modifications and therefore no color is developed. Recently[2] the triarylmethyl halides, whose carbon skeletons correspond to that of phenolphthalein, have also been studied as to their activated adsorption.

Experimental Conditions.—The experiments were carried out under qualitative analytical conditions. The metal hydroxide was precipitated by the addition of a 2 N or 0.2 N solution of sodium hydroxide to the 0.2 N solution of the metallic salt, collected on an ordinary filter and spotted with a 1% alcoholic solution of phenolphthalein.

As the adsorptive power of the precipitate was expected to vary according to the nature of the electrolyte kept in solution by the supernatant liquid, each metal hydroxide was prepared in two different ways, using a 10% excess of alkali and a 10% excess of metal salt, respectively. This excess was calculated from an empirical zero point fixed by rendering the salt solution alkaline toward phenolphthalein by means of a 0.1 N sodium hydroxide solution. Of course this zero point does not coincide with the equivalent point of the chemical reaction, owing to the formation of basic salts and to the presence of adsorbed material on the precipitate. When an excess of alkali was used the precipitate had to be freed from this excess before spotting; washing was therefore continued till the water gave no color with phenolphthalein.

The reactivity of the precipitates toward phenolphthalein decreases when they are allowed to remain on the filter for some time. Alcohol also hinders the reaction. This seems to agree with the fact that addition of alcohol to the aqueous solution shifts the end-point of phenolphthalein in the direction of higher alkalinity.[3] As in these experiments phenolphthalein is used in alcoholic solution, it is advantageous to moisten the precipitate with a few drops of water after spotting.

Results.—The colors obtained by spotting the hydroxides of the metals with phenolphthalein are given in Table I.

TABLE I

Metal	Hydroxide prepared with excess alkali	Hydroxide prepared with excess salt
Lead	Crimson	Crimson
Copper	Pastel blue	None
Cadmium	Crimson	Crimson
Cobalt	Mauve	Mauve
Nickel	Raspberry	Raspberry
Manganese^{++}	....	Red
Zinc	Crimson	Crimson
Magnesium	Red	Red
Bismuth	Bright crimson	None
Tin^{++}	None	None
Tin^{++++}	....	None
Antimony^{+++}	....	None
Antimony^{+++++}	None	None
Aluminum	None	None
Iron^{+++}	None	None
Chromium	None	None

The hydroxides of trivalent antimony and tetravalent tin as well as that of bivalent manganese could not be utilized when prepared using an excess of alkali, the first two because they ran through the filter as colloids when washed continuously, the third because it was oxidized during washing.

Of all the hydroxides examined only that of magnesium is soluble enough in water to render it alkaline toward phenolphthalein, so that its behavior calls for no remark. Some of the colors observed may be mixtures of the original color of the hydroxide and the color produced by the action of the indicator.

The hydroxides of bismuth and copper call for special mention in that they give distinct colors (with phenolphthalein) when prepared with excess of alkali but none when prepared with excess of metallic salt. Under the latter condition bismuth hydroxide becomes indeed slightly colored in the course of time, the color deepening gradually when the amount of precipitating alkali is increased.

Copper hydroxide also gave a pastel blue color

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[1] Kolthoff, *Kolloid-Z.*, **68**, 196 (1934); *J. Phys. Chem.*, **40**, 1027 (1936).

[2] E. Weitz and F. Schmidt, *C. A.*, **34**, 95 (1940); *Ber.*, **72B**, 1740 (1939); *C. A.*, **34**, 3258 (1940); *Ber.*, **72B**, 2099 (1939).

[3] R. Wegscheider, *Z. physik. Chem.*, **100**, 532 (1922).

when prepared with slight deficiency of alkali, but under these conditions, in spite of excess of copper, no copper ion was detectable in the filtrate by means of benzoin oxime. When the amount of alkali was further reduced, part of the precipitate passed through the filter, rendering the filtrate milky.

The behavior of cupric hydroxide also has been studied by Mehrota and Dhar[4] and by Hayek[4]; it may adsorb cupric salts or alkali hydroxide. Similarly, bismuth hydroxide precipitated by alkali is never free from bismuth salts.[5] One may deduce that, under these conditions, the hydroxides have their surfaces covered with a sheath of neutral or basic salts which prevent the phenolphthalein from being adsorbed.

Discussion.—It might be suspected that alkali retained by the hydroxide precipitate is responsible for the appearance of color. But the color is destroyed by continuous washing with water that has been freed from carbon dioxide by boiling, the water remaining colorless. The color returns by a renewed treatment with phenolphthalein. Another argument in support of the view that the hydroxide is itself dyed is found in the action of bismuth hydroxide on hydrogen peroxide. The catalytic decomposition of the latter involves the intermediate formation of bismuthic acid. If bismuth which has been dyed with phenolphthalein on the filter is treated with hydrogen peroxide solution, the dye is detached and may be regenerated by rendering the filtrate alkaline.

There seems to be some correspondence between the possibility of assuming a color and the structure of the freshly prepared precipitate.[6] Those hydroxides which as a result of X-ray examination are alleged to be crystalline in their initial state have been found to be colored by phenolphthalein. The hydroxides concerned are those of lead, cadmium, cobalt, nickel, magnesium and bismuth; whereas the hydroxides of aluminum, trivalent iron, chromium and tetravalent tin, which are amorphous in the initial state, remain colorless. It must be conceded however, that though stannic hydroxide is not changed by phenolphthalein, it turns yellow when spotted with phenol red, and that, as already pointed out, its examination when prepared with excess of alkali was not possible.

In view of the general results obtained by the action of phenolphthalein on insoluble hydroxides, it is of interest to note that an adsorbent of an acid character, *e. g.*, grains of casein, may show an acid reaction when touching indicator paper although no reaction is observed with the water which has been shaken with the adsorbent.[7]

In contrast to these adsorption phenomena W. M. Dehn[8] succeeded in producing definite addition compounds of metal hydroxides and phenolphthalein. The colors of these compounds mostly depend on whether they contain water or not, and are different from the colors described in this paper. The anhydrous addition compound of copper is brown-black, of cadmium red, of cobalt and manganese black and of zinc scarlet while the hydrated compound of copper is grass-green, of cadmium and zinc white, of cobalt white (red) and of manganese white (brown).

The work described in this paper was begun in Vienna, where I enjoyed the valuable help of Eugen Rosenberg, Theodor Kapsa, and Fritz Gortam; the work was completed at the University of Glasgow.

Summary

A number of insoluble metal hydroxides are colored by phenolphthalein. This is due to the activated adsorption of phenolphthalein on the hydroxide. Lead, cadmium, cobalt, nickel, manganese^{++}, zinc, and magnesium are colored, tin^{++}, tin^{++++}(?), antimony^{+++}(?), antimony^{+++++}, aluminum, iron^{+++}, and chromium are not. Copper and bismuth give the reaction only when the alkali used for their preparation exceeds a certain amount.

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[4] Mehrota and Dhar, *J. Phys. Chem.*, **33**, 216 (1929); Hayek, *Monatsh.*, **67**, 352 (1936).

[5] Thibault, *J. pharm. chim.*, [6] **12**, 559 (1900).

[6] Fricke, *Kolloid-Z.*, **69**, 312 (1935).

[7] Brailsford and Robertson, *J. Biol. Chem.*, **2**, 326 (1907).

[8] W. M. Dehn, THIS JOURNAL, **54**, 2947 (1932).