yellow oxide. The color, however, was much more red than the samples of the yellow oxide.

Further work is necessary before one can definitely attribute the free energy difference between the red and yellow forms to either difference in particle size, or to allotropy.

Summary

We have determined the solubility of red mercuric oxide in water, and in sodium hydroxide solutions, and of yellow mercuric oxide in water, and in sodium, potassium, lithium hydroxide solutions, and in alkaline salt solutions. These determinations have been made at $25 \pm 0.01°$.

The data indicate no minima in the solubility curves of red and yellow mercuric oxides in alkali solutions; in each case the solubility is a linear function of the alkali concentration up to approximately one normal alkali. The two curves are nearly parallel, the solubilities differing by about 5%.

The solubility curves in pure alkali establish the amphoteric nature of mercuric oxide by the constancy of the equilibrium constant, K_2

$$HgO + OH^- = HHgO_2^- \qquad (2)$$

A number of free energy calculations have been made with the aid of the solubility results. These include the ΔF of formation of mercuric oxide.

The first dissociation constant of mercuric acid has been evaluated from the data.

The dissociation constant of mercuric hydroxide as a base has been calculated, and found to be 1.8×10^{-22}, a fact which indicates an extraordinarily small degree of dissociation, namely, 0.002% in the saturated solution.

The data indicate that the difference in free energy between red and yellow mercuric oxide is only 31 cal./mole.

The data in alkaline salt solutions indicate that definite reactions are taking place between the oxide and the salts, probably the formation of basic salts. The data give no information concerning the ratio $\gamma_{OH^-}/\gamma_{HHgO_2^-}$.

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Organo-metallic Compounds of Indium[1]

BY WALTER C. SCHUMB AND H. IRVING CRANE

Of the elements in Group III of the Periodic Table which are known to form organo-metallic compounds, least attention appears to have been given to indium, due to the unavailability of this element until recent years, and to the ease of oxidation and of hydrolysis of its organo-metallic compounds.

Spencer and Wallace,[1a] studying the behavior of the aluminum group of metals with organic halides, found that indium reacted with iodobenzene and with α-bromonaphthalene, giving intermediate products, which were not isolated, but which gave benzene and naphthalene, respectively, on steam distillation. In 1910, Thiel and Kölsch[2] mentioned that they had worked with both the aliphatic and aromatic compounds of indium, but the subsequent complete paper has not appeared. They observed, however, that the alkyl compounds oxidized easily, the aryl compounds more sluggishly.

Goddard[3] refers to some otherwise unpublished work in which he prepared diphenylindium chloride and a basic phenylindium oxide. In 1934, Dennis[4] and his co-workers prepared trimethylindium and studied its physical properties, its oxidation and hydrolysis. In patents issued to Groll[5] mention is made of triethylindium, but no data are listed as to yields or properties.

The present paper is concerned chiefly with the preparation of triphenylindium, diphenylindium bromide and iodide, and of phenylindium dibromide and diiodide. A study of the properties of these substances indicates that in its organo-

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(1) Presented at the second annual symposium of the Division of Physical and Inorganic Chemistry, Cleveland, Ohio, Dec. 27–29, 1937.

(1a) J. F. Spencer and M. L. Wallace, *J. Chem. Soc.*, **93**, 1827 (1908).

(2) A. Thiel and H. Kölsch, *Z. anorg. allgem. Chem.*, **66**, 320 (1910).

(3) A. E. Goddard, editor, in J. N. Friend, "A Textbook of Inorganic Chemistry," Longmans, Green and Co., New York, 1928, Vol. XI, part 1, p. 235.

(4) L. M. Dennis, R. W. Work, E. G. Rochow and E. M. Chamot, THIS JOURNAL, **56**, 1047 (1934).

(5) H. P. A. Groll, U. S. Patents 1,938,179 and 1,938,180, Dec. 5, 1933.

metallic compounds indium is more closely related to aluminum and gallium than to thallium.

Experimental

Triphenylindium.—Two and one-half grams of metallic indium,[6] cut into small chips was placed in a tube with 8.5 g. of diphenylmercury; the tube was swept out with dry carbon dioxide and sealed. The mixture was held in an oil-bath at 130° overnight, when the solidification of the contents of the tube indicated that the reaction was practically complete. The tube was then opened in an atmosphere of dry carbon dioxide, and the contents extracted with chloroform. Filtration in the same inert atmosphere removed the mercury, indium amalgam and traces of oxidation or decomposition products; and evaporation to a small volume by a stream of carbon dioxide gave colorless needles of triphenylindium, the mother liquor containing in addition diphenylmercury and a trace of diphenyl. The yield of crude crystals was 2.5 g. (45%). The product, recrystallized from chloroform, melted at 291° with decomposition.

Triphenylindium is readily soluble in chloroform, benzene or pyridine, but is nearly insoluble in petroleum ether. In benzene, or especially in pyridine, it reacts very readily with air or moisture, precipitating amorphous basic phenylindium oxides of indefinite composition, wherein the ratio of carbon–indium bonds to total indium valence bonds is 1:9 or less. The chloroform solution is much more stable, as is the dry solid, although even these are fairly reactive. The triphenylindium solutions react instantly with iodine in benzene solution, and all three carbon–indium bonds may be broken in this manner, indium triiodide being precipitated as the final product.

Anal. Calcd. for $(C_6H_5)_3In$: In, 33.3; C, 62.4; H, 4.35. Ratio of C–In bonds to total In valence bonds, 3:3. Found: In, 33.10, 33.15; C, 62.1, 62.2; H, 4.10, 4.27. Ratio of C–In bonds to total In valence bonds, 3:3.06, 3:3.03.

Diphenylindium Bromide.—Triphenylindium was dissolved in benzene and an aliquot portion was titrated with a dilute solution of bromine in benzene, the bromine serving as its own indicator. To the remaining solution was added one-third of the amount of bromine required to split all three carbon–indium bonds; the diphenylindium bromide was then precipitated by addition of petroleum ether, filtered and washed in a dry carbon dioxide atmosphere, and recrystallized several times from benzene. The yield was approximately 80%. The product, a faint buff-colored powder, did not melt below 300°. Heated in the open upon a spatula a sample charred and later oxidized to In_2O_3. Diphenylindium bromide is readily soluble in benzene, ether and pyridine, somewhat soluble in chloroform, insoluble in petroleum ether. It is hydrolyzed at once by water forming flocculent indium hydroxide. It reacts with bromine or iodine, as would be expected.[7]

Anal. Calcd. for $(C_6H_5)_2InBr$: In, 32.90; C, 41.27; H, 2.89; Br, 22.93. Found: In, 32.45, 32.37; C, 41.50, 41.20; H, 2.63, 2.58; Br, 22.61, 22.70.

Phenylindium Dibromide.—This compound was prepared by the method described for diphenylindium bromide, except that the proportions of bromine used were changed so that two-thirds of the amount necessary for the complete oxidation of the triphenylindium was used. In its properties it resembles diphenylindium bromide. It also does not melt below 300°.

Anal. Calcd. for $C_6H_5InBr_2$: In, 32.64; C, 20.48; H, 1.43; Br, 45.45. Found: In, 32.30, 32.49; C, 20.63, 20.39; H, 1.10, 1.17; Br, 45.27, 45.43.

Diphenylindium Iodide.—The preparation and properties of this compound, as well as of phenylindium diiodide, are wholly analogous to those of the bromides, except that iodine solutions in benzene were substituted for the bromine used in the two previous cases.

Anal. Calcd. for $(C_6H_5)_2InI$: In, 29.00; I, 32.07; C, 36.38; H, 2.55. Found: In, 28.70, 28.84; I, 32.06, 31.97; C, 36.22, 36.48; H, 2.43, 2.39.

Phenylindium Diiodide. *Anal.* Calcd. for $C_6H_5InI_2$: In, 25.75; I, 56.96; C, 16.16; H, 1.13. Found: In, 25.51, 25.48; I, 56.80, 57.02; C, 16.25, 16.10; H, 1.02, 1.09.

Reaction of Indium with Methylene Iodide.—Methylene iodide readily loses its iodine to magnesium and copper, with the formation of methylene polymers, chiefly ethylene. In some cases, however, as with aluminum[8] and mercury,[9] organo-metallic compounds are formed, such as $CH_2{=}AlI$, $ICH_2{-}HgI$ and $CH_2(HgI)_2$.

Samples of indium in the form of small chips were allowed to stand under methylene iodide in sealed tubes at room temperature. In one experiment 1.601 g. of indium and 3.515 g. of methylene iodide were used. The reaction was very slow; after a week the liquid had become considerably more viscous and the metal had lost its luster. After a month a light brown solid began to deposit, but even after a year, when deposition appeared to have ceased, the amount was very small. On opening the tube, a slight pressure was noted and an odor of unchanged methylene iodide, although the amount of the latter was so small that none could be recovered by steam distillation; 1.00 g. of unchanged indium was found.

After steam distillation, the residue in the flask contained a precipitate of indium hydroxide, which was filtered, washed, ignited and weighed. This was considered to represent the carbon–indium bonds formed in the reaction, with a small correction for the hydrolysis of indium iodide. In the filtrate the indium which had been present as $=InI$ or $-InI_2$ was precipitated and determined, and finally the iodide ion formed was determined. The results follow:

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(6) Metallic indium of purity better than 99.99%, obtained from the Grasselli Company, Cleveland, Ohio, was used in most of the work here described. The Indium Corporation of America also supplied some of the metal of 99% purity, containing some zinc and lead.

(7) Since Goddard[8] had reported diphenylindium chloride as insoluble in organic solvents, it was thought probable that it could be prepared from the bromide in benzene solution, by metathesis with an organic chloride with a labile halogen. Tertiary butyl chloride was used for this purpose, but no precipitation occurred even on refluxing, as long as air and moisture were excluded. It would thus seem that Goddard's product may have been somewhat oxidized or hydrolyzed, thereby rendering it insoluble.

(8) Faillebin, *Compt. rend.*, **174**, 112 (1932); Thomas, *ibid.*, 464 (1922).

(9) Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); **39**, 485 (1881); Thomas, *Compt. rend.*, **132**, 1119 (1901).

(a) In_2O_3 by hydrolysis	0.1114 g. or 0.803 milliatom In
(b) In_2O_3 from filtrate	0.5719 g. or 4.120 milliatoms In
Total In	0.6833 g. or 4.923 milliatoms In
(c) AgI from filtrate	2.9789 g. or 12.69 milliatoms I

The atomic ratio $a:b$ = R–In bonds : In–I bonds = 1:5.13, showing that the carbon–indium bonds were about one-sixth of the total number of indium valence bonds. The atomic ratio $b:c$ = $In^{+++} : I^{-}$ = 1:3.08. If allowance is made for hydrolysis of InI_3, which would produce a little $In(OH)_3$, contaminating the precipitate in (a), the indium ion was approximately equivalent to the iodide liberated.

As 13.12 millimoles of methylene iodide was originally taken, none of which was recovered, and 12.69 milliequivalents of iodide was found after the reaction, it would appear that on the average each methylene iodide lost one atom of iodine, the net reaction being

$$3CH_2I_2 + 2In \longrightarrow InI_3 + \frac{2}{x}(CH_2)_x + ICH_2InI_2$$

Incidental to the work above described several new addition compounds of indium halides were prepared and analyzed. They will be described here briefly.

Indium Bromide Dioxanate, $InBr_3 \cdot 2C_4H_8O_2$.—Dioxane added to an ether solution of indium bromide precipitates this compound as a white, crystalline powder, which is only slightly soluble in cold dioxane, but moderately soluble in warm anhydrous dioxane, from which it may be crystallized as large needles, decomposing at about 140°. The crystals are very hygroscopic, very slightly soluble in ether, insoluble in hydrocarbon solvents.

Anal. Calcd. for $InBr_3 \cdot 2C_4H_8O_2$: In, 21.63; Br, 45.18. Found: In, 21.52, 21.35; Br, 44.96, 44.86.

Indium Iodide Pyridinate, $InI_3 \cdot 3C_5H_5N$.—When solid indium iodide is treated with anhydrous pyridine, considerable heat is evolved and the addition product separates as colorless needles, melting at 164°. The compound is readily soluble in hot pyridine, sparingly in the cold.

Anal. Calcd. for $InI_3 \cdot 3C_5H_5N$: In, 15.69; I, 52.04. Found: In, 15.54, 15.60; I, 51.93, 51.97.

In addition to the above account of experiments which led to the successful preparation of organic indium compounds, it should be added that a study was made of other types of reaction whereby organo-metallic compounds of other elements have been prepared, but in each case we were unsuccessful in isolating corresponding compounds of indium, due in some cases to difficulty in separating the desired substances from the mixture of reaction products, in other cases to the fact that the reaction proceeded, if at all, to products containing no carbon–indium bonds. A brief list of these experiments may not be out of place here: (1) metallic indium and organic halides, including ethyl bromide, ethyl iodide, benzyl chloride, *t*-butyl chloride, triphenylchloromethane, and bromobenzene; (2) sodium–indium alloy and bromobenzene; (3) tetraphenyllead or diphenylmercury with indium; (4) indium bromide (or iodide) with phenylmagnesium bromide, tetraphenyllead, or diphenylmercury.

Summary

1. A study has been made of various methods for the preparation of organo-metallic compounds of indium, in the course of which representatives of three classes, R_3In, R_2InX and $RInX_2$, have been prepared by methods successfully employed in the preparation of analogous compounds of other elements. These substances include triphenylindium, diphenylindium bromide, diphenylindium iodide, phenylindium dibromide and phenylindium diiodide.

2. The organo-metallic compounds of indium appear to be more closely related to those of aluminum and gallium, in their stability toward oxidation and hydrolysis, than to thallium.

3. Indium was found to react very slowly with methylene iodide. ICH_2InI_2 is believed to be one of the reaction products.

4. Incidental to the main purpose of the work the preparation of two new addition compounds of indium halides with solvent of crystallization has been described, indium bromide dioxanate, $InBr_3 \cdot 2C_4H_8O_2$, and indium iodide pyridinate, $InI_3 \cdot 3C_5H_5N$.

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