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NOTE

Low pressure synthesis of cobalt carbonyls

Introduction

High pressure methods for the preparation of cobalt carbonyls in large quantities and in good yield such as dicobalt octacarbonyl are well documented[1]. However, this preparative approach has rather obvious disadvantages. A number of methods are available for the preparation of some of these species at low pressure[2-5]; here the percentage yields are frequently in the 50% range, but these methods suffer from the fact that they cannot be used for larger scale preparations.

We describe a method wherein the basic reaction of Gilmont and Blanchard[2] is utilized in a novel fashion which allows cobalt carbonyl synthesis in the 10–100 g range.

Experimental

The basic apparatus was given very preliminary description earlier[6]. The heart of the apparatus is a 3 or 12 liter, three-necked flask equipped with a very efficient spray-agitator (Nester–Faust). The size of the flask to be used is determined by the quantity of product desired. (A creased flask may be desirable for large scale runs.) The larger vessel is only slightly less convenient to use than the smaller one. The spray-agitator is a Teflon cylindrical block equipped with two stiff plastic tubes extending through and slightly below the cylinder. The tubes are bent at the top and beveled at the bottom in such a way that when the cylinder is rotated, large quantities of solution or slurry are picked up at the bottom and thrown against the sides of the flask. The surface contact between liquid and gas is quite extensive. The connecting rod to this agitator enters the flask through an O-ring sealed gland. This gland is fitted into a 24/40 joint which is the upper part of an adaptor in the center neck that has a tube extending about halfway into the flask. This tube is equipped with a loose fitting Teflon ring to act as a bearing support which helps to stabilize the long connecting rod. A well-braced medium to high speed motor is used for the stirring.

The gas inlet is through one of the side necks. This neck is equipped with an addition funnel containing a T-bore stopcock, making it possible to add chemicals without exposing the flask to the atmosphere. The funnel is designed such that the inlet gas can be bubbled through the solutions in order to degas them before they are admitted to the flask as suggested by Gilmont and Blanchard[2]. Our yields are sufficiently varied, however, that it is not clear whether this served any significant function. It did seem important to purify further the C.P. carbon monoxide. This is done by passing the gas over copper wire heated to about 500° in a tube heated by a nichrome wire heater. This also removed the rather appreciable quantities of iron pentacarbonyl that are inevitably found in cylinder carbon monoxide. A water bubbler and a simple oil manometer on the inlet side are used for flow control and to check for pressure blockages during subsequent steps.

The gas is vented through a water bubbler from the outlet neck of the flask.

That neck is also equipped with a special dropping funnel (Kontes Glass, Cat. No. K-63460) through which potassium cyanide solution can be admitted slowly over the course of 24 to 72 h.

The bottom of the flask is equipped with a 6 mm Teflon stopcock so that solutions or water can be drained readily.

The apparatus is shown schematically in Fig. 1. Safety, of course, demands that the entire apparatus be contained within a well-vented hood.

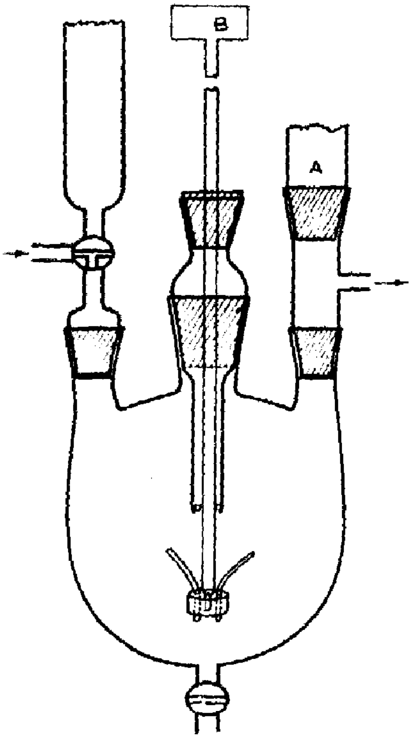

Fig. 1. Apparatus for the preparation of cobalt carbonyls. A is a dropping funnel and B is a stirring motor.

The preparation of $K[Co(CO)_4]$ solution is preliminary to the production of all other products. The flask is completely purged with carbon monoxide before the solutions are admitted. This is accomplished most simply by filling the flask with water, purging the necks with purified CO, and then slowly draining the flask while admitting CO. The relative quantities of chemicals are those used by Gilmont and Blanchard[2]. However, cobalt chloride is used in place of cobalt nitrate whenever the solution is to be subsequently acidified. This was done to avoid the oxidizing power of the nitrate ion in acid solution. In a typical small run in a 3 l flask, 29.8 g $CoCl_2 \cdot 6\ H_2O$ in 75 ml H_2O, 56.0 g KOH in 75 ml H_2O, and 8.0 g KCN in 35 ml H_2O are used. In the 3 l flask, these quantities can be increased 3-fold, and in a 12 l flask they can be increased perhaps 20-fold.

The cobalt chloride and potassium hydroxide are added to the flask, yielding pink gelatinous $Co(OH)_2$. Water is added at this time to obtain extensive agitation. The addition of water should be kept to a minimum, as an excess only serves to slow down the rate of reaction. The solution becomes much less viscous as the reaction proceeds. About 10% of the cyanide is added immediately to get the reaction started, and the rest is added slowly over the course of 24 to 72 hours, depending upon the scale of the reaction. Carbon monoxide is absorbed at a rate of 50–100 cc/min at first, and this absorption continues at only a slightly diminishing rate until the initial viscous pink suspension is converted into an orange-yellow solution containing a small quantity of a pinkish-white solid. If a reaction is not complete, the further addition of a few ml of cyanide will increase the rate of absorption, whereas if it is, a little gas may well be evolved. Usually, the reaction is complete before all of the cyanide has been added.

This solution is converted into the other products. For the production of hydride, 150 ml of concd. HCl are added slowly to the carbonyl cobaltate solution cooled in an ice bath. Large quantities of carbon dioxide are produced in the process, and the venting of this gas is the main factor limiting the rate of acid addition. Carbon monoxide is used to purge the CO_2 and $HCo(CO)_4$ from the system. The gas stream is dried over granular P_4O_{10} and then the hydride is condensed in a $-78°$ trap. A large bore trap is necessary to avoid plugging problems. It takes 12 to 36 h to sweep all of the hydride from the system in the larger runs. The hydride is a colorless to light yellow material.

The hydride is converted into dicobalt octacarbonyl by allowing the trap to warm slowly to room temperature while carefully venting the escaping gases. The best product results when the hydride is allowed to warm slowly to the decomposition temperature of about $-20°$. This can be accomplished by allowing the flask containing the hydride to warm in an empty dewar which had been cooled to the storage temperature of $-78°$. This slow decomposition during the course of several hours yields a product as a lump of large reddish-brown crystals on the bottom of the trap. These crystals are sufficiently stable to be handled briefly in air with little decomposition. The conversion is essentially quantitative.

Cobalt nitrosyl tricarbonyl is produced as described briefly earlier[6]. Cylinder nitric oxide, freed from NO_2 by a trap cooled to $-78°$, is passed into the $K[Co(CO)_4]$ solution either directly or after its partial neutralization by hydrochloric acid. The volatile compound is swept out of the system by a CO/NO gas mixture, dried by P_4O_{10} or 4A Molecular Sieves and trapped at $-78°$. The product is a red liquid with a freezing point of about 0°.

The mercury salt, $Hg[Co(CO)_4]_2$ is produced by adding $HgCl_2$ solution and nitric acid to the $K[Co(CO)_4]$ solution. The crude product is filtered and purified by recrystallization from acetone. The product had a melting point of 81.0–81.5°. This work was done with special attention toward obtaining high yields as an attempt to determine the amount of $K[Co(CO)_4]$ actually present in solution.

The yields of these products were somewhat variable, and it was never possible to really pinpoint the source of the variation. The recovery procedure is usually felt to result in considerable loss, especially with unstable species like $HCo(CO)_4$. The yields discussed below result from six to twelve preparations of each compound.

Cobalt carbonyl hydride, and from this dicobalt octacarbonyl, could be produced in about 7 to 13 g quantities representing 30 to 57% yields starting from 31.7 g of $CoCl_2 \cdot 6\ H_2O$. The production of these two carbonyls was scaled up further in a 12 l flask. As an example of two representative runs, 43.7 and 105 g of $HCo(CO)_4$ were produced from 149 and 597 g of $CoCl_2 \cdot 6\ H_2O$, respectively, for 40 and 24% yields. It is not certain that any particular significance can be placed on the lower yield of the larger scale run.

Cobalt nitrosyl tricarbonyl was produced in 6 to 11 g quantities in about 28 to 51% yields from 36.5 g quantities of $Co(NO_3)_2 \cdot 6\ H_2O$.

The mercury cobalt carbonyl was produced in quantities of 18 to 22 g with yields of 53 to 65% from 29.7 g of $CoCl_2 \cdot 6\ H_2O$. The ultimate amount of $Hg[Co(CO)_4]_2$ in the impure product was estimated to run as high as 80 to 85%.

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1 R. B. KING, *Organometallic Synthesis*, Vol. I, Academic Press, New York, 1965, p. 98.
2 P. GILMONT AND A. A. BLANCHARD, *Inorg. Syn.*, 2 (1946) 238; *J. Amer. Chem. Soc.*, 62 (1940) 1192.
3 G. W. COLEMAN AND A. A. BLANCHARD, *J. Amer. Chem. Soc.*, 58 (1936) 2160.
4 G. BOR AND B. MOHAI, *Acta Chem. Acad. Sci. Hung.* 8 (1956) 335; *Chem. Abstr.*, 50 (1956) 13643*e*.
5 W. HIEBER, E. O. FISCHER AND E. BÖCKLY, *Z. Anorg. Allg. Chem.*, 269 (1952) 308; W. HIEBER AND E. O. FISCHER, *Z. Anorg. Allg. Chem.*, 269 (1952) 292.
6 R. J. CLARK, *Inorg. Chem.*, 6 (1967) 299.

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