[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

The Chemistry of Metal Carbonyls. I. New Concepts Applied to Carbonyls of Cobalt

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The reactions of a variety of organic compounds with dicobalt octacarbonyl, previously assumed to proceed by the displacement of one or more moles of carbon monoxide by the entering organic molecule, are explicable on a common basis. The entering organic group, which always has an available pair of electrons, effects a homomolecular disproportionation of the dicobalt octacarbonyl into cobalt(II) ion and cobalt carbonyl anion according to the generalized equation: $12B + 3[Co(CO)_4]_2 \rightarrow 2[Co(B)_6][Co(CO)_4]_2 + 8CO$, where B is a base in the Lewis sense. The electrons necessary for the formation of the anion are secured at the expense of some of the cobalt. Situations also are described in which these electrons are furnished by an external source. The tendency to form the stable (rare-gas structure) cobalt carbonyl anion is probably the driving force for the reactions.

A study of the hydroformylation (oxo) reaction in this Laboratory required preparation of cobalt hydrocarbonyl, $HCo(CO)_4$. The methods for preparing this acid[1,2] are based on the formation of a metal salt of cobalt hydrocarbonyl and subsequent liberation of cobalt hydrocarbonyl by acid treatment. One such reaction involves the formation of cobalt(II) ion and cobalt carbonyl anion, $[Co(CO)_4]^-$, from dicobalt octacarbonyl according to equation (1)[3]

$$3[Co(CO)_4]_2 + 12NH_3 = 2[Co(NH_3)_6][Co(CO)_4]_2 + 8CO \quad (1)$$

In considering the details of this reaction, it occurred to the writers that it may be based on a reaction mechanism of general applicability in the field of metal carbonyl chemistry.

Equation (2) gives the general expression for

$$3[Co(CO)_4]_2 + xB \longrightarrow 2[Co(B)_x]^{++}[Co(CO)_4]_2^- + 8CO \quad (2)$$

the formation of cobalt carbonyl anion from dicobalt octacarbonyl. This reaction may be considered as a homomolecular disproportionation in which the uncharged dicobalt octacarbonyl disproportionates into cobalt(II) cation and cobalt carbonyl anion. B is a compound having an available unshared pair of electrons, *i.e.*, a base in the Lewis sense. As the coördination number of cobalt(II) ion is normally 6, x may be 6 or 3, depending upon the number of functional groups in B. Thus x is 6 for ammonia (equation (1)) and pyridine and 3 for *o*-phenanthroline. The function of B will be discussed in connection with the reaction mechanism.

The quantitative conversion of dicobalt octacarbonyl to cobalt cation and cobalt carbonyl anion according to equation (2) requires (a) the liberation of $2^2/_3$ moles of carbon monoxide per mole of dicobalt octacarbonyl, (b) the formation of $1^1/_3$ moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl, and (c) the conversion of one-third of the amount of cobalt present in dicobalt octacarbonyl to cobalt(II) ion. The data in Table I summarize the results obtained with methanol, ethanol, pyridine and *o*-phenanthroline, and these data are consistent with the stoichiometry required by equation (2).

TABLE I

Reagent added to $[Co(CO)_4]_2$	Reaction products a $\frac{\text{Moles CO}}{\text{Mole } [Co(CO)_4]_2}$	 b $\frac{\text{Moles } [Co(CO)_4]^-}{\text{Mole } [Co(CO)_4]_2}$	 c $\frac{\text{Grams Co(II)}}{\text{Gram total Co}}$
Methanol	2.66	..	0.334
Ethanol	2.87	1.40	...
Pyridine	2.80	1.41	...
o-Phenanthroline	2.86	1.34	...

The results listed in Table I suggest revision of the view[4,5,6] that the reaction between dicobalt octacarbonyl and compounds like methanol, ethanol, pyridine and *o*-phenanthroline involves the displacement of one or more carbon monoxide groups of the carbonyl by the base according to equations (3a), (4a), (5a) and (6a).

$$[Co(CO)_4]_2 + CH_3OH \longrightarrow Co_2(CO)_5 \cdot CH_3OH + 3\overline{CO} \quad (3a)$$

$$[Co(CO)_4]_2 + 1.5C_2H_5OH \longrightarrow Co_2(CO)_5 \cdot 1.5C_2H_5OH + 3\overline{CO} \quad (4a)$$

$$[Co(CO)_4]_2 + 4C_5H_5N \longrightarrow Co_2(CO)_5 \cdot (C_5H_5N)_4 + 3\overline{CO} \quad (5a)$$

$$[Co(CO)_4]_2 + 2\ o\text{-Phthr} \longrightarrow Co_2(CO)_6(o\text{-Phthr})_2 + 2\overline{CO} \quad (6a)$$

These reactions are correctly represented by equations (3b), (4b), (5b) and (6b)

$$3[Co(CO)_4]_2 + 12CH_3OH \longrightarrow 2[Co(CH_3OH)_6][Co(CO)_4]_2 + 8\overline{CO} \quad (3b)$$

$$3[Co(CO)_4]_2 + 12C_2H_5OH \longrightarrow 2[Co(C_2H_5OH)_6][Co(CO)_4]_2 + 8\overline{CO} \quad (4b)$$

$$3[Co(CO)_4]_2 + 12C_5H_5N \longrightarrow 2[Co(C_5H_5N)_6][Co(CO)_4]_2 + 8\overline{CO} \quad (5b)$$

$$3[Co(CO)_4]_2 + 6o\text{-Phthr} \longrightarrow 2[Co(o\text{-Phthr})_3][Co(CO)_4]_2 + 8\overline{CO} \quad (6b)$$

It will be noted that the stoichiometry of the paired equations (5a) and (5b) and (6a) and (6b) is approximately the same and the analytical data previously secured[4] to support equations (5a) and (6a) are also consistent with the new formulations (5b) and (6b). The stoichiometry of the paired equations (3a) and (3b) and (4a) and (4b) is considerably different as regards the quantity of alcohol consumed. We made no attempt to isolate the cobalt salts, but it is quite likely that the previous isolations and analyses[4] on which equations (3a) and (4a) were based are unreliable owing to the loss of

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[1] A. A. Blanchard and P. Gilmont, THIS JOURNAL, **62**, 1192 (1940); "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 238.

[2] W. Hieber and H. Schulten, *Z. anorg. u. allgem. Chem.*, **232**, 29 (1937).

[3] W. Hieber and H. Schulten, *ibid.*, **232**, 17 (1937).

[4] W. Hieber, F. Muhlbauer and E. A. Ehmann, *Ber.*, **65**, 1090 (1932).

[5] A. A. Blanchard, *Chem. Revs.*, **21**, 3(1937).

[6] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 2, Oxford at the Clarendon Press, 1950, p. 1423.

coördinatively bound alcohol during the course of the removal of solvent.

The action of *t*-butyl alcohol on dicobalt octacarbonyl differs from that of methanol and ethanol. Only 2.2 (instead of 2.67) moles of carbon monoxide are evolved per mole of dicobalt octacarbonyl; small brownish-black glistening crystals separate. These are similar in appearance and solubility in benzene[4] to the tetramer, tetracobalt dodecacarbonyl, $[Co(CO)_3]_4$, and the butanol solution contains no cobalt carbonyl anion. The reaction probably proceeds according to equation (7)

$$2[Co(CO)_4]_2 \longrightarrow [Co(CO)_3]_4 + 4CO \qquad (7)$$

The difference in the mode of action of *t*-butyl alcohol may be due to steric factors (see below).

Mechanism of the Homomolecular Disproportionation.—As the over-all reaction involves transfer of electrons between molecules of dicobalt octacarbonyl only, we have termed the formation of the cobalt salt of cobalt hydrocarbonyl from the dimer (equation (2)) a homomolecular disproportionation.

It is instructive to visualize equation (2) as occurring stepwise as follows, where B is a generalized base

$$3B + 3[Co(CO)_4]_2 \rightleftarrows \underset{\text{I}}{3[BCo(CO)_4]^+[Co(CO)_4]^-} \qquad (8)$$

$$\underset{\text{II}}{2[BCo(CO)_4]^+} \longrightarrow 2B + 2Co^{++} + 8CO + 2e^- \qquad (9)$$

$$[BCo(CO)_4]^+ + 1e^- \longrightarrow B + \cdot Co(CO)_4 \qquad (10)$$

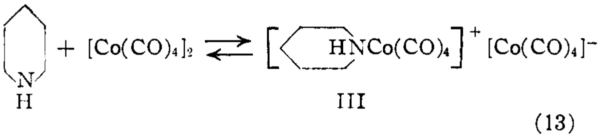
$$\cdot Co(CO)_4 + 1e^- \rightleftarrows [Co(CO)_4]^- \qquad (11)$$

$$3[Co(CO)_4]_2 \rightleftarrows 2Co[Co(CO)_4]_2 + 8CO \qquad (2a)$$

If the monomer, $\cdot Co(CO)_4$, dimerized to dicobalt octacarbonyl (equation (12)), it would react further in the stepwise sequence shown in equations (8–11).

$$2\cdot Co(CO)_4 \rightleftarrows [Co(CO)_4]_2 \qquad (12)$$

With weak bases, such as pyridine or methanol, II decomposes rapidly at room temperature. Experimental support for the existence of the salt, I, was obtained from a study of the reaction with piperidine. Following addition of this strong base in the cold to the dark solution of dicobalt octacarbonyl in xylene or toluene, the dark color changes to light red, indicating disappearance of the dimer. No gas is evolved, and a light greenish-yellow oil separates. The reaction is probably



(13)

The oil is readily soluble in water and contains one mole of cobalt carbonyl anion per mole of starting dicobalt octacarbonyl. Dropwise addition of dilute hydrochloric acid to III results in restoration of the color of dicobalt octacarbonyl caused by reversal of reaction 13 and removal of the piperidine as the hydrochloride.

The reaction of I with excess concentrated hydrochloric acid is of interest. Some reversal of reaction (8) probably occurs as in the case of dilute acid, but the high concentration of acid leads to formation of cobalt hydrocarbonyl. This acid is not stable and decomposes into hydrogen and dicobalt octacarbonyl[2] (equation (14))

$$2HCo(CO)_4 \longrightarrow H_2 + [Co(CO)_4]_2 \qquad (14)$$

The reaction of I with concentrated hydrochloric acid may be written

$$[[BCo(CO)_4]^+[Co(CO)_4]^-] + 2HCl \longrightarrow 2[BCo(CO)_4]^+ Cl^- + 2HCo(CO)_4 \qquad (15)$$

In this example, cobalt carbonyl anion is removed, and the cation (or the neutral molecule, $Co(CO)_4Cl$) decomposes according to the scheme previously outlined in equations (8–11). The experimental data are consistent with the over-all equation (16)

$$4[[BCo(CO)_4]^+[Co(CO)_4]^-] + 8HCl \longrightarrow 2H_2 + 8CO + 3[Co(CO)_4]_2 + 2CoCl_2 + 4BHCl \qquad (16)$$

Although kinetic data are lacking, it is instructive to regard the first step of the homomolecular disproportionation as a typical organic displacement reaction initiated by a base

$$\underset{\text{Initial state}}{B + [Co(CO)_4]:[Co(CO)_4]} \longrightarrow \underset{\delta^+ \quad \text{Transition state} \quad \delta^-}{B\ldots\ldots Co(CO)_4\ldots\ldots :Co(CO)_4} \longrightarrow \underset{\text{Final state}}{[BCo(CO)_4]^+[Co(CO)_4]^-}$$

The symmetrical cobalt carbonyl anion possesses the rare-gas structure, and its formation may furnish the driving force for the reaction. The cation also possesses a rare-gas structure; its lack of symmetry probably makes it less stable than the anion. The relative stability of various cations may depend upon the basicity and geometry of the entering group. Piperidine is quite basic and small enough to be fairly stable in the complex. With weaker bases, the cation has less stability and decomposes rapidly according to equations (9–11). The attacking base, B, may be neutral (an amine or an olefin) or it may be an anion (Cl^-) in which latter case the complex corresponding to the cation above would still possess the rare gas structure but would be the neutral entity, $Co(CO)_4Cl$.

Formation of Cobalt Carbonyl Anion by Electron Transfer.—Equation (11) implies that addition of an electron to cobalt carbonyl (or the dimer) leads to formation of the cobalt carbonyl anion. If this is correct, it should be possible to form cobalt carbonyl anion from dicobalt octacarbonyl by an external source of electrons. Such a reaction was achieved by shaking a benzene solution of dicobalt octacarbonyl with sodium amalgam. No gas was evolved and analysis of the reaction mixture showed that a quantitative conversion of dicobalt octacarbonyl to cobalt carbonyl anion had taken place according to equation (17).

$$2Na + [Co(CO)_4]_2 \longrightarrow 2Na[Co(CO)_4] \qquad (17)$$

Hieber and Schulten[3] reported that dicobalt octacarbonyl reacts with aqueous solutions of strong bases, *e.g.*, $Ba(OH)_2$ or NaOH principally according to equation (18).

$$\underset{\text{(dimer)}}{3Co(CO)_4} + 2OH^- \longrightarrow 2HCo(CO)_4 + \underset{\text{(polymer)}}{Co(CO)_3} + CO_3^{--} \qquad (18)$$

These authors reported that, even in strong alkaline solutions, the reaction did not proceed uniformly accordingly to equation (18) and that some carbon monoxide was evolved according to equation (19).

$$\underset{\text{(dimer)}}{3\mathrm{Co(CO)_4}} + 2\mathrm{H_2O} \longrightarrow 2\mathrm{HCo(CO)_4} + \mathrm{Co(OH)_2} + 4\mathrm{CO} \qquad (19)$$

In light of the new concepts, the reaction between dicobalt octacarbonyl and aqueous solutions of strong bases may conceivably consist of either an electron transfer and/or a homomolecular disproportionation, the former predominating at high hydroxyl ion concentrations equations (20a),[7] (20b) and (20c). At low hydroxyl ion concentrations, the water acts like ammonia in equation (1).

$$\begin{array}{lr} 4\mathrm{OH^-} \longrightarrow \mathrm{O_2} + 2\mathrm{H_2O} + 4e^-,\ E^0_B = -0.401 & (20a) \\ 2[\mathrm{Co(CO)_4}]_2 + 4e^- \longrightarrow 4[\mathrm{Co(CO)_4}]^- & (20b) \\ \hline 2[\mathrm{Co(CO)_4}]_2 + 4\mathrm{OH^-} \longrightarrow 4[\mathrm{Co(CO)_4}]^- + 2\mathrm{H_2O} + \mathrm{O_2} & (20c) \end{array}$$

This hypothesis is supported by the following experiments: A benzene solution of dicobalt octacarbonyl was treated with 4 *N* sodium hydroxide until the benzene solution had become colorless.[8] Analysis of the aqueous solution showed that 1.72 mole of cobalt carbonyl anion per mole of dicobalt octacarbonyl was formed. In a similar experiment in which distilled water was used in place of the sodium hydroxide solution, the amount of cobalt carbonyl anion formed corresponded to 1.48 moles per mole of dicobalt octacarbonyl. It should be pointed out that equations (18) and (19), suggested by Hieber and Schulten,[3] exclude formation of more than $1^1/_3$ moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl.

The electron-transfer concept may also help to explain the complicated reaction that constitutes one of the standard methods for the preparation of cobalt carbonyl anion.[1]

$$12\mathrm{KOH} + 2\mathrm{K_4Co(CN)_6} + 11\mathrm{CO} \longrightarrow 3\mathrm{K_2CO_3} + 12\mathrm{KCN} + 6\mathrm{H_2O} + 2\mathrm{KCo(CO)_4} \qquad (21)$$

In this reaction, cobalt(II) ion gains electrons in its transformation to the anion $\mathrm{Co(CO)_4^-}$, and these electrons probably are furnished by the alkali (equation (20a)). The appearance of carbonate is consistent with this view and is explained by the oxidation of the carbon monoxide.

Experimental

All reactions were carried out in an apparatus[9] that consisted of a gas buret and a 125-ml. erlenmeyer flask fitted with a ground-glass joint and a side-arm for addition of the reagent. A benzene solution, containing approximately the required amount of dicobalt octacarbonyl,[10] was placed in the weighed erlenmeyer flask, the benzene evaporated at room temperature in a current of carbon monoxide,[11] the flask stoppered, weighed, attached to the gas buret, and the system purged with nitrogen. The reagent was then added through the side-arm, the solution stirred by means of a magnetic stirrer, and the amount of gas evolved measured; gas samples were then withdrawn for analysis. The amount of cobalt carbonyl anion formed was determined by addition of aqueous nickel *o*-phenanthroline chloride ($[\mathrm{Ni}(o\text{-Phthr})_3][\mathrm{Cl}]_2$) solution to the reaction mixture, filtration of the precipitate, $[\mathrm{Ni}(o\text{-Phthr})_3][\mathrm{Co(CO)_4}]_2$, and determination of the amount of carbon monoxide in the latter by a gasometric procedure.[12]

Dicobalt Octacarbonyl and Methanol.—To 0.8805 g. (2.58 millimoles) of dicobalt octacarbonyl was added 20 ml. of absolute methanol, and the solution was stirred. The reaction was completed at room temperature in 3 hours, during which time 154 ml.[13] of carbon monoxide (6.88 millimoles) was evolved (2.66 moles of gas per mole of dicobalt octacarbonyl). About 72% of the gas was evolved during the first 15 minutes of the reaction.

In a second experiment, the amount of cobaltous ion was determined as follows: Dicobalt octacarbonyl (0.3852 g.) was treated with 10 ml. of methanol as above. After completion of the reaction, 69 ml. of oxygen-free water and 25 ml. of nickel *o*-phenanthroline chloride solution were added to remove the cobalt carbonyl anion, and the precipitate was filtered and washed with water. The combined filtrate and wash water were evaporated to dryness, ignited and dissolved in acid. After removal of nickel with dimethylglyoxime, the solution was electrolyzed.[14] The 0.0444 g. of cobalt obtained represents 33.4% of the amount of cobalt present in the dicobalt octacarbonyl. This result is in excellent agreement with equation (2), which requires that one-third of the amount of cobalt present in the dicobalt octacarbonyl be converted to cobaltous ion.

Dicobalt Octacarbonyl and Ethanol.—To 0.4800 g. of dicobalt octacarbonyl (1.40 millimoles) was added 15 ml. of ethanol. The reaction proceeded as described under methanol, and 90 ml. (4.02 millimoles) of carbon monoxide was evolved (2.87 moles per mole of dicobalt octacarbonyl). Analysis of the reaction mixture showed that 0.336 g. (1.97 millimoles) of cobalt carbonyl anion had been formed (1.40 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and Pyridine.—To 0.7723 g. of dicobalt octacarbonyl (2.26 millimoles) in 15 ml. of xylene was added 5.0 ml. of pyridine. The reaction was completed within a few minutes, with evolution of 142 ml. (6.34 millimoles) of carbon monoxide (2.80 moles of carbon monoxide per mole of dicobalt octacarbonyl). Analysis of the reaction mixture showed that 0.546 g. (3.18 millimoles) of cobalt carbonyl anion had been formed (1.41 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and *o*-Phenanthroline.—To 0.8645 g. (2.53 millimoles) of dicobalt octacarbonyl dissolved in 20 ml. of toluene was added 1.5 g. of *o*-phenanthroline dissolved in 70 ml. of toluene. A precipitate, ($[\mathrm{Co}(o\text{-Phthr})_3][\mathrm{Co(CO)_4}]_2$), was formed, and 162 ml. (7.24 millimoles) of carbon monoxide was evolved (1.86 moles of carbon monoxide per mole of dicobalt octacarbonyl). The precipitate contained 0.610 g. (3.56 millimoles) of cobalt carbonyl anion (1.34 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and *t*-Butyl Alcohol.—To 0.4770 g. (1.40 millimoles) of dicobalt octacarbonyl was added 15 ml. of *t*-butyl alcohol. The reaction was complete after 21 hours, during which time 69 ml. (3.08 millimoles) of carbon monoxide was evolved (2.20 moles of gas per mole of dicobalt octacarbonyl). In the course of the reaction, a small amount of brownish-black, glistening crystals precipitated from the solution. After the reaction was completed, water was added, whereupon the color lightened perceptibly, and more crystalline material separated. No trace of cobalt carbonyl anion could be detected in the aqueous solution. When the precipitate was treated with warm methanol, cobalt carbonyl anion was formed.

Dicobalt Octacarbonyl and Piperidine.—A solution of 10 ml. of toluene containing 0.7419 g. (2.17 millimoles) of di-

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(7) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 35.

(8) W. Hieber and H. Schulten[3] reported formation of tetramer when they treated solid dicobalt octacarbonyl with an aqueous $\mathrm{Ba(OH)_2}$ solution. Under the conditions of our experiment no tetramer was formed.

(9) M. Orchin and I. Wender, *Anal. Chem.*, **21**, 875 (1949).

(10) I. Wender, H. Greenfield and M. Orchin, THIS JOURNAL, **73**, 2656 (1951).

(11) For this operation, synthesis gas ($\mathrm{H_2}$ and CO in a ratio of 0.7:1) was ordinarily used because of its ready availability in this Laboratory. No difference was observed when this operation was carried out with commercial carbon monoxide containing approximately 2% hydrogen.

(12) H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, in press.

(13) All gas volumes corrected to N.T.P.

(14) We wish to thank W. Dieter and W. Oppenheimer for analytical assistance.

cobalt octacarbonyl was placed in the erlenmeyer flask, the flask attached to the gas buret, the system purged with nitrogen, and the gas volume recorded. The flask was immersed in Dry Ice, and 2.0 g. of piperidine dissolved in 13 ml. of toluene was slowly added to the flask. The Dry Ice bath was removed, the contents of the flask stirred by means of a magnetic stirrer, and the gas volume recorded after the solution had reached room temperature. No evolution of gas occurred. The dark solution turned light red, and a greenish-yellow oil separated. The addition of 20 ml. of water solubilized the oil, and the color changed to light yellow. After 5 minutes of stirring, 50 ml. of nickel *o*-phenanthroline chloride solution was added and the solution stirred for 5 minutes. After acidification with 10 ml. of 6 *N* hydrochloric acid, the solution was filtered. Analysis for cobalt carbonyl anion gave 0.341 g. (1.99 millimoles). This is 92% of the amount of anion predicted by equation (8).

I and Dilute Hydrochloric Acid.—A solution of 10 ml. of xylene containing 1.9680 g. (5.76 millimoles) of dicobalt octacarbonyl was cooled in a Dry Ice-bath as described above, 6.0 g. of piperidine dissolved in 19 ml. of xylene was added, the Dry Ice removed, and the solution allowed to warm to 0° in an ice–water-bath. A solution of 12 ml. of concentrated hydrochloric acid and 40 ml. of water was added slowly with stirring. Upon addition of the acid, the xylene solution turned dark brown, owing to the formation of dicobalt octacarbonyl according to equation (13). The gas evolved (52 ml.) consisted of 4 ml. of hydrogen and 48 ml. (2.14 millimoles) of carbon monoxide; this amounts to only 4.6% of the carbon monoxide present in the dicobalt octacarbonyl.

I and Concentrated Hydrochloric Acid.—To a solution of 10 ml. of xylene containing 1.500 g. (4.38 millimoles) of dicobalt octacarbonyl, cooled in a Dry Ice-bath as described above, was added 4.0 g. of piperidine dissolved in 19 ml. of xylene. The Dry Ice-bath was removed and, after the solution had reached room temperature, a solution of 12 ml. of concentrated hydrochloric acid and 11 ml. of water was rapidly added with stirring. The resulting aqueous layer was pink while the xylene solution was dark brown, indicating the presence of cobalt chloride and dicobalt octacarbonyl; the formation of both of these compounds is postulated in equation (16). The gas evolved (184 ml.) consisted of 20 ml. (0.89 millimole) of hydrogen and 164 ml. (7.32 millimoles) of carbon monoxide. This is 20.9% of the amount of carbon monoxide present in the dicobalt octacarbonyl; equation (16) requires the evolution of 25% of the amount of carbon monoxide in the dicobalt octacarbonyl. If the decomposition of cobalt hydrocarbonyl (equation (14)) had gone to completion, the amount of hydrogen (equation (16)) would have been 0.5 mole per mole of dicobalt octacarbonyl, or 2.19 millimoles. That the amount of hydrogen obtained in this experiment is lower than that predicted by equation (16) is consistent with the fact that cobalt hydrocarbonyl is fairly stable in aqueous solutions even in the presence of acids.[1]

Dicobalt Octacarbonyl and Sodium Amalgam.—To 0.4931 g. (1.44 millimoles) of dicobalt octacarbonyl in 12 ml. of toluene was added 130 g. of sodium amalgam containing approximately 1% sodium, and the mixture was stirred. The benzene solution was decolorized after 1 hour, indicating complete conversion of dicobalt octacarbonyl. Stirring was continued for 1 more hour. No gas was evolved during the reaction. Sixty ml. of water was added and the mixture stirred for 2 hours to decompose excess sodium and dissolve the sodium salt of cobalt hydrocarbonyl, $NaCo(CO)_4$. Analysis of the aqueous solution showed 0.465 g. (2.72 millimoles) of cobalt carbonyl anion (1.89 millimoles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and Sodium Hydroxide Solution.—To 0.5048 g. (1.48 millimoles) of dicobalt octacarbonyl dissolved in 20 ml. of toluene was added 20 ml. of a 4 *N* sodium hydroxide solution. During the reaction, which was completed in 8 hours, a total of 42 ml. of carbon monoxide was evolved. The toluene solution became colorless, and the aqueous solution turned from light blue-violet at the beginning to light straw-yellow at the end of the reaction. The aqueous solution contained 0.435 g. (2.55 millimoles) of cobalt carbonyl anion (1.72 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and Water.—To 0.54 g. (1.60 millimoles) of dicobalt octacarbonyl dissolved in 25 ml. of benzene, 15 ml. of water was added. Completion of the reaction required 48 hours, and during this time 105 ml. (4.70 millimoles) of carbon monoxide was evolved. The aqueous solution contained 0.405 g. (2.37 millimoles) of cobalt carbonyl anion (1.48 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Dimethylaminoboron Dichloride and Difluoride

BY JOHN F. BROWN, JR.

The reaction of triethylamine with dimethylamine–boron trichloride in benzene solution gave a 73% yield of dimethylaminoboron dichloride. Pyridine with dimethylamine–boron trichloride gave mainly a 1:1 adduct. There was no reaction between triethylamine and dimethylamine–boron trifluoride, but when dimethylamine–boron trifluoride was pyrolyzed, it gave a 31% yield of dimethylaminoboron difluoride dimer, along with the disproportionation products trimethylamine–boron trifluoride and tetramethylammonium fluoborate.

Dimethylaminoboron dichloride was first prepared by Wiberg[1] by mixing dimethylamine and boron trichloride. The process was represented by equation 1, although HCl was not found among the products.

$$(CH_3)_2NH + BCl_3 \longrightarrow (CH_3)_2NBCl_2 + HCl \quad (1)$$

Bis-dimethylaminoboron chloride and tris-dimethylaminoboron were also formed, and the yields of the amino dichloride were low.

It has now been found that good yields of dimethylaminoboron dichloride may be obtained by first forming dimethylamine–boron trichloride in benzene solution and then dehydrohalogenating it with triethylamine, according to equations 2 and 3. When the preparation is carried out in this way, no appreciable amounts of bis- or tris-aminoboron compounds appear to be formed, but a brown tar is obtained as a by-product.

$$(CH_3)_2NH + BCl_3 \longrightarrow (CH_3)NHBCl_3 \quad (2)$$

$$(CH_3)_2NHBCl_3 + (C_2H_5)_3N \longrightarrow (CH_3)_2NBCl_2 + (C_2H_5)_3NHCl \quad (3)$$

When pyridine is used instead of triethylamine, little dehydrohalogenation results, but instead a 1:1 dimethylamine–boron trichloride–pyridine adduct is formed.

Dimethylaminoboron difluoride, which does not seem to have been previously described, could not be prepared by this method. There was no evidence of any reaction between dimethylamine–boron trifluoride and triethylamine, even though the

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[1] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.*, **202**, 46 (1931); E. Wiberg and K. Schuster, *ibid.*, **213**, 77 (1933).