intensities as well as position of infrared absorption bands are required for an accurate estimate of the basicity of solvents.

3. In the nitrotoluene solutions, hydrogen chloride corresponds with the law of Henry and shows negative deviations from the law of Raoult. The data in these solutions are interpreted in terms of a reaction between solute and solvent. In the hexane solutions hydrogen chloride also corresponds with the law of Henry, but the deviation from the law of Raoult is positive.

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Preparation of Cobalt Carbonyl, Cobalt Nitrosyl Carbonyl and Cobalt Carbonyl Hydride by the Cyanide Method

BY ARTHUR A. BLANCHARD AND PAUL GILMONT

Brockway and Anderson[1] have prepared cobalt nitrosyl carbonyl for the purpose of electron diffraction studies by the method of Blanchard, Rafter and Adams,[2] saturating an alkaline suspension of cobaltous cyanide with carbon monoxide, but they state that on passing nitric oxide into the still alkaline solution no nitrosyl carbonyl is formed. They obtain this product only after acidification. This is contrary to the findings of Blanchard, Rafter and Adams, who found that cobalt nitrosyl carbonyl vapor could be swept from the still alkaline solution. The present studies confirm the latter statement. Furthermore, the product obtained by treating the alkaline solution with nitric oxide is undoubtedly purer than that obtained from the acidified solution.

Ewens and Lister[3] prepared cobalt carbonyl hydride, also for electron diffraction studies, by a modification of the method of Coleman and Blanchard[4] by saturating an alkaline suspension of cobaltous cyanide with carbon monoxide, then acidifying and sweeping the volatile hydride from the solution. The fact that the volatile hydride $HCo(CO)_4$ is obtained when cyanide is used as a carrier makes it seem probable that the fundamental reaction of oxidation and reduction is the same as when cysteine is the carrier, namely: $2CoCl_2 + 11CO + 12KOH \rightarrow 3K_2CO_3 + 2KCo(CO)_4 + 4KCl$. In absence of the carrier, no absorption of carbon monoxide takes place. The carrier, whether cysteine or cyanide, forms an intermediate complex containing carbon monoxide and cobalt; the latter reacts further to yield the salt of $HCo(CO)_4$ and the carrier is regenerated. Schubert[5] has very beautifully identified the intermediate complexes in the case of cysteine. Acidification liberates the volatile acid $HCo(CO)_4$ from its salt. Treatment with NO produces the volatile nitrosyl carbonyl, probably according to the reaction: $KCo(CO)_4 + NO + H_2O \rightarrow CO(CO)_3NO + CO + KOH + {}^1/_2\, H_2$.

Experimental

A large number of runs with varying proportions of cyanide and alkali were carried out and the proportions given in the following statements were found to produce the best results in the shortest time.

A shaking apparatus capable of keeping the liquid in the condition of a fine spray and yet allowing the passage of gases during the shaking is provided. It is swept out with carbon monoxide and approximately 50 ml. of a solution about 0.5 formal in cobalt nitrate, 0.5 formal in potassium cyanide and 4.0 formal in potassium hydroxide is introduced as follows: 7.3 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 15 ml. of water is allowed to enter through a side arm, then 5 cc. of water to wash the arm, then 11.2 g. of potassium hydroxide in 11 ml. of water, then 5 cc. of water, then 1.6 g. of potassium cyanide in 3 ml. of water and lastly, 5 cc. of water.

The exit stopcock is closed and the solution shaken. A total absorption of 2200 to 2600 cc. of carbon monoxide takes place in about seven hours, 2 liters in the first two to three hours, the rate falling during the next three to five hours. During this absorption the solution changes from a blue suspension, through a pink suspension, to a yellow solution almost free of suspended matter.

Cobalt Nitrosyl Carbonyl.—The yellow liquid is a solution of the potassium salt of cobalt carbonyl hydride. The carbon monoxide is displaced from the shaker by nitric oxide and the shaker is started. Soon the solution turns red and after a while a deep yellow gas begins to show in

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[1] Brockway and Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1937).

[2] Blanchard, Rafter and Adams, THIS JOURNAL, **56**, 16 (1934).

[3] Ewens and Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

[4] Coleman and Blanchard, THIS JOURNAL, **58**, 2160 (1936).

[5] Schubert, *ibid.*, **55**, 1877 (1933).

the shaker. This is the cobalt nitrosyl carbonyl and it is swept from the shaker by a very slow stream of nitric oxide, dried by passing through calcium chloride and phosphorus pentoxide, and frozen in a trap cooled with solid carbon dioxide and alcohol. Sweeping with nitric oxide at the rate of 2 liters per hour until no further product is obtained takes about five hours. A yield of 2.5 g. of $Co(NO)(CO)_3$ can be obtained or 58%.

Cobalt Carbonyl Hydride.—A solution of the potassium salt of cobalt carbonyl hydride is prepared as in the foregoing directions. A 500-ml. distilling flask fitted with an inlet tube reaching to the bottom and another short inlet tube and a drying train and trap leading from the side arm is provided. The long inlet tube is attached to the shaker and the apparatus is filled with carbon monoxide. The shaker is tilted and the solution is run into the flask. The flask is cooled with ice water and 30 ml. of 12 *N* hydrochloric acid is added slowly with hand shaking through the short tube. The surplus of hydrochloric acid after the surplus potassium hydroxide, potassium carbonate, potassium cyanide and $KCo(CO)_4$ have reacted gives a concentration of approximately 2.3 *N*. With a slow stream of carbon monoxide passing, the flask is allowed to come to room temperature, but care must be taken that the evolution of gas (carbon dioxide and $Co(CO)_4H$) does not carry the foam into the drying train. A slow stream of carbon monoxide is continued for ten hours to sweep the hydride from the solution. Sweeping at a lower temperature (10–15°) takes a longer time but produces a better yield of a cleaner product.

The cobalt carbonyl hydride condenses in the trap at −79° to a nearly white to light yellow solid. It melts at −33° to a light yellow liquid and begins to decompose above that temperature into cobalt tetracarbonyl and hydrogen. If it is sealed in a tube and brought to room temperature a high pressure results which will burst an ordinary tube. It is true that the presence of hydrogen tends to reverse the reaction.[6] The cobalt carbonyl hydride vapor in the tube has a deep yellow color. A yield of 2.2 g. of $Co(CO)_4H$[7,8] can be obtained or 44%.

Cobalt Tetracarbonyl $[Co(CO)_4]_2$.—The trap in which the hydride is collected should be connected through a tube of perhaps 100-ml. capacity with a sample tube and the system evacuated. Cooling the sample tube to −79° and removing the trap from the carbon dioxide ice, the hydride is distilled into the sample tube. The latter is allowed to come to room temperature and the hydride to decompose. The trap is again cooled to −79°, the hydrogen is pumped out and the remaining yellow cobalt carbonyl hydride vapor is condensed in the trap. The hydride is again distilled back into the sample tube and this process is repeated until, when no more yellow vapors appear after several days of standing, the sample tube is sealed off.

Summary

Carbon monoxide is absorbed almost quantitatively by an alkaline suspension of a cobalt salt to form $KCo(CO)_4$, but only when a carrier such as a small amount of a cyanide is present.

Nitric oxide displaces the volatile cobalt nitrosyl carbonyl $Co(NO)(CO)_3$ from the resulting solution even when the solution is distinctly alkaline.

Acids displace the volatile cobalt carbonyl hydride, $HCo(CO)_4$.

Cobalt tetracarbonyl $[Co(CO)_4]_2$ is obtained by allowing the hydride to decompose spontaneously at room temperature.

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(6) Hieber, Schulten and Marin, *Z. anorg. allgem. Chem.*, **240**, 261 (1939).

(7) It is noteworthy that cobalt carbonyl hydride vapor mixed with a large amount of carbon monoxide at room temperature can be carried through long connections and a drying train without showing any sign of decomposition.

(8) The odor of cobalt carbonyl hydride is so intolerable that the danger from inhaling it is much less than from nickel carbonyl. It is, however, probably equally poisonous and since there is no antidote and the injury resulting from inhaling it is permanent, the utmost caution should be used to keep it from escaping into the laboratory.