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Formation of Carbonyls and Related Compounds

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Windsor and Blanchard[1] studied the mechanism of the formation of nickel carbonyl from carbon monoxide and an aqueous alkaline suspension of nickel sulfide as reported by Manchot and Gall.[2] They explained the reaction on the basis of the postulate that nickel sulfide suffers a potential dissociation into nickel and sulfur and that in the presence of sulfur-removing agents such as hydroxyl and sulfide ions, the nickel potential can rise to the point of carbonyl formation. This paper reports some exploratory work upon the further possibilities of the formation of carbonyls and related nitrosyls in the light of the above working hypothesis.

Windsor and Blanchard had in fact already reported that nickel selenide would produce carbonyl under the same conditions as would the sulfide.

Nickel Carbonyl from Nickel Cyanide.—Nickel cyanide would have a potential dissociation of the same order of magnitude as nickel sulfide, and cyanogen, the dissociation product, would be removed by alkalies with about the same facility as sulfur.

A shaking apparatus was arranged to keep the suspension broken into the finest spray and yet allow the passage of gases without entraining the spray.[3] The apparatus was filled with carbon monoxide, and reagents were introduced to total 80 cc., 0.5 formal in $Ni(NO_3)_2$, 0.5 formal in KCN, and 2.0 formal in KOH. These react to give a suspension of nickel cyanide–nickel hydroxide in potassium hydroxide solution. On shaking, carbon monoxide was absorbed at first at a rate of 15 bubbles per minute, the rate soon decreasing. Sweeping with carbon monoxide was always followed by an increased rate of absorption, even up to 60 bubbles per minute after the earlier sweepings. Several hours of standing without shaking would always be followed by a noticeable carbon monoxide absorption on renewed shaking. In all, over one liter of carbon monoxide was absorbed during five days of intermittent shaking. All of the sweepings carrying nickel carbonyl vapor were passed through bromine water. The carbonyl reacts with bromine giving a very dense yellow appearing smoke consisting of nickel bromide, and this settles and dissolves in the water. Finally the excess bromine was boiled off, an excess of ammonia added and the nickel estimated colorimetrically: 6% of the nickel originally in the reaction chamber had been carried over as carbonyl.

Cobalt Carbonyl from Cobalt Cyanide

The foregoing experiment was repeated using cobalt salt (nickel free) instead of nickel. A considerable absorption of carbon monoxide, 175 cc. in sixteen minutes, and 480 cc. over several days of intermittent shaking, was noted but no more than a trace of volatile carbonyl passed over. Once or twice a faint mirror was produced when exit gases were passed through a hot glass tube. This was proved to be cobalt by melting the glass at the mirror and observing a cobalt blue color. Several efforts were made with solvents to extract cobalt carbonyl from the suspension, but very little success was achieved. However, the positive results obtained by the procedure in the following paragraph tend to confirm the formation here of some kind of a carbonyl.

Cobalt Nitrosyl Carbonyl

A suspension prepared as in the above paragraph and doubtless containing cobalt carbonyl was treated with nitric oxide. Immediately the apparatus became filled with a deep yellow-brown vapor which gave an intense mirror when passed through a heated tube. Alternation of nitric oxide and carbon monoxide, or passage of a mixture of the oxides, continued to produce this yellow brown vapor. Sweeping the vapor through phosphorus pentoxide and then through a vessel immersed in carbon dioxide snow, allowed the collection of the substance which is undoubtedly the cobalt nitrosyl tricarbonyl, $CoNO(CO_3)$, described by Mond and Wallis[4] and by Reiff.[5] In the most successful runs as much as 0.5 g. of the substance could be collected. When frozen it is an orange yellow crystalline substance. It melts sharply at approximately $-11°$ to a deep cherry red liquid the saturated vapor of which at this temperature shows a distinct yellow color.

This substance was also prepared by the action at room temperature of carbon monoxide and nitric oxide on active cobalt prepared by the careful heating of cobalt formate or cobalt nitrate on pumice in hydrogen. (The formate gave the more active cobalt.) The metal rapidly lost its activity but could repeatedly be reactivated by small doses of hydrogen sulfide. The cyanide method, however, was much more effective as a means of preparation.

When the active cobalt was first treated with carbon monoxide alone very little absorption occurred; nevertheless the sweepings with carbon monoxide gave a very faint mirror in a heated glass tube, and this mirror was identified as cobalt by its giving a cobalt blue glass when melted into the tube.

Vapor Pressure and Molecular Weight of Cobalt Nitrosyl Tricarbonyl.—The pressure of the saturated vapor over a limited range and with no attempt at much precision.

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[1] Windsor and Blanchard, THIS JOURNAL, **55**, 1877 (1933).

[2] Manchot and Gall, *Ber.*, **62**, 678 (1929).

[3] Rafter, Thesis, Massachusetts Institute of Technology, 1932.

[4] Mond and Wallis, *J. Chem. Soc.*, **121**, 29 and 32 (1922).

[5] Reiff, *Z. anorg. allgem. Chem.*, **202**, 375 (1931).

Temp., °C.	1	5	8	10	13	16	19	21
Vapor press., mm.	24	28	32	38	44	56	62	68

VAPOR DENSITY MEASUREMENTS

Sample, g.	Volume, cc.	Pressure, mm.	Temp., °C.
0.0666	175	40	28
.065	100	70	25

Molecular weight from data	177 and 178
Formula weight of $CoNO(CO)_3$	173

Blanchard and Gilliland[6] proposed an arrangement of electrons in molecules of the volatile carbonyls to account for the remarkable properties of these compounds. Reiff[5] proposed the rather vague conception of "effective atomic number" according to which carbonyl groups add two and nitrosyl groups add three to the atomic number of the central atom. Thus whenever the atomic number 36 of krypton is effected the forces within the molecule are self contained and the substance is volatile. According to both of these proposals cobalt nitrosyl tricarbonyl should be a volatile substance.

Reiff predicts that cobalt trinitrosyl $Co(NO)_3$ should be a stable volatile substance. Blanchard and Gilliland's proposal would not indicate that the existence of such a compound is possible. The most active sample of cobalt prepared in our experiments was subjected to the action of nitric oxide alone after displacing the hydrogen. No significant absorption took place over a period of several days. No trace of a volatile nitrosyl was swept along when a current of nitric oxide was passed. Failure of cobalt trinitrosyl to form under these conditions is of course by no means complete proof that it is incapable of existence.

Failures to prepare volatile carbonyls or nitrosyls were scored with several combinations which our working hypotheses had suggested:

Nickel iodide with excess of sodium thiosulfate as iodine removing agent shaken with carbon monoxide during several days gave no trace of volatile carbonyl. It is significant however that the solution contained no trace of suspended solid substance.

Ammoniacal nickel salt solutions and suspensions with varying amounts of ammonia, from enough to precipitate only a part of the nickel to more than enough to redissolve the nickel hydroxide precipitate, yielded no carbonyl.

Cobalt chloride, 0.5 formal, in sodium hydroxide, 2.0 formal, failed to absorb carbon monoxide.

Chromium salts, both chromic and chromous, in conjunction with sulfide and with cyanide and excess of alkali hydroxide resisted several attempts to prepare carbonyl and nitrosyl.

Failure to produce a substance may always be due to some minor inhibiting condition rather than to a fundamental impossibility of its formation. We feel that further attempts to prepare volatile chromium compounds are desirable; also a number of other experiments with nickel and cobalt as well as with other heavy metals are suggested by our working hypotheses.

Summary

Carbonyls of nickel and cobalt and cobalt nitrosyl tricarbonyl are prepared at room temperature and ordinary pressure by the treatment of alkaline suspensions of sulfide or cyanide with carbon monoxide or carbon monoxide–nitric oxide mixture.

Approximate vapor pressure and vapor density data for cobalt nitrosyl tricarbonyl are given. The vapor density closely approximates that corresponding to the formula $Co(CO)_3NO$.

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(6) Blanchard and Gilliland, THIS JOURNAL, **48**, 872 (1926).