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Nickel Carbonyl. A Study of the Mechanism of its Formation from Nickel Sulfide and Carbon Monoxide[1]

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The metal carbonyls generally may be prepared by direct synthesis from the metal and carbon monoxide. The extent of carbonyl formation on a compact metal surface is extremely small; very fine subdivision of the metal increases the amount, high pressure of carbon monoxide and a somewhat elevated temperature likewise increase the rate of carbonyl formation. These factors, particularly temperature and pressure, were used by Mond in his extensive work in preparing carbonyls.[2]

A fact, however, which Mond perhaps did not realize to the extent of its full importance was that the active condition of the metal surface is the most weighty factor, that at least in the preparation of nickel carbonyl a highly active nickel suffices to yield the product at a rapid rate even at room temperature and atmospheric pressure. This fact was thoroughly demonstrated by Gilliland, who prepared active nickel[3] by gently heating, in a current of hydrogen, nickel formate, which had been carefully precipitated, washed and dried. He allowed the carbon monoxide to pass downward into the active mass of nickel in a vertical tube. The liquid carbonyl actually flowed in a continuous stream into the receiving vessel when the carbon monoxide was supplied rapidly enough. The activity of the nickel depended in the highest degree however on the complete exclusion of air (presumably oxygen). Gilliland confirmed the fact, which was already known,[4] that hydrogen sulfide has an activifying action upon the finely divided nickel. The exclusion of air was so perfect in his manipulation that the nickel would usually remain active to a satisfactory extent without this expedient; nevertheless, he did provide a branch line through which a little hydrogen sulfide could be introduced when the activity of the nickel began to diminish. This always restored the activity of the material. Gilliland supposed that the effect of the hydrogen sulfide was due to its reaction with the "poisoning" film of oxygen (nickel oxide?).

Manchot and Gall[5] in 1929 discovered a method of preparation of nickel carbonyl which bears a most interesting relation to Gilliland's observations on the effect of hydrogen sulfide. They found that a solution of nickel sulfate to which two moles each of potassium acid sulfide and potassium

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(2) Mond, Hirtz and Cowap, *J. Chem. Soc.*, **97**, 798 (1910).

(3) Gilliland, Doctors' Research, Mass. Inst. Tech., 1926; THIS JOURNAL, **48**, 410 and 872 (1926).

(4) Mittasch, *Z. physik. Chem.*, **40**, 70 (1902).

(5) Manchot and Gall, *Ber.*, **62**, 678 (1929).

hydroxide were added, would absorb carbon monoxide quite freely when shaken with that gas, that thereupon sweeping with carbon monoxide would expel a considerable amount of nickel carbonyl, and that the suspension would then again absorb carbon monoxide freely. They expressed the opinion that a continuously working apparatus based upon this plan would furnish a practical method for the preparation of nickel carbonyl.

We repeated the experiment of Manchot and Gall according to their directions and completely confirmed their observations as to the formation of nickel carbonyl. We further tried their procedure in attempts to form chromium carbonyl and molybdenum carbonyl, but we obtained not a trace of these compounds. It thus was not altogether certain whether this "sulfide method" was merely applicable to the isolated case of nickel carbonyl or had possibilities as a general method of preparing carbonyls. We decided next to study the case of nickel carbonyl to find not only the most favorable conditions for its formation but also if possible some insight into the mechanism of the reaction.

First Method. Weighing Nickel Deposited on Heating Nickel Carbonyl.—A series of experiments was carried out in which the concentrations of the different reagents, nickel sulfate, sodium sulfide and sodium hydroxide, were varied, and other factors held approximately constant by a standardized procedure. A reaction tube mounted on a shaking machine was charged with the reagents and swept thoroughly with carbon monoxide. The exit was closed and the tube shaken at room temperature for a definite length of time (six hours) while attached to a supply of carbon monoxide. At the end of this time, the exit was opened and a definite volume (two liters) of carbon monoxide was used to sweep the vapor of the accumulated nickel carbonyl through a spiral tube that was heated. In this way the carbonyl was decomposed and the weight of the nickel deposited in the tube served as a measure of the amount of carbonyl that had been formed.

Temperature and rate of shaking not being closely controlled in the foregoing experiments, it is not surprising that duplicate results for the same concentration (Runs 3, 5, 9) vary a good deal among themselves; nevertheless, the effect of changing the concentration of each reacting component is clearly indicated.

Thus a comparison of Run 1 with Runs 2 and 12 shows that the rate of reaction is increased over thirty-fold by the presence of sodium hydroxide in 0.67 formal concentrations; further doubling of the sodium hydroxide concentration, Runs 3, 5, 9, increases the rate three times, and with 2 formal sodium hydroxide concentrations, Runs 7, 10, the rate of reaction is quite clearly lower than with 1.33 formal.

Presence of sodium sulfide in 0.67 formal concentration, from the addition of twice the amount of sodium sulfide needed to precipitate nickel

TABLE I

SERIES A—TWELVE HOURS OF EXPOSURE TO ATMOSPHERE OF CARBON MONOXIDE FOLLOWED BY SIX HOURS OF SHAKING. INITIAL CONTENT OF NICKEL, 5.8 G. IN EACH CASE

	Additions in f. w. per liter of mixture				
Run	$NiSO_4$	Na_2S	NaOH	S	Ni, mg.
1	0.67	0.67	..	..	4.5
4	.67	1.33	..	..	80
6	.67	1.33	..	..	122
2	.67	0.67	0.67	..	180
12	.67	.67	.67	..	100
8	.67	.67	.67	0.67	4
3	.67	.67	1.33	..	330
5	.67	.67	1.33	..	974
9	.67	.67	1.33	..	386
7	.67	.67	2.00	..	381
10	.67	.67	2.00	..	168
13	.445	.445	0.445	..	70

TABLE II

SERIES B—SIX HOURS OF SHAKING ONLY. INITIAL CONTENT OF NICKEL, 2.9 G. IN EACH CASE

	Additions in f. w. per liter of mixture			
Run	$NiSO_4$	Na_2S	NaOH	Ni, mg.
22	0.5	0.5	0.5	7
23	.5	.5	.5	11.5
30	.5	.5	1.0	293
31	.5	.5	1.0	326
14	.5	.5	1.5	365
15	.5	.5	1.5	301
18	.5	.5	2.0	268
19	.5	.5	2.0	242
20	.5	.5	2.5	90
24	.5	.5	2.5	143
25	.5	.5	2.5	147

sulfide from the nickel sulfate solution, in Runs 4, 6, causes an increase of rate of twenty times.

The presence of 0.67 formal sulfur dissolved in the reagents causes a decrease to one thirty-fifth the rate shown without the sulfur. Compare Run 8 with Runs 2 and 12.

Table II shows more completely than Table I the effect of sodium hydroxide concentration: for concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5, the rates are, respectively, 9, 309, 333, 255, 127. Very clearly the effect of sodium hydroxide reaches a maximum at about 1.5 normal and then diminishes.

We believe that the formation of nickel carbonyl can be regarded as a direct synthesis in the experiments under discussion just as in the obvious case of the combination of carbon monoxide with finely divided nickel metal. This of course postulates an infinitesimal dissociation, or a potential dissociation, of nickel sulfide into free nickel and free sulfur.

Obviously the activity of free nickel from this dissociation is not sufficient for carbonyl formation with carbon monoxide alone, but with sulfur-removing reagents present to lower the potential of the sulfur concentration, the nickel concentration can rise to the point of carbonyl formation. Sodium hydroxide will react with sulfur according to a somewhat involved train of reactions in which the primary step may be assumed to be

$$6NaOH + 3S \longrightarrow 2Na_2S + Na_2SO_3 + 3H_2O \quad (1)$$

After the sulfide and sulfite concentrations have been built up they too will increasingly tend to claim the sulfur to form polysulfide and thiosulfate, respectively. It is fairly apparent that sodium hydroxide should be more effective than an equivalent concentration of sodium sulfide in lowering the sulfur potential, and thus in increasing the rate of nickel carbonyl formation.

Two-thirds of the sulfur disposed of by sodium hydroxide in equation (1) is regenerated as sulfide, which may precipitate fresh nickel sulfide and the equation

$$3NiSO_4 + Na_2S + 6NaOH + 12CO \longrightarrow 3Na_2SO_4 + Na_2SO_3 + 3Ni(CO)_4 + 3H_2O \quad (2)$$

should represent the proportion in which the reagents are consumed.

RUN 11

Used: 0.1 f. w. $NiSO_4$, 0.01 f. w. Na_2S, 0.1 f. w. NaOH; volume 150 cc.

Wt. of nickel in nickel carbonyl formed, g.	0.925
Wt. of nickel calculated from equation (2) on basis of Na_2S, g.	1.75
Wt. of nickel calculated without regeneration of sulfide, g.	0.587

This run was prolonged for several days and nickel carbonyl was still being formed slowly when it was stopped.

To verify the supposed formation of sulfite (or thiosulfate) according to equation (1) or (2), the suspension left after the end of a run was filtered and the filtrate was acidified. The results were what would be expected upon acidification of a mixture of sulfide and sulfite: usually an odor of sulfur dioxide appeared with or without a separation of sulfur, sometimes an odor of hydrogen sulfide and a deposit of sulfur.

The decreasing yield of nickel carbonyl with sodium hydroxide concentrations greater than 1.5 formal appears not in agreement with our interpretation of the reaction. It might be that the extent of carbonyl formation was indeed greater (we had no device for accurately metering the carbon monoxide consumed) and that nickel carbonyl decomposed in concentrated sodium hydroxide to yield formate.[6] Careful tests for formate in the solution, however, failed to reveal the faintest trace. Furthermore, the following series of runs in which the extent of the reaction was determined by measuring the carbon monoxide consumption showed the same trend as when the nickel deposit was weighed.

Second Method. Measuring the Consumption of Carbon Monoxide

To each of a series of one-liter flasks was sealed a capillary mercury manometer; and the desired combination of solutions, in each case totaling 22.4 cc. in volume, was added. The flask was filled with carbon monoxide at atmospheric pressure and room temperature, and sealed. All of these flask experiments were started at the same time, kept side by side on the same shelf and subjected to the same treatment over a period of 188 days.

In the formation of nickel carbonyl four volumes of carbon monoxide react (Equation 2) to give 1 volume of nickel carbonyl (a gas at the temperature and partial pressure prevailing). Therefore the decrease of pressure should serve as a measure of the nickel

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[6] Blanchard and Gilliland observed the formation of a small amount of formate as a side reaction during the oxidation of nickel carbonyl by air, THIS JOURNAL, **48**, 878 (1926).

carbonyl formed. The pressure measurements made on all flasks at intervals were all corrected to 0°. The initial and final values (188 days) together with the difference between them ($-\Delta P$) are recorded in Table III.

Curves were drawn plotting the value of $-\Delta P$ at 30, 60, 90 and 188 days, respectively, against the varied concentration and the shape of the curve was practically the same whatever the lengths of time for which $-\Delta P$ was taken. Therefore the values of $-\Delta P$ in the table are fairly representative of the rate of reaction.

TABLE III

SUMMARY OF DATA ACCORDING TO METHOD 2

Experiment		I	II	III	IV	V
Additions (f. w./l.)	NaOH	0.5	1.0	1.5	2.0	2.5
	Na_2S	.16	0.16	0.16	0.16	0.16
	$NiSO_4$	.5	.5	.5	.5	.5
Formed	$Ni(OH)_2$	.25	.33	.33	.33	.33
	NiS	.16	.16	.16	.16	.16
	Excess Ni^{++}	.09	0	0	0	0
	Excess OH^-	0	0.33	0.83	1.33	1.83
P_0 (corr.), mm.		665	665	662	655	655
P after 188 days, mm.		465	330	474	455	453
$-\Delta P$, mm.		200	335	188	200	202
Compn. of residual gas (corr.)						
	% CO_2	23.3	22.9	1.9	0.6	0
	% $Ni(CO)_4$	13.5	34.4	10.8	8.3	7.7
	% CO	63.1	42.5	87.0	59.9	54.2
	% H_2	...	...	...	31.0	37.8
Total		99.9	99.8	99.7	99.8	99.7
Final pressure CO, mm.		293	140	412	272	245
CO used up, mm.		372	525	250	383	410
CO found in $Ni(CO)_4$, mm.		252	454	205	152	139
H_2, mm.		...	...	...	141	172

Experiment		VI	VII	XI	XII	XIII	XIV
Additions (f. w./l.)	NaOH	1.0	1.0	1.0	1.0	1.0	1.0
	Na_2S	0.1	0.2	0.16	0.16	0.16	0.16
	$NiSO_4$	.5	.5	.10	.25	.75	1.00
Formed	$Ni(OH)_2$	.4	.3	0	.09	.50	0.50
	NiS	.10	.2	0.10	.16	.16	.16
	Excess Ni^{++}	0	0	0	0	.09	.34
	Excess OH^-	0.2	0.4	1.00	0.82	0	0
P_0 (corr.), mm.		660	663	671	671	676	672
P after 188 days, mm.		315	299	476	465	327	376
$-\Delta P$		345	364	195	206	349	296
Compn. of residual gas (corr.)							
	% CO_2	31.4	10.6	0	0	56.0	37.1
	% $Ni(CO)_4$	43.5	30.6	8.0	9.9	30.1	29.4
	% CO	25.2	57.6	92.0	90.1	13.8	33.5
	% H_2	0	...	...	...	...	...
Total		100.1	98.8	100.0	100.0	99.9	100.0
Final pressure CO, mm.		79	173	440	419	45	126
CO used up, mm.		581	490	231	252	631	546
CO found in $Ni(CO)_4$, mm.		550	364	151	184	394	442

The quantities of reagents added and the amounts of substances which would immediately form on mixing these reagents are also given in the table—expressed in f. w. per liter of the mixed solution or suspension. It is to be noted that 22.4 cc. of 0.5 formal nickel sulfate would exactly consume 1 liter of carbon monoxide (0°, 760 mm.) if reaction (2) went to completion.

At the conclusion of the 188 days the residual gas in each flask was analyzed for carbon monoxide, nickel carbonyl, carbon dioxide, oxygen and hydrogen. The oxygen, where it appeared, was introduced as air through faulty manipulation in taking the sample for analysis and the gas volume unaccounted for was supposed to be nitrogen introduced with the oxygen. The percentages of the gases other than oxygen and nitrogen given in Table III have been reduced to an air-free basis. The carbon dioxide appears to come from the reagents. No particular precautions had been taken to use carbonate-free sodium hydroxide. In equation (2) each formula weight of nickel carbonyl formed accounts for the removal of two formula weights of sodium hydroxide so that toward the end of the reaction the residual nickel sulfate and sodium carbonate will react to give basic nickel carbonate and carbon dioxide. If the carbon dioxide had come from decomposition of nickel carbonyl, free carbon would have been deposited ($Ni(CO)_4 \longrightarrow Ni + 2CO_2 + 2C$); the residue was tested for free carbon and none was found.

The final amount of carbon monoxide, expressed in millimeters pressure in the liter flask, is calculated in each case from the analysis of the residual gas; also the amount of carbon monoxide, expressed in the same units, which has gone into the nickel carbonyl found by analysis. The difference, excluding Runs 4 and 5, although not constant, possesses about the same order of magnitude and averages 98 mm. This might easily be accounted for on the score of nickel carbonyl held by adsorption in the suspension. It seems to be a reasonable assumption therefore that except in Runs IV and V the carbon monoxide is used exclusively in the formation of nickel carbonyl. Subtracting this average difference from the difference in Runs IV and V leaves 133 and 173 mm. of carbon monoxide used up that does not appear in the form of nickel carbonyl; but in these runs there is a formation of hydrogen to the extent of 141 and 172 mm. It is significant that in these runs the hydroxyl-ion concentration is greatest, and hydroxyl ions would certainly favor the reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Experiments I to V show the effect of varying the amount of sodium hydroxide. The yield of nickel carbonyl is a maximum in Expt. II where the addition of sodium hydroxide is 1 f. w. per liter and the initial OH^- ion concentration is 0.33, and falls off steadily with further addition of sodium hydroxide. This accords with the findings from the first method. On the other hand, the consumption of carbon monoxide also shows a maximum in Expt. II, but although it falls off markedly in Expt. III it again rises somewhat through Expts. IV and V due to the entrance of the side reaction.

Experiments VI, II, VII vary only in the amount of sodium sulfide used and at that over only a small range (0.1, 0.16, 0.2 Na_2S). A decrease in carbon monoxide used up, also in nickel carbonyl formed, is shown for increasing sodium sulfide but this decrease is small and one cannot be entirely certain it is more than accidental variation.

Experiments XI–XIV together with II vary only in the amount of nickel salt used. The carbon monoxide consumption increases with the amounts of nickel salt except for a slight falling off in the last experiment. This trend is, at first glance, difficult to explain, especially since in the last two experiments the OH^- ion is all exhausted in precipitating nickelous hydroxide and there is actually a surplus of Ni^{++} ions in the solution. If in accordance with our hypothesis removal of free sulfur is essential to the continuance of carbonyl formation, the suspended nickelous hydroxide must be particularly effective in the removal of sulfur.

The seeming contradictions, however, become less disturbing when one considers that the reaction takes place on or within the surface of the suspended particles. The ratio of nickelous hydroxide to nickel sulfide in the suspension may well be a more potent influence than the free OH^- ions which diffuse into the surface. Furthermore, the falling off in rate of reaction at high OH^- ion concentrations might be caused by the effect of the electrolyte in altering the surface of the colloidal particles.

Substitution of Selenide for Sulfide.—Two experiments were performed, using the method of weighing the deposit of nickel, in which equivalent amounts of sodium selenide and of sodium sulfide were used (each 0.5 molal), with all other reagents the same. The weight of nickel obtained from the sulfide tube was 0.469 g., while that from the selenide tube was 0.276 g. This shows that the selenide is capable of forming the carbonyl, but less effectively than the sulfide.

Summary

The reaction reported by Manchot and Gall by which nickel carbonyl is formed by the action of carbon monoxide upon a suspension of nickel sulfide has been studied.

The optimum yield is obtained from the suspension obtained from 1 f. w. sodium hydroxide, 0.1 f. w. sodium sulfide and 0.5 f. w. nickel sulfate all in 1 liter.

It is suggested that a potential dissociation of nickel sulfide allows the formation of nickel carbonyl in the presence of a sulfur-removing reagent.

Incidentally in this work it is indicated that the reaction $CO + H_2O \longrightarrow H_2 + CO_2$ will take place at room temperature to a slight extent in presence of OH^- ions under the catalytic influence of nickel carbonyl.

Nickel selenide behaves similarly to nickel sulfide in yielding nickel carbonyl.

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