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Preparation and Properties of Manganese Carbonyl

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Manganese carbonyl, $Mn_2(CO)_{10}$, has been prepared by the reaction of manganese iodide, magnesium and carbon monoxide. It forms volatile, golden-yellow, monoclinic crystals, which are insoluble in water, but soluble in organic solvents. It reacts with iodine to form $Mn(CO)_5I$. X-Ray powder, single crystal Lauë and rotation patterns have been obtained for the carbonyl. Axial ratios, angle and unit cell dimensions are presented. Infrared spectra of the carbonyls and carbonyl iodides of both manganese and rhenium are shown. The spectra of the carbonyls suggest that dimerization does not occur through carbonyl bridges.

Introduction

Although rhenium carbonyl is known,[1] manganese carbonyl has not been isolated and characterized. Mond, Hirtz and Cowap[2] failed to obtain manganese carbonyl from pyrophoric manganese and carbon monoxide up to 500 atmospheres pressure and 450°. No other experimental work was reported until Hurd, Sentell and Norton[3] presented mass spectrographic evidence for a volatile carbonyl of manganese and its hydrocarbonyl. Hurd and co-workers reduced an ether suspension of manganous iodide with an unspecified Grignard reagent under pressure of carbon monoxide. The products were treated by the method[4] used for chromium carbonyl. They reported the recovery of transparent crystals containing manganese, but not in sufficient quantity to characterize them.

Manganese carbonyl has been prepared in this Laboratory by reducing manganese iodide at room temperature with magnesium in diethyl ether under a pressure of 1000–3000 p.s.i.g. of carbon monoxide. The only manganous halide which gave manganese carbonyl was a manganous iodide prepared by heating an excess of cuprous iodide with manganese metal. None of the following manganous halides gave manganese carbonyl under the same conditions: manganous iodide from iodine and manganese at 700°; manganous chloride from the tetrahydrate dehydrated under hydrogen chloride at 400°; or manganous chloride or bromide from the metal and corresponding cuprous halide. No substitute for diethyl ether was found. Temperatures up to 160° and carbon monoxide pressures over 3000 p.s.i.g. were without beneficial effect on the yield. Carbon monoxide pressures below 1000 p.s.i.g. failed to produce manganese carbonyl. The presence of hydrogen or carbon dioxide (in addition to the amounts of these gases usually present in commercial carbon monoxide) was without effect. Oxygen, on the other hand, when added to the carbon monoxide decreased the yield.

Although the yields in this method are low, sufficient quantities of the carbonyl have been isolated to characterize it and to study some reactions.

Experimental

Materials.—Manganese metal powder was obtained from A. D. Mackay, Inc. Cuprous iodide was purchased from Amend Drug and Chemical Company, Inc. Rhenium metal powder was purchased from the University of Tennessee at Knoxville, Tennessee. Carbon monoxide in cylinders was obtained from the Matheson Company, Inc., Rutherford, New Jersey.

Preparation of MnI_2.—A mixture of finely divided manganese metal (5.5 g.) and cuprous iodide (57 g.) was placed between glass wool plugs in a Pyrex tube (50 × 25 mm.) and heated slowly to 400–500° in an atmosphere of nitrogen. Reaction started at 300°, to give MnI_2 and Cu, and was complete after heating at 450° for one hour. The product was easily broken up when the temperature was increased slowly, but a hard mass was formed on rapid heating.

Preparation of $Mn_2(CO)_{10}$.—The intimate mixture of MnI_2 and Cu was ground to a slurry in ether. Magnesium metal powder (2.4 g.) was added to this slurry, and the mixture, with additional ether to make a total of 100 ml., was charged into a 300-ml., stainless steel, pressure vessel. About 50 half-inch, stainless steel balls were added which brought the total volume of the charge to 150 ml.

The vessel was flushed several times with carbon monoxide under 200–400 p.s.i.g. pressure. Carbon monoxide was then admitted to a pressure of 3000 p.s.i.g. Since oxygen was shown to decrease the yield, the carbon monoxide was purified by passage over copper heated to 300° and through a trap cooled to −78°. This treatment reduced the oxygen content from 1.2% to about 0.02%.

The autoclave was mounted horizontally and rotated for 15–17 hours at room temperature. After releasing the carbon monoxide, the vessel was opened, and the steel balls were separated from the slurry. Most of the ether was permitted to evaporate before treating the product with ice and cold, dilute sulfuric acid to destroy the unreacted magnesium. The hydrolysis mixture was steam distilled, and the residual ether was removed. As the pot temperature approached 100°, a yellow deposit of manganese carbonyl or an orange solid, a mixture of yellow carbonyl and red carbonyl iodide, appeared on the wall of the condenser.

Purification.—The yellow carbonyl was purified by sublimation under reduced pressure (<0.5 mm.) at room temperature. Well-formed, golden yellow crystals were obtained. When the product was orange colored, this sublimation led to golden-yellow and dark-red crystals of the carbonyl and carbonyl iodide, which were separated by hand with the aid of a microscope. Separate resublimation gave pure samples. The average recovery of sublimed crystals was about 1% of theory.

Analyses and Molecular Weight Determinations.—A sample of the yellow crystals was fused with sodium peroxide in a Parr bomb and the manganese was determined by the sodium bismuthate method.[5] The carbon was determined in a standard semi-micro combustion train. Calcd. for $Mn(CO)_5$: Mn, 28.2; C, 30.8. Found: Mn, 26.8, 28.3; C, 30.7, 30.8. Cryoscopic determination of the molecular weight in cyclohexane showed manganese carbonyl to be dimeric. Mol. wt. of $Mn_2(CO)_{10}$: calcd. 390; found 365, 393. Manganese carbonyl iodide was similarly analyzed for manganese and carbon. The iodine was determined on a separately fused sample by the standard potassium iodide sodium thiosulfate method,[6] after filtering the boiled, alka-

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[1] W. Hieber and H. Fuchs, *Z. anorg. Chem.*, **248**, 256 (1941).

[2] L. Mond, H. Hirtz and M. D. Cowap, Jr., *J. Chem. Soc.*, **97**, 798 (1910).

[3] D. T. Hurd, G. W. Sentell and F. J. Norton, THIS JOURNAL, **71**, 1899 (1949).

[4] B. B. Owen, J. English, H. G. Cassidy and C. V. Dundon, *ibid.*, **69**, 1723 (1947).

[5] G. E. F. Lundell, J. I. Hoffman and H. A. Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 190.

[6] W. W. Scott, "Standard Methods of Chemical Analysis," Fifth Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 458.

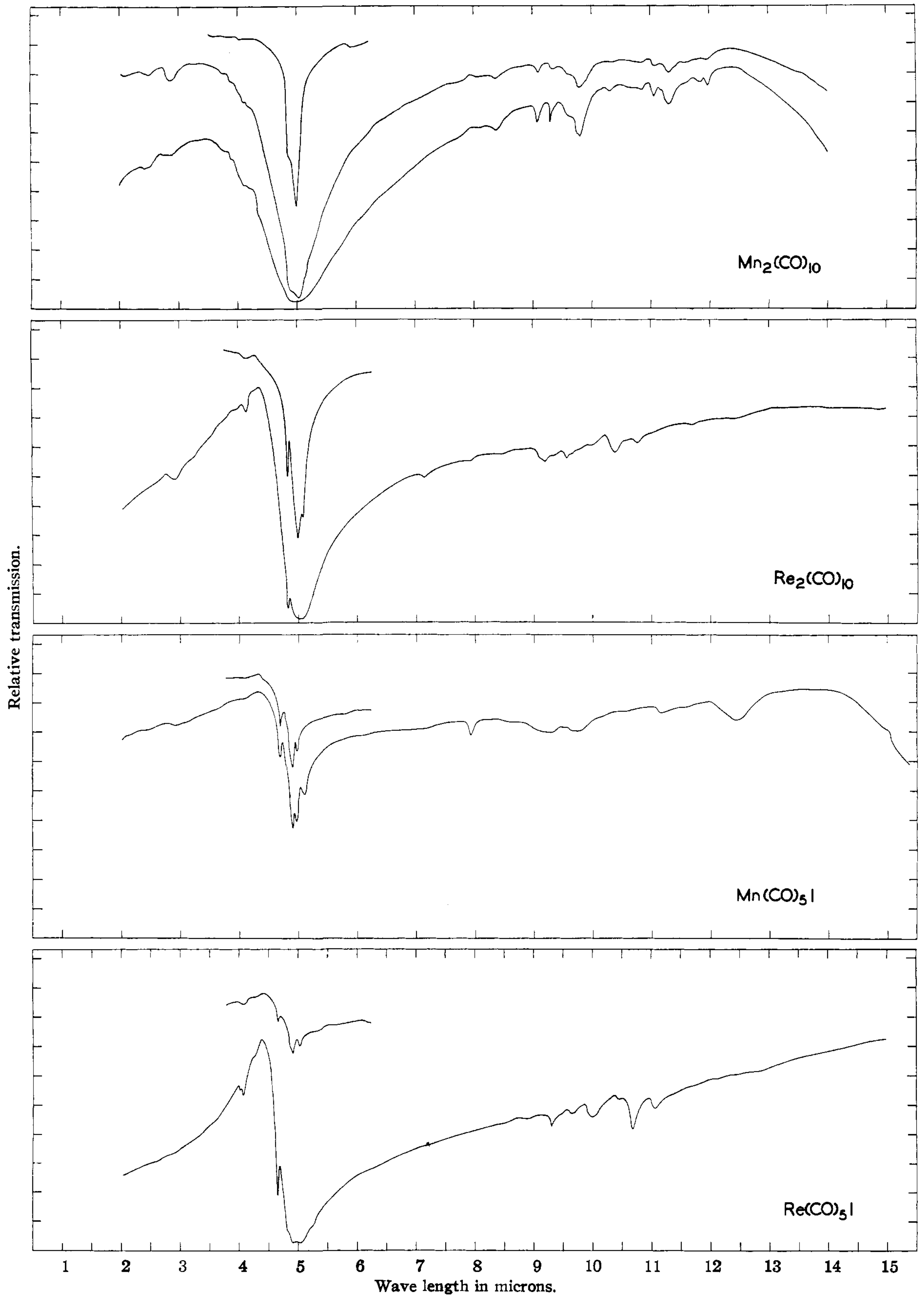

Fig. 1.—Infrared spectrum of the solids in pressed KI wafers (1.5 g.): manganese carbonyyl (0.8, 4 and 12 mg.); rhenium carbonyl (1, 6 mg.); manganese carbonyl iodide (2, 6 mg.); rhenium carbonyl iodide (5, 10 mg.).

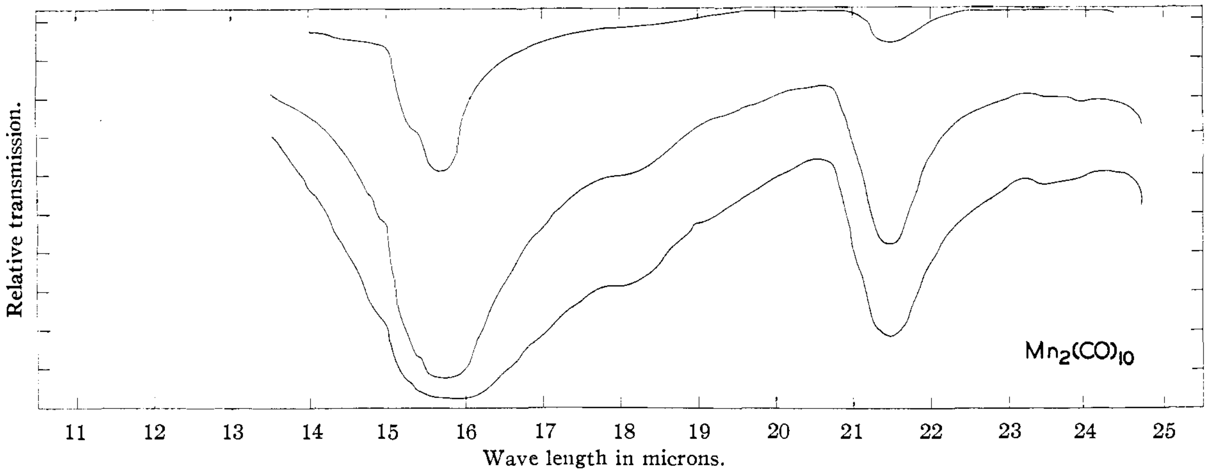

Fig. 2.—Infrared spectrum of manganese carbonyl in a pressed KI wafer (1.5 g.): manganese carbonyl (0.8, 4 and 12 mg.).

line solution to remove manganese dioxide. Calcd. for $Mn(CO)_5I$: Mn, 17.1; C, 18.6; I, 39.5. Found: Mn, 17.6; C, 17.3; I, 35.5. Cryoscopic measurements showed the carbonyl iodide to be monomeric in both benzene and cyclohexane solutions. Mol. wt. of $Mn(CO)_5I$: calcd. 322; found 300 in C_6H_6, 339 in C_6H_{12}.

Preparation of $Re_2(CO)_{10}$.—Rhenium metal was converted to the heptoxide by heating in pure oxygen. The oxide was purified by sublimation. The heptoxide was converted to carbonyl by the method of Hieber.[1] The dirhenium decacarbonyl was purified by vacuum sublimation.

Preparation of $Re(CO)_5I$.—Rhenium carbonyl absorbed iodine when heated in an evacuated, sealed tube at 130°. Colorless[7] crystals of rhenium carbonyl iodide were recovered by vacuum sublimation of the reaction product.

Properties

Physical. $Mn_2(CO)_{10}$.—Dimanganese decacarbonyl forms golden-yellow, transparent crystals which melt at 154–155° in a sealed tube. It is stable for prolonged periods under an atmosphere of carbon monoxide, and it is not decomposed up to 250° under 3000 p.s.i.g. pressure of carbon monoxide. In the absence of carbon monoxide it begins to decompose above about 110° and, when heated strongly, decomposes to give a metallic mirror. In air it slowly darkens at room temperature. It is not wet by water but is soluble in common organic solvents. These solutions are much less stable toward air, heat and light than the solid. By displacement of water the average density of these crystals was found to be 1.75 $g./cm.^3$ at 25°.

$Mn(CO)_5I$.—Manganese carbonyl iodide forms ruby-red, transparent crystals which melt in air at 115° with decomposition. It is somewhat less stable than the parent carbonyl and evolves iodine on exposure to air at room temperature. It is not soluble in water but dissolves in common organic solvents. These solutions are less stable toward air than the solid.

Chemical. $Mn_2(CO)_{10}$.—Dimanganese decacarbonyl reacted with iodine when heated to 130–140° in an evacuated, sealed tube. The orange liquid solidified on cooling. Sublimation of the product gave the same red crystals as frequently observed in the preparation of dimanganese decacarbonyl. When shaken with sodium amalgam, the yellow color of a benzene solution of the pure carbonyl was discharged. A small amount of white precipitate formed which was not isolated. It was probably the sodium salt of the hydrocarbonyl, $HMn(CO)_5$. A similar reaction[8] has been described for dicobalt octacarbonyl. Dimanganese decacarbonyl was not attacked by aqueous ammonia or by aqueous alkali at room temperature. Unlike cobalt carbonyl, no evolution of carbon monoxide was observed when it was dissolved in pyridine. The solution, however, darkened in a few minutes on heating to 100°.

Structure

X-Ray Investigation.—Using copper Kα radiation, the X-ray diffraction pattern of powdered manganese carbonyl has been obtained. For comparison the pattern for rhenium carbonyl was obtained. The *d*-values and the relative intensities based on the most intense line equal to 10 are presented in Table I.

TABLE I

$Mn_2(CO)_{10}$				$Re_2(CO)_{10}$			
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
7.07	6	3.24	1	7.11	8	2.998	6
6.79	2	3.17	3	6.38	10	2.941	2
6.31	10	3.09	3	5.90	8	2.872	8
5.71	5	3.02	3	5.07	10	2.787	1
5.01	7	2.94	6	4.44	4	2.706	2
4.38	2	2.90	3	3.906	1	2.623	4
3.80	1	2.84	3	3.817	1	2.530	2
3.56	3	2.80	5	3.546	6	2.503	2
3.40	3	2.70	4	3.158	6	2.447	1
3.31	1	2.62	2	3.053	4	2.385	3

X-Ray single crystal Laué and rotation patterns of manganese carbonyl show the cell is monoclinic with axial ratios[9] $a_0:b_0:c_0 = 1.036:1:0.5054$ (notation of Davey); angle, 75°; and lattice constants $a_0 = 14.68$ Å., $b_0 = 14.16$ Å., and $c_0 = 7.16$ Å. From these lattice constants and an experimental density of 1.75 $g./cm.^3$ at 25°, it was calculated that the unit cell contains 4 molecules of $Mn_2(CO)_{10}$. This leads to a calculated X-ray density of 1.79 $g./cm.^3$.

Infrared Spectra.—The absorption spectra of manganese and rhenium carbonyls and carbonyl iodides have been obtained in the 2–15 μ region and for manganese carbonyl in the 15–35 μ region. These compounds do not have sufficient vapor pressure at room temperature to obtain acceptable spectra of their vapors in a 10-cm. cell. Spectra are shown in Figs. 1–3 for the crystalline solids,[10] and their solutions in carbon tetrachloride or cyclohexane (manganese carbonyl and carbonyl iodide were more stable in the latter). The spectra were obtained with a Perkin–Elmer, Model 21, double-beam spectrometer.

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(7) Hieber reports yellow crystals which may have been due to the incomplete removal of iodine.

(8) I. Wender, H. W. Sternberg and M. Orchin, THIS JOURNAL, **74**, 1216 (1952).

(9) The optical crystallographic values of Steinberg[1] for monoclinic rhenium carbonyl were $a_0:b_0:c_0 = 1.045:1:2.045$, with an angle of 76°28'.

(10) The solid spectra were obtained using the alkali halide-wafer technique of Sisters Miriam M. Stinson and Marie J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

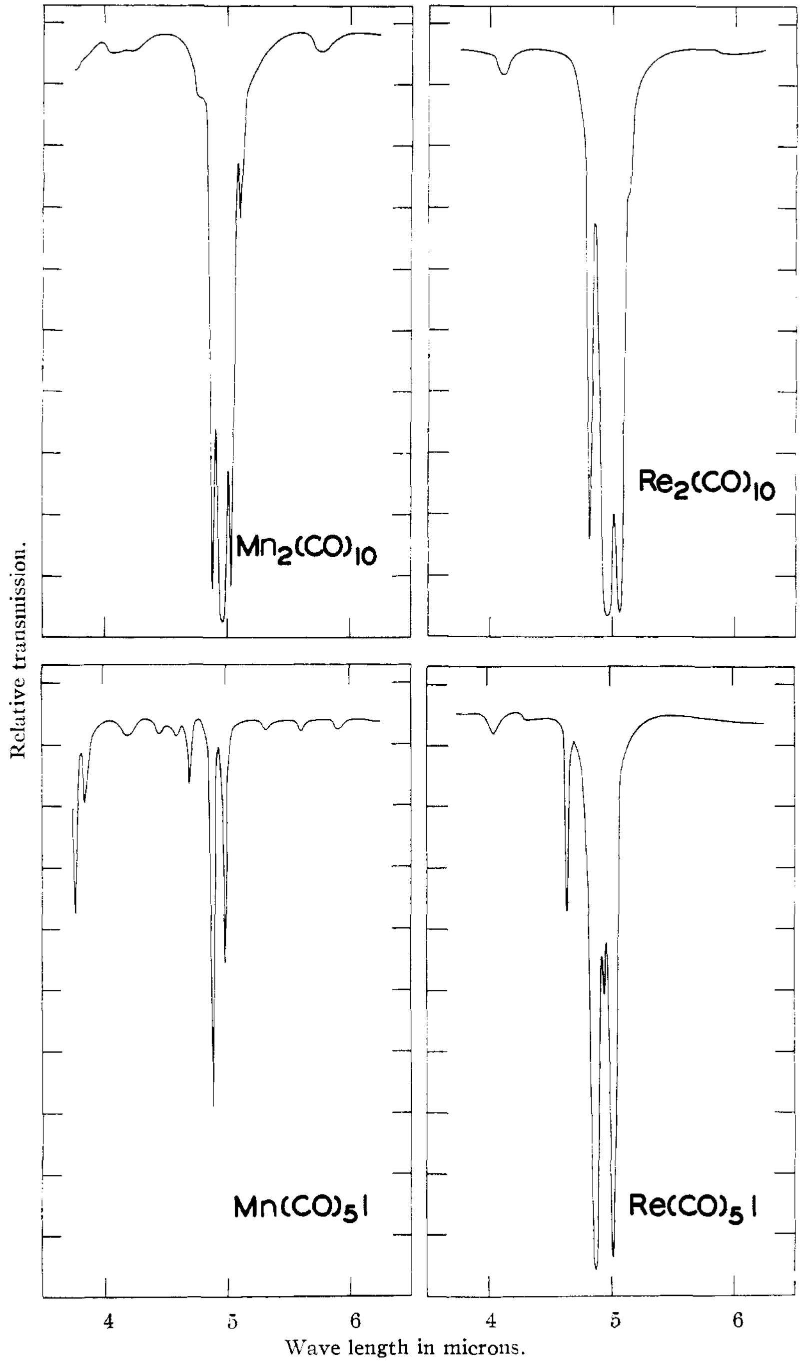

Fig. 3.—Infrared spectrum of saturated solutions in 0.001-in. cells: manganese carbonyl (C_6H_{12}); manganese carbonyl iodide (C_6H_{12}); rhenium carbonyl (CCl_4); rhenium carbonyl iodide (CCl_4).

Sheline and Pitzer observed an absorption band at 5.47 μ in the infrared spectrum of iron enneacarbonyl, $Fe_2(CO)_9$, whose structure is known to contain bridging carbonyl groups. Since ketones usually show an absorption between 5.7 and 6.0 μ, they attributed this band at 5.47 μ to the bridging carbonyls. It is possible, although it has not been established, that absorption near 5.5 μ is characteristic for bridging carbonyl groups in all polymeric metal carbonyls.[11] If so, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, which do not absorb near 5.5μ, must dimerize

(11) C. A. Coulson, Victor Henri Mem. Vol., "Contribution a l'etude de la structure moleculaire," Desoer, Liege, 1948, p. 26, has pointed out that in the ketone carbonyl group in diacetyl the amount of s character and hence the strength of the carbon-oxygen, σ (sigma) bond increases as the opposite angle between the hybrid orbitals decreases from 120°. Another example pointed out by Professor R. C. Lord (M.I.T.) is cyclobutanone which probably contains a 90° skeletal angle and, therefore, an angle between the hybrid orbitals approaching this value. It has an absorption band near 5.6 μ. See J. D. Roberts and C. W. Sauer, This Journal, **71**, 3925 (1949), for the spectrum of cyclobutanone. In $Fe_2(CO)_9$ the Fe–C–Fe angle is less than 90°. The angle between the hybrid orbitals is unknown but probably approaches this value of 90° quite closely. This would give the carbon-oxygen, σ (sigma) bond considerable s character and, in strengthening it, would shift the absorption to shorter wave length.

through formation of metal–metal bonds. It may be significant in this connection that the dimeric carbonyls, and the monomeric carbonyl iodides which can have no bridging groups, have very similar bands in the region about 5 μ.

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Heats of Formation of Nickel and Cobalt Oxides (NiO and CoO) of Combustion Calorimetry

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The heats of formation of nickel and cobalt oxides (NiO and CoO) were determined as $\Delta H_{298.16} = -57.3 \pm 0.1$ and $\Delta H_{298.16} = -57.1 \pm 0.3$ kcal./mole, respectively, by combustion calorimetry. The corresponding free energies of formation from the elements are -50.6 and -50.4 kcal./mole.

The heats of formation of nickel and cobalt oxides have been determined previously by combustion calorimetry and from reaction equilibria. The data, summarized by Brewer[1] and in the N. B. S. tables,[2] cover ranges of 2.8 and 3.1 kcal./mole, respectively; and those from combustion calorimetry are not of high precision. This paper reports new experiments in combustion calorimetry, which yield heats of formation of these oxides valid to within ±0.1 and ±0.3 kcal./mole.

Materials.—The nickel was a specially purified product in the form of a small bar.[3] Analysis showed 0.03% iron, 0.003% silicon, 0.001% cobalt and 0.002% sulfur as the only detectable impurities. In a series of preliminary experiments, using filings and fine lathe turnings from this bar, the metal either failed to ignite or showed only superficial combustion under conditions prevailing in the calorimeter bomb. It was discovered, however, that the presence of a small amount (*ca.* 0.1%) of cobalt had a markedly beneficial effect in promoting combustion.[4] This led to adoption of the following procedure for preparing the metal used in the reported measurements. Lathe turnings from the bar (cut with a Carboloy tool) and pure cobalt sponge, in amount equal to 0.1% of the nickel, were dissolved in concentrated reagent grade nitric acid, and the solution was diluted and filtered. The filtrate was evaporated to dryness and the resulting cake transferred to a porcelain dish and ignited at 1,150°. The oxide from this process was finely ground and reduced to metal in a stream of pure hydrogen at 650°. When reduction was complete, the hydrogen stream was discontinued and replaced by a stream of pure helium in which the metal was allowed to cool to room temperature. This metal, consisting of 99.9% nickel and 0.1% cobalt, was used in all the reported measurements. X-Ray diffraction showed only lines corresponding to the normal nickel structure.

The cobalt was a Johnson, Matthey and Co. product. Their analysis showed 0.003% silicon, 0.0005% aluminum, 0.0002% magnesium, 0.0001% copper, 0.0001% manganese and less than 0.001% iron. Other metallic impurities, including nickel, were not present in amounts large enough for detection. The metal, as received, contained a small amount of oxygen. This was eliminated by reduction in a stream of pure hydrogen at 750°, followed by cooling to room temperature in a stream of pure helium. The X-ray diffraction pattern contained no lines other than those of the normal cobalt structure.

Measurements and Results.—The measurements were conducted with the calorimetric equipment described by Humphrey.[5] Benzoic acid (N. B. S. sample No. 39g) was used in determining the energy equivalent of the calorimeter, which was 32,415.1 (±0.01%) cal./ohm for the nickel combustions and 32,435.4 (±0.01%) for the cobalt combustions, the difference being attributable to minor apparatus repairs. All weighings were reduced to vacuum and all heat values are expressed in defined calories (1 cal. = 4.1840 abs. joules).

The metal samples for combustion were held in unlined silica-glass capsules, the use of nickel and cobalt oxide linings being precluded by possible changes in composition resulting from exposure to oxygen in the bomb during combustion of the metal. The capsules were attacked by the combustion products, superficially in the nickel combustions and appreciably in the cobalt combustions. In the latter case, a special procedure for correcting for silica contamination of the combustion products was devised, as will be described later.

All heat measurements were made at a calorimeter temperature of 303.16°K. The initial oxygen pressure in the bomb was 40 atm. for the nickel combustions and 25 and 30 atm. (mostly 30 atm.) for the cobalt. In all instances the bomb walls remained clean, the total combustion product being contained in the capsule. Ignition was by means of an electrically heated platinum spiral and a filter paper fuse, for which appropriate corrections were applied. The bomb gases after combustion were tested for oxides of nitrogen. The amount found was negligible, yielding a correction of less than 0.001% in the heat values. Exposure tests of the metals to oxygen, conducted under bomb conditions, showed that no oxidation occurred before ignition of the fuse.

Completion of combustion was determined from the difference in mass of the combustion product and the metal sample. The percentage completions of the nickel combustions ranged from 87.33 to 92.92, the average O:Ni atomic ratio of the combustion products being 0.9036. X-Ray diffractions of the nickel combustion products showed the lines of ordinary nickel oxide (NiO) and a few faint lines of nickel. The energy values were corrected to correspond with complete formation of NiO by assuming direct proportionality with the oxygen contents of the combustion products. It was mentioned previously that the attack of the silica-glass capsules by the nickel combustion products was only superficial. This was confirmed by analysis of these products for silica.

The cobalt combustion products had O:Co atomic ratios greater than unity in all instances. They ranged from 1.0312 to 1.0365, the average being 1.0338. Correction of the results to correspond to

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(1) L. Brewer, *Chem. Revs.*, **52**, 1 (1953).

(2) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Natl. Bur. Standards Circular* 500, 1952.

(3) This metal was furnished by T. H. Hazlett, Division of Mineral Technology, University of California.

(4) This phenomenon was first noted by G. L. Humphrey, formerly of this Laboratory.

(5) G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).