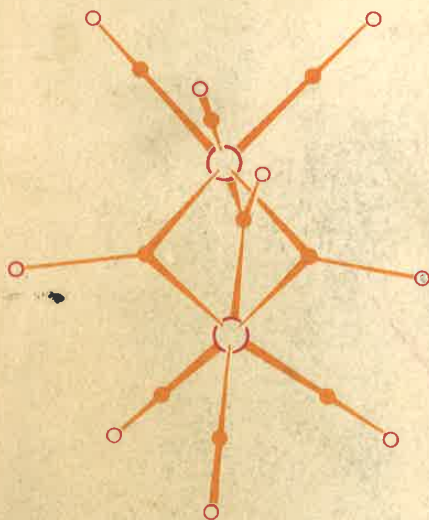


WENDER
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VOLUME I
ORGANIC SYNTHESSES VIA METAL CARBONYLS



INTERSCIENCE



IRVING WENDER
PIERO PINO
Editors

**ORGANIC
SYNTHESSES
VIA
METAL
CARBONYLS**

VOLUME I

Organic Syntheses via Metal Carbonyls

Volume 1

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38 Metal Carbonyls: Preparation, Structure, and Properties

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III. PHYSICAL AND THERMODYNAMIC DATA OF METAL CARBONYLS

A. Introduction

Some physical properties of the metal carbonyls are presented in Table 1. The vapor pressure values are also tabulated in Table 2, since a similar compilation has never appeared before. Knowledge of the vapor pressures of the metal carbonyls at different temperatures has important practical utility for safety reasons and for operations involving distillation and sublimation. Moreover, the vapor pressure measurements represent the first step toward the determination of important thermodynamic properties.

TABLE 1
Selected Physical Data of Metal Carbonyls

Compound	Color	Mp (°C)	Solubility at room temperature	
			Hydrocarbons	THF
Ni(CO) ₄	Colorless	-19.3 (bp 42.1)	Very good	Very good
Fe(CO) ₅	Yellow	-20.5 (bp 103-104) ^a	Very good	Very good
Fe ₂ (CO) ₉	Orange	100 dec.	Extremely low	Reacts
Fe ₃ (CO) ₁₂	Black-green	140-150 dec.	Moderate	—
Ru(CO) ₅ ^b	Colorless	-22	Good	—
Ru ₃ (CO) ₁₂	Orange-red	150 dec. (in air)	Moderate	—
[Ru(CO) _x] _n ^b	Green	—	Extremely low	—
Os(CO) ₅ ^b	Colorless	-15 ~	—	—
Os ₃ (CO) ₁₂	Yellow-orange	224	Good	—
Co ₂ (CO) ₈	Orange	51-52 dec.	Good	Reacts
Co ₄ (CO) ₁₂	Black	—	Very low	Reacts
Co ₆ (CO) ₁₆ ^b	Black	100-110 dec.	Very low	—
Rh ₂ (CO) ₈ ^b	Orange	76 dec.	—	—
Rh ₄ (CO) ₁₂	Brick red	150 dec.	—	—
Rh ₆ (CO) ₁₆	Black	> 220 dec.	Low	—
[Ir(CO) ₄] _n ^b	Yellow-green	—	—	—
Ir ₄ (CO) ₁₂	Canary yellow	210 dec.	Very poor	Poor
Mn ₂ (CO) ₁₀	Golden yellow	154-155	Moderate	Good
Tc ₂ (CO) ₁₀	Colorless	159-160	≥ 5%	—
Re ₂ (CO) ₁₀	Colorless	177	—	—
[Re(CO) ₄] _n ^b	Colorless	Subl. 100°/0.1 mm	Very low	Very low
Cr(CO) ₆	Colorless	130 dec.	Very low	Low
Mo(CO) ₆	Colorless	—	Very low	Low
W(CO) ₆	Colorless	—	Very low	Low
V(CO) ₆	Black-green	~ 70 dec.	~ 2% (w/v) ^c	Reacts

^a Extrapolated.

^b No other reports known apart from that of the discoverers.

^c Reacts very slowly with aromatic hydrocarbons.

B. Vapor Pressures and Heats of Vaporization

The vapor pressures in mm Hg at different temperatures were calculated using the empirical equations numbered below.

TABLE 2
Vapor Pressures of Some Metal Carbonyls

Compound	Vapor pressure (mm Hg)													
	10°C	15°C	20°C	30°C	40°C	50°C	60°C	70°C	100°C	110°C	120°C	130°C	140°C	150°C
Ni(CO) ₄	211.8	262.7	322.9	478.8	692.0									
Fe(CO) ₅	11.8	15.7	20.8	35.4	58.2	92.7	143.7	217.1	655.9					
Ru(CO) ₅			~ 50 ^a											
Os(CO) ₅			~ 4.5											
Co ₂ (CO) ₈			0.07											
Mn ₂ (CO) ₁₀										3.0 ^a	5.1	8.5	13.6	21.3
Re ₃ (CO) ₁₀								0.04 ^a	0.36	0.7	1.3	2.4	4.3	7.4
Cr(CO) ₆				0.28 ^a	0.69 ^a	1.63	3.64	7.76	58.9	107.9	191.5	330.4		
Mo(CO) ₆				0.27 ^a	0.63 ^a	1.43	3.06	6.26	42.8	75.9	130.9	219.3	358.9	
W(CO) ₆				0.06 ^a	0.14 ^a	0.35	1.25	1.74	14.1	26.2	47.4	83.2	142.0	236.6

^a Extrapolated.

For $\text{Ni}(\text{CO})_4$, valid from -35 to 45°C (1):

$$\log p = 7.690 - 1519/T \quad (1)$$

Another equation has been reported (2):

$$\log p = 7.878 - 1574.49/T$$

For $\text{Fe}(\text{CO})_5$, the following equation has been found (3):

$$\log p = 8.3098 - 2050.7/T \quad (2)$$

The equation proposed by Dewar and Jones (4), $\log p = 7.349 - 1681/T$, gives too high values of the vapor pressures and too low values of the heat of vaporization. The most probable value of the heat of vaporization is 8.9 kcal/mole, as suggested in a publication of the U.S. Bureau of Standards (5). Trautz and Badstübner's data (3) give a molar entropy of vaporization of 23.7 eu compared with that of 20.4 eu given by Dewar and Jones. The accepted value (5) of the entropy of vaporization of $\text{Fe}(\text{CO})_5$ is 23.5 cal deg^{-1} mole $^{-1}$. These entropy change values suggest that $\text{Fe}(\text{CO})_5$ behaves approximately as a Troutonian liquid.

The variation of vapor pressures with temperature for a number of other metal carbonyls is given below.

For $\text{Mn}_2(\text{CO})_{10}$ between 102 and 146°C (6):

$$\log p = 9.225 - 3262.6/T \quad (3)$$

For $\text{Re}_2(\text{CO})_{10}$ between 78 and 135.5°C (7):

$$\log p = 10.68 - 4152/T \quad (4)$$

For $\text{Cr}(\text{CO})_6$ between 50 and 140°C (8):

$$\log p = 11.832 - 3755.2/T \quad (5)$$

For $\text{Mo}(\text{CO})_6$ between 55 and 145°C (8):

$$\log p = 11.174 - 3561.3/T \quad (6)$$

For $\text{W}(\text{CO})_6$ between 55 and 145°C (8):

$$\log p = 11.523 - 3872.0/T \quad (7)$$

The vapor pressures of the hexacarbonyls of the sixth group have also been determined by Rezhukhina and Shvyrev (9). The relations given by these authors are:

$$\text{Cr}(\text{CO})_6: \log p = 11.475 - 3622.9/T; \text{ between } 46.1 \text{ and } 138.4^\circ\text{C}$$

$$\text{Mo}(\text{CO})_6: \log p = 11.727 - 3788.3/T; \text{ between } 50.5 \text{ and } 129.6^\circ\text{C}$$

$$\text{W}(\text{CO})_6: \log p = 10.947 - 3640.4/T; \text{ between } 65.6 \text{ and } 137^\circ\text{C}$$

The three latter equations give vapor pressures normally lower than those reported by Hieber and Romberg. The largest discrepancy between the two sets of values is found for $\text{Mo}(\text{CO})_6$. The heats of sublimation (see Table 3) increase in the order $\text{Mo}(\text{CO})_6 < \text{Cr}(\text{CO})_6 < \text{W}(\text{CO})_6$ according to Hieber and Romberg (8) and in the order $\text{Cr}(\text{CO})_6 < \text{W}(\text{CO})_6 < \text{Mo}(\text{CO})_6$ according to other workers (9).

TABLE 3
Heats of Vaporization of Some Metal Carbonyls

Compound	Heat of vaporization, ΔH_v (kcal/mole)	Reference
$\text{Ni}(\text{CO})_4$	7.20	2
	6.92	1
	6.50	19
	7.0	5
$\text{Fe}(\text{CO})_5$	8.9	5
	9.38	3
	7.71 ^a	—
	15.0	6
$\text{Mn}_2(\text{CO})_{10}$	19.0	7
$\text{Re}_2(\text{CO})_{10}$	17.18	8
$\text{Cr}(\text{CO})_6$	16.57	9
	18.2	10
	16.29	8
	17.33	9
$\text{Mo}(\text{CO})_6$	17.39	20
	16.66	21
	17.71	8
	16.66	9

^a Calculated from the vapor pressure data given in ref. 4.

Vapor pressures of $\text{Cr}(\text{CO})_6$ between 27.6 and 42.3°C have been measured by Cordes and Schneider (10) using the Knudsen effusion method. The relation $\log p = 12.7 - 3980/T$ was found by these authors, who also give a heat of vaporization of 18.2 kcal/mole. The vapor pressures of $\text{Cr}(\text{CO})_6$ at different temperatures given by Windsor and Blanchard (11) are too high, and therefore probably not properly corrected for the carbon monoxide pressure formed by the decomposition of the carbonyl; this reaches 10 mm Hg at temperatures around 130°C (9).

A redetermination of the vapor pressure of $\text{Cr}(\text{CO})_6$ between 0 and 37.5°C has appeared (9a). The value of the heat of sublimation was found to be 17.09 kcal/mole, in good agreement with that reported by Hieber and Romberg (8).

C. Heats of Combustion and Formation

In spite of the numerous experimental difficulties, the heats of formation of some metal carbonyls have been determined.

Some selected values of heats of formation of metal carbonyls are given by Skinner (12).

Some of the older values obtained for $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ have also been critically reviewed (13,14).

For $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and the hexacarbonyls of group VI, the more recent values of Cotton, Fischer, and Wilkinson are reported in Table 4.

TABLE 4
Heats of Combustion and Formation of Some Metal Carbonyls
(Reference numbers in parentheses)

Compound	Heat of combustion (kcal/mole)	Heat of formation ^a (kcal/mole)	Mean dissociation energies ^b of M—C bond
$\text{Ni}(\text{CO})_4$	-282.2 (13) ^c	-148.7 (24) -151.6 (13) -151.0 (25)	35.2 (14)
$\text{Fe}(\text{CO})_5$	-386.9 (14) ^c	-182.6 (14) -187.8 (5)	27.7 (14)
$\text{Mn}_2(\text{CO})_{10}$	-777.0 (22) ^d	-400.9 (22)	15.7
$\text{Cr}(\text{CO})_6$	-443.1 (23) ^c	-257.5 (23)	27.1 (14) $\text{Cr}_2\text{O}_3 = -272.7$
$\text{Mo}(\text{CO})_6$	-507.5 (23) ^c	-234.8 (23)	35.9 (14) $\text{MoO}_3 = -178.0$
$\text{W}(\text{CO})_6$	-537.8 (23) ^c	-227.2 (23)	42.1 (14) $\text{WO}_3 = 200.84$

^a Heats of formation of the metal carbonyl in the liquid state ($\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$) or the solid state (all the others) from the solid metal, graphite, and oxygen gas.

^b For the equation $\text{M}_{(g)} + n\text{CO}_{(g)} = \text{M}(\text{CO})_{n(g)}$. The value for $\text{Mn}_2(\text{CO})_{10}$ was calculated from the heat of formation in the literature, the heat of vaporization of the metal, the heat of vaporization of the metal carbonyl, and the metal-metal bond energy given in ref. 6 (34 ± 13 kcal/mole). The metal-metal bond dissociation energy was found to be 18.9 kcal/mole by mass spectrometric methods (26).

^c For the combustion to metal oxides with oxygen.

^d For the reaction: $\text{Mn}_2(\text{CO})_{10} + 4\text{HNO}_3$ (in $16\text{H}_2\text{O}$) + $6\text{O}_{2(g)} = 2\text{Mn}(\text{NO}_3)_2$ (in $10.309\text{H}_2\text{O}$) + $10\text{CO}_{2(g)} + 2\text{H}_2\text{O}$ (liq.).

In order to get a rough estimate of the relative metal-carbon bond strength in metal carbonyls the above-mentioned authors have calculated the enthalpy change of the following processes:

$$\frac{1}{n} \text{M}(\text{CO})_{n(g)} = \frac{1}{n} \text{M}_{(g)} + \text{CO}_{(g)} \quad (\Delta H) \quad (8)$$

which gives the values in the last column of Table 4. The latter are in good agreement with the average bond dissociation energies obtained from the results of electron impact measurements (27).

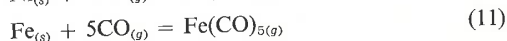
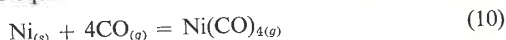
The mean metal-CO dissociation energies for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ (35.2, 27.7, and 27.1 kcal/mole, respectively) are, however, inconsistent with the usually higher reactivity of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ compared with $\text{Cr}(\text{CO})_6$ and with the fact that $\text{Ni}(\text{CO})_4$ was found to exchange its carbonyl groups (15) with ^{14}CO at a much faster rate than $\text{Fe}(\text{CO})_5$ (16) and $\text{Cr}(\text{CO})_6$ (17). It has been pointed out (14) that a more realistic evaluation of bond energies is obtained by taking into account the promotion energies of the metal and ligands to their corresponding valence states, i.e.,

$$\frac{1}{n} \text{M}(\text{CO})_{n(g)} = \frac{1}{n} \text{M}_{(g)}^* + \text{CO}_{(g)}^* \quad (\Delta H^*) \quad (9)$$

This calculation has been carried out for $\text{Cr}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Ni}(\text{CO})_4$ and values for ΔH^* of 87, 89, and 77 kcal/mole, respectively, have been found.

It is interesting to note that although, according to the heats of formations calculated with Eq. 8, $\text{Fe}(\text{CO})_5$ appears to be less stable than $\text{Ni}(\text{CO})_4$, the opposite order of stability is found for the two metal carbonyls when the promotion energies as defined above are also taken into account. From the data of Table 4, it would also appear that stability increases regularly from $\text{Cr}(\text{CO})_6$ to $\text{W}(\text{CO})_6$.

The thermodynamic equilibrium constants for the reactions:



have been calculated by using the known standard heats of reaction and the entropies deduced from spectroscopic data (18). The equations relating equilibrium constants to temperature are, for $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, respectively:

$$\log K = 8546/T - 21.64 \quad (12)$$

$$\log K = 8940/T - 30.09 \quad (13)$$

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IV. STRUCTURE OF METAL CARBONYLS

A. Introduction

The structures of several metal carbonyls have been elucidated in recent years, especially by Dahl and his co-workers, by x-ray diffraction

ORGANIC SYNTHESSES VIA METAL CARBONYLS

VOLUME I

Edited by IRVING WENDER, U.S. Department of the Interior; and PIERO PINO, University of Pisa, Italy.

Although research involving the metal carbonyls has necessarily been an interdisciplinary endeavor, the organic chemist has not played as large a part in this area as perhaps he should. The next decade will see dozens of new compounds and syntheses made possible by the use of organometallic complexes of the transition metals. ORGANIC SYNTHESSES VIA METAL CARBONYLS (a two volume work) invites the organic chemist to join the team of inorganic chemists and catalyst researchers who are already reaping a magnificent harvest in this field.

Volume I features:

- a long, extremely detailed chapter on the preparation, structure, and chemical properties of the metal carbonyls and their derivatives — the most comprehensive of coverage of its kind to date.
- a treatment of reactions of acetylenes and metal carbonyls that summarizes a complicated field of endeavor and brings the principle of ligand synthesis into focus.
- a chapter covering alkyl and acyl metal carbonyls and some novel organic syntheses via the insertion of carbon monoxide into a carbon-metal bond. This section emphasizes cobalt reactions.
- a summary and discussion of the reactions of nitrogen compounds with carbon monoxide, with a short section on the fixation of nitrogen by soluble transition metal complexes.
- a chapter dealing with the catalytic cyclization of acetylenes.

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