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Thermochemistry of Metalcarbonyl Compounds
I. Complexes $W(CO)_{6-n}(CH_3CN)_n$ (n = 1,2,3)

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It is shown that DSC measurements can be used for the determination of the heats of reactions of substitution reactions.

The heats of reactions have been determined for:

$$W(CO)_{6-n}(CH_3CN)_n + nCO \rightarrow W(CO)_6 + nCH_3CN \quad (n = 1,2,3)$$

Combination of these data with measured heat capacities and sublimation energies and with the known standard enthalpies of formation of $W(CO)_6$*, CO and* CH_3CN *afforded the standard enthalpies of formation of each member of the series,* $W(CO)_{6-n}(CH_3CN)_n$*. These values are discussed in the light of the observed disproportionation behaviour of this series.*

The tungsten–acetonitrile bond energies have been derived and are shown to be of the order of 45 kcal/mol, which is comparable to the bond energy of the tungsten–carbonyl bond.

Introduction

While organometallic chemistry has experienced an enormous growth, thermochemical investigations[1] in this field have lagged far behind, partly owing to a lack of interest and partly owing to a lack of a variety of precise methods of measuring thermochemical data from which metal–ligand bond strengths can be derived.

Recent advances in the field, however, have yielded some results on the bond strengths of M–CO[2–6], $M–CH_3$[7], $M–C_6H_5$[8], $M–C_2H_4$[9], and M–π-allyl[10]. In our laboratory new precise techniques, such as DSC and an advanced thermobalance apparatus are used to obtain bond energy values by means of substitution reactions and to correlate these results if possible, with mass spectrometric, photoelectron spectroscopic and other spectroscopic data.

In the first part of the series, which mostly deals with the substitution reactions of $M(CO)_{6-n}L_n$ with CO (M = Cr, Mo, W), the results for the complexes $W(CO)_{6-n}(CH_3CN)_n$ are reported and compared with data for other metal–ligand bonds.

In the experimental part, some detailed information is given on more precise methods of preparation and on the methods of measurement, as some of them have been developed by us while others needed some developments and adaptations.

Experimental

Preparation

The complexes $W(CO)_5(CH_3CN)$ and $W(CO)_4(CH_3CN)_2$ were prepared using a modification of previously described methods[11], while $W(CO)_3(CH_3CN)_3$ was prepared according to Tate *et al.*[12]. The methods are described below, as extremely pure compounds were needed to carry out the thermochemical measurements. Great care was spent on the purification of the compounds and of the solvents, which were used oxygen-free.

$W(CO)_5(CH_3CN)$

5 g $W(CO)_6$ (14 mmol) was dissolved in 300 ml benzene (as solvent and as photosensitizer) and 1.5 ml acetonitrile (29 mmol) was added. In the centre of the reaction vessel a medium pressure Hg lamp (Hanovia 12669) was placed, while the lamp was surrounded by a cooled ethylacetate filter ($\lambda < 250$ nm is absorbed). The reaction mixture was irradiated for 2.5 hr at 60° C. Subsequently the solvent was removed by distillation at 20° C (2 mm Hg). After stirring the yellow solid with 50 ml acetonitrile and then filtration, the solid was shaken with portions of 20 ml n-heptane to remove $W(CO)_6$. After evaporation of the acetonitrile at 20° C (2 mm Hg) the product was dried in a stream of argon at 20° C. Yield: 35%; *analysis* (calcd): C, 23.17 (23.03); H, 0.95 (0.83). The ν(CO) are (for identification purposes) 2080 cm^{-1} A_1^2 (w), 1943 cm^{-1} E (s) and 1900 A_1^1 (m).[13]

$W(CO)_4(CH_3CN)_2$

4.4 g $W(CO)_6$ (12.5 mmol) in 300 ml acetonitrile, was irradiated for 22 hr with a medium pressure Hg

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lamp (Hanovia) at 60° C. The reaction mixture was filtered at 20° C and the solvent was removed at 20° C (2 mm Hg). After the appearance of yellow crystals the solution was kept overnight at –30° C. The resulting yellow solid was filtered off at –30° C. The complex was recrystallized twice according to the same method. The product was dried in a stream of argon at 20° C. Yield: 33%. *Analysis* (calcd): C, 25.60 (25.42); H, 1.51 (1.60).

The CO stretching frequencies (Nujoll mull) are 2022 cm^{-1} A^2 (m), 1900 cm^{-1} A^1 (s); 1880 B (sh), 1839 cm^{-1} B_2 (s)[13].

$W(CO)_3(CH_3CN)_3$

This compound was prepared as described previously[12]. Since the product is unstable in acetone[14], the complex was recrystallized from acetonitrile rather than from acetone/n-hexane Yield: 30%. The analysis could not be carried out properly owing to the great oxygen sensitivity of the compound. The purity was checked by spectroscopic means and was sufficient in view of the thermochemical results. The CO stretching frequencies are 1885 cm^{-1} A (s) and 1778 cm^{-1} E (s)[13].

B. *Differential Scanning Calorimetry*

The enthalpies of the substitution reactions of acetonitrile in $W(CO)_{6-n}(CH_3CN)_n$ by CO were measured using a DSC calorimeter (Dupont, type 990) under isobaric conditions.

In order to obtain reliable enthalpy values the following procedures should be strictly adhered to:

1. Series of measurements should be performed in succession with samples of approximately the same weight (2.0–4.5 mg).
2. The calorimeter should be calibrated every day (melting of In as standard[15]) by using the same experimental conditions as for the compounds under investigation. The average value is taken of three measurements on three different samples.
3. It is extremely important that the calorimeter is clean in order to avoid noise. Also, no other compounds should be investigated during a series of measurements. If noise is observed, the calorimeter should be cleaned as described by Plato[16], while traces of methanol must be removed, as this may cause serious damage.
4. Overnight the calorimeter was kept at the upper limit of the temperature range used, while a small stream of pure CO was passed through the calorimeter.

Before the actual measurement the sample and the reference were placed in the calorimeter, after which the chamber was purged for 20 min with pure CO. The CO was purified by passing it successively through silicagel–potassium hydroxide-R 3-11 catalyst (BASF) at 120° C–silicagel and finally phosphorous pentoxide. The DSC pans were of Aluminium (Dupont 900656).

Since the weights of the samples were small an empty Aluminium pan was used as a reference.

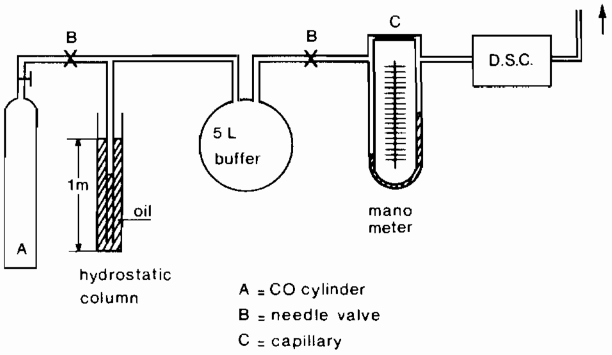

Figure 1. Gas flow system.

During the measurements the CO gas flow should be very well controlled. Therefore, a gas flow system as shown in Fig. 1 was used.

The choice of the capillary C allowed gas flows of 0.5–10 l/hr.

The DSC peak area is a measure of the enthalpy of reaction[17]. Calibration by melting In afforded the enthalpy in terms of energy units (kcal). The areas were measured with a Hewlett–Packard digitizer (9864 A) in combination with the Hewlett–Packard calculator (type 9810 A).

Determination of the Heat Capacity at Constant Pressure

All Cp measurements were performed in a N_2 atmosphere with a controlled gas flow of 2 l/hr in temperature ranges of 20° C where the samples showed no decomposition or phase changes. The Cp values at higher temperatures were derived by assuming a linear dependence of Cp on temperature.

When the experiment was started, it was essential to have a good linear isothermal baseline. The commercial cooling accessory (Dupont 990135) had to be adapted* to work isothermally to –100° C (see Figure 2).

Thermogravimetric Measurements

Meaningful reaction enthalpies are only obtained when the initial and final compound(s) are well defined.

To this end a Thermobalance (Mettler type 1) was used in combination with a gas chromatograph (Perkin Elmer, F30), which was fitted with a heating valve (no. 3920) with a loop of 10 cm^3. A column of Poropak (Waters Associates Inc) was used to identify acetonitrile and a Chromosorb W (J.M. Celite Division) with 20% squalane column for identification of $W(CO)_{6-n}(CH_3CN)_n$[18]. All substitution experiments were performed in a dynamic CO atmosphere with a controlled gas flow of 5 l/hr, while the rates of temperature increase ranged from 1 to 10° C/min.

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* Developed in our laboratory by Mr. H.J. van Ballegoy, Mr. P.C. van Ommen and his coworkers.

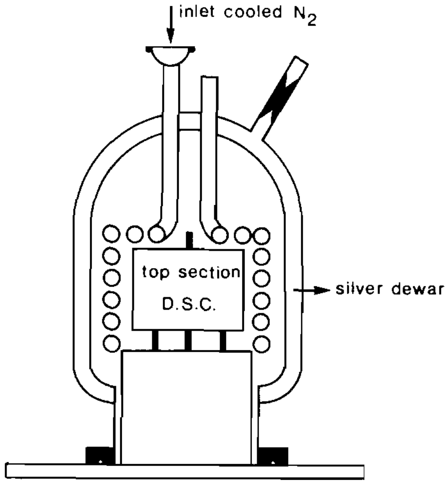

Figure 2. Cooling accessory DSC.

Vapour Pressure Measurements

Vapour pressures were measured under equilibrium conditions with an automatic apparatus developed in this laboratory[19]. A small amount of $W(CO)_{6-n}(CH_3CN)_n$ was introduced at 0° C into the sample section of the isoteniscope with exclusion of oxygen. Owing to the thermoinstability, the normal procedure of degassing[20] could not be used. Instead, a slow stream of very pure argon was passed during 48 hr at 0° C through the sample inside the isoteniscope. Thereafter the sample was cooled to the starting temperature and evacuated twice for five min. At −196° C the sample section was again evacuated and sealed off.

Spectra

IR spectra were recorded on Beckman IR-7 and IR-12 spectrophotometers.

Analysis

The C and H analyses were carried out in this Laboratory.

Results and Discussion

The thermobalance results show that under isobaric conditions the following substitution reactions proceed quantitatively:

$$W(CO)_{6-n}(CH_3CN)_n + nCO \rightarrow W(CO)_6 + n(CH_3CN)$$

$\Delta H_r(n)$ = enthalpy of reaction
$n = 1,2,3$

The products were identified by IR and gas chromatography. From the thermogravimetric curves and their derivatives it was deduced that only one reaction step could be observed. The DSC curves are given in Figure 3.

The form of the curve in Fig. 3A is remarkable in view of the thermogravimetric results, as in the shaded temperature ranges the IR spectra indicate the presence of only the starting compound and $W(CO)_6$. The presence of the five-coordinate intermediate $W(CO)_5$[21] in the decomposition of $W(CO)_5(CH_3CN)$ might be the reason for the shape of the curve in Figure 3A.

The enthalpies of reaction were obtained by comparing the shaded areas with the calibration areas for the melting of In[15]. No correction was made for the nonlinearity of the base line[22], since the method given in the reference is only applicable over small temperature ranges. The results are given in Table I.

The heat capacities Cp, which were obtained by linear extrapolation, are given in Table II (*N.B.* Some irregularity was observed with relation to the additivity relation of Cp and molar weight). They were used for the calculation of the values of Table I. Since the corrections from reaction temperature to standard conditions (25° C) are only small, the irregularity of C_p had little influence.

Combination of the sublimation energy data, obtained from vapour pressure measurements as a function of temperature (Table III) with the $\Delta H^\circ_r(n)$ values and the known ΔH°_f values for $W(CO)_6$[23], CO[23] and CH_3CN[24] afforded the values for $\Delta^g H^\circ_f(n)$, which are recorded in Table IV.

It is concluded that the thermodynamic stability of the substituted compounds is less than that of $W(CO)_6$[1,3]. This is mainly caused by the difference in the heats of formation of CO and CH_3CN. A difference of 47.1 kcal/mmol would be expected for the substitution of a CH_3CN by a CO group. This emerges from Table IV, which shows, in the column "stabilization energies", that the substitution of CH_3CN by CO and *vice versa* should be fairly easy, from a thermodynamic point of view, in the series $W(CO)_{6-n}(CH_3CN)_n$ ($n = 1,2,3$). This is experimentally borne out by the observed disproportionation reactions[25] and the difficulties encountered in obtaining pure members of the series. These experimental observations further indicate that the activation energies for the substitution reactions are also approximately the same. The relative stabilities are reflected in the DSC curves of Figures 3B and 3C. Comparison with Figure 3A is difficult, as a different heating rate had to be used.

The principal aim of these studies is to determine metal–ligand bond energies in dependence of the electronic state of the metal, the coordination number and the type of ligand.

Therefore the tungsten–acetonitrile bond energy was calculated from the equation:

$$-n\Delta^g H(W\text{–}CH_3CN) = \Delta^g H^\circ_f(W(CO)_{6-n}(CH_3CN)_n - \Delta^g H^\circ_f(W(CO)_{6-n}) - n^g\Delta H^\circ_f(CH_3CN)$$

$(n = 1,2,3)$

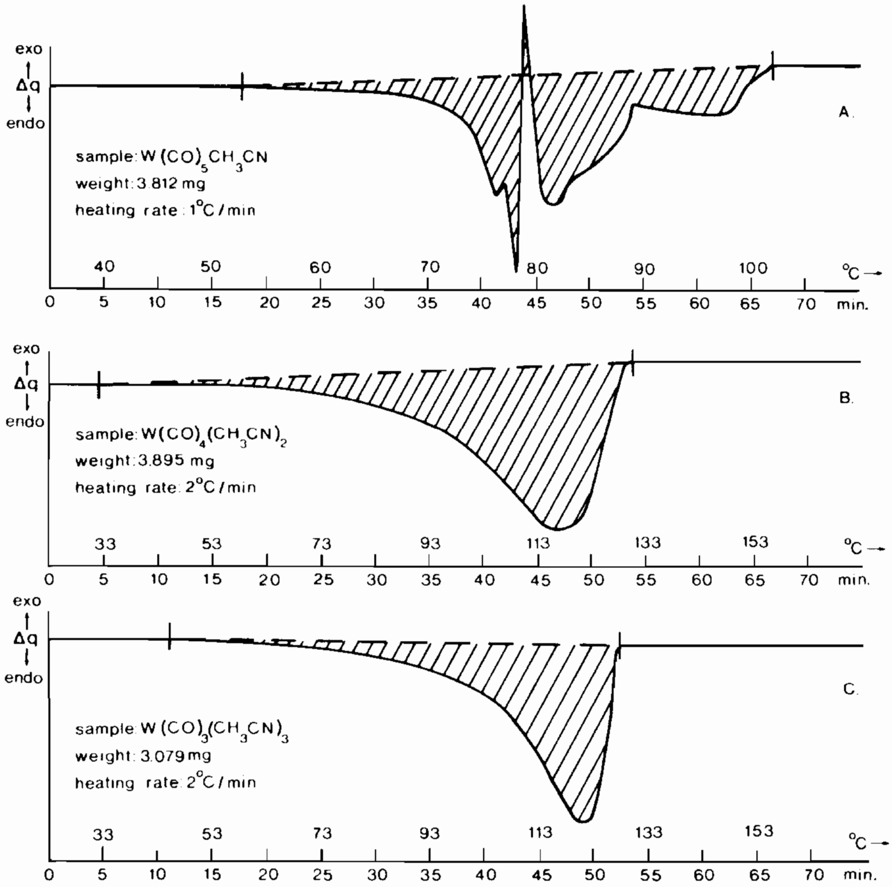

Figure 3. DSC curve for CO substitution in $W(CO)_{6-n}(CH_3CN)_n$. Dynamic CO atmosphere, gasflow 2 l/h.

TABLE I. Standard Enthalpies of Formation of $W(CO)_{6-n}(CH_3CN)_n$ (kcal/mol).

Compound	n[b]	$\Delta H_r(n)$[c]	$\Delta H^\circ_r(n)$[d]	s[e]	$\Delta^s H^\circ_f(n)$[f]	$\Delta^g H^\circ_f(n)$[g]
$W(CO)_5(CH_3CN)$	14	16.9	16.9	0.6	–179.4	–167.9
cis-$W(CO)_4(CH_3CN)_2$	15	17.8	17.3	0.9	–132.7	–119.0
cis-$W(CO)_3(CH_3CN)_3$	13	17.3	17.4	1.2	–85.7	–75.2
$W(CO)_6$[a]		0	0	–	–227.3	–209.6

[a] See ref. 1. [b] n = number of experiments. [c] $\Delta H_r(n)$ = measured enthalpy of the substitution reaction. [d] $\Delta H^\circ_r(n)$ = as c, but at standard conditions (25° C). [e] s = standard deviation, defined as a = $\sqrt{\sum_i \Delta_i^2/(n-1)}$, where Δ_i is the deviation from the mean. [f] $\Delta^s H^\circ_f(n)$ = standard enthalpy of formation for the solid state. [g] $\Delta^g H^\circ_f(n)$ = standard enthalpy of formation for the gaseous state.

The values $\Delta^g H^\circ_f(W(CO)_{6-n})$ are unknown for n = 1,2,3, while the standard enthalpy of formation is known for $W(CO)_6$[1,3]. The standard enthalpies of formation of the radical ions $W(CO)_5^+$, $W(CO)_4^+$ and $W(CO)_3^+$, however, are known from mass spectrometric measurements[26,27] (Table V).

Knowledge of the ionization potentials would be necessary to derive the values for the neutral species $W(CO)_{6-n}$ (n = 1,2,3). Ionization potentials on these unstable species are not known, while theoretical calculations of the IP values are not reliable enough, since the bond distances in the radicals are unknown[28].

TABLE II. Approximate Heat Capacity at Constant Pressure of $W(CO)_{6-n}(CH_3CN)_n$.

Compound	Cp Equation	Temperature Range Used (° K)
$W(CO)_5(CH_3CN)$	57.2 + 0.312(T–298)	298–328
cis-$W(CO)_4(CH_3CN)_2$	74.3 + 0.118(T–298)	303–323
cis-$W(CO)_3(CH_3CN)_3$	68.9 + 0.221(T–298)	303–343
$W(CO)_6$[a]	57.9 + 0.063(T–298)	

[a] See ref.[23].

TABLE III. Enthalpy of Sublimation of $W(CO)_{6-n}(CH_3CN)_n$.

Compound	ΔH Sublimation (kcal/mol)	Temp. Range ° K
$W(CO)_5(CH_3CN)$	11.5	228–279
cis-$W(CO)_4(CH_3CN)_2$	13.7	257–296
cis-$W(CO)_3(CH_3CN)_3$	10.5	228–266
$W(CO)_6$[a]	17.7	315–373

[a] See ref.[34].

TABLE IV. Values for $\Delta^g H^\circ_f$ (kcal/mol) for $W(CO)_{6-n}(CH_3CN)_n$ (n = 1,2,3).

Compound	$\Delta^g H^\circ_f$ (cald)[a]	$\Delta^g H^\circ_f$ (experimental)	"Stabilization" Energy
$W(CO)_5(CH_3CN)$	–162.5	–167.9	–5.4
$W(CO)_4(CH_3CN)_2$	–120.8	–119.0	+1.8
$W(CO)_3(CH_3CN)_3$	–71.9	–75.2	–3.3
$W(CO)_6$	–209.6	–209.6	–

[a] Calculated by substraction for each substitution of a value of 47.1 kcal/mol (= difference in ΔH°_f of CO and CH_3CN).

TABLE V. Standard Enthalpies of Formation of $W(CO)_{6-n}^+$ and $W(CO)_{6-n}$ (n = 0,1,2,3) (kcal/mol).

Radical Species	$\Delta^g H^\circ_f$	Ref.	Neutral Species	$\Delta^g H^\circ_f$ Neutral Species
$W(CO)_6^+$	–20.9	1,30	$W(CO)_6$[a]	–209.6
$W(CO)_5^+$	+46	26	$W(CO)_5$	–142.6
$W(CO)_4^+$	+117	26	$W(CO)_4$	–71.6
$W(CO)_3^+$	+184	26	$W(CO)_3$	–4.6

[a] IP $W(CO)_6$ = 8.18 eV[30] = 188.6 kcal/mol.

TABLE VI. Mean Bond Energy (kcal/mol) W–CH_3CN in $W(CO)_{6-n}(CH_3CN)_n$ (n = 1,2,3).

Mean Bond Energy	$W(CO)_5$ (CH_3CN)	$W(CO)_4$ $(CH_3CN)_2$	$W(CO)_3$ $(CH_3CN)_3$
W–CH_3CN	–46.0	–44.4	–44.2

It was therefore decided to use the suggestions of Junk and Svec[29], who concluded that the trend observed for bond energies of ionic species correlates well with the bond energies of neutral species. Thus, if the IP value of $W(CO)_6$ (well known from photoionization measurements[30] and photoelectron spectra[31,32]) can also be used for the species $W(CO)_{6-n}$, the $\Delta^g H^\circ_f$ values for the neutral $W(CO)_{6-n}$ species can be approximated (Table V). Furthermore, if as usual[10,33] one neglects the energy difference between the $W(CO)_{6-n}$ species and the $W(CO)_{6-n}$ group in the molecule $W(CO)_{6-n}(CH_3CN)_n$ one may derive the tungsten–acetonitrile bond energy values (Table VI).

These values of about 44–46 kcal/mol are remarkably constant in the series and appear therefore to be almost independent of the degree of substitution for n = 1,2 and 3. As very few other bond energy data for tungsten compounds are known, few comparions can as yet be made. It is, however, clear that the tungsten–acetonitrile bond is as strong as or only slightly stronger than the W–CO bond, which seems at first sight surprising in view of the great difference in both σ- and π-bonding tendencies of the CO and the CH_3CN groups.

Further discussions of these aspects will be left to the following report in this series dealing with the thermochemical and vibrational data for the analogous Cr- and Mo compounds, which will be compared with those of the W compounds.

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