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THERMAL DEGRADATION OF TRANSITION METAL CARBONYL COMPLEXES. PART II:

Thermogravimetry and Differential Scanning Calorimetry of Monosubstituted Pyridine Carbonyls of Chromium, Molybdenum and Tungsten

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The thermal degradation of three monosubstituted hexacarbonyl complexes, $M(CO)_5py$ (where M = Cr, Mo, and W; py = pyridine) has been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) and their results reported. It was found that for each of the three complexes studied, the starting material $M(CO)_6$ was formed which immediately sublimed unchanged with or without concomitant loss of carbonyl (CO) ligands to give the first large weight loss step. This was closely followed by the volatilisation of the pyridine ligands and at higher temperatures the loss of further CO ligands. The enthalpy changes associated with the above-mentioned steps are reported. The conversion of $M(CO)_5py$ to $M(CO)_6$ and other products was confirmed by the analysis of residue after pyrolysis in a tube furnace under conditions similar to those observed in TG experiments.

The field of organometallic chemistry has grown very rapidly in the last two decades. This is largely due to the increasingly important roles of these compounds, particularly metal carbonyl complexes, in homogeneous and heterogeneous catalysis [1–3], thermal and photochemical polymerization reactions [4–6], and selective organic syntheses with low energy input requirements [7–8]. Many of these metal carbonyl complexes contain phosphorus and amine ligands which can greatly influence the rate and product of the reactions.

Dissociation of a two electron ligand from eighteen electron species leading to sixteen electron intermediates plays a very important role in organometallic compounds. Therefore, the knowledge on the thermal stabilities of the metal

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carbonyl and other metal-ligand bonds is very crucial to the understanding of their roles in the above-mentioned applications. Despite its importance, studies on the thermal decomposition mechanism of metal carbonyls are lacking, especially in the solid state.

So far only a small number of thermal degradation pathways of metal carbonyls in the solid state has been studied. One such study is the thermogravimetry–mass spectrometry analysis (TG–MS) of mono- and polynuclear metal carbonyls [9]. A more recent study involving thermogravimetry (TG) and differential scanning calorimetry (DSC) on the $M(CO)_5dppm$ system where M = Cr, Mo, and W; and dppm = bis-(diphenylphosphino)-methane) has been carried out by Chan and Hor [10].

The investigation of the thermal behaviour of the $M(CO)_5py$ (where M = Cr, Mo, W, and py = pyridine) by TG and DSC in the present work is an extension of the work initiated in this laboratory. The decomposition mechanism of the complexes will be discussed based on the weight loss, rate of weight loss and enthalpy changes. Whenever possible, comparison with past work, including those in solution, will be made.

Experimental

Chemicals and reagents

Solvents were reagent grade and degassed before the reactions were allowed to proceed. $M(CO)_6$ where M = Cr, Mo, and W were purchased from Alfa Products Co. while pyridine was obtained from Merck Schushandt Chem. Co. Trimethylamine-N-oxide dihydrate (TMNO) was purchased from Aldrich Chem. Co. and Tokyo Kasai Kogyo Co. They were used without further purification. The syntheses of the complexes $M(Co)_5py$ was reported in the literature but the methods.have been modified in the present work.

General procedure

All reactions were carried out under dry nitrogen unless otherwise stated. Proton NMR spectra were recorded either on a Joel FX 90Q or a Perkin–Elmer R32 NMR spectrometer at 90 MHz using $Si(CH_3)_4$ as internal standard. The samples were run in deuterated chloroform. Infrared spectra were run on a Unicam SP1000 spectrophotometer as solution or Nujol mull. Melting points were determined by a Thomas Hoover Capillary Melting Point apparatus and were uncalibrated. Spectroscopic data are given in Table 1. Elemental analyses wewe carried out by the

Table 1 Spectroscopic data of $M(CO)_5L$ prepared

Compounds	Solution IR, cm^{-1}		Ref.	^{1}H-nmr Chem. shift, ppm
	expt. values	lit. values		
A. $Cr(CO)_5py$	2080w	2073w		8.59(d)
	1980w	1987w	15	7.68(t)
	1940vs	1944vs		7.23(t)
	1900m(sh)	1890m(sh)		
B. $Mo(CO)_5py$	2080vw	2079w		8.66(d)
	1990w	1987m	15	7.78(t)
	1945vs	1944vs		7.28(t)
	1910m(sh)	1890m(sh)		
C. $W(CO)_5py$	2078w	2076w		8.83(d)
	1933w	1980m	15	7.81(t)
	1902m	1933vs		7.27(t)
		1895m(sh)		

Table 2 Physical properties of $M(CO)_5L$ prepared

Compounds	Colour	Yield, %	Melting point, °C			Ref.
			lit.	found	DSC	
A. $Cr(CO)_5py$	yellow	45	95–96	95–96	98	12
B. $Mo(CO)_5py$	yellow	42	83–84	84–86	86	13
C. $W(CO)_5py$	bright yellow	52	114	115–117	111	14

Microanalytical Laboratory in the Department. The physical properties of the complexes are summarized in Table 2.

Thermal analysis

All TG experiments were conducted on a DuPont 9900 Thermal Analyser in nitrogen. The nitrogen flow was at 75 cc/min. The samples were heated from room temperature to 1000 °C at the rate of 10 °C/min. DSC experiments were also carried out on a DuPont 9900 Thermal Analyser calibrated to have a cell constant of 1.19. Nitrogen flow was at 50 cm^3/min and temperature range was from room temperature to 600°. The heating rate employed here was also 10 deg/min. The enthalpy values were generated by computer with indium as the reference.

To support the evidence provided by TG and DSC experiments, analyses of the residues were carried out in a Carbolite electric tube furnace. The complexes were heated to a certain desired temperature and the intermediate products formed were analysed using solution and Nujol mull IR. Experimental conditions were kept as close as possible to those employed in TG and DSC. Heating rate was approximately 10 deg/min and the nitrogen flow was at 50–75 cm^3/min.

Reactions

$Cr(CO)_5py$ (A)

$Cr(CO)_6$ (0.5006 g, 2.27 mmoles) and TMNO (0.2627 g, 2.37 mmoles) were added to tetrahydrofuran (THF) (30 ml) with stirring. A yellow solution was observed. Addition of excess pyridine (0.2 ml) turned the solution into cloudy brown colour. After 2 hours of stirring, the resulting yellow solution was evaporated to dryness under reduced pressure. The yellow solid so obtained was dissolved in minimum amount of dichloromethane (CH_2Cl_2). The solution was filtered and hexane was added. The mixture was reduced in volume at the vacuum pump to produce yellow microcrystals. Further recrystallization was carried out in CH_2Cl_2/hexane. Yield: 0.28 g (45%). Melting point: obsd. 92–94 °C; lit. 95.5–96.5 °C [12]. Elemental analysis, found: C, 44.19; H, 1.59; N, 5.11; calcd.: C, 44.3; H, 1.86; N, 5.17.

$Mo(CO)_5py$ (B)

Addition of $Mo(CO)_6$ (0.4996 g, 1.89 mmoles) and TMNO (0.2103 g, 1.90 mmoles) to THF (30 ml) produced a clear yellow solution. Upon addition of excess pyridine (0.4 ml), the solution turned cloudy. After 3 hours of stirring, the solvent was evaporated off under pressure leaving behind a yellow residue. The solid was redissolved in CH_2Cl_2, followed by addition of hexane. Yellow microcrystals were formed when the volume of the mixture was reduced at the vacuum pump. Recrystallization was carried out in CH_2Cl_2/hexane. The microcrystals isolated were bright yellow. Yield: 0.25 g (42%). Melting point: obsd. 84–85 °C; lit. 83–84 °C [13]. Elemental analysis, found: C, 38.78; H, 1.54; N, 4.50; calcd.: C, 38.12; H, 1.6; N, 4.44.

$W(CO)_5py$ (C)

$W(CO)_6$ (0.4976 g, 1.41 mmoles) and TMNO (0.1609 g, 1.50 mmoles) were added to 30 ml of THF. The resultant yellow solution changed to orange when excess pyridine (0.4 ml) was introduced to the mixture. After 2.5 hours of stirring, a clear yellow solution was observed. The solvent was then evaporated to dryness under reduced pressure. CH_2Cl_2 was added to the dissolved resultant yellow solid which was followed by the addition of hexane. The precipitated solid was recrystallized from CH_2Cl_2/hexane to produce bright yellow microcrystals. Yield: 0.52 g (52%). Melting point: obsd. 115–117°; lit. 114° [11]. Elemental analysis, found: C, 29.7; H, 1.09; N, 3.57; calcd.: C, 29.8; H, 1.25; N, 3.48.

Results and discussion

(i) Thermal analysis

All three samples of $M(CO)_5py$ show similar TG curves. Weight losses occur at two main steps, both below 250°. The first very steep step shows a large percentage weight loss (values for complex A, B and C are 50, 38, and 48%, respectively). The second stage registers a smaller weight loss. The large percentage weight loss in the first step could not be accounted for if only simple cleavage of ligand or CO were considered as these would have constituted much smaller weight loss. In an attempt to explain the TG and DSC results, the following mechanism is proposed prior to reactions responsible for the large weight loss observed.

$$2M(CO)_5py \rightarrow M(CO)_6 + M(CO)_4(py)_2$$

Since $M(CO)_6$ are known to have high vapour pressure [17], they are likely to undergo either sublimation or simple volatilisation during the subsequent thermal process. This is confirmed by the weight loss curve for $Mo(CO)_6$ in Fig. 1 which

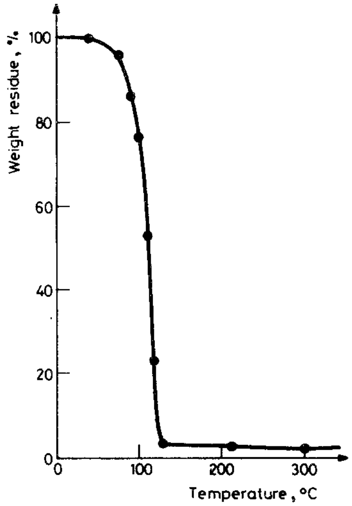

Fig. 1 TG curve of $Mo(CO)_6$ in nitrogen

shows a sharp one step loss starting at about 70°. The following calculations and interpretations of DSC and TG results are based on the stoichiometry of the overall reaction as shown above.

$Cr(CO)_5py$ (A)

TG—In Fig. 2, the weight loss at about 90 °C corresponds to the overlapping expulsion of one equivalent mole of $Cr(CO)_6$ and two equivalent moles of CO (obsd. 49.9%, calcd. 50.8%, at a rate of 22% min^{-1}). Another weight loss starts at about 145 °C which may be due to the elimination of two moles of pyridine (obsd. 29.6%, calcd. 29.3%, at a rate of 18% min^{-1}). A further loss of one equivalent mole of CO is registered at about 205 °C (obsd. 4.9%, calcd. 5.2%, at a rate of 1.5% min^{-1}). The percentage of the residue at 900 °C corresponds to Cr(CO) (obsd. 15.2%, calcd. 14.9%).

DSC—The sharp endothermic peak at 90 °C in Fig. 3 is made up of three overlapping reactions, i.e., the melting of complex (A), evolution of two moles of

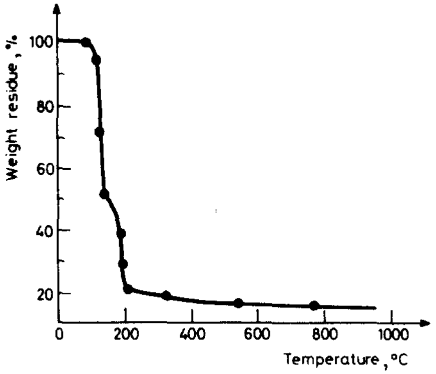

Fig. 2 TG curve of $Cr(CO)_5py$ in nitrogen

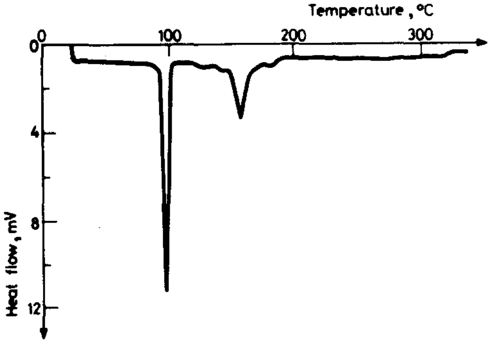

Fig. 3 DSC curve of $Cr(CO)_5py$ in nitrogen

CO and sublimation of $Cr(CO)_6$. The energy required is 24.9 kJ mol^{-1}. The endothermic peak at about 150 °C indicates that the elimination of two moles of pyridine is accompanied by the release of 18.1 kJ mol^{-1}. The small endothermic peak at around 175 °C may be attributed to the loss of one CO ligand.

$$2Cr(CO)_5py \xrightarrow{90\text{–}145^\circ} Cr(CO)_6 + [Cr(CO)_2(py)_2] + 2CO \qquad \Delta H = 24.9 \text{ kJ mol}^{-1}$$

$$[Cr(CO)_2(py)_2] \xrightarrow{150\text{–}200^\circ} [Cr(CO)_2] + 2py \qquad \Delta H = 18.1 \text{ kJ mol}^{-1}$$

$$[Cr(CO)_2] \xrightarrow{200\text{–}400^\circ} [Cr(CO)] + CO$$

$Mo(CO)_5py$ (B)

TG—In Fig. 4 the weight loss equivalent to the sublimation of $Mo(CO)_6$ is shown to occur at about 70° (obsd. 39.2%, calcd. 41.9%, at a rate of 25% min^{-1}). The next step of weight loss at about 110° indicates the concurrent loss of one mole of CO and two moles pyridine (obsd. 31.6%, calcd. 29.4%, at a rate of 10% min^{-1}). It is difficult to determine the sequence of the breakdown from the TG curve. Following that, a weight loss of 3.9% is observed between 160–300° which can be attributed to the expulsion of another CO (calcd. 4.4%). The percentage of the residue at about 700° corresponds to $Mo(CO)_2$ (obsd. 24.4%, calcd. 24.1%) which decomposes further at 800°.

DSC—Figure 5 indicates a sharp endothermic peak at 86° which corresponds to the melting point of complex (B) with the enthalpy of 8.1 kJ mol^{-1}. The exothermic peak immediately after that at about 88° could indicate the solidification of the

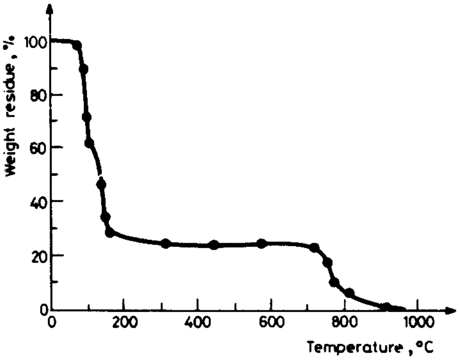

Fig. 4 TG curve of $Mo(CO)_5py$ in nitrogen

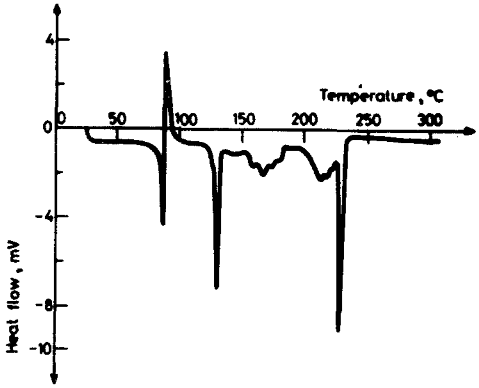

Fig. 5 DSC curve of $Mo(CO)_5py$ in nitrogen

intermediate product formed. Another sharp endothermic peak at about 130° may be responsible for either the sublimation or melting of the intermediate compound. The enthalpies for the solidification and sublimation are -10.3 and 15.6 kJ mol^{-1}, respectively. The overlapping decomposition of one mole of CO and two moles of pyridine and the evolution of another CO at a higher temperature correspond to the next two endothermic peaks at 150° and 200° with combined enthalpies of 30.5 kJ mol^{-1}. The sharp endothermic peak at about 230° may be due to expulsion of a CO ligand.

$$2Mo(CO)_5py \xrightarrow{70\text{–}110^\circ} Mo(CO)_6 + Mo(CO)_4(py)_2$$

$$Mo(CO)_4(py)_2 \xrightarrow{110\text{–}160^\circ} [Mo(CO)_3] + CO + 2py$$

$$\Delta H = 30.5 \text{ kJ mol}^{-1}$$

$$[Mo(CO)_3] \xrightarrow{160\text{–}300^\circ} [Mo(CO)_2] + CO$$

$W(CO)_5py$ (C)

TG—At about 100° in Fig. 6, a weight loss corresponding to the simultaneous elimination of one equivalent mole of $W(CO)_6$ and one CO ligand are observed (obsd. 46.1%, calcd. 46.9%, at a rate of 27% min^{-1}). The next weight loss at about 150° can be attributed to the overlapping eliminations of two equivalent moles of CO and two moles of pyridine (obsd. 26.2%, calcd. 26.7%, at a rate of 10% min^{-1}). The percentage of the residue at 300° corresponds to W(CO) (obsd. 27.0%, calcd. 26.3%) with no further expulsion of CO ligand.

DSC—The endothermic peak at about 110° (Fig. 7) is probably due to the

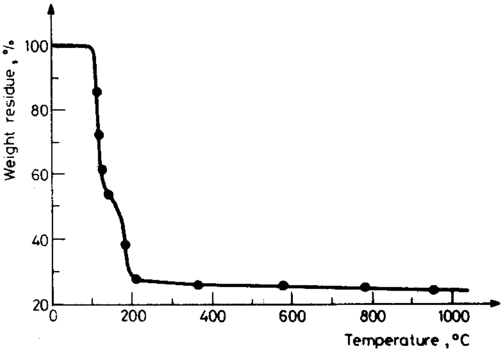

Fig. 6 TG curve of $W(CO)_5py$ in nitrogen

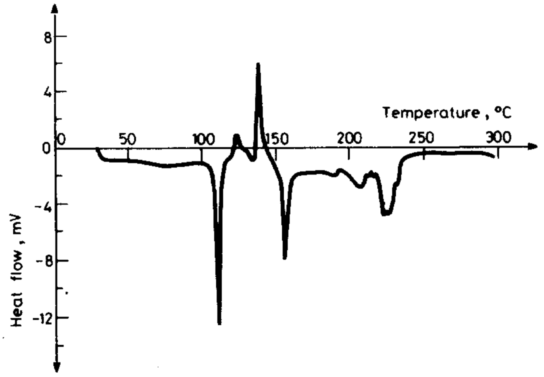

Fig. 7 DSC curve of $W(CO)_5py$ in nitrogen

overlapping reactions involving the melting of complex (C) with simultaneous evolution of $W(CO)_6$ and CO. The enthalpy involved in these reactions is 22.6 kJ mol^{-1}. The existence of two exothermic peaks at about 120° and 140° following that could be due to the solidifications of $W(CO)_6$ and $W(CO)_4(py)_2$ formed. The two remaining endothermic peaks at about 160° and 230° correspond to the losses of two moles each of CO and pyridine with the combine enthalpies of 41.5 kJ mol^{-1}.

$$2W(CO)_5py \xrightarrow{100\text{–}145^\circ} W(CO)_6 + [W(CO)_3(py)_2] + CO$$

$$\Delta H = 22.6 \text{ kJ mol}^{-1}.$$

$$[W(CO)_3(py)_2] \xrightarrow{150\text{–}215^\circ} [W(CO)] + 2CO + 2py$$

$$\Delta H = 41.5 \text{ kJ mol}^{-1}.$$

ii) Tube furnace experiment

Further studies were carried out to verify the validity of the mechanism proposed to explain the TG and DSC results. Heating of complex (C) in flowing dry nitrogen in a Carbolite electric furnace to 125° over a period of an hour was carried out. The weight loss registered was 46%. Solution and Nujol mull of the residue (Fig. 8) indicated that there were absorptions bands at 1905(m) cm^{-1}, 1870(vs) cm^{-1}, 1830(s) cm^{-1}, 1820(s) cm^{-1} and 1790(m) cm^{-1} which indicated the presence of a mixture of $W(CO)_4(py)_2$ and $W(CO)_3(py)_3$ [15]. Residue of complex (B) was obtained in a similar fashion at 40% weight loss. IR analysis indicated absorption peaks at 1916(m) cm^{-1}, 1881(vs) cm^{-1} and 1838(s) cm^{-1} (Fig. 9) which showed the presence of $Mo(CO)_4(py)_2$ [15]. When heated in a small round bottom flask over an oil bath in a slow stream of flowing nitrogen, complex (B) was observed to melt but immediately solidified to give a brown solid which subsequently sublimed during the heating as a white solid at the top of the flask. Solution IR (Fig. 10) showed a strong absorption band at 1990 cm^{-1} suggesting that the white solid was $Mo(CO)_6$ [18]. The above physical transition from liquid to solid was also observed during the determination of melting point. These observations were confirmed by

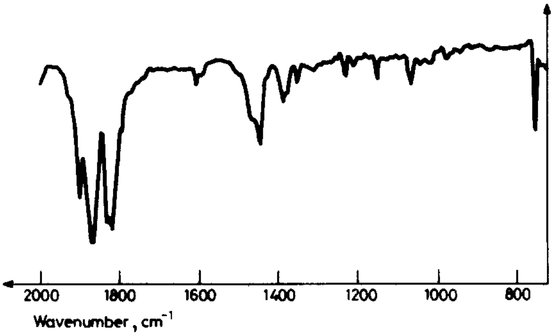

Fig. 8 IR spectrum of $W(CO)_5py$ residue at 46% weight loss

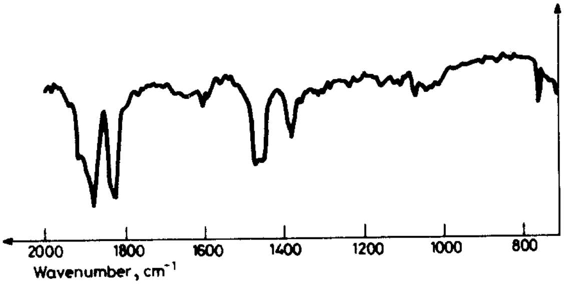

Fig. 9 IR spectrum of $Mo(CO)_5py$ residue at 45% weight loss

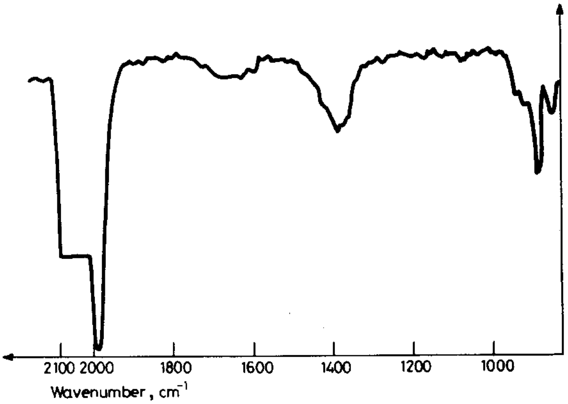

Fig. 10 IR spectrum of white sublimed solid from $Mo(CO)_5py$

the exothermic peaks in Figs 5 and 7, respectively. These observations together with the spectroscopic and DSC results strongly suggest that the sample $M(CO)_5py$ undergoes a conversion back to the starting material, $M(CO)_6$ together with other products which could be $M(CO)_4(py)_2$ and $M(CO)_3(py)_3$. The mechanism of conversion to $M(CO)_6$ is similar to what was found by Darensburg and Brown [16]. They reported that the thermal decomposition of $Mo(CO)_5L$ (L = py and piperidine) in hexane proceeds via a rate determining dissociation step resulting in the highly reactive $[Mo(CO)_5]$ which would then react with another mole of $Mo(CO)_5L$.

$$Mo(CO)_5L \xrightarrow{\text{SLOW}} [Mo(CO)_5] + L$$

$$Mo(CO)_5L + [Mo(CO)_5] \xrightarrow{\text{FAST}} Mo(CO)_6 + Mo(CO)_4L$$

Darensburg and Brown [16] confirmed the formation of $Mo(CO)_6$ but failed to detect $Mo(CO)_4L_2$.

All three complexes, $Cr(CO)_5py$ (A), $Mo(CO)_5py$ (B) and $W(CO)_5py$ (C) give similar TG curves with the loss of about 40–50% of the original weight in the first step. The weight loss is attributed to the sublimination or volatilization of $M(CO)_6$ (where M = Cr, Mo, W) formed with or without concomitant loss of CO. Subsequent loss of other CO and pyridine occur at a later stage. The weights of the residue at 800° correspond to $Cr(CO)$, $MO(CO)_2$ and $W(CO)$. Thermogravimetry–Mass spectrometry (TG–MS) study by Fillman and Tang [9] has shown that $M(CO)_6$ (where M = Cr, Mo, W) exhibits one step weight loss to completion which is indicative of sublimation or decompositional volatilization.

The $M(CO)_6$ were observed to start subliming or volatilizing below 100° and were completely sublimed at about 180°. This is consistent with the results obtained in the present work.

In two of the complexes (A) and (C), concomitant evolutions of CO (one or two moles) are observed in the first step below 200°. Pyridine only dissociates in the second decomposition step. This indicates that at least one CO in $M(CO)_4(py)_2$ is labile. As pyridine is a poorer π-acceptor, substitution of CO by pyridine will make the CO trans to pyridine experience greater backbonding and strengthen the M–CO bond resulting in the labilization of the remaining CO groups.

Another factor that contributes to the labilization of CO is attributed to the difference in relative "hardness" of the CO and pyridine bases. Pyridine, being a relative "harder" base is known to increase the lability of the remaining CO groups [19] while relative "softer" base like CO appear to have no such effect. The labilization is judged to be due to the stabilization of the transition state in the CO dissociation step by the hard base.

The weight of the residues show that at least one CO is still attach to M (where M = Cr, Mo, W) despite the fact that they are unstable carbonyl complexes. The percentage weight of the residues at 800 °C correspond to Cr(CO), $Mo(CO)_2$ and W(CO). The first two are consistent with the findings in the thermal degradation of $M(CO)_5$dppm [10] where M = Cr, Mo, and W and dppm = bis-(diphenylphosphine)-methane.

The existence of such highly unsaturated species (Cr(CO), Mo(CO), W(CO)), which are highly unstable and reactive, in our experimental condition is far from certain. It is possible that polymeric species such as $[Cr(CO)]_n$ or even some oxo species are formed. Nevertheless, our experimental findings strongly suggested that complete depletion of carbonyl ligand did not occur in all three cases.

References

1 M. J. Workulich and J. D. Atwood, J. Organomet. Chem., 219 (1981) 53–59.

2 A. K. Smith, J. M. Basset and P. M. Maitlis, J. Mol. Catal., 2 (1977) 223.

3 W. A. Zanobi, E. Mantoni and N. Palladino, J. Mol. Catal., 3 (1977/78) 285.

4 W. Strohmeier and P. Hartman, Z. Naturforsch., 19b, 10 (1964) 65w.

5 W. Strohmeier and P. Hartman, Z. Naturforsch., 19b (10) (1964) 822–6.

6 W. Strohmeier and H. Gruebel, Z. Naturforsch., B21 (8) (1966) 807–8.

7 M. F. Farona and V. W. Motz, J. Chem. Soc., Chem. Comm., 22 (1976) 930–1.

8 V. M. Motz and M. F. Farona, Inorg. Chem., 16 (10) (1977) 2545.

9 L. M. Fillmand and S. Tang, Therm. Chim. Acta, 75 (1984) 71–84.

10 H. S. O. Chan, A. T. S. Hor, C. S. M. Chiam and T. C. Chong, Submitted for publication, J. Thermal Anal. (1986).

11 W. Strohmeier, K. Gerlach and G. Matthias, Z. Naturforsch. 15b (1960) 621–2.

12 H. Behrens and W. Klek, Z. Anorg. Allgem. Chem., 292 (1957) 151–61.
13 H. D. Murdoch and R. Henzi, J. Organomet. Chem., 2 (1963) 463–9.
14 T. A. Magee, C. N. Matthews, T. S. Wang and J. H. Wotiz, J. Am. Chem. Soc., 83 (1961) 3200–3.
15 C. S. Kraihanzel and F. A. Cotton, Inorg. Chem., 2 (1963) 533.
16 D. J. Darensbourg and T. L. Brown, Inorg. Chem., 7 (1968) 1679–80.
17 G. Wilkinson, F. G. A. Stone and E. W. Abel (eds), Comprehensive Organometallic Chemistry, Vol. 3, 1982, Pergamon Press.
18 D. J. Darensbourg and T. L. Brown, Inorg. Chem., 7 (1968) 959–66.
19 R. J. Angelici and J. R. Graham, J. Am. Chem. Soc., 87 (1965) 5586–90.

Zusammenfassung — Der thermische Abbau von drei monosubstituierten Hexacarbonylkomplexen der allgemeinen Formel $M(CO)_5py$ (mit M = Cr, Mo und W; py = Pyridin) wurden mittels TG und DSC untersucht. Von jeder der drei Komplexe wird die Ausgangssubstanz $M(CO)_6$ erhalten, die sofort unverändert mit oder ohne gleichzeitigem Verlust an Carbonyl (CO)-Liganden sublimiert und die erste große Gewichtsverluststufe ergibt. Diesem Schritt folgt gleich die Verflüchtigung des Pyridinliganden und bei höheren Temperaturen die Abgabe weiterer CO-Liganden. Die mit den genannten Schritten einhergehenden Enthalpieveränderungen werden mitgeteilt. Die Umwandlung von $M(CO)_5py$ zu $M(CO)_6$ und anderen Produkten wurden durch Analyse des Rückstandes nach der Pyrolyse in einem Röhrenofen unter ähnlichen Bedingungen wie in den TG-Versuchen bestätigt.

Резюме — Методами ТГ и ДСК изучено термическое разложение трех монозамещенных гексакарбонильных комплексов $M(CO)_5py$, где M = хром, молибден и вольфрам, а py = пиридин. Найдено, что разложение комплексов протекает с образованием исходного гексакарбонила, который сразу же сублимируется неизменным или же с сопутствующей потерей карбонильных лигандов, давая тем самым первию стадию с большой потерей веса. Близко к этой стадии происходило выделение пиридиновых лигандов, а при более высоких температурах происходило дальнейшее выделение карбонильных лигандов. Приведены изменения энтальпии для вышеупомянутых стадий. Образование гексакарбонилов металлов и других продуктов разложения было подтверждено анализом конечных продуктов пиролиза в трубчатой печи в условиях подобных таковым, как и в методе ТГ.