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THERMAL DECOMPOSITION OF METAL CARBONYLS: A THERMOGRAVIMETRY-MASS SPECTROMETRY STUDY

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ABSTRACT

A thermogravimetry-mass spectrometry study of the decompositional behavior of binary transition metal carbonyls—$M(CO)_6$ (M = Cr, Mo, W), $M_2(CO)_{10}$ (M = Mn, Re), $Fe_2(CO)_9$, $Co_2(CO)_8$, $M_3(CO)_{12}$ (M = Fe, Ru, Os), $M_4(CO)_{12}$ (M = Co, Rh, Ir), $Rh_6(CO)_{16}$—has been carried out. Although the thermogravimetry often shows an apparent continuous monotonic weight loss, the CO thermal evolution profiles as seen by the quadrupole mass spectrometer indicated that the actual decomposition may be much more complex than successive CO stripping, and in several instances relatively stable intermediates are formed.

INTRODUCTION

Transition metal carbonyls are being used in the preparation of a variety of heterogeneous catalysts [1-3]. Various approaches are possible: ligand attachment of the metal carbonyl to the support surface; metal decomposition onto the support by thermal decomposition of the metal carbonyl; or entrapment of the metal carbonyl inside the pores of the support. In all cases, thermal rearrangement of the metal carbonyl could occur, be it at the preparation, calcination, reaction, or regeneration stage of the catalyst preparation. However, in spite of its importance, knowledge of the thermal decomposition mechanisms of various metal carbonyls, mononuclear or polynuclear, is lacking. Furthermore, metal carbonyl clusters are also being considered as models for small catalyst particles or catalytic surfaces [4], and knowledge of the details of the thermal degradation pathways of the carbonyl clusters should aid in the understanding of these systems. Psaro et al. [5], recently examined several carbonyl metal clusters by thermogravimetry and IR spectroscopy. They found that although the thermogravimetric traces showed that the neutral metal carbonyl clusters appeared to decompose in a smooth monotonic one-step fashion, the infrared spectroscopy indicated in several instances the existence of discrete complex intermediates. They

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attributed this difference to a matrix isolation effect of the KBr support for the IR experiments. In order to shed some light on the question of the existences of these intermediates, we undertook a combined thermogravimetry–mass spectrometry (TG–MS) study of several series of binary transition metal carbonyls: $M(CO)_6$ (M = Cr, Mo, W), $M_2(CO)_{10}$ (M = Mn, Re), $Fe_2(CO)_9$, $Co_2(CO)_8$, $M_3(CO)_{12}$ (M = Fe, Ru, Os), $M_4(CO)_{12}$ (M = Co, Rh, Ir), $Rh_6(CO)_{16}$. Furthermore, with the TG–MS study of these metal carbonyls, we hoped to delineate the similarities and differences in the mode of thermal degradation of the transition metal carbonyls in order to suggest guidelines for the preparation of supported metal carbonyl catalysts. The results of this study are reported here.

EXPERIMENTAL

Apparatus

The thermogravimetry–mass spectrometry studies were carried out using a DuPont 951 thermogravimetric analyzer interfaced to a Balzers QMG511 quadrupole mass spectrometer. The thermogravimetric analyzer is controlled by a DuPont 1090 thermal analyzer. The pressure reduction from the atmospheric pressure of the thermogravimetric analyzer to the operating pressure of the mass spectrometer ($< 10^{-4}$ Torr) is accomplished through a 0.30-mm I.D. capillary of a Balzers GES010 non-discriminating gas inlet system. Data from the QMG511 quadrupole mass spectrometer is collected on floppy disks by a Digital PDP 11/03 minicomputer system.

Procedure

Typically, the sample (20–70 mg) was placed in the open platinum pan of the thermogravimetric analyzer and heated at 10°C min^{-1} from 30 to 525°C under a dynamic oxygen-free argon flow at atmospheric pressure and a rate of 50 ml min^{-1}. The quadrupole mass spectrometer PDP 11/03 can monitor up to ten masses in one experiment, typically examining each set of masses once every 10 s. The sets of digital data can be output on an 8-pen plotter or on a line printer following data processing (normalization, smoothing, truncation) with in-house programs.

RESULTS AND DISCUSSIONS

Thermogravimetry has traditionally been employed as a rapid technique for observing the thermal degradation or volatilization behavior of solid materials. When combined with mass spectrometry, which can identify and quantify the thermally evoluted products, it becomes an extremely powerful tool for elucidating the thermolytic degradation pathway of the material under study. The usefulness of the TG–MS technique for studies on coals, shales, and polymers has been well documented [6]. However, to our knowledge, this technique has not been applied to the study of organometallic complexes. The metal carbonyls represent the "simplest" of the organometallic complexes since the major thermal evolution species is inevitably carbon monoxide. Other common ligands, such as π-allyl, NO, carbenes, cyclopentadiene, etc., are not present. However, we have found, as a group, the neutral transition metal carbonyls studied exhibited a high degree of diversity in the manner by which the carbonyl ligands are thermally stripped from the metal centers. The carbonyl ligands may evolve all at once from some complexes, while for others, they evolve in discrete or overlapping steps. This variability points to the rich chemistry involved even in just the thermal decomposition of the simple metal carbonyls.

Table 1 collects the thermogravimetry data for the metal carbonyl complexes studied. Only three of the binary metal carbonyls ($Mn_2(CO)_{10}$, $Co_2(CO)_8$, and $Rh_4(CO)_{12}$) showed bimodal weight loss while the remaining compounds all exhibited single-step weight loss. Table 2 summarizes the

TABLE 1

Thermogravimetric analysis of transition metal carbonyl complexes

Compound	Thermogravimetry [a]			
	Weight loss midpoint (°C) [b]	Major weight loss range (°C) [c]	Observed weight loss (%)	Theoretical weight loss (%) [d]
$Cr(CO)_6$	131	50–165	99.8	76.4
$Mo(CO)_6$	140	65–175	99.8	63.7
$W(CO)_6$	146	70–173	99.8	47.8
$Mn_2(CO)_{10}$	68, 171	25–187	99.5	71.8
$Fe_2(CO)_9$	115	80–140	93.0	69.3
$Co_2(CO)_8$	90, 160	35–190	71.2	65.5
$Re_2(CO)_{10}$	190	115–207	99.9	42.9
$Fe_3(CO)_{12}$	150	30–280	41.0	66.7
$Ru_3(CO)_{12}$	215	115–305	57.8	52.6
$Os_3(CO)_{12}$	251	175–305	96.3	37.1
$Co_4(CO)_{12}$	183	110–220	58.9	58.8
$Rh_4(CO)_{12}$	127, 228	95–260	54.9	55.0
$Ir_4(CO)_{12}$	305	220–395	48.4	30.4
$Rh_6(CO)_{16}$	210	145–255	40.4	42.0

[a] Heating rate, 10° min^{-1}; argon flow.

[b] Temperature at which 50% of observed weight loss of step has occurred.

[c] Temperature range during which 99% of the observed weight loss occurred.

[d] Computed for complete evolution of CO, leaving $metal^0$.

TABLE 2
TG and QMS thermal evolution summary

Compound	Thermogravimetry	QMS
$Cr(CO)_6$	1 step with complete volatilization	Broad CO-evolution beyond volatilization point
$Mo(CO)_6$	1 step with complete volatilization	Multiple CO-loss peaks (1 major)
$W(CO)_6$	1 step with complete volatilization	Broad CO-evolution beyond volatilization point
$Mn_2(CO)_{10}$	2 step with nearly complete volatilization	Rapid CO-loss (maybe bimodal)
$Fe_2(CO)_9$	1 step with nearly complete volatilization	1 major CO-loss peak
$Co_2(CO)_8$	2 step with partial volatilization	2 distinct major CO-loss peaks
$Re_2(CO)_{10}$	1 step, complete sublimation	No CO-loss peak
$Fe_3(CO)_{12}$	1 step, less than theoretical weight loss	1 major CO-loss peak
$Ru_3(CO)_{12}$	1 step with partial volatilization	Multiple CO-loss peaks with high initial loss
$Os_3(CO)_{12}$	1 step with nearly complete volatilization	Bimodal CO-loss peak
$Co_4(CO)_{12}$	1 step to Co^0	Multiple overlapping CO-loss peaks
$Rh_4(CO)_{12}$	2 steps to Rh^0	2 distinct CO-loss peaks
$Ir_4(CO)_{12}$	1 step with partial volatilization	Trimodal CO-loss peak
$Rh_6(CO)_{16}$	1 step to Rh^0	Shoulder on 1 major CO-loss peak

information obtained from both thermogravimetry and quadrupole mass spectrometry (QMS). the results indicate that in several cases sequential CO losses can be detected by the QMS, thus implicating discrete "stable" intermediates, even though the TG showed only a smooth, monotonic decomposition.

Mononuclear—$Cr(CO)_6$*,* $Mo(CO)_6$*,* $W(CO)_6$

The thermogravimetric traces of the three Group VIB mononuclear carbonyls ($Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$) are shown in Fig. 1a while the QMS data on the carbon monoxide evolution (CO^+, *m/z* 28) of the three complexes are shown in Fig. 1b. All three compounds exhibited one-step weight loss to completion, indicative of sublimation, or rapid decomposi-

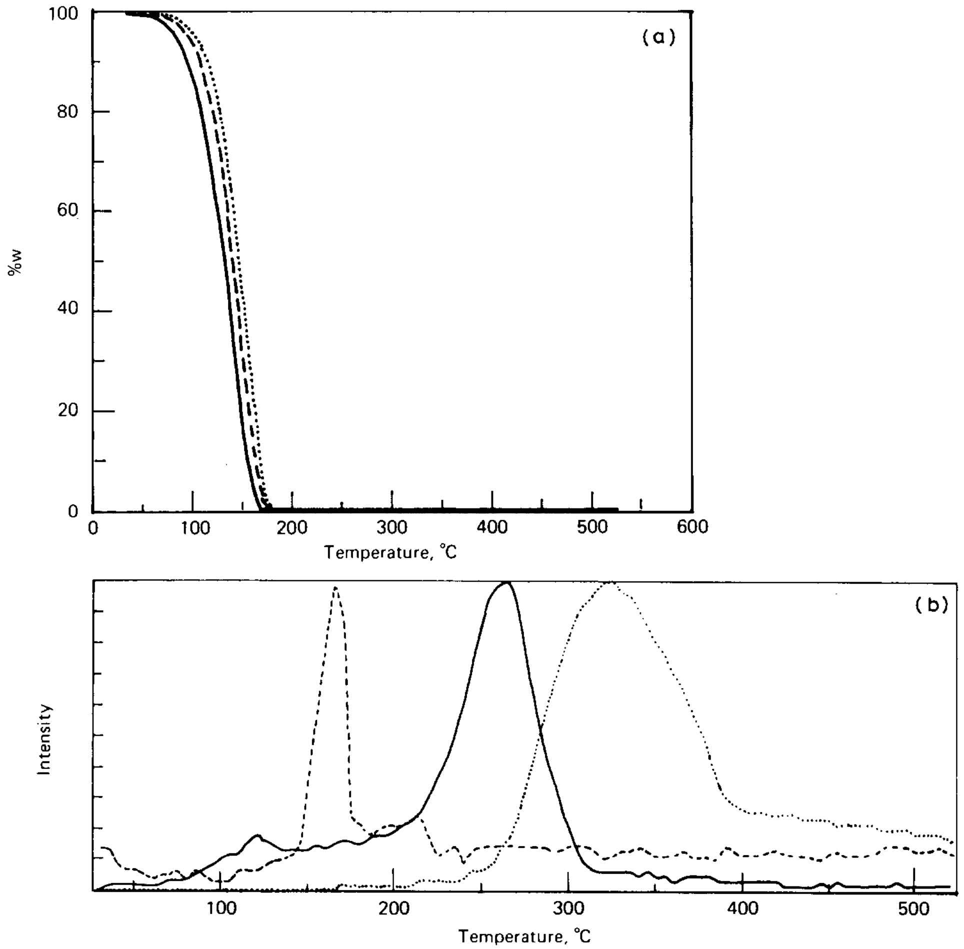

Fig. 1. (a) TG curves in argon atmosphere of $Cr(CO)_6$ (———); $Mo(CO)_6$ (- - - - - -); and $W(CO)_6$ (· · · · · ·). (b) QMS thermal evolution profiles of CO for $Cr(CO)_6$ (———); $Mo(CO)_6$ (- - - - - -); and $W(CO)_6$ (· · · · · ·).

tional volatilization. The CO evolution profiles, however, are quite different. The most stable of the three compounds, tungsten carbonyl, apparently sublimes without decomposition as indicated by the lack of CO evolution up to 180°C. However, a broad CO evolution profile was seen at a higher temperature; this can be attributed to the gaseous W(CO)$_6$ entering into the mass spectrometer and subsequently decomposing in the ionization chamber. Molybdenum carbonyl, on the other hand, decomposes during the volatilization process while chromium carbonyl shows a slight loss of CO during the volatilization process (small peak at 130°C), but the major CO evolution did not occur until the sublimation process had been completed, analogous to the tungsten carbonyl case.

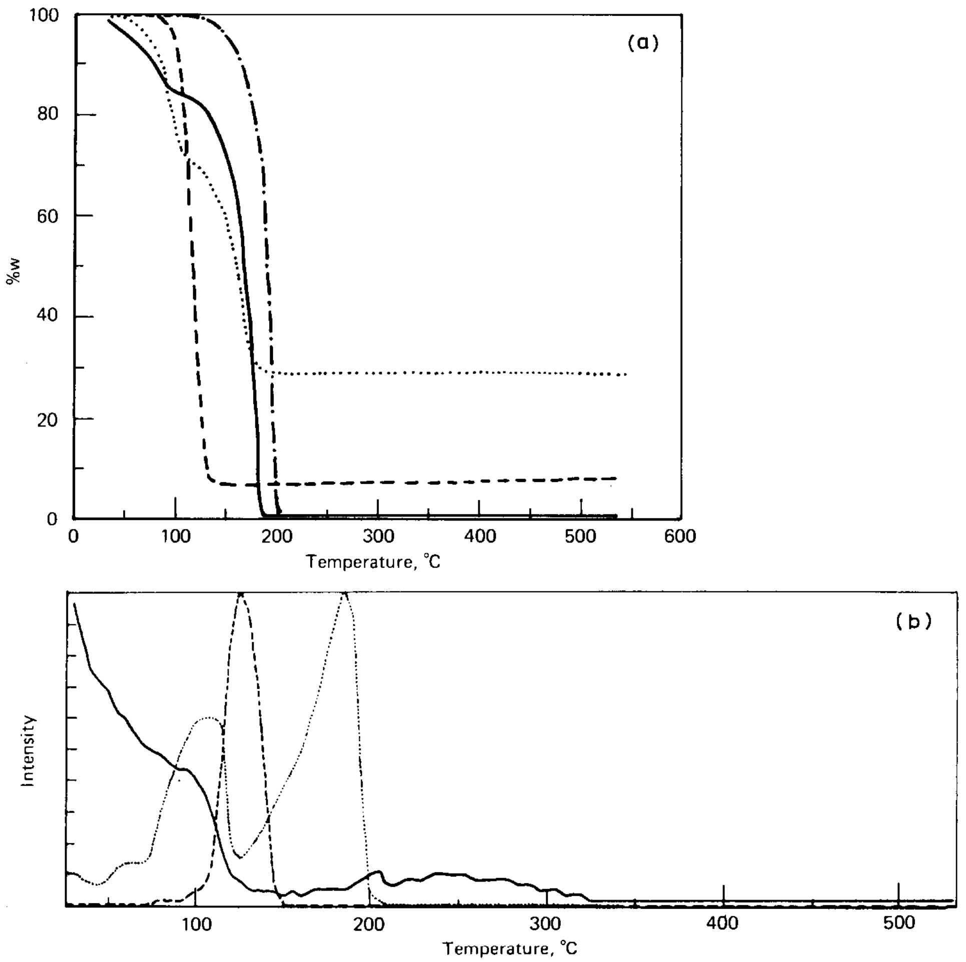

Fig. 2. (a) TG curves in argon atmosphere of Mn$_2$(CO)$_{10}$ (———); Fe$_2$(CO)$_9$ (- - - - - -); Co$_2$(CO)$_8$ (· · · · · ·); and Re$_2$(CO)$_{10}$ (–·–·–·–). (b) QMS thermal evolution profiles of CO for Mn$_2$(CO)$_{10}$ (———); Fe$_2$(CO)$_9$ (- - - - - -); and Co$_2$(CO)$_8$ (· · · · · ·).

Binuclear—$Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Re_2(CO)_{10}$

Of the four neutral binuclear metal carbonyl compounds studied, two ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$) are in Group VIIB with no bridging carbonyls, and two ($Fe_2(CO)_9$, $Co_2(CO)_8$) are in Group VIII with three and two bridging carbonyl ligands, respectively. The TG–MS traces of the four complexes are shown in Fig. 2.

In spite of having three bridging carbonyls, diiron nonacarbonyl exhibited no stable intermediate state; carbonyl evolution occurred in a single step. The small quantity of residue left (7.0%) indicated that evolution of iron-containing species occurred simultaneously with CO loss. It is well known that the thermolysis of $Fe_2(CO)_9$ in solution gives $Fe(CO)_5$ and the triplet radical $Fe(CO)_4$ [7], and the same mechanism is likely to be operative in the present case. Iron pentacarbonyl is quite volatile, thus accounting for the iron loss, and the CO evolution is likely to be due to $Fe(CO)_5$ decomposition to give $Fe(CO)_4$ plus CO and further CO-stripping.

Cobalt carbonyl exhibited two very distinct decomposition steps, both in the thermogravimetric trace and in the CO mass spectral profile. The total weight loss was greater than expected if only CO had evolved, indicating a small amount of concurrent sublimation, as expected for dicobalt octacarbonyl. Based on literature information, the intermediate likely is $Co_2(CO)_6$, since it is known from pyrolysis studies that reaction (1) readily occurs [7]. Concurrently, the saturated (18-electron) metal fragment $Co(CO)_4$ would probably have been formed from $Co_2(CO)_8$. Thus, the second large CO peak may be the decomposition of $Co_2(CO)_6$ superimposed on the sequential CO loss from $Co(CO)_4$.

$$Co_2(CO)_8 \xrightarrow{50°C} Co_2(CO)_6 + 2\ CO \qquad (1)$$

Of the two Group VIIB carbonyls, $Mn_2(CO)_{10}$ both sublimes and decomposes, while only sublimation was observed for $Re_2(CO)_{10}$. The manganese carbonyl is quite unstable, with CO loss commencing at room temperature, and with no discernible stable intermediate. The mechanism of decomposition of $Mn_2(CO)_{10}$ has been shown earlier to be homolytic fission followed by CO-loss [8]. Manganese carbonyl is also extremely hydroscopic, since it was the only compound studied in which a significant quantity of water was detected by the mass spectrometer.

Trinuclear—$Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$

The common neutral trinuclear carbonyl clusters ($Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$) are all in the iron triad, and all possess triangular cluster molecular structure. Triosmium dodecacarbonyl is isomorphous with $Ru_3(CO)_{12}$ with four CO ligands attached to each metal center, while

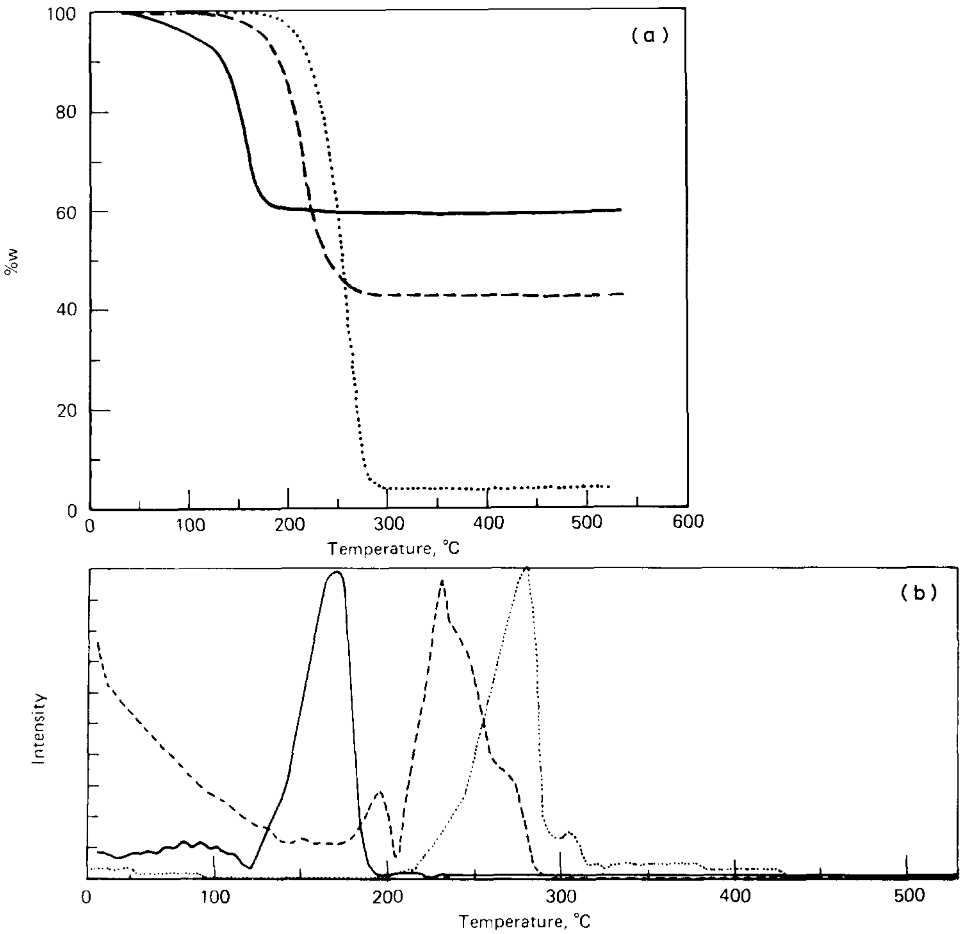

Fig. 3. (a) TG curves in argon atmosphere of $Fe_3(CO)_{12}$ (———); $Ru_3(CO)_{12}$ (- - - - - -); and $Os_3(CO)_{12}$ (· · · · · ·). (b) QMS thermal evolution profiles of CO for $Fe_3(CO)_{12}$ (———); $Ru_3(CO)_{12}$ (- - - - - -); and $Os_3(CO)_{12}$ (· · · · · ·).

$Fe_3(CO)_{12}$ has two bridging CO's between two of the three metal centers. The thermogravimetric traces of the three clusters (Fig. 3a) all showed approximate single-step weight loss centered at 150, 215, and 251°C, respectively. This increase is as expected since the strength of metal–metal bonds increases upon descending a column of the periodic table. The QMS CO evolution profiles are shown in Fig. 3b. All three compounds exhibited some initial decomposition as evidenced by the CO loss from the start of the experiment, followed by a major CO evolution. In the case of iron carbonyl, this major CO loss is a single peak, while it is a trimodal peak for ruthenium carbonyl, and a bimodal peak for osmium carbonyl.

Eady et al. [9], have found that the pyrolysis (90–114°C) of $Fe_3(CO)_{12}$ in sealed evacuated tubes led to the formation of $Fe(CO)_5$ and metallic iron.

This does not seem to be entirely the case with $Fe_3(CO)_{12}$ in an argon atmosphere. The rapid decrease in weight and the concomitant observed CO loss commencing at room temperature suggests a facile decomposition, perhaps to $Fe(CO)_5$; however, metallic iron cannot be the final product since the total weight loss is less than that expected theoretically for a decomposition to metal. Also, since no increase in weight was observed, it is unlikely that pyrophoric iron was produced and reacted with oxygen impurity as suggested by Eady et al. [9]. The alternative explanation of iron carbide and iron oxide formation from CO dissociation is more likely.

Contrary to the earlier results of Banditelli et al. [10], but in agreement with Psaro et al. [5], we found that $Ru_3(CO)_{12}$ under argon does not simply decompose to metallic ruthenium since the observed weight loss is higher than expected for straightforward complete CO loss to metal. Eady and coworkers [9] found that the pyrolysis of $Ru_3(CO)_{12}$ in a sealed evacuated tube below 180°C gave exclusively the hexanuclear carbide-cluster, $Ru_6(CO)_{17}C$, while at a higher temperature, total conversion to ruthenium metal was observed. Our data is in agreement with the formation of $Ru_6(CO)_{17}C$ from $Ru_3(CO)_{12}$ in that the CO-evolution profile indicated an initial loss of 6 CO's up to approximately 180°C. Beyond 180°C, the CO-evolution profile indicated a complicated sequence of decomposition with several intermediates. The weight loss beyond the predicted metal level is presumably due to volatilization of one of these intermediates.

With the trinuclear cluster $Os_3(CO)_{12}$, sublimation of itself or its transformation species is the major occurrence as seen from the high weight loss. Eady et al. [9], found that the pyrolysis of $Os_3(CO)_{12}$ in a sealed tube at 210°C for 12 h gave a variety of polynuclear carbonyl clusters as $Os_5(CO)_{16}$, $Os_5(CO)_{15}C$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$, $Os_8(CO)_{23}$, and $Os_8(CO)_{21}C$ with $Os_6(CO)_{18}$ (80%) being the major product. A similar occurrence is likely to be the case in the present study as surmised from the multi-terrace feature of the CO-loss profile.

For the trimetal dodecacarbonyls $M_3(CO)_{12}$ ($M = Fe$, Ru, or Os), it has been suggested that the initial degradation takes place via the ejection of a saturated (18-electron) metal fragment $M(CO)_5$, based on gas phase studies for $Fe_3(CO)_{12}$ and the disproportionation reactions to form mixed metal clusters [11]. Thus, for the case of $Fe_3(CO)_{12}$, reaction (2) initially takes

$$Fe_3(CO)_{12} \rightleftharpoons \text{“}Fe(CO)_7\text{”} + Fe(CO)_5 \qquad (2)$$

place, thus accounting for the invariable contamination of $Fe(CO)_5$ in $Fe_3(CO)_{12}$. However, the arrangement of carbonyl groups around two of the Fe atoms in $Fe_3(CO)_{12}$ (each with 3 terminal and 2 bridging = 5 CO's) renders $Fe_3(CO)_{12}$ ideally suitable for the above degradation pathway (via reaction 2), but the same is not true for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, which have no bridging carbonyls and only 4 CO's around each metal center. It is more likely that for the latter two compounds, decomposition does not involve the ejection of $M(CO)_5$ (M = Ru, Os), but rather involves the initial loss of CO, followed by subsequent aggregation (or polymerization) of the CO-poor fragments to form higher-nuclearity metal clusters. The formation of these polynuclear carbonyl clusters has been previously observed [9].

Further evidence favoring initial CO loss rather than $M(CO)_5$ ejection from $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is that the mass spectra of the two compounds exhibit all possible ions of the type $M_3(CO)_n^+$, ($n = 0$–12) [12,13], indicating that the metal–metal bonds are stronger than the metal–carbonyl bonds. The same was not found for the mass spectrum of $Fe_3(CO)_{12}$ [11,12], which indicated rupture of the iron triangle as required for the ejection of $Fe(CO)_5$.

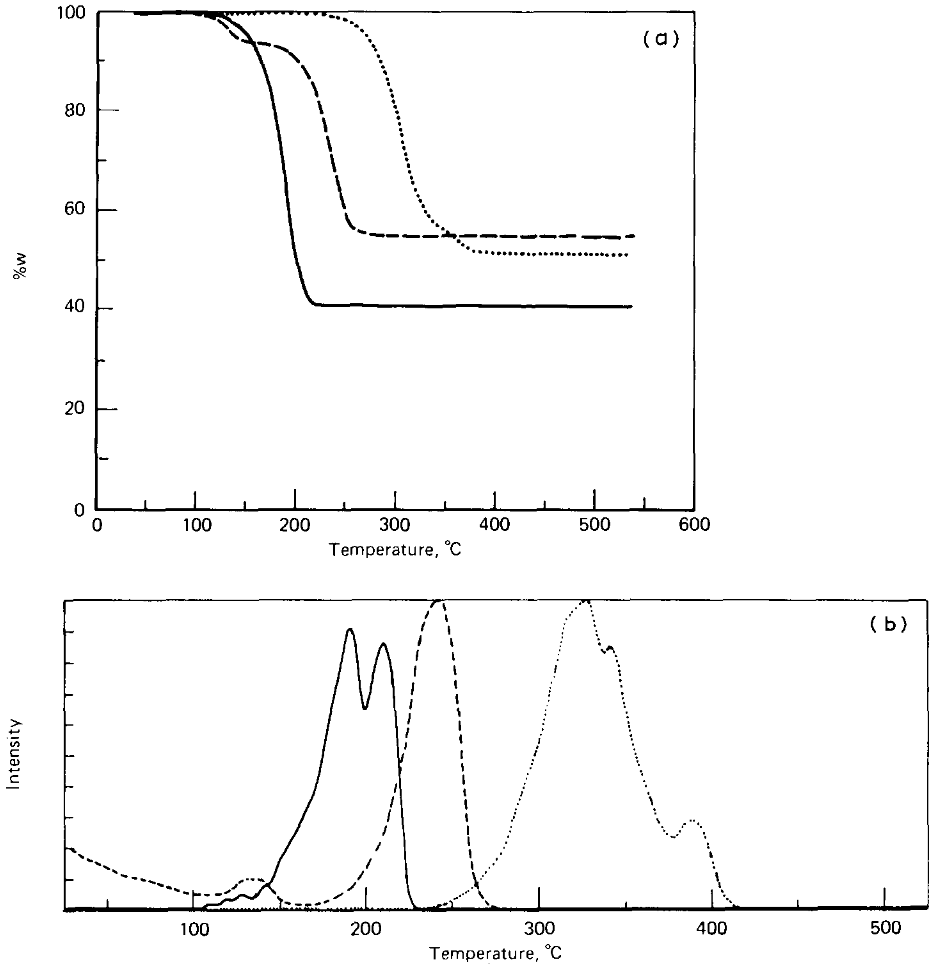

Fig. 4. (a) TG curves in argon atmosphere of $Co_4(CO)_{12}$ (———); $Rh_4(CO)_{12}$ (- - - - -); and $Ir_4(CO)_{12}$ (· · · · · ·). (b) QMS thermal evolution profiles of CO for $Co_4(CO)_{12}$ (———); $Rh_4(CO)_{12}$ (- - - - -); and $Ir_4(CO)_{12}$ (· · · · · ·).

Tetranuclear—$Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Ir_4(CO)_{12}$

The homometallic tetrametal dodecacarbonyls $M_4(CO)_{12}$ (M = Co, Rh, Ir) all possess tetrahedral metal center structure. Tetrarhodium dodecacarbonyl is isomorphous with tetrahedral dodecacarbonyl with three carbonyls bridging the base of the tetrahedron, while iridium dodecacarbonyl has no bridging carbonyl and three carbonyls on each metal center.

The three tetranuclear carbonyl clusters showed complex decomposition profiles, as seen in Fig. 4. The QMS carbonyl evolution profiles showed a multifeature CO loss for $Co_4(CO)_{12}$, two distinct CO evolution steps for $Rh_4(CO)_{12}$, and a trimodal CO loss for $Ir_4(CO)_{12}$. From the observed thermogravimetric weight loss, $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ clearly decom-

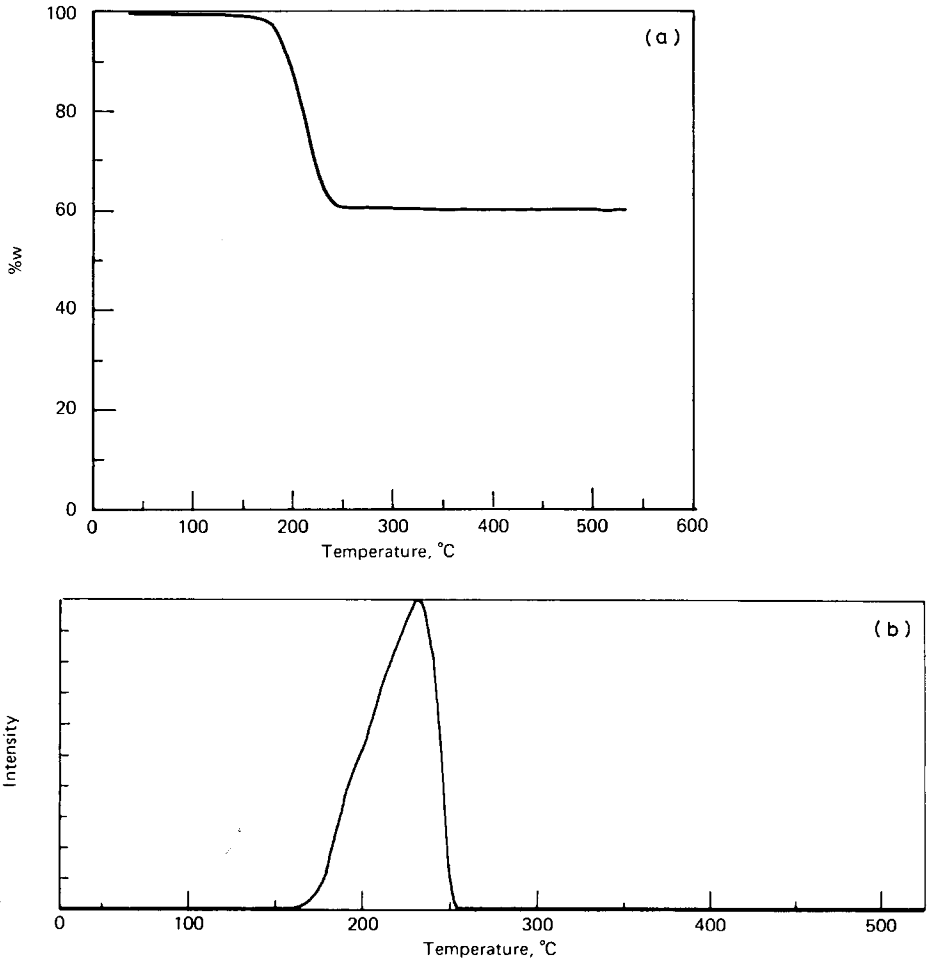

Fig. 5. (a) TG curve in argon atmosphere of $Rh_6(CO)_{16}$. (b) QMS thermal evolution profile of CO for $Rh_6(CO)_{16}$.

posed to metallic cobalt and rhodium, respectively, while $Ir_4(CO)_{12}$ decomposed to an intermediate with sufficient volatility such that the theoretical weight loss to metal is exceeded. This phenomenon was also observed by Psaro et al. [5] who found a certain amount of sublimation occurring with $Ir_4(CO)_{12}$ at heating rates above 1°C min^{-1}.

The decomposition process for rhodium carbonyl compound seems to be the most clearcut; both the TGA and the QMS CO-evolution profile indicated a distinct two-step decomposition. The relative quantity of CO evolved for step 1 vs. step 2 was found to be approximately 1 : 3, highly suggestive that three carbonyl ligands, probably the three bridging carbonyls, were lost, giving rise to a stable intermediate cluster $Rh_4(CO)_9$, which subsequently decomposes from 150 to 260°C completely to metallic rhodium. The isomorphous tetracobalt dodecacarbonyl, as seen from the multiple peaks in the CO-evolution profile, seem to lose CO's almost one-by-one initially, followed by a major loss to arrive at (from the relative areas of the peaks) the cluster $Co_4(CO)_8$ or the dimer $Co_2(CO)_4$, which subsequently decomposes completely to metallic cobalt.

The distinctly trimodal CO-evolution profile of $Ir_4(CO)_{12}$ indicates several relatively stable intermediates, with the last one corresponding perhaps to small metal particles covered with CO since the metal to carbonyl ratio at that point is nearly 1 : 1.

Hexanuclear—$Rh_6(CO)_{16}$

The hexanuclear binary rhodium carbonyl $Rh_6(CO)_{16}$ has an octahedral metal center structure with four triply bridging CO's and twelve terminal CO's, two on each metal center. While the thermogravimetry showed a single-step decomposition to metallic rhodium, the QMS thermal CO-evolution profile indicated a slight shoulder on the low-temperature side of the broad CO-loss peak (Fig. 5). The hexanuclear cluster $Rh_6(CO)_{16}$ is readily formed from $Rh_4(CO)_{12}$ by polyhedral expansion under CO pressure [14]. It is possible that one of the intermediates in the decomposition of $Rh_6(CO)_{16}$ is $Rh_4(CO)_{12}$ with the loss of 4 CO's, but the temperature has reached such a point that the latter rapidly decomposes. With the hexanuclear osmium cluster $Os_6(CO)_{18}$, Psaro et al. [5] found highly complex IR spectra during the former's thermal decomposition, suggesting possible stable intermediates.

CONCLUSIONS

Based on the results of this TG–MS study, several conclusions can be made. Firstly, for the binary metal carbonyls, in spite of the fact that the thermogravimetry may show only an apparent single-step weight loss, the actual decomposition may be much more complex than simple sequential

CO loss. The thermogravimetric trace is often a composite of sublimation, volatilization of intermediates, and loss of ligand, and its sensitivity is apparently too low to perceive the presence of relatively stable intermediates. The CO thermal evolution profiles as seen by the QMS are able, however, to detect the subtle differences in the volatilization rate, and thus give a more detailed picture of the sequence of events occurring in the degradation process. Therefore, the formation of stable intermediates during the decomposition need not require a matrix as was suggested in an earlier study [5], nor is a matrix necessary to retard the volatilization in order for the intermediates to be detected (see above).

Secondly, the thermolytic pathways often do not follow simple reversible ligand dissociation, but involve in many cases metal–metal bond heterolysis and nucleophilic attack of the metal atom on the carbon of a CO ligand, as, for example, in the case of $Ru_3(CO)_{12}$ to give $Ru_6(CO)_{17}C$.

On the more pragmatic side, the results of this study suggest that, if binary metal carbonyls are used to prepare heterogeneous catalysts, difficulties may be encountered with using .$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Re_2(CO)_{10}$ and $Os_3(CO)_{12}$ due to their tendencies for sublimation or complete volatilization. Only $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Ir_4(CO)_{12}$, and $Rh_6(CO)_{16}$ would be considered good candidates for immobilization onto supports if total decomposition to metal after high temperature calcination is the intended aim. However, if the preparation of coordinatively-unsaturated supported-metal species or semi-metal particles with attached CO's is desired, then polynuclear carbonyls such as $Co_2(CO)_8$, $Ru_3(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$ which showed multi-step CO-loss as a function of temperature should perhaps be used. Experimental verification of these conclusions would be necessary.

Lastly, TG–MS has been shown to be a useful technique for the study of organometallic complexes. In the present case, only decomposition and only binary metal carbonyls were examined. The QMS can be used to detect, of course, not only CO, but a variety of ligands such as NO, CS_2, C_6H_6, as well as the volatile metal-containing fragments themselves.

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