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THERMAL DEGRADATION OF TRANSITION METAL CARBONYL COMPLEXES. PART IV: THERMOGRAVIMETRIC STUDIES OF VARIOUS STOICHIOMETRIC MIXTURES OF TRIMETHYLAMINE *N*-OXIDE DIHYDRATE AND HEXACARBONYL MOLYBDENUM

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ABSTRACT

The effect of $(CH_3)_3NO \cdot 2H_2O$ on the thermal degradation of $Mo(CO)_6$ in nitrogen was studied by thermogravimetry (TG) and derivative thermogravimetry (DTG). Pure $Mo(CO)_6$ and $(CH_3)_3NO$ readily sublime without decomposition. On mixing and heating, oxidative decarbonylation readily occurs, followed by substitution. This yields $Mo(CO)_{6-n}[(CH_3)_3N]_n$ and CO_2. The substituted carbonyl complexes undergo further ligand cleavage and disintegrate into metal residue. In a stoichiometric ratio of greater than 3:1 for $(CH_3)_3NO \cdot 2H_2O:Mo(CO)_6$, free and excess amine oxide are detected in the TG profile, which lends strong support to the formation of the tricarbonyl $Mo(CO)_3[(CH_3)_3N]_3$, but not the higher substituted analogues.

INTRODUCTION

This paper is the fourth in a series devoted to the study of the thermal degradation of transition metal carbonyl complexes [1–3].

Catalytically active carbonyl compounds constitute an important chapter in the current trends of research in organometallic chemistry [4–6]. Coordination unsaturation is among the commonly acknowledged criteria for a complex to be catalytically functional [7–10]. The classical activation process demands the use of stringent thermal and photolytic techniques [11–14]. In recent years, reagent-induced decarbonylation using, for example, $CoCl_2$, sodium benzoquinone, $(CH_3)_3NO$, etc. has been developed into a viable alternative for such studies [15–22]. The use of chemical reagents in the activation step often involves a low-energy pathway which is particularly valuable for thermally unstable systems. Unfortunately most of the current

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investigations are devoted to solution studies which offer little information on solid state interactions or solvent-free processes [23–26].

$Mo(CO)_6$ is one of the earliest characterized binary carbonyls in the literature [27]. Under normal or reduced pressure conditions, the complex sublimes prior to decomposition and hence is unsuitable for the normal gas-flow-type thermogravimetric (TG) analysis. In this paper we report the effect of trimethylamine *N*-oxide dihydrate (TMNO), which is a well-documented decarbonylating agent in solution studies [4,8,28–34], on the thermal decomposition of $Mo(CO)_6$ using TG analysis. The oxidative decarbonylation action of TMNO is demonstrated by varying the stoichiometry of the reaction mixtures.

EXPERIMENTAL

Molybdenum hexacarbonyl and trimethylamine *N*-oxide dihydrate were supplied by Aldrich Chemical Co. The substrates were finely ground and mixed in different stoichiometric ratios. All the TG experiments were conducted on a Du Pont 9900 thermal analyser in dry nitrogen. The nitrogen flow was 75 cm^3 min^{-1} and the heating rate was 10 °C min^{-1}. All samples were run from room temperature to 400 °C.

RESULTS

TG analysis

Neat $Mo(CO)_6$ (Fig. 1) and TMNO (Fig. 2)

Under a nitrogen atmosphere, sublimation of $Mo(CO)_6$ commences at approximately 40 °C and is complete at about 140 °C. Practically no residue is left behind. This is in accordance with the literature [27]; the complex undergoes little decomposition over this temperature range.

The TG profile and, in particular, the DTG profile of TMNO reveal a two-step process, namely dehydration followed by sublimation.

$$(CH_3)_3NO \cdot 2H_2O \xrightarrow{75-160\,^\circ C} (CH_3)_3NO + 2H_2O$$

$$(CH_3)_3NO \xrightarrow{160-240\,^\circ C} \text{Sublimation}$$

This sublimation is virtually complete and no residue is deposited beyond 240 °C.

$Mo(CO)_6$ + TMNO (3 : 1) (Fig. 3)

Weight loss commences at 30 °C and is complete at 115 °C. A residue (2.1%) is deposited which is likely to be molybdenum metal. The weight loss

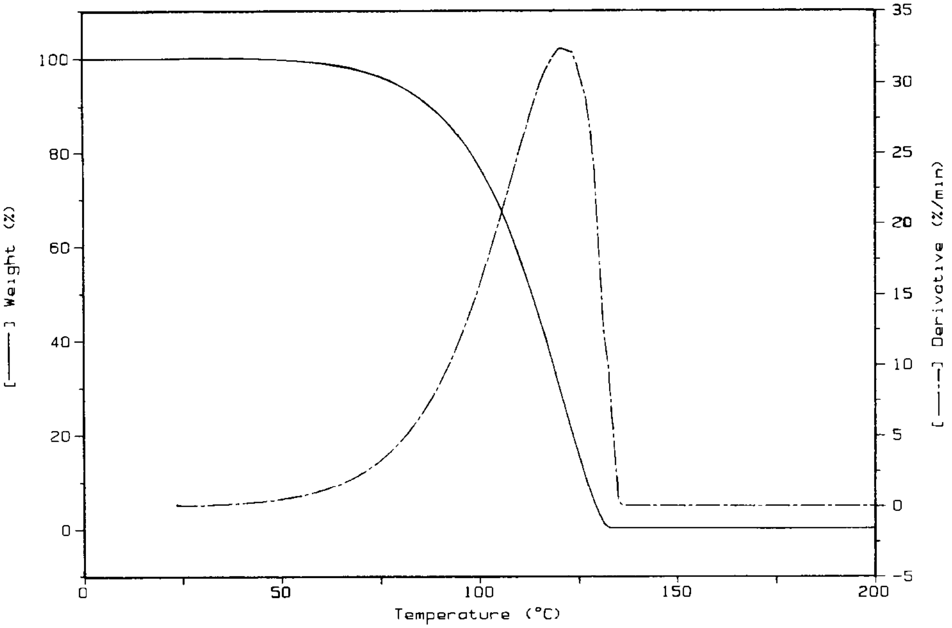

Fig. 1. TG/DTG of $Mo(CO)_6$.

occurs via a multi-step process which is interpreted to be an initial oxidative decarbonylation of $Mo(CO)_6$, yielding $[Mo(CO)_5]$ or $Mo(CO)_5[(CH_3)_3N]$, which is accompanied by the rapid elimination of CO molecules. A concom-

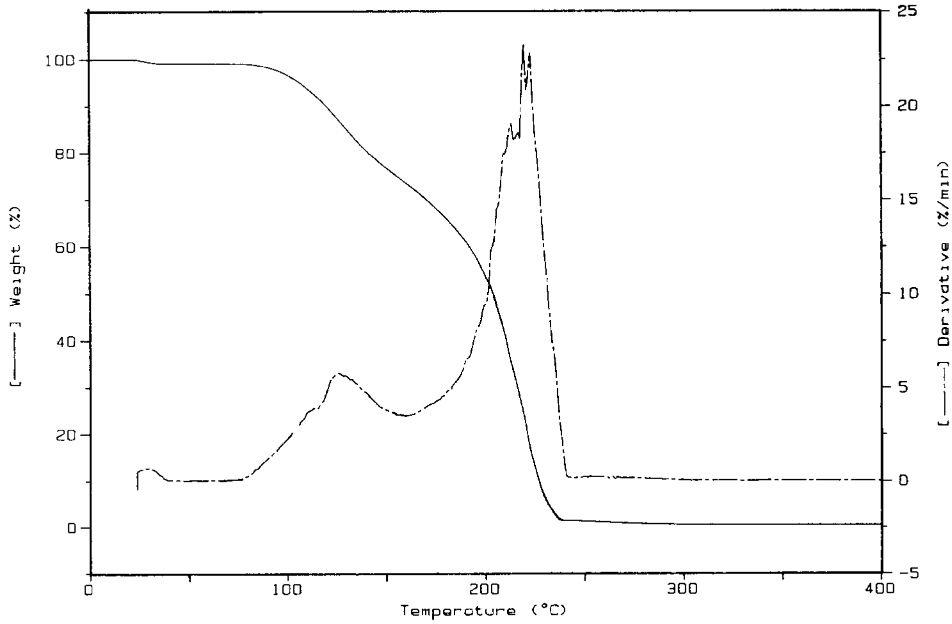

Fig. 2. TG/DTG of TMNO.

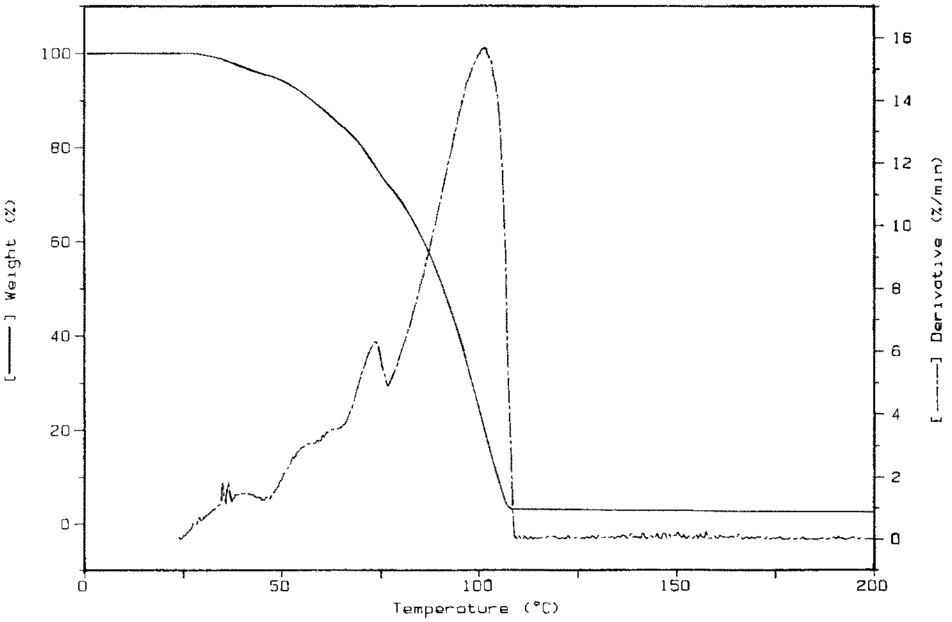

Fig. 3. TG/DTG of $Mo(CO)_6$ + TMNO (3 : 1).

itant overlapping process which takes place is the sublimation of the excess $Mo(CO)_6$ in the mixture. The overall equation can be represented as

$$3Mo(CO)_6 + (CH_3)_3NO \cdot 2H_2O \rightarrow 2Mo(CO)_6 + Mo(CO)_5[(CH_3)_3N] + 2H_2O + CO_2$$

$$2Mo(CO)_6 \rightarrow \text{Sublimation}$$

$$Mo(CO)_5[(CH_3)_3N] \rightarrow 5CO + (CH_3)_3N + Mo(\text{obs., } 2.1\%\text{; calc., } 10.6\%)$$

Elimination of the volatile substances, such as CO, CO_2, H_2O and $(CH_3)_3N$, is understandably facile and explains the rapid loss in weight. The absence of free TMNO in the mixture is clearly discernible when a comparison is made with Fig. 2. A possible intermediate for this thermal reaction is $Mo(CO)_5[(CH_3)_3N]$ which is notoriously unstable with respect to the elimination of the labile $(CH_3)_3N$ [4,8,35]. A residual deposit of 2.1% is small, but not negligible, which is interesting in view of the 0% residue in both of the neat substrates. The value of 2.1% is in poor agreement with the calculated value of 10.6% based on the above equations. However, this discrepancy is not unexpected owing to the incompletion of the reaction between the substrates and hence the excessive escape of $Mo(CO)_6$ from the reaction mixture through volatilization.

$Mo(CO)_6$ + TMNO (1 : 1) (Fig. 4)

Degradation commences at about 35 °C and is complete at 120 °C giving 4.9% of metallic residue. The striking similarity between the TG decomposi-

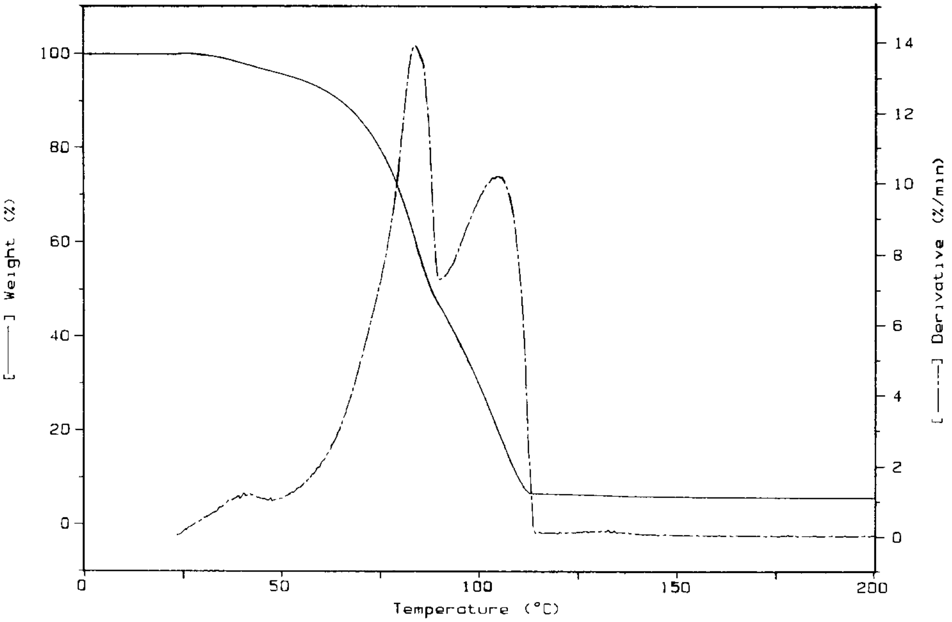

Fig. 4. TG/DTG of $Mo(CO)_6$ + TMNO (1 : 1).

tion curve of this equimolar mixture (Fig. 4) and the mixture with excess $Mo(CO)_6$ (Fig. 3) lends further evidence to the mechanism proposed above. A similar reaction scheme can be represented here

$Mo(CO)_6 + (CH_3)_3NO \cdot 2H_2O \rightarrow Mo(CO)_5[(CH_3)_3N] + CO_2 + 2H_2O$
$Mo(CO)_5[(CH_3)_3N] \rightarrow 5CO + (CH_3)_3N + Mo$(obs., 4.9%; calc., 25.6%)

Again, the low observed percentage of metal residue is not surprising and is a likely consequence of other side reactions in which further substitution occurs and gives rise to other carbonyls such as $Mo(CO)_4[(CH_3)_3N]_2$ and $Mo(CO)_3[(CH_3)_3N]_3$ [27]. This would permit the escape of excess $Mo(CO)_6$, thus resulting in a reduction in the metallic deposit.

$Mo(CO)_6$ + TMNO (1 : 3) (Fig. 5)

On mixing and heating, the substrates decompose rapidly giving a residue of 17% at 120 °C. Prolonged heating to 700 °C reduces the residue to 11.8%, which is the highest recorded for all the stoichiometries tested. The TG curve shows no sign of dehydration or sublimation attributable to free TMNO. This may be interpreted as a 1 : 3 stoichiometric reaction between $Mo(CO)_6$ and TMNO thus resulting in the tricarbonyl. This observation further supports our earlier proposal that a higher degree of substitution can be achieved with an excess of TMNO in the mixture. The reaction and degradation can be represented as

$Mo(CO)_6 + 3(CH_3)_3NO \cdot 2H_2O \rightarrow Mo(CO)_3[(CH_3)_3N]_3 + 6H_2O + 3CO_2$
$Mo(CO)_3[(CH_3)_3N]_3 \rightarrow 3CO + 3(CH_3)_3N + Mo$(obs., 11.8%; calc., 16.1%)

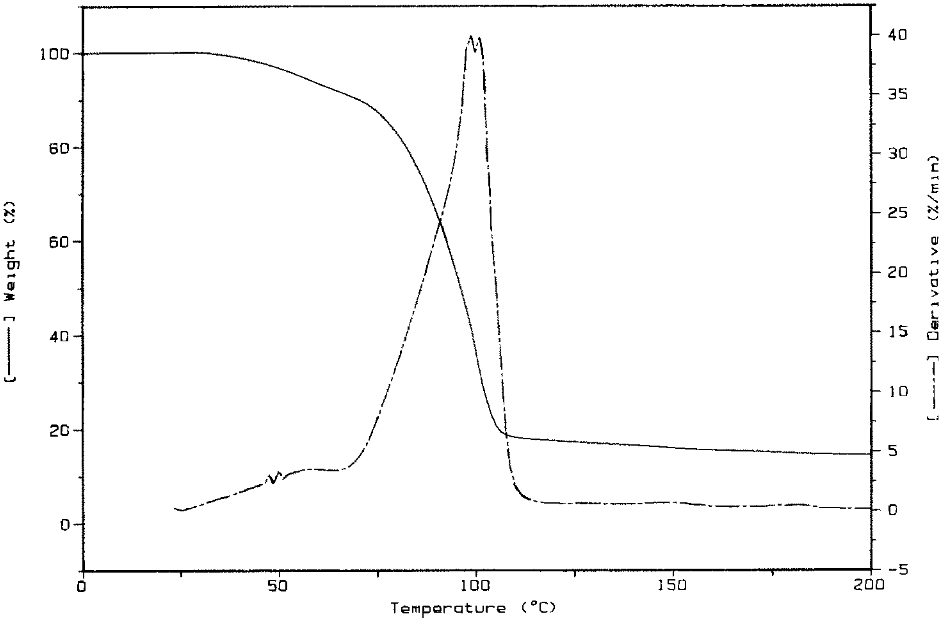

Fig. 5. TG/DTG of Mo(CO)$_6$ + TMNO (1 : 3).

Mo(CO)$_6$ + TMNO (1 : 4) (Fig. 6) (1 : 6) (Fig. 7)

Two distinctly different TG profiles are observed in these cases when TMNO is present in excess. A steep weight loss in the first step is followed

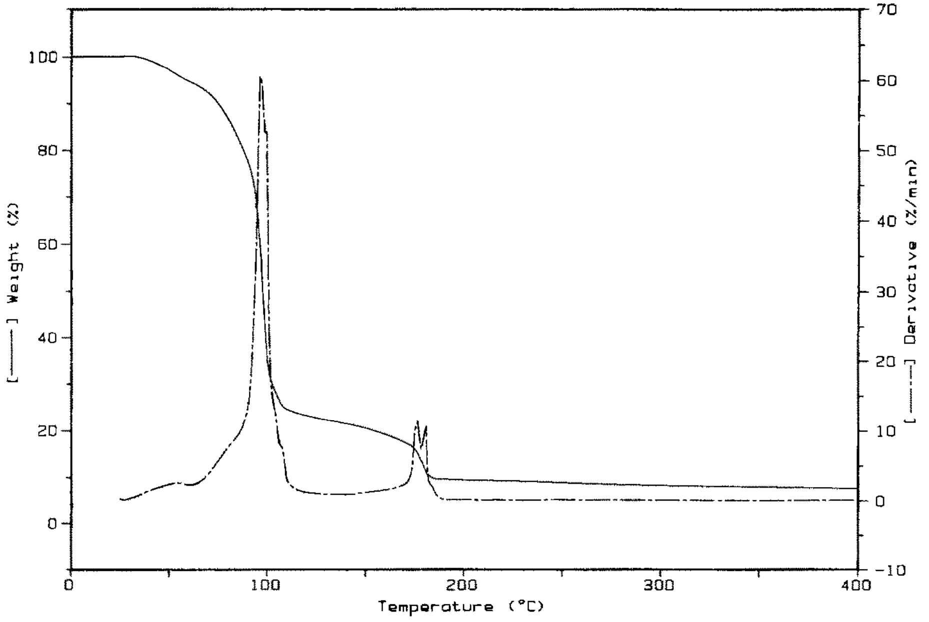

Fig. 6. TG/DTG of Mo(CO)$_6$ + TMNO (1 : 4).

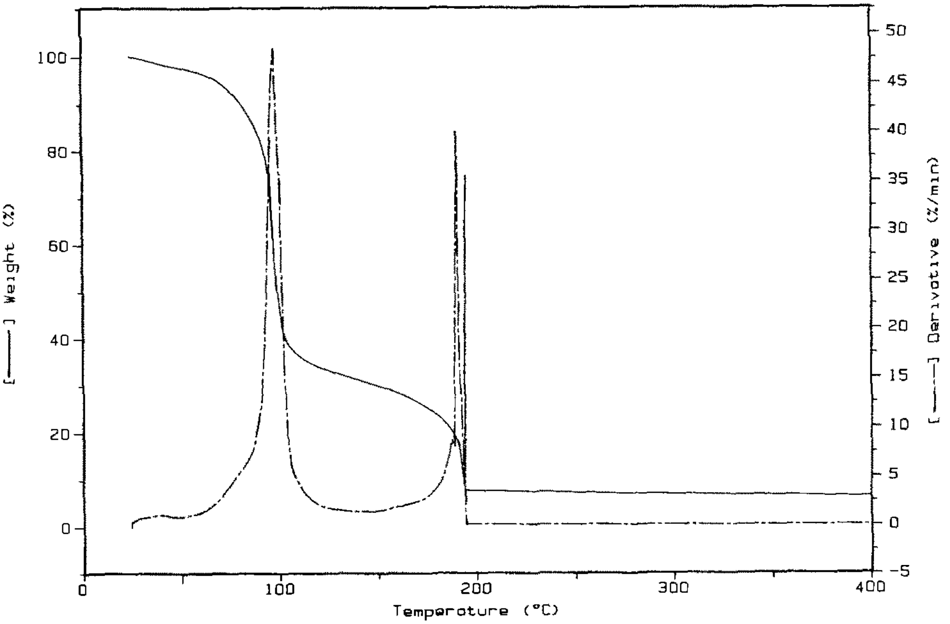

Fig. 7. TG/DTG of $Mo(CO)_6$ + TMNO (1 : 6).

by a more gradual loss. Both mixtures display very similar inflexion points (approximately 120 ° C) and similar temperatures at which decomposition is complete (approximately 190 ° C). This is understood in terms of similar reaction/decomposition mechanisms in both mixtures. The first step is attributed to the formation of the tricarbonyl followed by rapid ligand dissociation. The second step indicates the volatilization of excess unreacted TMNO. The equations are represented below

$$Mo(CO)_6 + 4(CH_3)_3NO \cdot 2H_2O \xrightarrow{45-120\,°C} Mo(CO)_3[(CH_3)_3N]_3 + 8H_2O$$
$$+ 3CO_2 + (CH_3)_3NO$$

(obs., 13.0%; calc., 10.6%)

$$Mo(CO)_6 + 6(CH_3)_3NO \cdot 2H_2O \xrightarrow{45-120\,°C} Mo(CO)_3[(CH_3)_3N]_3 + 12H_2O$$
$$+ 3CO_2 + 3(CH_3)_3NO$$

(obs., 26.0%; calc., 24.2%)

The discrepancies in the percentage of $(CH_3)_3NO$ may be understood in view of the partial hydration (or incomplete dehydration) of $(CH_3)_3NO$ at the point of inflexion, i.e. 120 ° C.

DISCUSSION

TG analysis indicates that both $Mo(CO)_6$ and TMNO lose their identity when present in the form of a mixture. In agreement with the results of solution studies, the interaction between these two substrates in a solvent-free state gives rise to the amine-substituted carbonyls $Mo(CO)_{6-n}[(CH_3)_3N]_n$ via an oxidative decarbonylation pathway. The major compound formed is likely to be the trisubstituted derivative, i.e. $Mo(CO)_3[(CH_3)_3N]_3$. Our results unequivocally establish that further substitution is resisted and, despite the presence of a sixfold excess of TMNO, there is no evidence of the generation of species $Mo(CO)_2[(CH_3)_3N]_4$ and $Mo(CO)[(CH_3)_3N]_5$. This observation can easily be explained by the increase in metal-to-ligand π back-bonding and hence the Mo–C bond strength on higher substitution [27]. These amine-substituted carbonyls are thermally unstable and, once formed, rapidly disintegrate into CO molecules, $(CH_3)_3N$ and metallic residue.

The decomposition temperature range of all the mixtures examined is significantly lower than that at which sublimation of either $Mo(CO)_6$ or TMNO occurs. This finding may have an interesting application in the research of in situ metal decomposition in conductive polymers [36,37[. In general, owing to the occurrence of the overlapping substitution reactions and the high volatility of $Mo(CO)_6$, the experimental percentage of metal residue is much lower than that expected for a single decomposition pathway. Nevertheless, results in our laboratory indicate unambiguously that TG analysis offers a simple, yet superior, technique for the optimization of the reaction stoichiometry and the amount of metal deposit in some decarbonylation reactions.

CONCLUSION

The use of TG analysis in the investigation of the stoichiometry, the optimum reaction conditions and the nature of decomposition products is of immense potential. In this report, we have substantiated this idea by demonstrating that a volatile binary carbonyl such as $Mo(CO)_6$ can be doped and thermally degraded at normal pressure. The thermal data thus generated will be of use not only to organometallic investigations but also to research in polymers and catalysis. Similar studies on other binary carbonyl complexes are currently being performed in our laboratory.

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