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Substituted metal carbonyls

X *. Thermogravimetric and quantitative studies of the oxidative decarbonylation of tungsten hexacarbonyl

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Abstract

Thermogravimetric and Derivative Thermogravimetric Analyses have been carried out on different stoichiometric mixtures of $W(CO)_6$ and $(CH_3)_3NO \cdot 2H_2O$ (TMNO) under nitrogen. The studies indicate that the optimum reactant ratio (W : TMNO) is close to 1 : 4, at which there is a single-step weight loss in the region 50–90 °C and a residue (ca. 13%) is left. The rapid loss in weight is attributed to the ready decomposition of the primary product $W(CO)_{6-n}(Me_3N)_n$ ($n > 1$). At W : TMNO ratios, 1 : n, where n is smaller or greater than four, unchanged $W(CO)_6$ on TMNO, respectively, were observed from the thermal profiles. The liberation of CO_2 was quantified during separate experiments. The amount of gas released is proportional to the concentration of TMNO present. When the latter is present in a 15-fold excess, four moles of CO_2 are released per mole of the parent hexacarbonyl.

Introduction

Catalytically active carbonyl complexes have attracted much attention in recent years [1–3]. Most of such complexes are coordinatively unsaturated [4–7]. The activation of saturated complexes by use of various deligating strategies such as thermolysis, photolysis [8–11] and reagent-induced [12–19] decarbonylation, has been studied extensively. It is in situation where thermally or UV sensitive species are encountered or where selectivity and specificity are of prime concern that the reagent induced decarbonylation is particularly suited. The most successful de-

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carbonylating agents are the mild oxidants such as dimethylsulphoxide, n-butylphosphine oxide, cobalt chloride, sodium diphenyl ketyl and many aromatic and aliphatic amine oxides especially trimethylamine *N*-oxide (TMNO). Arguably the most versatile is TMNO; its uses are well described in the literature [5,20–23]. In spite of the abundance of literature reports on this subject, little is known about the reactions that are free from interference by the solvents [24–27] or about the quantitative effect of TMNO in such systems.

Here we evaluate the thermogravimetric (TG) and derivative thermogravimetric (DTG) behaviour of varying the stoichiometric solid-state mixtures of $W(CO)_6$ and TMNO. The possibility of establishing the stoichiometry of the solid-state reaction from the TG and DTG profiles is examined. In a separate experiment, the amount of CO_2 liberated from the various mixtures has been determined. $W(CO)_6$ is chosen because of the notorious strength of the W–CO bonds. Highly substituted complexes have rarely been obtained directly from oxidative decarbonylation of the parent hexacarbonyl in solutions.

Results and discussion

Pure $W(CO)_6$ sublimes at temperatures between 35–141° C without significant decomposition or deposition. Hydrated TMNO first undergoes dehydration at 100–150 ° C and then sublimes. Complete sublimation is achieved at ca. 235 ° C and leaves practically no residue. However, when the two components are ground and mixed in different stoichiometric ratios and the resultant mixtures subjected to TG and DTG analyses, the degree of sublimation is substantially inhibited. Oxidative decarbonylation occurs upon heating and in all mixtures a residue remains when heated to 750 ° C. The amount of residue depends on the stoichiometry. Results are listed in Table 1.

Table 1

Thermal data of different stoichiometric mixtures of $W(CO)_6$ and trimethylamine *N*-oxide (TMNO)

Stoichiometric mixtures of $W(CO)_6$: TMNO	% Weight loss with respect to $W(CO)_6$	% Weight loss with respect to TMNO	No of moles of CO_2 released per mole of $W(CO)_6$ in the mixture	% Deposit at 750 ° C
3:1	73	–	0.8	2.3
2:1	63	–	0.4	7.7
1:1	54	–	0.6	7.7
1:2	25	–	1.0	11.5
1:3	17	–	1.4	12.3
1:4	–	–	2.2	13.2
1:5	–	< 5	2.4	12.9
1:6	–	15	2.2	12.2
1:7	–	19	3.3	11.7
1:8	–	25	3.4	13.4
1:10	–	33	2.8	10.7
1:15	–	52	3.9	7.7
1:18	–	57	5.6	6.0

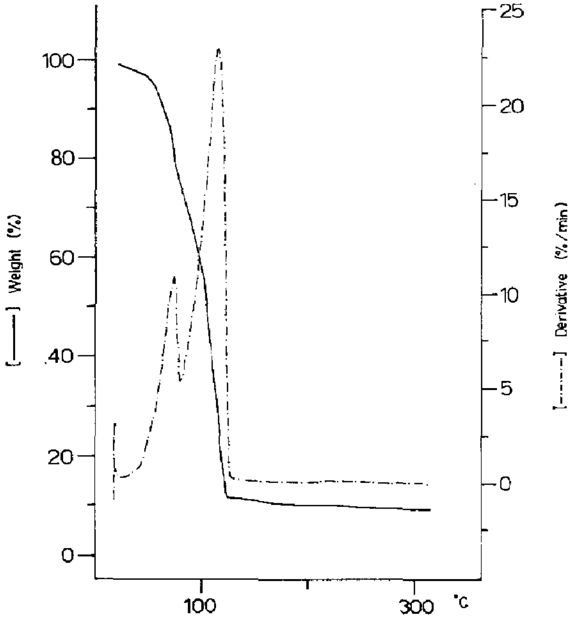

Fig. 1. TG and DTG curves of a mixture of $W(CO)_6$: TMNO (2 : 1) showing the typical profiles for the liberation of excess $W(CO)_6$.

The two reagents react slowly upon grinding and mixing at 20°C; this is reflected in the gradual weight loss that commences with heating. The three mixtures having the stoichiometries 3 : 1, 2 : 1 and 1 : 1 for $W(CO)_6$: TMNO display similar patterns in their profiles (Figs. 1 & 4). Two steps are usually observed, one in the range 50–75°C and the other in the range 80–125°C. The initial loss is attributed to the rapid reaction of the two components which liberates CO_2 and possibly Me_3N as gaseous effluents. Such an interaction involves an excess dosage of $W(CO)_6$; this is exemplified in the second weight loss, attributable to the sublimation of $W(CO)_6$. The escape of $W(CO)_6$ can be easily proved by differential scanning calorimetry (DSC), profiles of which show a sharp endothermic peak at 171°C corresponding to the superheating of the carbonyl. Further support is gained from the absence of free TMNO in the TG profiles and by the fact that the percentage of weight losses for the second stage decreases in the order 3 : 1(73%) > 2 : 1(63%) > 1 : 1(54%) for the three different $W(CO)_6$: TMNO mixtures. The major products of the reaction are probably $W(CO)_{6-n}(Me_3N)_n$ [28] with $n > 1$. Such species are unlikely to be stable under these thermal conditions and hence will decompose rapidly after formation. The percentage of residue thus formed depends on the quantity of the substituted carbonyls generated in the system. A deposit of 2.3% for the 3 : 1 mixture is the lowest amount of residue left by any of the mixtures studied; this is understandable in view of the high deficiency of TMNO. The other two mixtures registered a residue of 7.7%.

The above decomposition pattern persists in those mixtures having higher concentrations of TMNO, viz. at the ratios of 1 : 2 and 1 : 3 the weight losses are increased to 52% and 62%, respectively, and the amount of unchanged $W(CO)_6$ decreases to 25% and 17% respectively (Fig. 4). Such a two-step degradation pathway is however not found when the concentration of TMNO is increased to

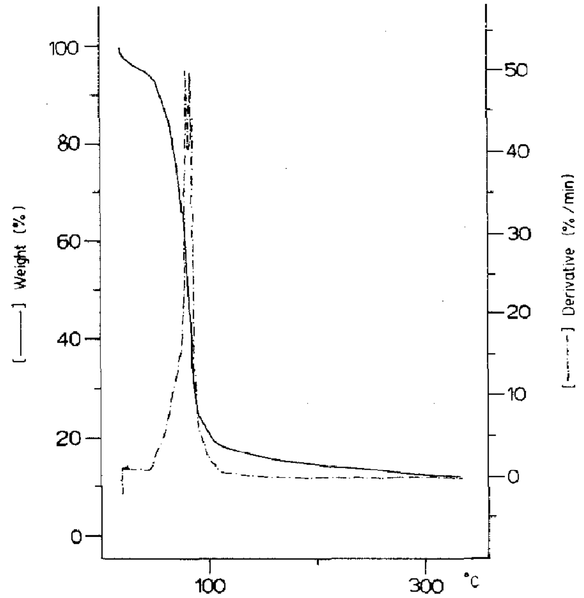

Fig. 2. TG and DTG curves of a mixture of W(CO):TMNO (1:4) showing the typical profile for the decomposition of the primary product in the absence of an excess of $W(CO)_6$ or TMNO.

give ratios of 1 : 4 and 1 : 5 (Figs. 2 & 4). In these cases, a unique one-step process and a steep weight loss are observed below ca. 90 ° C, after which the loss in weight is relatively small up to 750 ° C. Accordingly, the DTG profiles show a sharp peak just below 90 ° C. These ratios represent the optimum stoichiometric ratios for the solid-state reaction under the present conditions. In these two reaction mixtures, neither TMNO nor $W(CO)_6$ is liberated in significant quantities, and the steep loss in weight is a consequence of the degradation of the primary product(s) between the two components. The steepness of the loss in weight suggests that the highly volatile decomposition products such as CO_2 and Me_3N are liberated and that the product mixture from $W(CO)_6$ and TMNO may be dominated by a major species. The exact nature of this species is not clear but doubtless it decomposes much more readily than either $W(CO)_6$ or TMNO. The liberation of CO gas from these mixtures is indicated by the darkening of $PdCl_2$-impregnated paper but too little is produced to be quantified. In accord with the TG findings, the IR spectra (Nujol and CH_2Cl_2) of the residues show only terminal carbonyl absorptions for both mixtures at 90 ° C, which indicates incomplete decarbonylation.

As expected, when the molar ratio $W(CO)_6$: TMNO is 1 : > 5, the decomposition pathway reverts to the two-phase pattern (Figs. 3 & 4) but, in this case the second step is attributed to the sublimation of unchanged TMNO. Both the TG and DTG profiles reveal that the excess TMNO sublimes in the range 100–165 ° C, which is substantially lower than that observed for pure TMNO. Similar lowering of the sublimation temperature is also observed in the case of $W(CO)_6$. This can be attributed to the weakening of the intermolecular forces in the molecular lattice in the reaction matrix.

The TG and DTG data provide a direct and convenient means to estimate the optimum stoichiometries for the oxidative decarbonylation of $W(CO)_6$ by TMNO. However, they fail to prove categorically that CO_2 is generated and if so in what

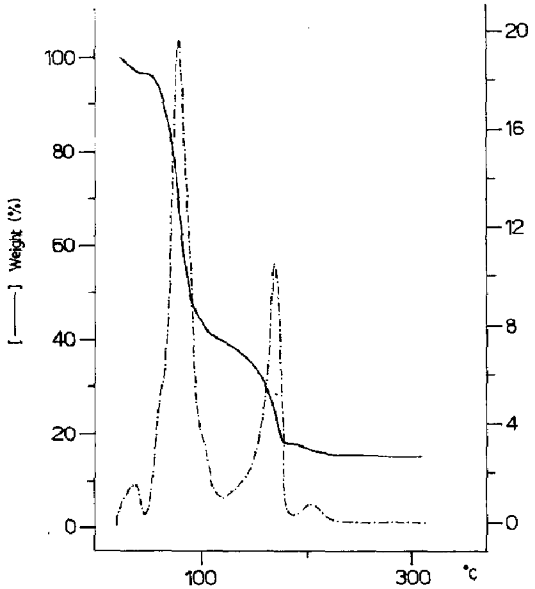

Fig. 3. TG and DTG curves of a mixture of $W(CO)_6$: TMNO (1 : 8) showing the typical profiles for the liberation of excess TMNO.

quantities. Hence in a separate modelling experiment, we simulated the TG conditions by carrying out a series of thermal decomposition studies on solid mixtures in Schlenk flasks under a controlled dynamic atmosphere of nitrogen. The gas liberated readily gives a white precipitate upon contact with $Ba(OH)_2$ solution. The identity of the decomposition residue has not been established but its analytical data

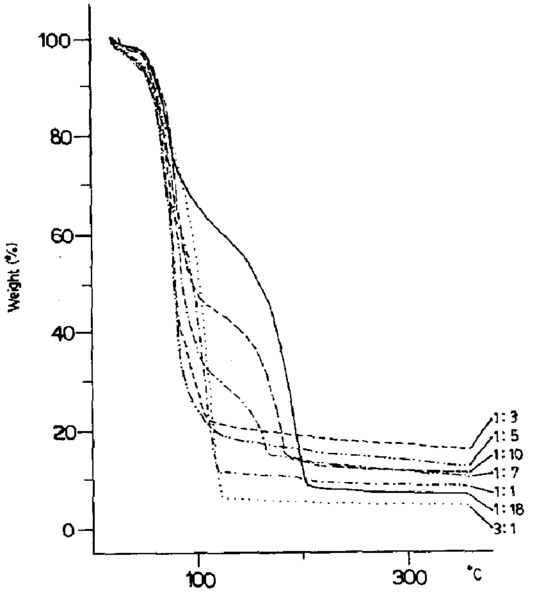

Fig. 4. TG decomposition curves for the selected mixtures of $W(CO)_6$: TMNO, stoichiometric ratios ranging from 3 : 1 to 1 : 18. [3 : 1 · · · ; 1 : 1, · — · —
; 1 : 3 - - - - - -; 1 : 5 — · · —; 1 : 7 —— · ——; 1 : 10, — — - - — —; 1 : 18, ———].

indicate a high metal content viz. ca. 70% and ca. 8.7, 1.6 and 2.8% of carbon, hydrogen and nitrogen respectively. The presence of nitrogen is interesting and suggests the occurrence of cleavages within the Me_3N ligand; the nitrogen is incorporated into the metal coordination sphere. In our attempts to quantify the CO_2 liberated in different solid mixtures, the gas was trapped in cold aq. NaOH and standard titrations with HCl were employed to determine the molarity of Na_2CO_3 formed. The results are summarised in Table 1.

It is clear from the Table that the stoichiometric ratio at which CO_2 release is at its maximum does not correspond to the optimum ratios as found from the TG profiles. This is not surprising in view of the complication by side-reactions which probably does not involve the oxidation of the carbonyl ligands. It can however be concluded that such side-reactions are largely inhibited in a matrix that has a high concentration of TMNO. The loss of $W(CO)_6$ by sublimation is also expected to be much less severe in such a matrix.

In view of these considerations, the molarity of CO_2 liberated does not necessarily reflect the precise number of M–CO bonds cleaved in each $W(CO)_6$ molecule. Our results, however, unequivocally demonstrate that TMNO is an effective decarbonylating agent even in a solvent-free environment. Apart from some slight irregularities which could be a result of imperfect homogeneity of the matrix, the degree of decarbonylation is proportional to the concentration of the TMNO present. At ratios of $W(CO)_6$: TMNO of 1 : 15 and above, over four moles of CO_2 are formed for each mole of $W(CO)_6$. This is perhaps surprising in light of the strength of the W–CO bond and that such extensive decarbonylation has not been observed in solution studies on $W(CO)_6$ in the absence of strong chelating ligands or donor solvents.

Conclusion

The use of TG and DTG in the investigation of stoichiometries of organometallic reactions shows much potential. The data thus generated would complement those obtained from classical solution studies. Our interest in the oxidative decarbonylation of metal carbonyls is not confined to synthetic studies; another of our research objectives is to design suitable metal dopants in the formulation of conductive polymers [29–32]. The use of metal carbonyls in this area would be greatly facilitated if one could activate such species without subjecting the sample to stringent processes such as photolysis which causes polymer degradation. Group 6 metal binary carbonyls are unsuitable dopants because they readily sublime, but results in this paper suggest that in the presence of suitable decarbonylating agents, they would be good candidates for in situ metal or metallic deposition. The exact stoichiometry of the oxidative decarbonylation of $W(CO)_6$ with TMNO cannot be ascertained owing to the occurrence of side-reactions, but the optimum ratio for complete reaction between the reactants can be deduced from the TG and DTG profiles. The information thus obtained is invaluable in the formulation of the dopants.

Experimental

All the thermal experiments were conducted under pure dry dinitrogen. Tungsten hexacarbonyl and trimethylamine *N*-oxide dihydrate were supplied by Aldrich

Chemical Co. and used without further purification. The substrates were finely ground and mixed at 20 °C in the various stoichiometric ratios. All the TG and DTG experiments were conducted by use of a Du Pont 9900 thermal analyser in dry dinitrogen. The gas flow was 75 $cm^3 min^{-1}$ and heating rate 10 °C min^{-1}. All experiments were carried out between 20 to 750 °C. Sample residual weight (in %[total weight]) vs. temperature curves and their derivatives (DTG, %[total weight] min^{-1}) were generated by the Du Pont software programs. About 13 mg of a finely ground powder mixture was used. DSC experiments were performed with the same instrument over a temperature range of 20–500 °C and calibrated to have a cell constant of 1.19. The corresponding modelling experiments were conducted similarly by use of Schlenk flasks and larger sample quantities (ca. 0.5 g $W(CO)_6$); the heating range was 25–280 °C. The CO_2 liberated was trapped in 1.0 *M* or 0.5 *M* NaOH (100 cm^3) solution, cooled in an ice bath, then the mixtures were titrated with 0.5 *M* HCl by a published procedure in order to determine the carbonate content [33]. At least three independent runs were performed for each mixture and the average value is cited. Control experiments were performed on the pure substrates and the standard NaOH solution and any residual CO_2 was accounted for and adjusted accordingly. All the relevant data are summarised in Table 1. The solid sublimates and residues were subjected to IR analysis on a Perkin–Elmer 1310 spectrometer. Microanalyses of the solid residues were carried out in this Department.

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