

THERMAL DECOMPOSITION OF A SERIES OF TETRANUCLEAR CARBONYL CLUSTERS $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, $\text{RhCo}_3(\text{CO})_{12}$ AND $\text{Co}_4(\text{CO})_{12}$

R. PINCE, R. QUEAU and D. LABROUE

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par convention à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse (France)

(Received November 20th, 1985)

Summary

Decarbonylation of the unsupported clusters $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, $\text{RhCo}_3(\text{CO})_{12}$ and $\text{Co}_4(\text{CO})_{12}$ in a stream of hydrogen has been investigated by temperature programmed decomposition. Kinetic parameters for the thermal decomposition are presented, and the stabilities of the clusters are discussed. The profile for evolution of CO from $\text{Rh}_4(\text{CO})_{12}$ indicates that a stable intermediate is formed. In all four cases methane is formed stepwise until most of the CO groups are evolved.

Introduction

Impregnation of metal oxides with carbonyl compounds followed by thermal decarbonylation is a common way of preparing supported catalysts. Knowledge of the decomposition steps is limited, and temperature programmed decomposition (TPDE) offers a valuable technique for providing information in this area [1]. We have shown previously that quantitative data from multiple TPDE runs can be used to determine the kinetics of decarbonylation of $\text{Co}_4(\text{CO})_{12}$ [2]. The method has now been extended to the isostructural series of clusters, $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, and $\text{RhCo}_3(\text{CO})_{12}$.

Results and discussion

CO evolution

The experimental procedure was the same as described earlier [2] except for the hydrogen pressure. In the present series of experiments, the H_2 pressure was kept constant at 1 atm, whereas previously [2] the pressure increased with temperature. Figure 1 illustrates the TPDE profiles obtained with a 40 ml/min hydrogen flow for the series of clusters. $\text{Rh}_4(\text{CO})_{12}$ is the only one which gives a double maximum in

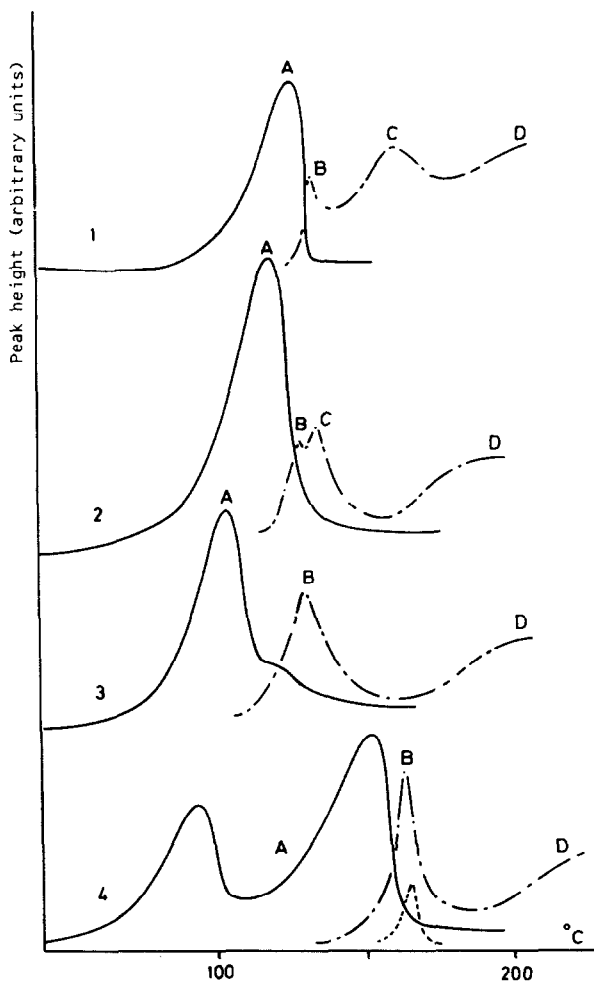


Fig. 1. Profiles for gas evolution in TPDE experiments. H_2 flow: 40 ml/min, atmospheric pressure; heating rate: $6^\circ\text{C}/\text{min}$. 1: $\text{Co}_4(\text{CO})_{12}$ 2.24 mg; 2: $\text{Co}_3\text{Rh}(\text{CO})_{12}$ 1.90 mg; 3: $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ 1.86 mg; 4: $\text{Rh}_4(\text{CO})_{12}$ 5.92 mg. Evolved gas: CO (—), CH_4 (---), C_2H_6 (-·-·-·).

the CO gas profile. Such a shape was previously noted by Tang et al. in thermogravimetric studies [3]. Their suggestion was that the first peak was related to loss of the three bridging carbonyl ligands, to give the stable intermediate cluster $\text{Rh}_4(\text{CO})_9$.

Owing to the large difference between the two maxima (ca. 60°C) decarbonylation can be stopped just after the first peak and a sample analysed. The IR spectrum shows that the well known $\text{Rh}_6(\text{CO})_{16}$ cluster is quantitatively formed, not $\text{Rh}_4(\text{CO})_9$, as the first step in the TPDE of $\text{Rh}_4(\text{CO})_{12}$ ($\nu(\text{CO})$ in CH_2Cl_2 : 2076.2 vs. 2044.2 w, 1806 m). Reaction 1 was recognized previously during pyrolysis of



$\text{Rh}_4(\text{CO})_{12}$ in sealed evacuated tubes [4].

The CO evolution profiles for the four isostructural clusters do not enable any

distinction to be made between terminal and bridging carbonyl ligands and give no information about the nature of the metal centre, but only give insight into the formation of stable intermediates.

It is noteworthy that $\text{Co}_4(\text{CO})_{12}$ was reported to behave rather like $\text{Rh}_4(\text{CO})_{12}$, showing multiple peaks in the CO evolution profile, and formation of the postulated $\text{Co}_4(\text{CO})_8$ intermediate after an almost one-by-one CO loss [3]. Despite many attempts, we were not able to reproduce that observation; the explanation for this may be related to the difference in the initial mass of samples used in the decarbonylation reaction, in our experiments being 10 times lower.

Even with a carefully purified sample of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ the TPDE peak is followed by a shoulder. No intermediate could be characterized, but a plausible suggestion is that this shoulder is related to the formation of hexanuclear species such as $\text{Rh}_4\text{Co}_2(\text{CO})_{16}$, as reported by Martinengo et al. for thermal transformation of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ in heptane solution [5].

T_m position

In our earlier TPDE study on $\text{Co}_4(\text{CO})_{12}$ [2] we showed that the temperature of the peak maximum (T_m) is governed by the heating rate (β) and by the initial mass of the sample (m_0). The same parameters determine T_m values for all the clusters $\text{RhCo}_3(\text{CO})_{12}$, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$, and preliminary results on various carbonyl compounds indicate that it is a general property of this class of complexes. When the β and m_0 effects operate together, the T_m shift may be quite large, with values over 20°C (Table 1). Hence caution must be taken in identifying unknown species from comparisons of T_m values. Erroneous clues can be avoided only if experimental conditions, including β , m_0 , gas flow, gas pressure, and also the crystallinities of the compared samples, are identical.

Linear plots of $2 \log T_m - \log \beta$ versus $1/T_m$ at constant initial sample mass give the activation energies (E_a) for the decarbonylations of the clusters. A different set of T_m values measured for a different initial sample mass is necessary to arrive at

TABLE 1

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED T_m VALUES ^a

	m_0 (mg)	β (°C min ⁻¹)	T_m obs.	T_m calcd.
$\text{Rh}_4(\text{CO})_{12}$	4.75	6	79.7	79.65
$\text{Rh}_4(\text{CO})_{12}$	6.77	6	81.6	81.8
$\text{Rh}_4(\text{CO})_{12}$	4.75	2	69.85	69.90
$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	1.39	6	81.7	81.95
$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	4.25	6	90.9	90.65
$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	4.20	1	72.7	72.65
$\text{Rh}_3\text{Co}(\text{CO})_{12}$	3.20	6	113.7	113.6
$\text{Rh}_3\text{Co}(\text{CO})_{12}$	1.90	6	109.2	108.9
$\text{Rh}_3\text{Co}(\text{CO})_{12}$	1.90	2	91.45	91.30
$\text{Co}_4(\text{CO})_{12}$	3.20	6	122.3	122.1
$\text{Co}_4(\text{CO})_{12}$	4.85	6	127.0	127.05
$\text{Co}_4(\text{CO})_{12}$	4.82	2	109.6	109.75

^a 40 ml/min H_2 flow at atmospheric pressure.

TABLE 2

VALUES OF THE KINETIC PARAMETERS FOR THE DECARBONYLATION REACTION FOR THE $M_{4-x}M'_x(\text{CO})_{12}$ CLUSTERS

	E_a (kcal mol ⁻¹)	A (min ⁻¹ mg ¹⁻ⁿ)	n
Rh ₄ (CO) ₁₂ ^a	26.6	10 ^{16.7}	0.34
Rh ₂ Co ₂ (CO) ₁₂	24.0	10 ^{14.6}	0.24
RhCo ₃ (CO) ₁₂	15.8	10 ^{8.7}	0.47
Co ₄ (CO) ₁₂ ^b	18.0	10 ^{9.8}	0.26

^a Values calculated for the first CO peak. ^b Co₄(CO)₁₂ values are different from ref. 2 because gas pressure was changed (atmospheric pressure in these experiments).

the global reaction order (n). The preexponential factor (A) is calculated from the formula:

$$2 \log T_m - \log \beta = E/RT_m + \log(E/AR) + \log\left(\frac{1}{n} m_{max}^{1-n}\right).$$

When the E_a , n , and A parameters have been determined (Table 2), the T_m values

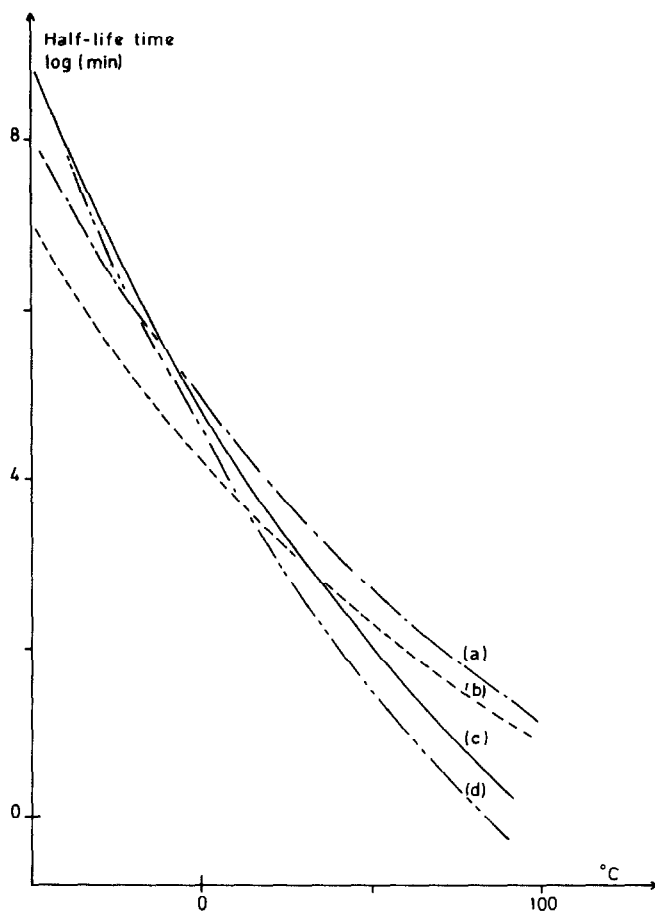


Fig. 2. Isothermal decomposition: half life time for 1.748×10^{-5} mole of carbonyl clusters (~ 10 mg) (a) Co₄(CO)₁₂; (b) Co₃Rh(CO)₁₂; (c) Co₂Rh₂(CO)₁₂ and (d) Rh₄(CO)₁₂.

can be derived for any m_0 sample by numerical solution of the equation $dm/dt = -km^n$ (eq. 2) with $k = Ae^{-E/RT}$ and with temperature (T) a linear function of time (t): $T = T_0 + \beta t$. The calculated and observed values of T_m are in good agreement, as can be seen from Table 1.

Isothermal decarbonylations can be analysed by solving the differential equation 2. The residual fraction m of an initial sample m_0 remaining after heating at $T^\circ\text{C}$ for t minutes is then expressed as:

$$m = ((n-1)A e^{-E/RT}t + m_0^{1-n})^{1/1-n} \quad (3)$$

To provide comparisons of the thermal stabilities of the clusters, the half-life times are plotted in Fig. 2.

$\text{Rh}_4(\text{CO})_{12}$ which is the most stable cluster at -50°C , appears to be the least stable at $+50^\circ\text{C}$, underlining the fact that relative thermal stabilities are not governed solely by the activation energies when A and n are significantly different.

Reactivity of the CO ligands

Two features were revealed when GC analysis was performed on the flowing gas. The first involves most of the carbonyl ligands, which are eliminated as carbon monoxide (peak A, Fig. 1), with no reaction with hydrogen, either for terminal or bridging CO. The second feature, which is much more complex, involves the successive stepwise formation of hydrocarbon species. Only preliminary studies were performed in this area, and these are reported below.

The first step is located just after T_m (peak B, Fig. 1) and is characterized by the formation of a sharp hydrocarbon peak, mainly composed of CH_4 , with traces of C_2H_6 in the case of $\text{Rh}_4(\text{CO})_{12}$ and $\text{RhCo}_3(\text{CO})_{12}$. For all four clusters, the hydrocarbon peak B has a maximum which seems to be closely correlated to the position of T_m and not to the reactor temperature (Table 3); this suggests that the reactivity of the remaining CO on the $\text{M}_4(\text{CO})_x$ solid formed during the decarbonylation process is governed by the CO/metal ratio, as noted by Dalmon and Martin [6] for CO methanation of silica-supported Ni. These authors were able to conclude that the rate-determining step of the reaction involves the collision of a H_2 molecule with a site composed of approximately 13 adjacent Ni atoms free from inactive adsorbed CO species.

TABLE 3
VALUES OF T_m AND THE TEMPERATURE OF THE FIRST MAXIMUM IN CH_4 EVOLUTION (peak B, Fig. 1)

	T_m ($^\circ\text{C}$)	CH_4 peak ($^\circ\text{C}$)	$\text{CH}_4 - T_m$
$\text{Rh}_4(\text{CO})_{12}$	130.6 ^a	140.0	9.4
$\text{Rh}_4(\text{CO})_{12}$	155.8 ^a	165.3	9.5
$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	110 ^b	118	8
$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$	124.1 ^b	132.1	8
$\text{RhCo}_3(\text{CO})_{12}$	95	108.5	13.5
$\text{RhCo}_3(\text{CO})_{12}$	113.7	127.7	14
$\text{Co}_4(\text{CO})_{12}$	114.7	120.2	5.5
$\text{Co}_4(\text{CO})_{12}$	123.0	128.6	5.6

^a T_m values of the higher temperature peak. ^b Position of T_m on the shoulder.

The second step (peak C) appears only with $\text{Co}_4(\text{CO})_{12}$ and $\text{RhCo}_3(\text{CO})_{12}$ (respective maxima at 160–170°C and 110–130°C, depending upon the experimental conditions). The third step (peak D) is characterized by CH_4 formation over a large range of temperature. When isothermal conditions are maintained (ca. 300°C), the CH_4 concentration in the gas flow slowly decreases to zero during one or two hours.

Our results provide no indication on the form adopted by the reactive carbon species which give rise to hydrocarbon formation. When TPDE is performed under a helium flow, CO_2 is detected at temperatures above T_m , showing that C formation occurs by CO disproportionation.

The mass balances for the least sublimable clusters, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$, provide additional confirmation that some carbon remains in the metallic part of the sample after TPDE conducted under hydrogen.

The existence of various carbon species of differing reactivities deposited on metals, is an actively studied topic [7–9]. It can be suggested that peaks B, C and D are related to the forms of non-oxygenated carbon identified by Duncan et al. [8], and designated by C_α , $\text{C}_{\beta 1}$ and $\text{C}_{\beta 2}$.

Under H_2 , $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ deposited on alumina give CH_4 at 150°C with a CH_4 /metal ratio of 1.3 for $\text{Co}_4(\text{CO})_{12}$ and 1.5 for $\text{Rh}_4(\text{CO})_{12}$ [10]. In our experiments with the unsupported clusters, only a CH_4 /metal ratio of 0.14 was observed for $\text{Co}_4(\text{CO})_{12}$ for peaks B, C and D combined with a contribution of only 0.016 from peak B. This result throws light on the large effect of the support in the methanation reaction, since the production of CH_4 is enhanced 10 times by impregnation on alumina.

When decarbonylation is over, most of the cobalt is deposited as a metallic mirror on the wall of the glass reaction in the case of $\text{Co}_4(\text{CO})_{12}$, whereas $\text{RhCo}_3(\text{CO})_{12}$, $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ give solid residues of metallic appearance. Preliminary studies indicate that these aggregates are active for catalytic methanation of CO.

References

- 1 T.J. Thomas, D.A. Hucul and A. Brenner, Am. Chem. Soc. Symposium Series, 192 (1982) 268.
- 2 D. Labroue, R. Pince and R. Queau, J. Organomet. Chem., 249 (1983) 405.
- 3 L.M. Fillman and S.C. Tang, Thermochemica Acta, 75 (1984) 71.
- 4 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1975) 2606.
- 5 S. Martinengo, P. Chini, V.G. Albano, F. Cariati and T. Salvatori, J. Organomet. Chem., 59 (1973) 379.
- 6 J.A. Dalmon and G.A. Martin, J. Catal., 84 (1983) 45.
- 7 C.H. Bartholomew and C.K. Vance, J. Catal., 91 (1985) 78.
- 8 T.M. Duncan, P. Winslow and A.T. Bell, J. Catal., 93 (1985) 1.
- 9 C. Mirodatos, J.A. Dalmon and G.A. Martin, Stud. Surf. Sci. Catal., 19 (1984) 19.
- 10 D.A. Hucul and A. Brenner, J. Am. Chem. Soc., 103 (1981) 217.