DETERMINATION OF KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION REACTION OF CARBONYL COMPLEXES BY TPDE METHOD; APPLICATION TO UNSUPPORTED $Co_4(CO)_{12}$ IN FLOWING HYDROGEN

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Summary

A method for determining the activation energies, rate constants and reaction orders for the thermal decomposition of carbonyl complexes by temperature programmed decomposition studies is proposed. The heating program involves a linear variation of the sample temperature with time ($T = T_0 + \beta t$). Decomposition occurs in a H_2 flow as carrier gas and the evolved gases are analysed by gas chromatography. The temperature T_m of the maximum decomposition rate is not only characteristic of the carbonyl cluster but is also dependent on two experimental parameters, β and the initial mass sample m_0. The application of the method to $Co_4(CO)_{12}$ is described.

Introduction

Pyrolysis under vacuum or under hydrogen of carbonyl clusters deposited on metal oxides is currently used to produce catalysts [1]. Temperature-programmed decomposition (TPDE) is a technique developed by Brenner and Hucul [2] in which the evolution of gas is monitored during thermal activation of the cluster to provide information on the formation of subcarbonyl species and on the stoichiometric reactions which occur between the support and the absorbed complex.

The TPDE technique has been applied to most of the commonly available carbonyl complexes deposited on various metal oxides [3,4], but no detailed studies have been published for unsupported clusters. We describe below a study of the temperature-programmed decomposition of metal carbonyls in a stream of carrier gas, leading to the determination of the reaction order, the value of the activation energy, and the pre-exponential factor. The application of the method to the decomposition of $Co_4(CO)_{12}$ in a stream of hydrogen is used to illustrate the procedure.

Results

The temperature-programmed desorption of gas with linear temperature increase is usually represented by eq. 1, where T_m is the temperature of the peak maximum [5].

$$2 \log T_m - \log \beta = E_d/2.303 \, R \, T_m + \log(E_d/AR) \tag{1}$$

The variation of the temperature with time is given by eq. 2.

$$T = T_0 + \beta t \tag{2}$$

In eq. 1 E_d is the activation energy for desorption, R is the gas constant, and A is the pre-exponential factor. This equation has been used to calculate E_d and A varying β and measuring the corresponding T_m.

Application of eq. 1 to the temperature-programmed decomposition of a metal carbonyl will be valid only if the decomposition reaction is a first order reaction. In the general case of a carbonyl complex $M_x(CO)_y$ the reaction order is n and eq. 1 must be recalculated. At a given time the mass of the sample during its decomposition is given by eq. 3:

$$dm/dt = -km^n \tag{3}$$

The temperature dependance is given by the Arrhenius law:

$$k = A \exp(-E/RT) \tag{4}$$

With a flow rate F of the carrier gas, the concentration c of CO in the gas phase at any time is:

$$c = ykm^n/MF \tag{5}$$

where M is the molecular weight of the carbonyl complex $M_x(CO)_y$. Equation 3 can be transformed in eq. 6

$$-\beta dm/dT = km^n \tag{6}$$

Differentiation of c in eq. 5 with respect to T gives:

$$dc/dT = \frac{y}{MF}\left(m^n \frac{dk}{dT} + knm^{n-1} \frac{dm}{dT} \right) \tag{7}$$

The maximum concentration of CO in the carrier gas will be reached at the temperature T_m at which $dc/dT = 0$. Equations 6 and 7 then give:

$$k_m = \frac{\beta E m_{max}^{1-n}}{nRT_m^2} \tag{8}$$

which can be rearranged into:

$$2 \log T_m - \log \beta = E/2.303 \, RT_m + \log(E/AR) + \log\left(\frac{1}{n} m_{max}^{1-n}\right) \tag{9}$$

Equation 9 shows that when n is different from unity T_m is a function of m_{max}, which is the mass of carbonyl cluster remaining at the temperature of the peak maximum. A reasonable value of m_{max} can be derived from the profile of the TPDE curve and related to the initial mass of cluster m_0.

For $Co_4(CO)_{12}$ (Fig. 1), the relation was $m_{max} = 0.25 \, m_0$. The observed experi-
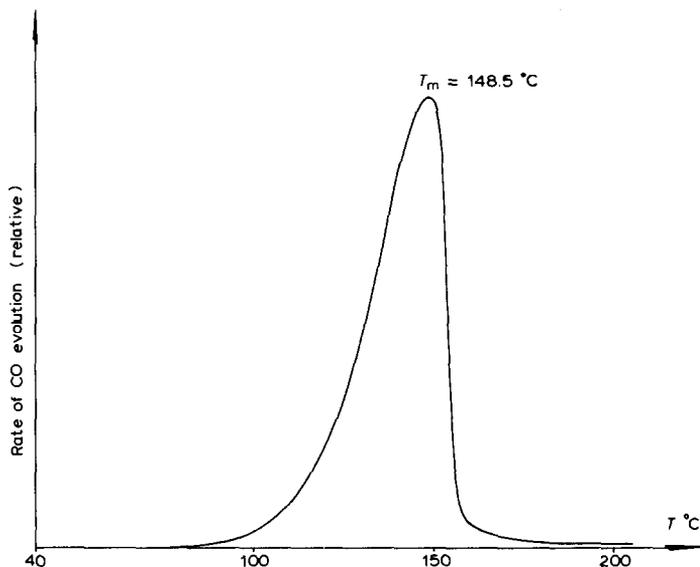
Fig. 1. TPDE of $Co_4(CO)_{12}$ (m_0 9.0 mg; β 6°C/min).

mental temperature dependence of T_{max} with the initial quantity of $Co_4(CO)_{12}$ (Table 1) shows that decomposition of $Co_4(CO)_{12}$ is not a first order reaction.

TABLE 1

TPDE OF $Co_4(CO)_{12}$ IN FLOWING H_2; VARIATIONS OF T_m WITH β

β (°C/min)	T_m (m_0 4.7 mg) (°C)	T_m (m_0 10 mg) (°C)
1	109.5	118
2	120.5	130.5
4	136.5	147.5
6	142.5	152
8	146	154.5

Determination of the reaction order

According to eq. 9, a plot of $2 \log T_m - \log \beta$ versus $1/T_m$, at constant m_0, must give a straight line. Another set of values for a different m_0 and same β gives a parallel straight line. The distance Δ between the two lines, measured along the y axis, allows calculation of the reaction order n (Fig. 2).

$$n = 1 - \Delta/\log(m_1/m_2) \tag{10}$$

When E and A have been determined, the variation of T_m as a function of m_0 can be derived (for a given value of β) from eq. 9. Fitting the experimental curve $T_m = f(m_0)$ to one of the lines of the calculated set (Fig. 3) allows an evaluation of the reaction order n.
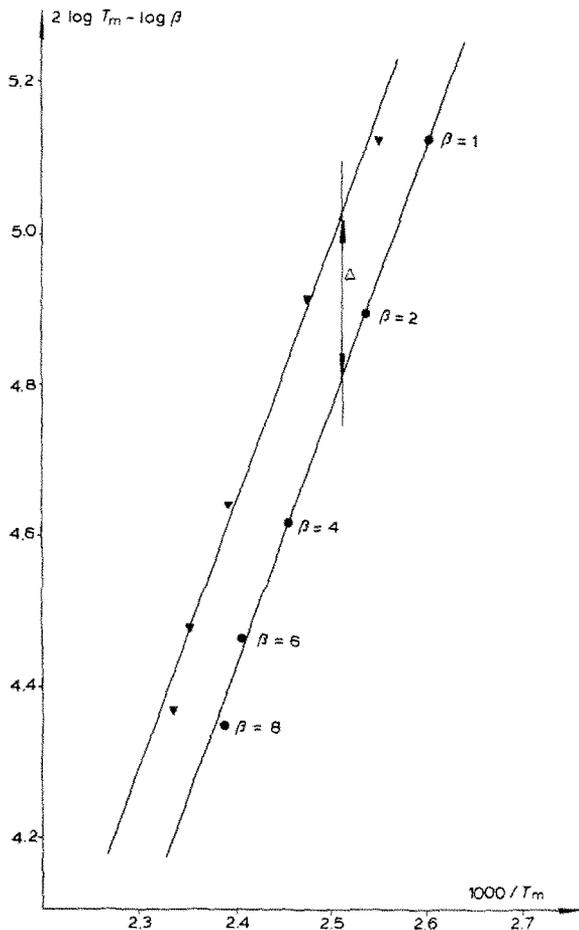
Fig. 2. Plots of $(2 \log T_m - \log \beta)$ against $1/T_m$ for m_0 4.7 mg($\bullet$) and m_0 10 mg ($\blacktriangledown$).

For $Co_4(CO)_{12}$ this method leads to $n = 0.36 \pm 0.02$, whereas calculation from eq. 10 gives $n = 0.37 \pm 0.04$. Such a fractional reaction order, differing from unity by far more than the experimental uncertainty, means that no simple mechanism can be proposed to describe the decomposition of $Co_4(CO)_{12}$.

Determination of the activation energy

The activation energy of decomposition, E, can be evaluated from the slope of the linear relation between $2 \log T_m - \log \beta$ and $1/T_m$ (eq. 9, Fig. 2). For $Co_4(CO)_{12}$ the E value was 15.9 ± 0.2 kcal mol^{-1}.

Determination of the pre-exponential factor

When n and E are determined as previously, A is readily calculated from eq. 9, this gives a value of A $10^{8.2}$ s^{-1} mg^{1-n} when m_0 is expressed in mg. These values of E and A for unsupported $Co_4(CO)_{12}$ are somewhat lower than those calculated for carbonyl complexes deposited on refractory oxides [6] ($E \sim 30$ kcal mol^{-1}; $A = 10^{13}$
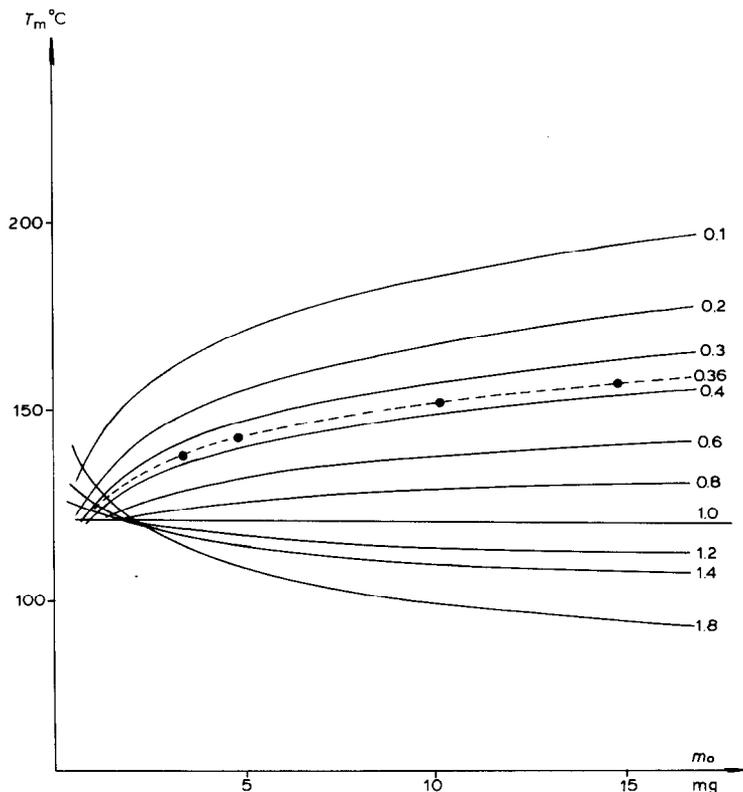
Fig. 3. Calculated curves T_m: $f(m_0)$ for $\beta = 6$; $A = 10^{8.2}$ and $E = 15.9$ kcal mol^{-1}. (●) Experimental values of T_m.

s^{-1}). However, we must point out that in the latter calculation the cleavages of the M–CO bonds were assumed to be unimolecular, with a pre-exponential factor equal to $10\ kT_m/h$, whereas we conclude that the decomposition of $Co_4(CO)_{12}$ is not first order.

Experimental

Tetracobaltdodecacarbonyl was prepared by refluxing a toluene solution of dicobalt octacarbonyl and was recrystallized prior to use. High purity hydrogen was used without further purification.

Apparatus

The reactor, a 60 mm long and 6 mm o.d. Pyrex glass tube, was heated in the oven of a gas chromatograph IGC 120 ML. The H_2 flow rate was maintained at 30 ml/min in all experiments.

The total amount of gas obtained during the programmed decomposition was measured with a thermal conductivity detector connected to a ICR 1B integrator, this gave the T_m value and the peak area.

The composition of the evolved gas was analyzed with a second chromatograph IGC 16 equiped with a 5 Å molecular sieve (40/60 mesh) or a Porapak Q (80/100 mesh) column (1/8'' o.d. and 2 m lenght).

Procedure

A precisely weighted amount of $Co_4(CO)_{12}$ (1 to 15 mg range) was introduced into the Pyrex tube and held between two cotton glass plugs. The TPDE was started at 40°C and terminated at 250°C. The sweep rate was in the range 0.2 to 10°C/min.

Careful measurements were made to determine the true temperature of the cluster sample inside the Pyrex tube, and also the dead volume between the cluster sample an the T.C. detector in order to minimize most of the experimental errors which might affect the determination of T_m [7]. At the end of the TPDE run, decomposition of $Co_4(CO)_{12}$ was complete and a cobalt mirror of small surface area was deposited inside the Pyrex tube. Only a very small amount of CH_4 was formed during the decomposition and so integration of the TPDE peak can be regarded as referring only to CO. 11 ± 0.5 of the carbonyl groups of the $Co_4(CO)_{12}$ were accounted for. This observation is in agreement with earlier thermogravimetric experiments [8] where up to 11.7 CO per molecule of $Co_4(CO)_{12}$ were evolved at β 10°C/min.

Conclusion

TPDE studies of unsupported $Co_4(CO)_{12}$ show that the weight of the sample (m_0) is as important a parameter as the heating rate β in determining the temperature of the peak maximum (T_m). A plot of $2 \log T_m - \log \beta$ against $1/T_m$ for two sets of m_0 indicated a reaction order of 0.36, and gave a value of the activation energy E of 15.9 kcal mol^{-1}. The fractional value of n indicates the limitation of the analogy which can be drawn between desorption of CO absorbed on a metal and decomposition of a carbonyl cluster.

Bibliography

1 (a) M. Ichikawa, J. Cat, 59 (1979) 67;
  (b) M. Ichikawa, Bull. Chem. Soc. Jap., 51 (1978) 2268.
2 D.A. Hucul and A. Brenner, J. Am. Chem. Soc., 103 (1981) 217 and ref. therein.
3 A. Brenner and D.A. Hucul, J. Am. Chem. Soc., 102 (1980) 2484.
4 L. Guczi, Z. Schay, K. Lazar, A. Vizi and L. Marko Surface Sci., 106 (1981) 516.
5 R.J. Cvetanovic and Y. Amenomiya, Advances in Catalysis, vol. 17, p. 103, Academic Press, New York, 1967.
6 A. Brenner and D.A. Hucul, Inorg. Chem., 18 (1979) 2836.
7 A. Brenner and D.A. Hucul, J. Catal., 56 (1979) 134.
8 R. Psaro, A. Fusi, R. Ugo, J.M. Basset, A.K. Smith and F. Hughes J. Mol. Catal., 7 (1980) 511.