The non-isothermal decomposition kinetics of palladium(II) chloride complexes with sulphoxides $R-SO-C_6H_4CH_3$ and thioethers $R-S-C_6H_4CH_3$

Zhengrong Lu and Li Yang

The Central Laboratory, Suzhou University, Suzhou, Jiangsu 215006 (People's Republic of China)

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Abstract

The thermal decomposition under a nitrogen atmosphere of two new series of palladium(II) chloride complexes with sulphoxides $R-SO-PhCH_3$ and thioethers $R-S-PhCH_3$ ($R = C_4H_9$, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ and $C_{12}H_{25}$) was examined by means of non-isothermal gravimetric measurements. The values of the kinetic parameters, such as activation energy E, frequency factor A and reaction order n, obtained using the Coats–Redfern, Freeman–Carroll and Kissinger equations, are in good agreement. In addition, the values of the activation entropy ΔS were calculated. The E values for the complexes with thioether ligands were found to be somewhat higher than those of the complexes with sulphoxides. A qualitative relationship between the E values and the alkyl group in the ligand molecules was established. Finally, the thermal behaviour of both series of complexes was carefully observed and is discussed.

INTRODUCTION

Thermoanalytical methods are being employed increasingly in the investigation of complex properties. Among these methods, the thermogravimetric technique has a very important role in the kinetic study of the thermal decomposition processes of complexes, and many scientists [1–3] have made valuable contributions to this field. In the present work we investigated the thermal behaviour and estimated the kinetic parameters for the thermal decomposition of two new series of palladium(II) chloride complexes with sulphoxides and thioethers: $PdL_2^1Cl_2$ and $PdL_2^2Cl_2$ ($L^1 = R-SO-PhCH_3$ and $L^2 = R-S-PhCH_3$; $R = C_4H_9$, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ and $C_{12}H_{25}$). The Freeman–Carroll [4], Coats–Redfern [5] and Kissinger [6,7] methods were used for this purpose, and the kinetic parameters were then obtained by a least-squares regression analysis of the experimental data [8].

EXPERIMENTAL DETAILS

Chemicals

All the compounds investigated in this work were newly prepared and kindly presented by the Department of Chemistry, Suzhou University. The

identity and quality of the compounds were checked by elemental analysis (performed on a Carlo Erba model 1106 elemental analyser) and IR spectrophotometry (on an Alpha Centauri IR spectrometer).

Apparatus

The TG–DTG runs, under non-isothermal conditions, were carried out on a Perkin–Elmer TGA-7 Delta series thermogravimetric analyser equipped with a 3700 data station, in a dynamic atmosphere of pure N_2 flowing at 20 ml min^{-1}. The sample mass range was 3–5 mg. A heating rate of 5°C min^{-1}, unless otherwise specified, was employed within the temperature interval from 50 to 700°C.

THEORETICAL

In recent years, because of its advantages, there have been more applications of non-isothermal gravimetry than of isothermal gravimetry in the determination of the rate-dependent parameters of solid state decomposition reactions. Several methods have been proposed for this purpose [4,5,9–11], and have been discussed and compared [1,12,13]. These approaches are derived using different approximations of the formal kinetic equation [14]

$$-\,\mathrm{d}X/\mathrm{d}t = kX^n \tag{1}$$

where X is the amount of substance under reaction, n is the order of reaction, and the specific rate of reaction k is assumed to follow the Arrhenius equation for temperature dependency [15]:

$$k = A\,\exp(-E/RT) \tag{2}$$

where A is the frequency (or pre-exponential) factor, E the activation energy and R the universal gas constant.

Freeman and Carroll equation [4]

The Freeman–Carroll equation is one of the most well known and widely used approaches [16]. Its expression for practical calculation is in the form

$$\frac{-(E/2.3R)\,\Delta T^{-1}}{\Delta \log W_r} = \frac{\Delta \log(\mathrm{d}W/\mathrm{d}t)}{\Delta \log W_r} - n \tag{3}$$

where $W_r = (W_c - W)$ with W_c being the mass loss at completion of the reaction and W the mass loss at time t. Hence the equation can now be plotted in the form $\Delta \log(\mathrm{d}W/\mathrm{d}t)/\Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r$ to obtain the intercept on the y axis at $x = 0$, equal to the value of n, and a slope of $-E/2.3R$, to obtain E.

Coats and Redfern equation [5]

The equation derived by Coats and Redfern is

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{\Phi E}\left(1-\frac{2RT}{E}\right) - \frac{E}{2.3RT} \tag{4}$$

for $n \neq 1$, whereas for $n = 1$ the left-hand side reduces to $\log[-\log(1-\alpha)/T^2]$, where α is the fraction decomposed and Φ is the heating rate. The graph of the left-hand side of the equation vs. the reciprocal absolute temperature $(1/T)$ is thus a straight line of slope $-E/2.3R$ for the correct value of n. The main difficulty in this method is finding the optimum value of n, unknown in advance. This can usually be done by computer, using a trial and error method. The Coats–Redfern method, therefore, is considered more accurate but is considerably time consuming [12].

Kissinger equation [6,7]

In general, the Kissinger method is listed among the approaches treating DTA instead of TG–DTG curves [16]. So far, few articles have reported the results of thermogravimetric studies of decomposition kinetics by this method [17]. With regard to some similarities and comparabilities between DTA and DTG curves [16], however, the Kissinger method may be used here for complementary information purposes, despite some possible differences between them [16]. Besides, the question as to whether the Kissinger method applies to the DTG data in the present study intrigued us. The equation is

$$\frac{d\log(\Phi/T_s^2)}{d(1/T_s)} = -\frac{E}{2.3R} \tag{5}$$

where Φ is the heating rate and T_s is the corresponding peak temperature of the DTG curves obtained at various heating rates. Equation (5), after integration, becomes

$$\log\frac{\Phi}{T_s^2} = -\frac{E}{2.3R}\left(\frac{1}{T_s}\right) + c \tag{6}$$

where c is an integration constant. It is thus obvious that a plot of $\log \phi/T_s^2$ against $1/T_s$ will provide the E value.

RESULTS AND DISCUSSION

Data processing

In the present study, the Freeman–Carroll equation, eqn. (3), was first used to determine the order of the decomposition reactions, but as in other

similar observations made by several authors [18–20], it failed to provide the correct n value for subsequent use in eqn. (4). The Coats–Redfern equation, eqn. (4), was then applied, and n was determined by a trial and error method using a computer program, which gave quite good results and revealed that, for all the compounds in this study, 0.25 seems to be the optimum value of n, resulting in the best correlation coefficient r. In order to estimate E values by the Kissinger method, TG measurements at various heating rates (2.5, 5.0, 10, 15 and 20 °C min^{-1}) were performed on every sample under experimental conditions that were as close as possible. Thus, the corresponding T_s values were read from various DTG curves. The graphs provided by this method had good linearity.

Thus the n value was obtained on the basis of the best trial value in eqn. (4), and A was calculated from the intercept of the plot defined by the same equation. In all cases, E was calculated from the slope for eqns. (3), (4) and (5), and the activation entropy ΔS was calculated using the equation [21]

$$\Delta S = R \ln(Ah/kT_s) \tag{7}$$

where k is the Boltzmann constant, h is the Planck constant and T_s is the DTG peak temperature, in this study, at a heating rate of 5 °C min^{-1}. The least-squares linear regression method was used during the above calculations.

All the results obtained are given in Table 1 which shows that the values of E obtained for each sample using the three equations do not differ by more than 10%.

TABLE 1

Kinetic parameters determined using the Freeman–Carroll, Kissinger and Coats–Redfern methods

Complex	Kinetic parameters							
	Freeman–Carroll		Kissinger		Coats–Redfern			
	E (kJ mol^{-1})	r	E (kJ mol^{-1})	r	E (kJ mol^{-1})	A	ΔS (J K^{-1} mol^{-1})	r
PdL$_2^1$Cl$_2$ (L^1 = RSOPhCH$_3$)								
R = C$_4$H$_9$	47.75	0.9904	44.55	0.9981	43.10	8.3×10^1	−211	0.9995
R = C$_6$H$_{13}$	50.21	0.9916	46.27	0.9987	46.02	1.5×10^2	−206	0.9995
R = C$_8$H$_{17}$	59.78	0.9982	56.05	0.9981	53.63	1.5×10^3	−188	0.9996
R = C$_{10}$H$_{21}$	71.11	0.9923	70.52	0.9991	70.06	7.4×10^4	−156	0.9998
R = C$_{12}$H$_{25}$	76.34	0.9945	72.31	0.9938	71.10	8.5×10^4	−155	0.9994
PdL$_2^2$Cl$_2$ (L^2 = RSPhCH$_3$)								
R = C$_4$H$_9$	48.80	0.9930	45.61	0.9994	43.51	9.5×10^1	−211	0.9998
R = C$_6$H$_{13}$	53.18	0.9913	50.91	0.9956	48.74	2.4×10^2	−203	0.9997
R = C$_8$H$_{17}$	61.21	0.9898	60.69	0.9979	58.13	4.5×10^2	−198	0.9997
R = C$_{10}$H$_{21}$	83.69	0.9915	82.35	0.9930	80.13	3.9×10^5	−142	0.9993
R = C$_{12}$H$_{25}$	85.75	0.9976	83.85	0.9986	83.68	4.1×10^5	−142	0.9995

General features of the decomposition

The general information about the thermal behaviour of the complexes, in terms of stability ranges, peak temperatures and weight-loss values is listed in Table 2. Both series of complexes are stable up to about 155 °C; then their single-step decompositions begin, and are completed at around 650 °C. Inspection of Table 2 demonstrates that the DTG peak temperatures of L^2 complexes are, on the whole, somewhat higher than those of L^1 complexes. Moreover, it decreases in the order $R = C_{12}H_{25} > C_{10}H_{21} > C_8H_{17} > C_6H_{13} > C_4H_9$ for both series, where R is the alkyl group in the ligands L^1 or L^2. Meanwhile, the activation energy value also varies in exactly the same way (Table 2). These phenomena are expected from chemical considerations: the existence of a more electronegative oxygen atom brings about a reduction in the electron density surrounding the corresponding sulphur atom, thus leading to a decrease in the polarity and, further, in the strength of the Pd–S bond; in comparison, the complexes with sulphoxide L^1 are somewhat unstable. In contrast with an oxygen atom, alkyl groups, R, are generally considered to be somewhat electron-donating [22], and increasing the chain length of R could, to a certain extent, lead to a stronger Pd–S bond. Therefore complexes with a larger R in any ligand series tend to be more stable.

TABLE 2

The thermal behaviour of the complexes

Complex	Temperature (°C)			Weight loss (%)	
	T_i	T_f	T_s	Calc.	Found
$PdL_2^1Cl_2$ ($L^1 = RSOPhCH_3$)					
$R = C_4H_9$	152	625	180.7	81.32	81.09
$R = C_6H_{13}$	154	630	187.9	83.00	83.25
$R = C_8H_{17}$	157	630	196.5	84.39	83.84
$R = C_{10}H_{21}$ stage I	160	264.4	207.9	75.97 [a]	75.08
stage II	264.4	640	–	85.58	84.89
$R = C_{12}H_{25}$ stage I	166	283.6	228.1	77.67 [a]	76.81
stage II	283.6	650	–	86.60	86.62
$PdL_2^2Cl_2$ ($L^2 = RSPhCH_3$)					
$R = C_4H_9$ stage I	155	252.7	213.9	67.03 [a]	66.59
stage II	252.7	630	–	80.22	81.15
$R = C_6H_{13}$ stage I	158	252.9	219.1	70.10 [a]	69.79
stage II	252.9	640	–	82.07	81.79
$R = C_8H_{17}$	162	645	238.2	83.62	83.15
$R = C_{10}H_{21}$	165	650	240.3	84.93	84.21
$R = C_{12}H_{25}$	170	650	263.7	86.03	86.92

[a] Values calculated based on release of L from the complexes in stage I.
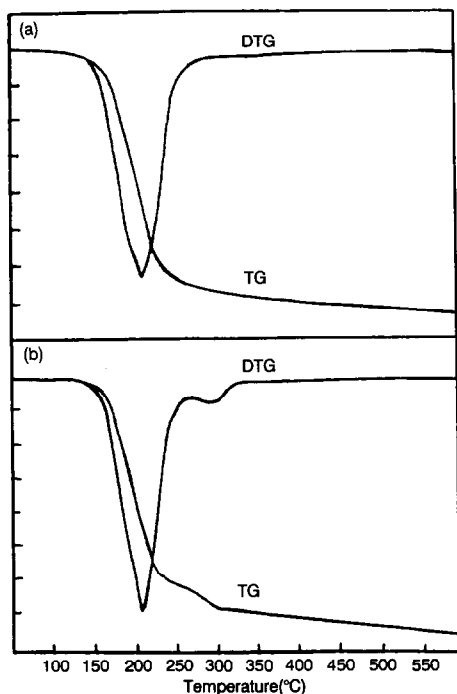
Fig. 1. TG–DTG curves of $[Pd(R–SO–PhCH_3)_2]Cl_2$: (a) $R = C_8H_{17}$; (b) $R = C_{10}H_{21}$.

A close observation of the TG curves reveals that varying R results in a tendency towards a two-step decomposition mode. Moreover, it is very interesting to note that the tendency to two-step decomposition grows with increasing chain length of R for L^1 complexes, but that the opposite occurs for L^2 complexes. Figures 1 and 2 show the two opposite situations. Figure 1 shows the TG–DTG curves of two L^1 complexes; we can see that when R is as large as C_8H_{17}, the complex has a single-step decomposition mechanism; but when $R = C_{10}H_{21}$, the indication of a two-step mode becomes discernible. Figure 2 is for the L^2 complex series; the DTG curves show the reverse tendency more clearly.

The interpretation of this phenomenon seems to be beyond our knowledge at present. From the TG curves of the complexes, it could be stated that the intermediates of the decomposition are unstable within the temperature range. Analysis of the weight losses (Table 2) suggests that, in the case of single-step decomposition, the complexes release both ligand molecules and chlorine atoms almost simultaneously, while in the case of two-step decomposition the complexes release the ligands first, then, immediately, the chlorine atoms. As none of the second stages of decomposition are sufficiently distinguishable (even at a very low heating rate) to present convincing data for evaluation of significant kinetic parameter values, no attempt to do this was made.
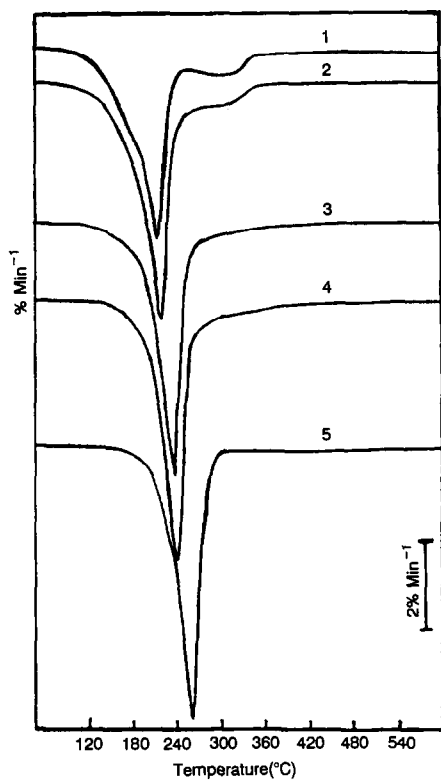
Fig. 2. DTG curves of $[Pd(R-S-PhCH_3)_2]Cl_2$: curve 1, $R = C_4H_9$; curve 2, $R = C_6H_{13}$; curve 3, $R = C_8H_{17}$; curve 4, $R = C_{10}H_{21}$; curve 5, $R = C_{12}H_{25}$.

CONCLUSIONS

From the results of the present study, the following conclusions may be drawn.

(1) The satisfactory value of r ($r \approx 1$) and the general agreement of the E values imply that all three methods, the Freeman–Carroll, Coats–Redfern and Kissinger equations, are applicable to this study for estimating kinetic parameters. The Coats–Redfern method seems to be the most helpful of the three, as it provided the most information.

(2) Both the activation energies and decomposition temperatures of $[PdL_2^2]Cl_2$, represented by the DTG peak temperatures, are somewhat greater than those of $[PdL_2^1]Cl_2$; these parameters fall in the order $R = C_{12}H_{25} > CF_{10}H_{21} > C_8H_{17} > C_6H_{13} > C_4H_9$ for both $[PdL_2^1]Cl_2$ and $[PdL_2^2]Cl_2$, where R is the alkyl group in the ligands. An attempt to interpret this has been made above.

(3) In general, these complexes decompose in a single step to leave residual Pd atoms. All these processes follow 1/4-order kinetics. However, a tendency to two-step decomposition was found. In the L^1 complexes this

tendency decreases in the order $R = C_{12}H_{25} > C_{10}H_{21} > C_8H_{17} > C_6H_{13} > C_4H_9$; this is the reverse order to that observed for the L^2 complexes.

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