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THERMAL BEHAVIOUR AND DECOMPOSITION KINETICS FOR TWO PALLADIUM(II) COMPLEXES WITH 1-AMINOPYRENE AND ITS DERIVATIVE

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Abstract

The thermal decomposition studies for two palladium(II) complexes $Pd(apyr)_2Cl_2$ and $Pd(pmpa)Cl_2$ (*apyr*=1-aminopyrene and *pmpa*=N-(2-pyridylmethylene)-1-pyrenylamine) were carried out in pure nitrogen using TG-DTG techniques. The non-isothermal kinetic parameters for the two complexes were evaluated employing the method suggested by Málek, Šesták, Koga *et al*. Based on the above results, thermal behaviour of the complexes were carefully discussed, which showed that not only the parameters value, but also the decomposition pattern and mechanism for complex 1 are different from complex 2.

Keywords: 1-aminopyrene (apyr), N-(2-pyridylmethylene)-1-pyrenylamine (pmpa), kinetics, palladium(II)

Introduction

The palladium(II) complexes with 1-aminopyrene(apyr) and its derivative are a new type of charge transfer with condensed aromatic compounds, in which there are relatively short distances between the donor and acceptor planes. Due to its special structure, both of the iodine doped complexes showed semiconductor properties [1–3].

In previous paper [3], we reported the preparation of the title complexes, their IR and UV-vis spectra and conductivities. Many efforts have been made to culture their single crystal, but unfortunately which was in vain for lack of a suitable solvent.

As an extension of our studies of the title complexes, the present paper is devoted to their thermal behaviour and the non-isothermal decomposition kinetics of the complexes under a dynamic nitrogen atmosphere by using the TG-DTG technique, the kinetic parameters and the mechanism have also been evaluated and studied by employing a more suitable method [4], i.e. one suggested by Málek, Šesták *et al.* [5–7], all the results were obtained with the aid of the computer program written by us. Based on the above results of two complexes, their thermal stability, decomposition pattern and mechanism are described.

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Experimental

The preparation and characterisation for the compounds were previously reported [3].

Thermal analyses of the complexes were performed on a Perkin Elmer Delta series TGA-7 thermogravimetric analyser in pure nitrogen flowing at a rate of 20 ml min^{-1}. The samples were heated at 2.5, 5.0, 10.0 and 15.0°C min^{-1} from 35 to 700°C, with approximately the same sample mass of 3–6 mg, respectively.

Theory

Kinetic investigations of solid state reactions have shown that the processes involved are generally complex [9, 10]. Recently a new complete method has therefore been proposed by Málek, Šesták, Koga and co-workers, allowing reliable kinetic analysis and interpretation of non-isothermal TG-DTG data. The method has been thoroughly described in the cited literature [5–8]. Here we give only a brief outline, referring the reader to the original papers for further details.

The general kinetic equation in non-isothermal studies is

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT) f(\alpha) \qquad (1)$$

where α, T, A, E and R are those in common use. β the heating rate and $f(\alpha)$ a function depending on the actual reaction mechanism. The most frequently used $f(\alpha)$ functions [11] are summarized in Table 1.

Table 1 Kinetic models

Model	Symbol	$f(\alpha)$
Šesták-Berggren equation	S$B(m, n)$	$\alpha^m(1-\alpha)^n$
Johnson-Mehl-Avrami equation	JMA (n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Reaction order equation	RO (n)	$(1-\alpha)^n$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$
Jander equation	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{2/3}]$
Ginstling-Brounshtein equation	D4	$1.5[(1-\alpha)^{-1/3}-1]$

Because of the strong mutual interdependence of the parameters E in Eq. (1) [12, 13]. In this paper, firstly, the Kissinger and Ozawa methods were carried out to calculate the activation energy E at different heating rates. In addition, the Ozawa method was also used to check the invariance of E with respect to different α, which is one of the basic assumptions in kinetic analysis [6].

Secondary, determination of the most probable kinetic model was performed by the two special functions $Y(\alpha)$ and $Z(\alpha)$ [6, 7, 8]

$$Y(\alpha) = \frac{d\alpha}{dt} \exp(X) \tag{2}$$

$$Z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\left(\frac{T}{\beta}\right) \tag{3}$$

where $X=E/RT$

$$\pi(x) = \frac{X^3 + 18X^2 + 88X + 96}{X^4 + 20X^3 + 120X^2 + 240X + 120} \tag{4}$$

which can easily be obtained by simple transformation of the experimental data and the shape of function $Y(\alpha)$ with both the parameters α_M and α_P^∞ at which the functions $Y(\alpha)$ and $Z(\alpha)$ have a maximum respectively.

Then the kinetic exponents n (or m) can be calculated for the determined kinetic model [7].

Finally, the pre-exponential factor (A) was obtained by using the following equation [7]:

$$A = -\frac{\beta x_p}{Tf'(\alpha_p)} \exp(x_p) \tag{5}$$

where α_p and x_p is the degree of conversion and reduced activation energy at the maximum of TA peak.

Results and discussion

Thermal behaviour

The temperature range and DTG peaks, together with the percentage of mass loss measured at various heating rates and decomposition products, are summarized in

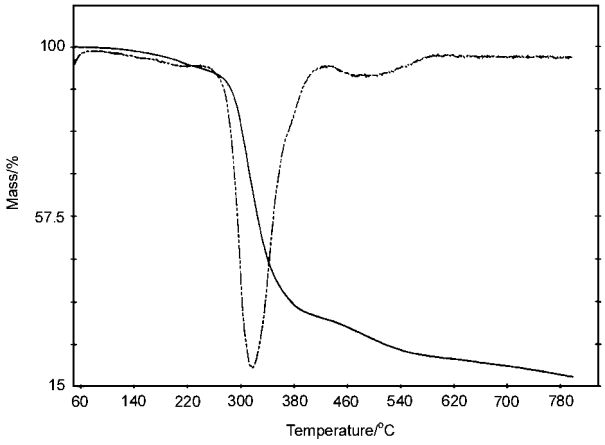

Fig. 1 The TG and DTG curves for $Pd(apyr)_2Cl_2$ at β=5.0 K min^{-1}

Table 2. The TG-DTG curves for two complexes are shown in Figs 1 and 2. It is obvious that complex 2 is more stable than complex 1, it can be explained by the difference in their structure.

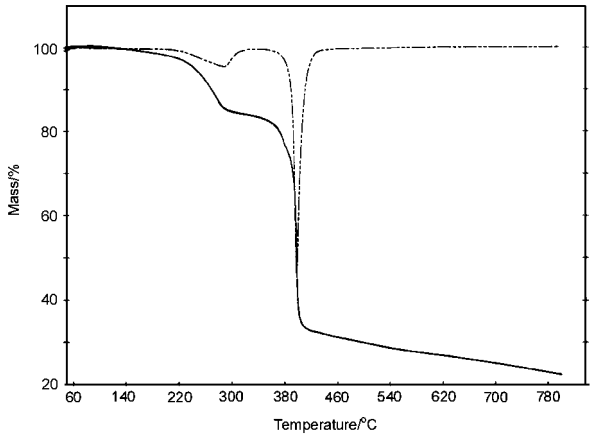

Fig. 2 The TG and DTG curves for $Pd(pmpa)Cl_2$ at β=5.0 K min^{-1}

Table 2 Thermal data

Complex		Heating rate/ K min^{-1}	Temp./oC		Mass loss/%		Decomposition product
			range	peak	found	calc.	
$Pd(apyr)_2Cl_2$	I	2.5	90–425	238.49	70.81	71.03	2 apyr
		5.0	107–432	257.22	70.36		
		10.0	123–440	265.42	69.68		
		15.0	125–456	274.73	69.84		
	II	2.5	425–785	463.42	10.45	11.62	2Cl
		5.0	432–790	470.66	10.76		
		10.0	440–793	476.46	11.24		
		15.0	456–795	478.54	10.88		
$Pd(pmpa)Cl_2$	I	2.5	142–279	272.44	15.66	16.15	C_5H_4N
		5.0	135–315	285.32	16.04		
		10.0	120–320	297.03	15.87		
		15.0	130–330	306.33	15.78		
	II	2.5	279–764	394.23	51.60	51.90	pmpa[a]+2Cl
		5.0	315–780	402.42	50.95		
		10.0	320–784	404.76	51.45		
		15.0	330–800	411.70	51.78		

[a]The remainder of pmpa ligand after the first stage

The TG-DTG curves for complex 1 show two decomposition stages. The first step, loss of mass 70.81% (calc. 71.03%) at a scanning rate of 2.5°C min^{-1}, corresponds to the removal of two apyr molecules, followed by the step of releasing Cl_2. The DTG curve for complex 2 shows two peaks. The first step, loss of mass 15.66% (calc. 16.15%) at a scanning rate of 2.5°C min^{-1}, corresponds to the decomposition of the pyridyl group from the pmpa ligand. From the point of view of bond strength [14], it seems reasonable for a possible break to occur at the pyridyl–C bond, because the C–C bond has almost the lowest bond energy (345.6 kJ mol^{-1}) in all the concerned bonds of pmpa molecule, namely C–H (411.0 kJ mol^{-1}), C–C (345.6 kJ mol^{-1}), C=N (614.5 kJ mol^{-1}). The second step, loss of mass 51.60% (calc. 51.90%), corresponds to the removal of the remainder of the pmpa ligand and the two chlorine atoms. The phenomenon that the pyridyl group was first broken suggests that the bond of nitrogen atom on the pyridyl coordinated with palladium is weaker than that which joined with pyrenyl in complex 2. It can be explained by the difference in chemical surroundings of the two nitrogen atoms in the ligand molecule.

The residue mass for the two complexes studied after the final decomposition is in good agreement with the calculated value of Pd, which is consistent with the results in our previous work [15].

Thermal decomposition kinetics

Kinetic studies have been made for the step corresponding to the loss of ligands (or its remainder), that is the first stage decomposition reaction for complex 1 and 2.

Table 3 The values of E (in kJ mol^{-1}) calculated using the Kissinger and Ozawa methods

Complex		Kissinger	Ozawa					
			α=0.25	0.42	0.55	0.80	0.91	Av.
$Pd(apyr)_2Cl_2$		108.3	110.8	112.9	111.1	104.5	108.9	109.6
$Pd(pmpa)Cl_2$	I	131.7	132.6	133.7	138.7	146.0	143.5	138.9
	II	392.1	416.2	392.8	397.5	425.6	406.9	407.8

The activation energy values E for all the studied decompositions determined by the Kissinger and Ozawa methods, are summarized in Table 3. The values of parameter E by two methods are in reasonable agreement, and the E values calculated employing Ozawa method are generally independent of the value of α, which has provided a check for the constancy of E during the course of reaction. The activation energy value in the second-step is much larger than that in the first-step for complex 2, which possibly indicates that the strength of two N–Pd bonds in the planar molecule are different, as described above.

Figures 3 and 4 show functions $Y(\alpha)$ and $Z(\alpha)$ dependences for several sets of kinetic data obtained at various heating rates. The important feature and parameter values, such as α_M and α_p^∞, corresponding to the maxima of the $Y(\alpha)$ and $Z(\alpha)$ curves, respectively, as well as the shape of $Y(\alpha)$ are summarized for the studied complexes in Table 4.

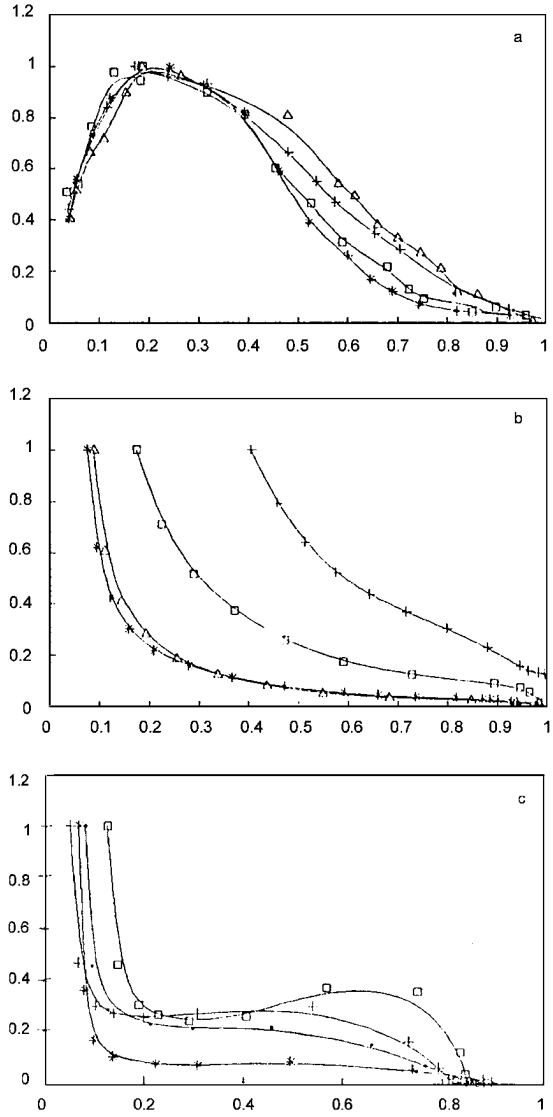

Fig. 3 Normalized $Y(\alpha)$ functions corresponding to the ligands decomposition kinetic data for studied complexes a – complex 1, b – first-step for complex 2 and c – second-step for complex 2. The heating rates are shown by various points, Δ – 2.5, + – 5.0, * – 10 and □ – 15 K min^{-1}

It is clear that there is a maximum of the $Y(\alpha)$ function at $\alpha_M \in (0, \alpha_P)$ for complex 1, and that the $Y(\alpha)$ function for the first-step reaction of complex 2 decreases steadily and has a maximum at $\alpha_M=0$. However, there are two maxima of the $Y(\alpha)$ function for the second-step decomposition of complex 2 at $\alpha_M=0$ and $\alpha_M \in (0, \alpha_P)$,

respectively, thus its kinetic model cannot be determined by the cited method. It is possible that the second step of decomposition is not a single but an overlapping reaction. It may be due to the simultaneous break of the both bonds of N–Pd and Pd–Cl which leads to a very complicated mechanism.

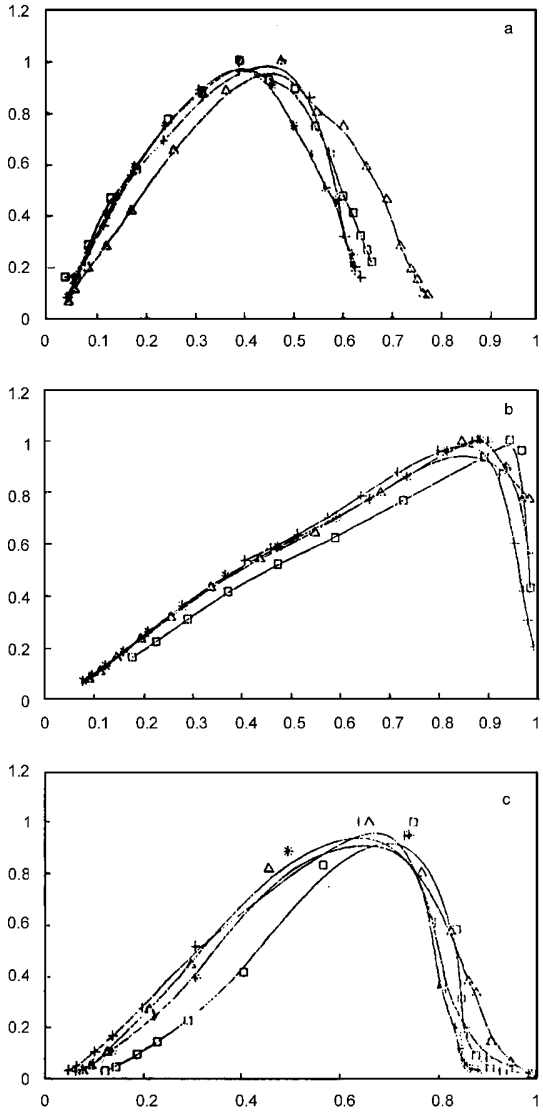

Fig. 4 Normalized $Z(\alpha)$ functions corresponding to the ligands decomposition kinetic data measured for studied complexes a – complex 1, b – first-step for complex 2 and c – second-step for complex 2. The heating rates are shown by various points, Δ – 2.5, + – 5, * – 10 and □– 15 K min^{-1}

Table 4 values of α_M and α_p^∞ at various heating rates (β)

Complex		β/K min^{-1}	α_M	α_p^∞	KM[a]	*m*	*n*	ln(*A*)/s^{-1}
$Pd(apyr)_2Cl_2$	I	2.5	0.1841	0.4782	SB	0.646	2.915	22.433
		5.0	0.1708	0.4803	SB	0.692	3.186	22.546
		10.0	0.1785	0.4803	SB	0.656	3.017	22.764
		15.0	0.1863	0.3919	SB	0.603	2.815	22.489
$Pd(pmpa)Cl_2$	II	2.5	0	0.8470	RO	–	0.140	30.498
		5.0	0	0.8802	RO	–	0.175	30.430
		10.0	0	0.8852	RO	–	0.180	30.442
		15.0	0	0.9828	RO	–	0.150	30.719

[a]Kinetic model

It is evident that the values of these parameters conform to the SB (*n, m*) model for complex 1, and the RO ($n<1$) model for the first-step of complex 2. The kinetic parameters calculated for these models are presented in Table 4. Considering these results, the decomposition process for complex 2 seems to be more complicated than that for complex 1. Two palladium(II) complexes with aminopyrene and its derivative would be linked by a strong infinite stacking of the pyrene planes to form a polymer structure.

As seen from Table 4, it is interesting to note that not only the value of *E*, but also the decomposition pattern and mechanism of complex 1 is different from that of complex 2.

Conclusions

The nitrogen atom in complex 1 is tetrahedral, and there is no conjugation of the pyrenyl π-electron with d-electrons of metal, whereas the amine nitrogen in complex 2 is planar and coordinates to metal atom forming a conjugation planar molecule. For this reason, complex 2 is more stable than complex 1. Their decompositions are complete at a temperature range of 760–800°C. Thermal decomposition kinetic parameters and mechanism have been studied (except the second-step for complex 2) in this work, their decomposition pattern can be described by the SB model for complex 1 and RO ($n>1$) model for the first stage of complex 2, respectively.

References

1 C. K. Prout and I. J. Tickle, J. Chem. Soc. Perkin Trans., (1973) 734.
2 L. F. Veiros, M. J. Calhorda and E. Canadell, Inorg. Chem., 33 (1994) 4290.
3 J. Dai, J. P. Sun and Z. R. Lu, J. Coord. Chem., 38 (1996) 281.
4 Z. Lu, L. Yang and J. Sun, J. Thermal Anal., 44 (1995) 1391.
5 J. Málek, Thermochim. Acta., 200 (1992) 257.
6 N. Koga, J. Málek, J. Šesták and H. Tanaka, Netsu Sokutei, 20 (1993) 210.
7 J. Šesták and J. Málek, Solid State Ionic, 63 (1993) 245.
8 G. I. Senum and R. T. Yang, J. Thermal Anal., 11 (1977) 445.

9 W. E. Brown, D. Dallimore and A. K. Galwey, in C. H. Bamford and C. F. H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam 1980.
10 J. Šesták, V. Satava and W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
11 J. Šesták, Thermophysical Properties of Solids, Their measurement and Theoretical Analysis, Elsevier, Amsterdam 1984.
12 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
13 T. Ozawa, J. Polym. Sci., Part C, 6 (1964) 183.
14 F. R. Hartley, The Chemistry of Platinum and Palladium. Applied Science Publishers Ltd, London 1973, p. 112.
15 Z. Lu and L. Yang, Thermochim. Acta, 188 (1991) 135.