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Thermal Study of Pd(II) Complexes Containing *Bis*-(Diphenylthiophosphenyl)methane

FATIH DOGAN*, SELMIN YANAR and SEVIL IRISLI
Department of Chemistry, Faculty of Science, Ege University, 35100, Izmir, Turkey
Fax: (90)(233)3888264; Tel: (90)(232)3388264; E-mail: fatih.dogan@ege.edu.tr

The TG-DTG and DTA study of dipositive palladium(II) complexes of the general formula $[Pt(L\text{-}L)(dppmS_2)](ClO_4)_2$, where $dppmS_2 = Ph_2P(S)CH_2P(S)Ph_2$ and L-L = dppm ($Ph_2PCH_2PPh_2$), dppe ($Ph_2PCH_2CH_2PPh_2$) and dppp ($Ph_2PCH_2CH_2CH_2PPh_2$), were studied by thermogravimetric analysis from ambient temperature to 1273 K in nitrogen atmosphere. The decomposition occurred in one stage for all complexes. The values of activation energy, E, frequency factor, A, reaction order, n, entropy change, $\Delta S^{\neq}$, enthalpy change, $\Delta H^{\neq}$ and Gibss free energy, $\Delta G^{\neq}$ of the thermal decomposition were calculated by means of Coats-Redfern (CR), MacCallum-Tanner (MC) and Horowitz-Metzger (HM) methods. The activation energy value obtained by CR, MC and HM methods were in good agreement with each other.

Key Words: *Bis*-(Diphenylthiophosphenyl)methane, Thermal behaviour, Pd(II) complexes, Activation energy.

INTRODUCTION

There has been considerable interest in studying metal complexes with bidentate tertiary phosphine chalcogenides. Complexes have been studied mainly with the bidentate ligands $Ph_2P(E)(CH_2)nP(E)Ph_2$ and $Ph_2P(CH_2)nP(E)Ph_2$ (E = S, Se, n = 1,2,3). One of these derivatives, $Ph_2P(S)CH_2P(S)Ph_2$ (=$dppmS_2$) exhibits monodentate S, bidentate or bridging S, S coordination to the metals as a neutral ligand. A large number of complexes of different metals have been reported for these chalcogenide ligands[1-4].

The lability of the chalcogen-metal bonds can give rise to dynamic processes and thus renders these ligands appropriate for catalytic application[5]. In recent years, however, most studies have focused on the use of soluble Pd complexes with various types of P ligands[6,7] with the aim of increasing the effectiveness of the catalysts. The palladium complex of the $Ph_2PCH_2P(S)Ph_2$ ligand has been tested as catalyst in the alternating copolymerization of ethylene and carbonmonoxide[8].

We report here, TGA analyses of cationic palladium (II) complexes containing $Ph_2P(S)CH_2P(S)Ph_2$ [$dppmS_2$ = *bis*(diphenylthiophosphenyl)-methane] of the type $[Pd(L\text{-}L)\ dppmS_2]\ (ClO_4)_2$ [L-L=dppm ($Ph_2PCH_2PPh_2$) (1), dppe ($Ph_2PCH_2CH_2PPh_2$) (2), dppp ($Ph_2PCH_2CH_2CH_2PPh_2$) (3)].

EXPERIMENTAL

Solvents were dried according to the methods given in the literature and were purified under inert conditions[9]. All synthesis were carried out using Standard Schlenk tube techniques under inert atmosphere. The starting complexes, $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene)[10], which is used for preparing the $[PdCl_2(L\text{-}L)]$ complexes [L-L=dppm ($Ph_2PCH_2PPh_2$), dppe ($Ph_2PCH_2CH_2PPh_2$), dppp ($Ph_2PCH_2CH_2CH_2PPh_2$)[11], $dppmS_2$ ($Ph_2P(S)CH_2P(S)Ph_2$)[12] and final complexes of the type $[Pd(L\text{-}L)dppmS_2](ClO_4)_2$ [L-L= dppm (1), dppe (2), dppp (3) were synthesized according to the methods given in the literature[13].

Thermal analysis: The DTA and TG curves are obtained with TG-DTA Perkin-Elmer diamond system apparatus. The measurements were performed by using a dynamic nitrogen atmosphere at a flow rate of 60 mL min^{-1} up to 1273 K. The heating rate was 10 °C min^{-1} and the sample sizes ranged in mass about 5 mg contained in platinum crucible. α-Al_2O_3 is used as a reference material.

RESULTS AND DISCUSSION

Palladium(II) cationic complexes containing $Ph_2P(S)CH_2P(S)Ph_2$ ($dppmS_2$ = *bis*(diphenylthiophosphenyl)methane) of the type, $[Pt(L\text{-}L)dppmS_2](ClO_4)_2$ (L-L= dppm (1), dppe (2) and dppp (3)], were studied by thermogravimetric analysis from ambient temperature to 1273 K in nitrogen atmosphere. Typical TG-DTA curves for all of these complexes are present in Figs. 1 and 2. The initial and final temperatures and total

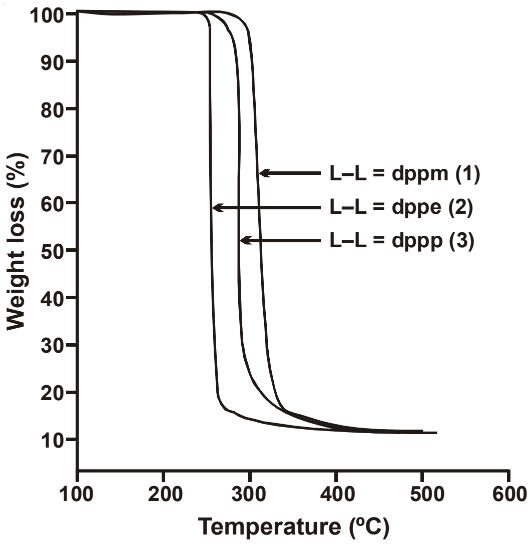

Fig. 1. TG curves of Pd(II) complexes (**1**, **2** and **3**)

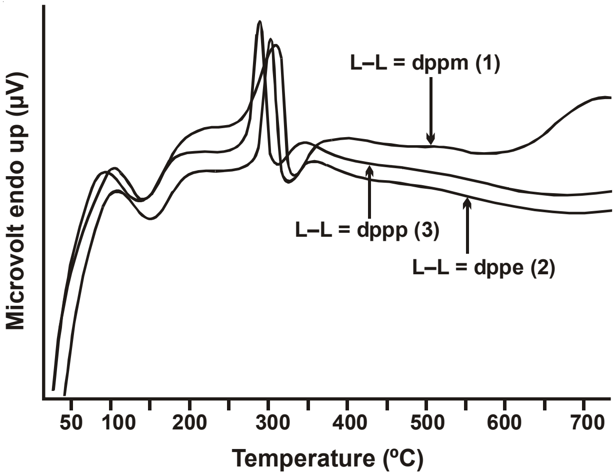

Fig. 2. DTA curves of Pd(II) complexes (**1**, **2** and **3**)

mass loses for each step in the thermal decomposition of complexes are given Table-1, together with temperatures of maximum rate of decomposition (DTG_{max}). The decomposition of all the complexes were very similar in character and occurs in one-stage. Complex (**2**) decomposes in one step in the temperature range 529-553 K giving mass loses of 87.6 %. In all complexes, the initial rate of decomposition is fast. Complexes (**1**), (**2**) and (**3**) are thermal stable up to 561, 529 and 539 K, respectively. From DTA profile, it was found that pyrolytic decomposition occurs together with the melting for all of complexes.

TABLE-1
TG, DTG AND DTA DATA FOR Pd(II) COMPLEXES

Complex	Step	Temp. of DTA peak max. (K)	DTG_{max} (K)	Temp. range (K)	DTA	Residue weight loss (%)
1	I Residue	583 > 591	581	561-591	exo	14.3
2	I Residue	457 > 553	550	529-553	exo	12.4
3	I Residue	553 > 566	562	539-566	exo	13.7

From the TG curve for complex (**1**), it appears that the sample decomposes in one stage over the temperature range 561-591 K with a mass loss 85.7 % in weight. The end product shows that corresponding to PdS by the comparison of experimental and theoretical data. The decomposition process of all complexes is similar to each other. The stability of complex (**1**) is higher than complex (**2**) and (**3**) and decomposes at 561 K.

From the corresponding DTA profiles, one exothermic peak for (**1**) and one exothermic peak for (**3**) are noted. The maximas of these peaks which is due to the pyrolytic decomposition together with the melting of all complexes (**1, 2, 3**) are found to be 583, 547 and 553 K, respectively.

The complex (**2**) is stable up to 529 K. At this stage the complex (**2**) simultaneously melts and decomposes and loses 87.6 % of its mass and the end product corresponding to metallic palladium. The DTA study of complex (**2**) showed one exothermic at 547 K.

Among these three complexes (**1**, **2** and **3**) having similar decomposition steps, the most stable complex (**1**) as compared to (**2**) and (**3**).

The kinetics of heterogeneous condensed phase reactions that occur in nonisothermal conditions is usually described by equation,

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(\frac{-E}{RT}\right) \tag{1}$$

where α = degree of conversion, β = linear heating rate, A = pre-exponential factor and $f(\alpha)$ = differential conversion function. For calculate kinetic parameters, the different reaction models may be used. The fraction mass loss, α and corresponding $(1\text{-}\alpha)^n$ are calculated from TG curves, Where '*n*' depends upon the reaction model. In studying the decomposition kinetic, five methods in the literature were chosen: Coats-Redfern (CR), Horowitz-Metzger (HM), MacCallum-Tanner (MC) methods may be expressed by following equations,

The Coats-Redfern method[14]

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left\{\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right\}-\left(\frac{E}{RT}\right) \tag{2}$$

Horowitz-Metzger method[15]: The Horowitz-Metzger method introduced a characteristic temperature T_m and a parameter θ such that

$\theta = (T\text{-}T_m)$

If the reaction order is 1, T_m is defined as the temperature at which $(1\text{-}\alpha)_m = 1/e = 0.368$ and the final expression is:

$$\ln\ln g(\alpha) = \frac{E\theta}{RT_m^2}$$

If the reaction order is unknown, T_m is defined for the maximum heating rate.

when $\theta = 0$, $(1\text{-}\alpha) = (1\text{-}\alpha)_m$ and $(1\text{-}\alpha)_m = n^{1/1-n}$ and

$$\ln[g(\alpha)] = \ln\frac{ART_m^2}{\beta E}-\frac{E}{RT_m}+\frac{E\theta}{RT_m^2} \tag{3}$$

A plot of ln $g(\alpha)$ *vs.* θ can yield activation energy

The MacCallum-Tanner method[16]:

$$\log[g(\alpha)] = \log\left(\frac{AE}{\beta R}\right) - 0.4828E^{0.4351} - \left(\frac{0.449 + 0.217E}{10^{-3}T}\right) \qquad (4)$$

In the equations above, α, g(α), T_m, E, n, A, R, β are the degree of conversion, integral function of conversion, DTG peak temperature, activation energy (kJ mol^{-1}), reaction order, pre-exponential factor, gas constant (8.314 J mol^{-1} K^{-1}) and heating rate, respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations (eqns. 2 and 4) against 1/T. The values E and A were calculated from the slope and intercept of the straight lines, respectively.

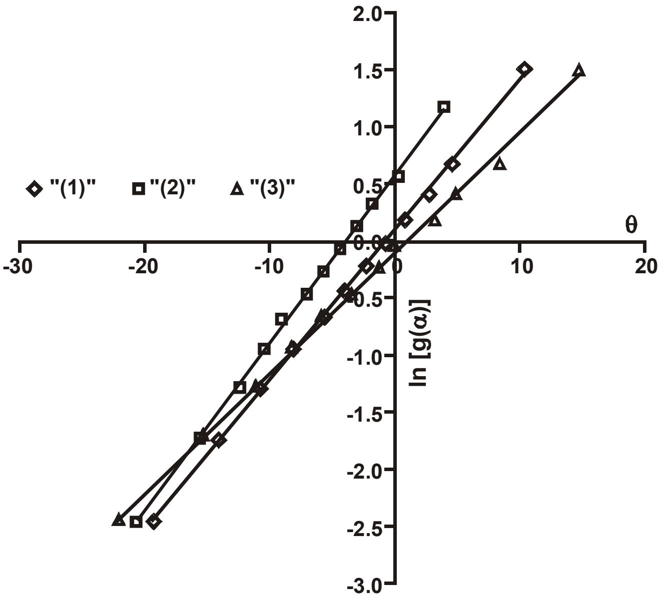

Fig. 3. Horowitz-Metzger plots of palladium(II) complexes

Fig. 3 shows activation energy determined by the method of Horowitz-Metzger in nitrogen for weight loss thermograms of 10 ºC min^{-1}. The activation energies can be calculated from slopes of the ln [g(α)] against θ plot.

The MacCallum-Tanner method also provides an approximated from of the rate of degradation as a function of temperature. The rate of degradation can thus be expressed by eqns. 4. Fig. 4 represent a plot of log [g(α)] against 1/T obtained using this approach. From the plot it is possible to calculate the activation energies from the slopes. The activation energies of Pd(II) complexes are between 277-363 kJ/mol.

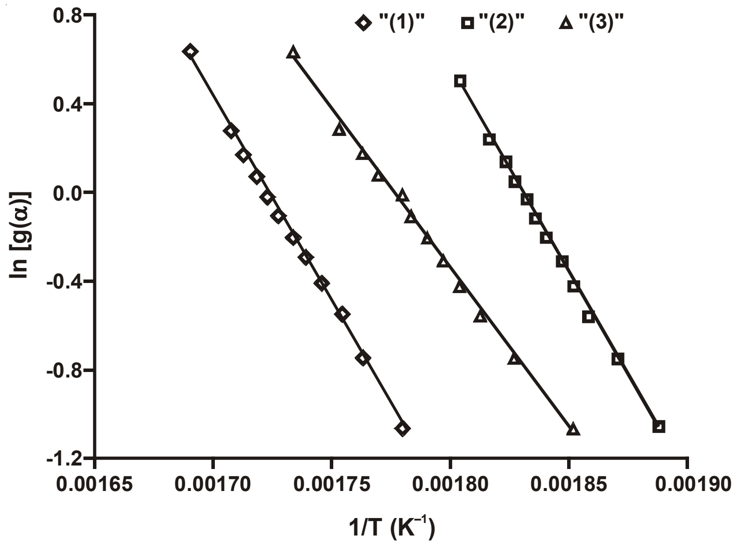

Fig. 4. MacCallum-Tanner plots of Pd(II) complexes

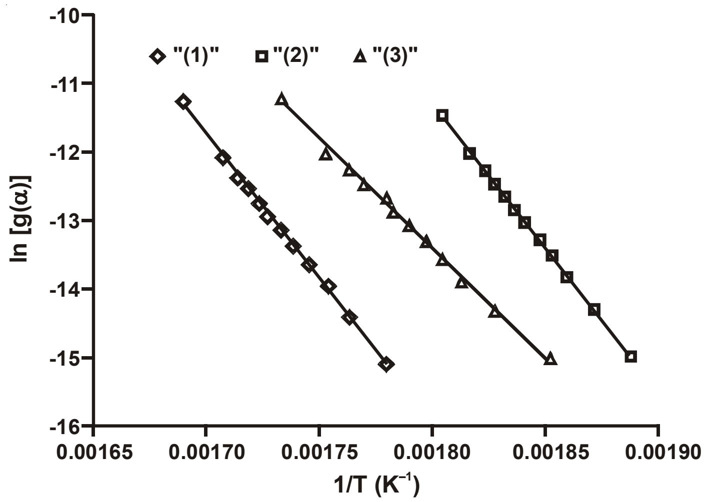

Fig. 5. Coats-Redfern plots of Pd(II) complexes

According to Coats and Redfern method, the plot of ln $(g(\alpha)/T^2)$ *vs.* 1/T gives straight line with slope equals to -E/R. The activation energies of complexes were calculated from Fig. 5 and given Table-2.

For all methods, determination of the pre-exponential factor and reaction order is possible from the expression of g(α) in above equations and $n \neq 1$:

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$$

TABLE-2
KINETIC DATA ON Pd(II) COMPLEXES (**1**, **2** AND **3**)

Method	Complexes	n	E (kJ/mol)	ln A (min^{-1})	Correlation coefficient (r)	$\Delta S^{\neq}$ ($J\ mol^{-1}\ K^{-1}$)	$\Delta H^{\neq}$ ($J\ mol^{-1}\ K^{-1}$)	$\Delta G^{\neq}$ ($J\ mol^{-1}\ K^{-1}$)
HM	1	0.8	367.11	12.99	0.99376	-142.44	362.27	445.04
	2	0.7	370.17	13.45	0.99243	-137.97	365.68	440.18
	3	0.8	279.21	12.50	0.99745	-146.23	274.53	356.71
MC	1	0.8	363.34	77.65	0.99675	395.26	358.50	128.85
	2	0.7	361.00	82.31	0.99231	434.58	356.51	121.83
	3	0.8	277.37	62.17	0.99841	266.83	272.69	122.73
CR	1	0.8	351.53	68.25	0.99743	317.10	346.69	162.46
	2	0.7	349.98	72.97	0.99641	356.96	345.49	152.72
	3	0.8	266.35	53.09	0.99753	191.24	261.67	154.19

The linear curves of Pd(II) complexes were obtained using the methods mentioned above and presented in Figs. 3-5. Moreover, Table-2 summarizes the reaction order (*n*), pre-exponential factor (A), correlation coefficient (r), the activation energy (E), entropy change ($\Delta S^{\neq}$), enthalpy change ($\Delta H^{\neq}$), and Gibss free energy ($\Delta G^{\neq}$) obtained by the three different methods examined in this study. The results are in good agreement with the values obtained from all of them. The results indicate that the values of all methods are comparable.

As seen in Table-2, the value of correlation coefficients of linear curves of Pd(II) complexes are *ca.* 1.00. The kinetic data obtained by different methods agree with each other. The enthalpy ($\Delta H^{\neq}$), activation entropy($\Delta S^{\neq}$) and the free energy of activation ($\Delta G^{\neq}$), of Pd(II) complexes were calculated using the following relations[17]:

$$\Delta S^{\neq} = 2.303\ \log\left(\frac{Ah}{kT}\right)R$$

$$\Delta H^{\neq} = E - RT$$

$$\Delta G^{\neq} = \Delta H - T\Delta S^{\neq}$$

where h = the planck constant and T = the temperature, A = the pre-exponential factor. The thermodynamic parameters calculated were reported in Table-2.

Conclusion

A study on the thermal decomposition of Pd(II) complexes was carried out by using three kinetic methods. The decomposition kinetics was investigated by evaluating the dynamic thermogravimetric data obtained at a single heating rate. The activation energy (E), reaction order (n), pre-exponential factor (A), entropy change ($\Delta S^{\neq}$), enthalpy change ($\Delta H^{\neq}$) and Gibbs free energy change ($\Delta G^{\neq}$) were calculated from the results of thermogravimetry analysis. It was found that the thermal stabilities and activation energies of all complexes follow the order **1** > **3** > **2**, $E_{(\mathbf{3})} < E_{(\mathbf{2})} \approx E_{(\mathbf{1})}$, respectively.

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