THERMAL STUDIES ON SOME COMPLEXES OF Pd(II)

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The formulae suggested for a series of complexes of Pd(II) with various amino acids have been verified by thermal methods using a derivatograph. A correlation of the obtained kinetic parameters with the structures suggested by electronic and IR spectra of the substances has been attempted.

In an earlier paper the synthesis and chemical analysis of some complexes of palladium(II) with different amino acids (ligands) were described [1]. Now, the authors wish to present the results of a thermal study carried out on some of these substances.

The determinations have shown that the decomposition takes place in several stages and leads finally to metallic palladium by the decomposition of intermediate PdO in the last stage at 825°. The thermal decomposition of the complexes, studied in the temperature range 20°—900°, can be described by the following overall reactions:

For chelate complexes of the type PdA_2 by:

$$PdA_2 \rightarrow Pd + 2 A \; (HA = \text{amino acid})$$
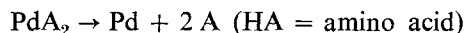
and for those of types $PdA(AH)X$ and $Pd(AH)_2X_2$ by:

$$[Pd(AH)_2X_2] \rightarrow Pd + 2 AH + X_2 \; (X = Cl, NO_2)$$

A typical derivatogram taken by a derivatograph of the Paulik—Paulik—Erdey, MOM type, is given in Fig. 1, while the analytical results that follow from these derivatograms are given in Table 1. The weight of sample (except when such quantity was not available) was in most cases 20 mg, and the heating rate 12°/min.

The derivatograms of the Pd(II) complexes were taken parallel with those of the free ligand and of the Pd(II) complexes

$$K_2[PdCl_4] \text{ or } Na_2[Pd(NO_2)_4]$$

used as starting materials.

From the experimental data obtained, shown in Table 1, it follows that there is a possibility to confirm thermogravimetrically the structures suggested previously from the chemical analyses and the IR spectra [2, 3]. In addition, the kinetic

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Table 1

Complex	Sample weight mg	Residue mg	Residue %	
			theoretical	practical
1. Pd(Val)$_2$	20.0	6.4	31.0	32.0
2. Pd(Val)$_2$	19.8	6.1	31.0	30.5
3. Pd(Val)(ValH)(NO$_2$)	14.8	4.4	27.0	30.9
4. Pd(Ty)(TyH)Cl	9.9	2.4	21.2	24.6
5. Pd(TyH)$_2$Cl$_2$	18.8	3.1	19.7	16.4
6. Pd(Tr)(TrH)Cl (green)	20.7	4.0	19.4	19.3
7. Pd(Tr)(TrH)Cl (grey)	19.4	3.5	19.5	18.3
8. Pd(Tr)(TrH)(NO$_2$)	19.8	3.8	19.1	19.3
9. Pd(TrH)$_2$(NO$_2$)	19.9	4.0	17.5	20.2
10. Pd(Phal)$_2$ · H$_2$O	20.1	4.4	23.6	21.7
12. Pd(aAsp)$_2$	20.1	5.7	29.0	27.6

interpretation of the derivatograms may provide supplementary data about the structures of the complexes studied.

The apparent activation energy and the reaction order for the principal decomposition processes of the complex compounds were estimated from the obtained thermal curves by the usual methods.
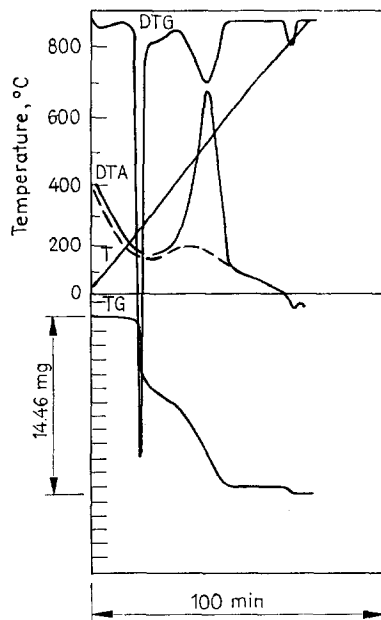

Fig. 1. A typical derivatogram of one of the complexes of Pd(II) with amino acids

The activation energy was evaluated using exclusively the data corresponding to the conditions of the maximum decomposition rate. This method was preferred to other calculation methods indicated in the literature, because under dynamic conditions of reaction (i.e. when the temperature changes during the process) pure stationary reaction conditions are realised only in cases when the decomposition proceeds according to a complex reaction mechanism [4] (cf. in our case the great differences in the reaction order n given in Table 2).

Table 2

Compound	T max °K	E kcal/mole	n obs.	
Valine	573	35	0.43	
Pd(Val)$_2$	533	32	0.35	
Pd(Val)(ValH)(NO$_2$)	523	36	1	I stage
Pd(Val)(ValH)(NO$_2$)	551	111	4	II stage
Tyrosine	563	96.5	1.5	
Pd(TyH)$_2$Cl$_2$	516	85	2	
Pd(Ty)(TyH)Cl	523	133	2	
Tryptophane	551	95.5	1.7	
Pd(Tr)(TrH)Cl (grey)	541	172	2.3	Isomer I
Pd(Tr)(TrH)Cl (green)	523	223	2.25	Isomer II
Phenylalanine	543	38	0,75	
Pd(Phal)$_2$ · H$_2$O	490	120	2	

Supposing that the overall reaction of the thermal decomposition obeys the kinetic law:

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

in which α is the transformation degree at time t, n is the reaction order, E the overall activation energy and β the constant heating rate, then from the condition of the maximum reaction rate $\frac{d^2\alpha}{dT} = 0$, we can estimate both the activation energy [5]:

$$E = \frac{\left(\dfrac{d\alpha}{dT}\right)_M \cdot nRT_M}{1 - \alpha_M}$$

and the reaction order [6]:

$$(1 - \alpha)_M = n \cdot \frac{1}{1 - n}$$

The results for the first decomposition stage, except for the complex Pd(Val)(ValH)(NO$_2$) which shows two decomposition processes in the first stage, are listed in Table 2.

It appears from Table 2 that when the ligands are linked only coordinatively to the central metal, the apparent activation energy corresponding to the first decomposition stage of the complex is, within the limits of experimental error, close to the apparent volatilization energy of the pure ligand. This statement holds satisfactorily for all the complexes studied. For example, Pd(Val)$_2$ decomposes with $E = 32$ kcal/mole while pure valine volatilizes with $E = 35$ kcal/mole. Pd(Val)(ValH)(NO$_2$) on the other hand, decomposes in two stages, the first stage with an apparent activation energy 36 kcal/mole similar to the heat of volatilization of valine, while the second stage needs 111 kcal/mole. To explain this it can be assumed that in the first stage the first coordinatively linked valine molecule is released, the energy of the breaking of the coordinate bond being probably so small as to have no noticeable influence upon the value of the apparent volatilization energy of the pure ligand; in the second decomposition stage the release of the second valine molecule linked covalently to Pd through the oxygen of the carbonyl group necessitates an increased energy.

Assuming that the apparent activation energy of the second stage is given by the sum of the energy corresponding to the breaking of the Pd—O covalent bond and that of the volatilization of the pure ligand, then a value of about 75 kcal/mole for the breaking of the Pd—O link could be obtained.

Similar values were found in the cases of the presumed first isomer of tryptophane, 75.5 kcal/mole, and phenylalanine, 82 kcal/mole.

For the second complex with tyrosine [PdTy(TyH)Cl], the existence of two distinct decomposition processes during the first stage could not be observed although the two tyrosine molecules are differently linked; hence the apparent activation energy corresponding to the breaking of the covalent bond was probably equally distributed on the two simultaneously released tyrosine molecules. For this reason the difference between the apparent volatilization energy of tyrosine, 96.5 kcal/mole, and the apparent activation energy of the thermal decomposition of the complex should be only $75/2 = 37.5$ kcal/mole. The corresponding experimental value is 36.5 kcal/mole. Consequently, relying on the experimental results, we may attribute the value of 75 kcal/mole to the apparent activation energy necessary for breaking the Pd—O covalent link.

On the other hand, the energy of the breaking of the Pd—N coordinative link is probably so small that it does not influence remarkably the apparent volatilization energy of the pure ligand.

Concerning the two presumed isomers of [Pd(Trp)(TrpH)Cl] it must be stressed that, although they can be distinguished according to their method of preparation, the IR spectra (recorded with a Perkin—Elmer 337 spectrophotometer) have not confirmed the existence of two geometric isomers. However, the difference between the apparent activation energies of the first step of the thermal decomposition seems to plead for the existence of two different isomers.

In conclusion it may be stated that the thermal method is useful for the study of the complexes not only from the analytical point of view but also because it gives useful information about the structure of the complex studied but which should be interpreted with a certain reserve.

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RÉSUMÉ — On a vérifié par thermogravimétrie des formules brutes proposées pour les combinaisons complexes du Pd(II) avec divers acides aminés. On a examiné la correlation entre les paramètres cynétiques obtenus et les structures déduites des spectres IR et electroniques.

ZUSAMMENFASSUNG — Es wurden Formeln für eine Serie von Komplexverbindungen des Pd(II) mit verschiedenen Aminosäuren vorgeschlagen und thermogravimetrisch bewiesen. Die Übereinstimmung zwischen den erhaltenen kinetischen Parametern und den durch ERS und Infrarotspektroskopie angedeuteten Strukturen wurde geprüft.

Резюме. — Путём дериватографического анализа проведена применимость формул, предложенных для ряда комплексов Pd(II) с различными аминокислотами. Исследована корреляция кинетических параметров, полученных для структур, чпредложенных на основании ЭТР и ИК спектра веществ.