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Kinetics of the thermal decomposition of clathrates of tetracyano complexes $\mathrm{CdenPd(CN)_4 \cdot 2G}$ (en type) and $\mathrm{Cd(NH_3)_2Hg(CN)_4 \cdot 2G}$ (Td type)

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Abstract

The kinetics of thermal liberation of the components included in two structurally different types of clathrates of tetracyano complexes were investigated using isothermal thermogravimetry. The liberation of the included component is always the first one-step process of thermal decomposition. In all cases it was found that the reaction order was equal to 2/3 ($n = 2/3$). The values obtained for the activation energy are discussed with reference to the properties for the included clathrate components as well as the structure of the coordination components of the compounds studied.

INTRODUCTION

The clathrates of tetracyano complexes represent an important class of inclusion compounds. The methods of preparation, the identification of the nature of the thermal decomposition and the structure of these compounds are well documented in the literature [1–4]. The results concerning the kinetics of liberation of the clathrate-included components from the clathrate structure are less well known, although some information concerning the kinetics of thermal decomposition derives from the more detailed investigations of these compounds [5,6]. The values of the kinetic parameters are frequently affected by the method of investigation; therefore the same method was used here for the whole group of compounds. This method was analogous to those employed for the study of coordination compounds with similar types of coordination components [7–9].

EXPERIMENTAL

Eight clathrates of tetracyano complexes, of two different structural types, were the subject of this study. The complexes of Hofmann en type were

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$CdenPd(CN)_4 \cdot 2C_6H_5OH$, $CdenPd(CN)_4 \cdot 2C_6H_6$, $CdenPd(CN)_4 \cdot 2C_4H_5N$, $CdenPd(CN)_4 \cdot 2C_4H_4S$. The complexes of Hofmann Td type were $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5OH$, $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$, $Cd(NH_3)$-$Hg(CN)_4 \cdot 2C_4H_5N$, $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_4S$. The preparation, identification and stoichiometry of the complexes for thermal decomposition showed that they were of sufficient purity and suited for kinetic measurements. Under dynamic conditions the first stage of thermal decomposition involves the liberation of the clathrate-included components. This is always a one-step process irrespective of the rate of heating, and is accompanied by a weak endothermic effect [4]. This liberation is distinctly different from the succeeding thermal decomposition.

To investigate the kinetics of liberation of the clathrate-included components, isothermal thermogravimetry was used. The isothermal decompositions took place in a laboratory furnace, in an air atmosphere and on flat crucibles at temperatures up to 200 ° C. The temperature was regulated with a precision of $\pm 1°C$. The changes in mass were recorded by means of a Derivatograph OD-102. The particle size of the samples was under 0.06 mm. The weighed amounts were always exactly 100 mg. The time of the decompositions investigated was 80 min in all cases.

RESULTS AND DISCUSSION

To study the kinetics of thermal liberation of the clathrate-included components, the mass decrease was correlated to the common differential equation $d\alpha/dt = k(1-\alpha)^n$. The best agreement was obtained for $\alpha = 2/3$. This means that the equation describing the overall course of decomposition assumes the form $d\alpha/dt = k(1-\alpha)^{2/3}$ and its integrated form is $1-(1-\alpha)^{1/3} = k't$. Because of factors of influencing the beginning and the end of the decomposition, the kinetics were not investigated until 20 min had elapsed. Then the decomposition was followed to 80% decomposition, corresponding to liberation of the clathrate-included component. The time dependence of the mass decrease at selected temperatures is shown in Figs. 1–4.

The dependence of the mass loss on time was used to calculate the values of α and $1-(1-\alpha)^{1/3}$. The plots of $1-(1-\alpha)^{1/3}$ against time, which were linear, were processed by the method of least squares. In this way, the values of the rate constants given in Table 1 were obtained. The plots of $\log k$ vs. $1/T$ were linear and consistent with the Arrhenius equation. They were also processed by the method of least squares (Figs. 5 and 6) and thus the values of the activation energies for the individual decompositions given in Table 2 were obtained.

The reaction order determined, $n = 2/3$, indicated that the rate-determining reaction step was the decomposition of the coordination component which proceeds from the surface to the centre of the crystals. However, the

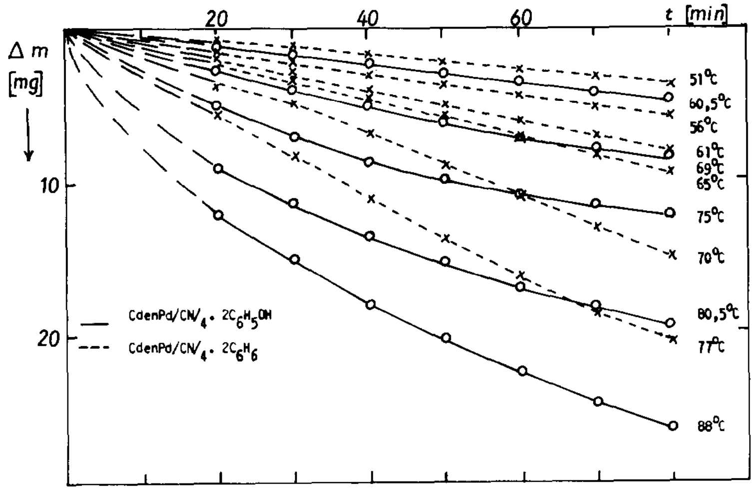

Fig. 1. Graphical representation of the isothermal decomposition of compounds $CdenPd(CN)_4 \cdot 2C_6H_5OH$ and $CdenPd(CN)_4 \cdot 2C_6H_6$.

reaction order suggests only a "rough" mechanism and is significantly dependent on experimental conditions. For this reason, the conclusions resulting from its value must be viewed carefully. A comparison between both structural types of clathrates shows that the higher values of E_A were found for the Hofmann clathrates of en type. This could by explained by the more compact structure of this type of clathrate in which the horizontal networks of $M(CN)_4^{2-}$ are bonded vertically and directly through the en

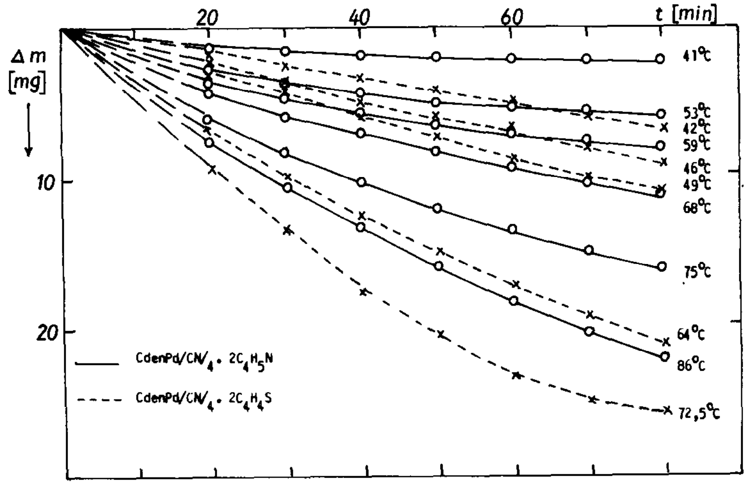

Fig. 2. Graphical representation of the isothermal decomposition of compounds $CdenPd(CN)_4 \cdot 2C_4H_5N$ and $CdenPd(CN)_4 \cdot 2C_4H_4S$.

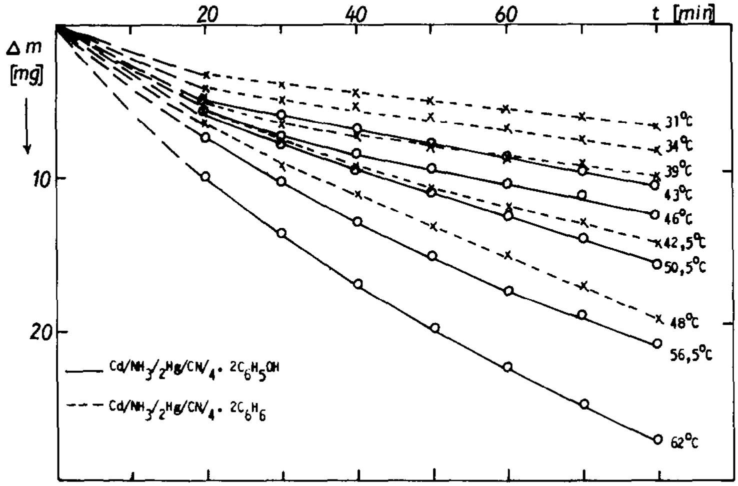

Fig. 3. Graphical representation of the isothermal decomposition of compounds $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5OH$ and $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$.

ligands. This structure also exhibits a greater thermal stability when compared to the thermal stability of the clathrates of Td type. The lower values of E_A observed for the Td type of compounds are to be attributed not only to the thermally less stable tetrahedral structure but also to a lower stability of the Hg(II) complexes, which is also confirmed by the values of the complex stability constants, e.g. in comparison with analogous cyano complexes of Pd(II) or Ni(II).

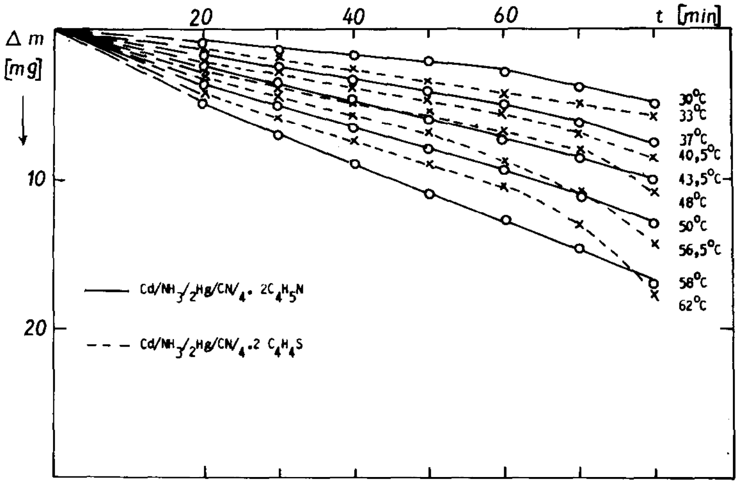

Fig. 4. Graphical representation of the isothermal decomposition of compounds $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_5N$ and $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_4S$.

TABLE 1

Values of rate constants at given temperatures

Compound	T (K)	$1/T \times 10^{-3}$	k (min)
$CdenPd(CN)_4 \cdot 2C_6H_5OH$	333.5	2.998	5.93×10^{-4}
	342	2.923	1.13×10^{-3}
	348	2.873	1.49×10^{-3}
	353.5	2.828	2.63×10^{-3}
	361	2.770	4.80×10^{-3}
$CdenPd(CN)_4 \cdot 2C_6H_6$	324	3.086	6.40×10^{-4}
	329	3.039	9.70×10^{-4}
	334	2.994	1.45×10^{-3}
	338	2.958	1.74×10^{-3}
	343	2.915	3.08×10^{-3}
	350	2.857	4.68×10^{-3}
$CdenPd(CN)_4 \cdot 2C_4H_5N$	314	3.184	3.10×10^{-4}
	326	3.067	8.86×10^{-4}
	332	3.012	1.31×10^{-3}
	341	2.932	2.00×10^{-3}
	348	2.873	3.36×10^{-3}
	359	2.785	5.90×10^{-3}
$CdenPd(CN)_4 \cdot C_4H_4S$	315	3.174	1.17×10^{-3}
	319	3.134	1.49×10^{-3}
	322	3.105	1.88×10^{-3}
	337	2.967	4.16×10^{-3}
	345.5	2.894	6.13×10^{-3}
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5OH$	316	3.164	1.28×10^{-3}
	319	3.134	1.73×10^{-3}
	323.5	3.091	2.61×10^{-3}
	329.5	3.034	4.05×10^{-3}
	335	2.985	6.04×10^{-3}
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$	304	3.289	1.19×10^{-3}
	307	3.257	1.73×10^{-3}
	312	3.205	2.04×10^{-3}
	315.5	3.169	2.53×10^{-3}
	321	3.115	3.70×10^{-3}
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_5N$	303	3.300	1.01×10^{-3}
	310	3.225	1.63×10^{-3}
	316.5	3.159	2.27×10^{-3}
	323	3.095	3.04×10^{-3}
	331	3.021	4.71×10^{-3}
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_4S$	306	3.267	9.50×10^{-4}
	313.5	3.189	1.40×10^{-3}
	321	3.115	2.10×10^{-3}
	329.5	3.034	3.06×10^{-3}
	335	2.985	3.99×10^{-3}

Regardless of the type of structure, the values of activation energies are in the order: $E_A(C_6H_5OH) > E_A(C_6H_6) > E_A(C_4H_5N) > E_A(C_4H_4S)$. This order may be related to steric factors of the clathrate-included components,

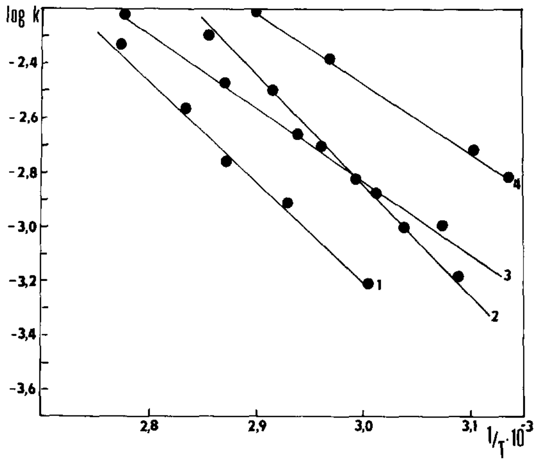

Fig. 5. Variation of rate constant with reciprocal value of temperature: curve 1, $CdenPd(CN)_4 \cdot 2C_6H_5OH$; curve 2, $CdenPd(CN)_4 \cdot 2C_6H_6$; curve 3, $CdenPd(CN)_4 \cdot C_4H_5N$; curve 4, $CdenPd(CN)_4 \cdot 2C_4H_4S$.

as suggested by the values for the molar volumes of these components (Table 2). An anomaly is exhibited by pyrrole for which a high activation energy value was observed even though its molar volume is lower than that of thiophene. This may be caused by the free electron pair on the nitrogen in pyrrole which, though orientated inside the pyrrole ring, is able to produce a

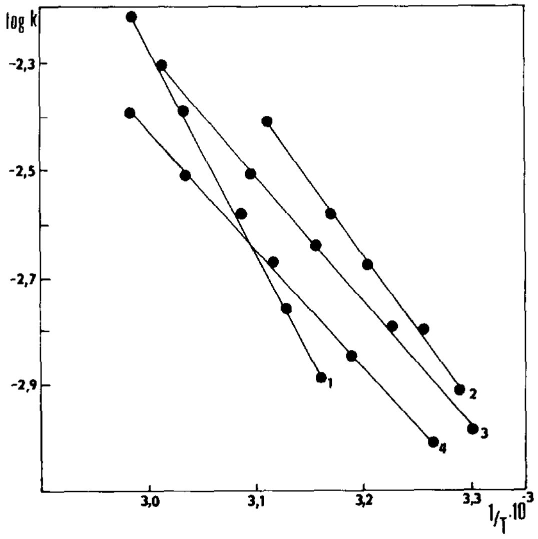

Fig. 6. Variation of rate constant with reciprocal value of temperature: curve 1, $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5OH$; curve 2, $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$; curve 3, $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_5N$; curve 4 $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_4S$.

TABLE 2

Values of activation energies, reaction order and molecular volumes

Compound	Mol. vol. of G [a] (cm^3 mol^{-1})	Structure	n	E_A (kJ mol^{-1})
$CdenPd(CN)_4 \cdot 2C_6H_5OH$	89	en type	2/3	75
$CdenPd(CN)_4 \cdot 2C_6H_6$	88			68
$CdenPd(CN)_4 \cdot 2C_4H_5N$	72			61
$CdenPd(CN)_4 \cdot 2C_4H_4S$	78.5			48
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5OH$	89	Td type	2/3	61
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$	88			54
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_5N$	72			44
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_4H_4S$	78.5			40

[a] G = C_6H_5OH, C_6H_6, C_4H_5N and C_4H_4S.

slightly increased interaction between pyrrole and the coordination component of the clathrate because of its higher electronegativity value with respect to sulphur. This relationship also manifests itself in kinetics studies of the thermal decomposition of tetracyano complex clathrates of other structural types [4] under analogous experimental conditions.

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