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THERMAL DISSOCIATION PROCESSES FOR CLATHRATES $[CuPy_4(NO_3)_2]\cdot 2G$ (*G*=TETRAHYDROFURANE, CHLOROFORM)

E. A. Ukraintseva [1], *V. A. Logvinenko* [1*], *D. V. Soldatov* [1,2] *and*
T. A. Chingina [1]

[1]Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Ac. Lavrentyev Ave. 3, 630090 Novosibirsk, Russia
[2]Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Dr.,
K1A 0R6 Ottawa, Canada

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Abstract

The thermal dissociation processes of clathrates $[CuPy_4(NO_3)_2]\cdot 2G$ (*G*=tetrahydrofuran, chloroform) were studied. Thermodynamic parameters (ΔH^0_{av},ΔS^0_{298} and ΔG^0_{298}) of the processes, producing solid host complex $[CuPy_4(NO_3)_2]$ and gaseous guest (*G*), were determined from the strain measurements. These data are compared with previous data for clathrates of the host complex with benzene and pyridine. Quasi-equilibrium thermogravimetry was used to investigate the step-by-step character of the dissociation processes. Kinetic studies were carried out for clathrate $[CuPy_4(NO_3)_2]\cdot 2THF$.

Keywords: chloroform, clathrate, Cu(II), kinetic parameters, Q-thermogravimetry, tetrahydrofuran, thermal dissociation, thermodynamic parameters, vapour pressure

Introduction

Soft supramolecular materials, such as molecular clathrates, have attracted a great deal of attention because of their structural variability and selectivity, transient response to external stimuli and mimicry of living matter [1]. Thermoanalytical, thermodynamic and kinetic studies have been performed on a wide range of such materials to provide fundamental information about their nature, stability and important properties [2–12].

Supramolecular compound $[CuPy_4(NO_3)_2]\cdot 2Py$ which forms in the pyridine (Py)–copper(II) nitrate system belongs to a large family of isomorphous clathrates $[MPy_4X_2]\cdot 2Py$ [13–15]. These compounds, previously referred to as 'metal hexapyridine complexes', were found to have only four pyridine ligands coordinated to the metal (*M*), with the rest two pyridine molecules included in the crystal framework [13–22]. The interest in this new family is the wide variability of the host complex constituents (*M*

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[*] Author for correspondence: E-mail: val@che.nsk.su

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Akadémiai Kiadó, Budapest
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and *X*) that maintain the structural similarity of the resulting inclusion compounds. The possibility to substitute for guest component was also reported [23, 24].

In spite of many of the $[MPy_4X_2]\cdot 2Py$ compounds have been studied X-ray structurally, little was made regarding the stoichiometry and stability region determinations for these compounds. Our recent studies concentrated on the properties of the clathrates of the $[MPy_4(NO_3)_2]\cdot 2Py$ series (*M*=Mn, Co, Ni, Zn, Cu, Cd) [25–28]. It was found that the removal of guest pyridine causes decomposition of the host complexes in the majority of the systems. The $[MPy_4(NO_3)_2]$ complexes are unstable and do not exist as guest-free solids but appear as host species in the clathrate structures. This type of thermodynamic stabilization of unstable molecules was referred to as 'contact stabilization phenomenon' [29, 30]. The $[CuPy_4(NO_3)_2]$ complex is the only exception; it forms a stable guest-free solid [24, 28] and it forms inclusion compounds with guests other than pyridine: $[CuPy_4(NO_3)_2]\cdot G$, where *G*=benzene, terahydrofuran and chloroform [23, 24, 31].

The purpose of this investigation was to study thermal and thermodynamic stability of the clathrates $[CuPy_4(NO_3)_2]\cdot 2G$, where *G*=tetrahydrofuran (THF) and chloroform. Determination of thermodynamic parameters for dissociation of the clathrates made it possible to compare these new data with previous data for isomorphous inclusion compounds with benzene [31] and pyridine [28]. In addition, kinetic parameters of the thermal dissociation of the tetrahydrofuran clathrate have been examined.

Experimental

Synthesis and analysis of the clathrates were performed as described previously [23, 24]. Results of analyses for copper(II) were as follows (mass%):

Calculated for $[CuPy_4(NO_3)_2]\cdot 2THF$: 9.80, found: 9.82(5);

Calculated for $[CuPy_4(NO_3)_2]\cdot 2CHCl_3$: 8.56, found 8.60(7).

Pressure measurement

Vapour pressure was measured by the static method, using spoon-type membrane null-manometers [32, 33]. The sensitivity of the membranes varied within 0.05–0.1 torr (1 torr=1 mm Hg=133.322 Pa). The accuracy of the temperature measurement was 0.05 K. Other details of this technique were given elsewhere [33, 34]. Two series of experiments were carried out for every clathrate. Pure as-synthesized compounds, $[CuPy_4(NO_3)_2]\cdot 2THF$ and $[CuPy_4(NO_3)_2]\cdot 2CHCl_3$, were used in first series. Before the second series of measurements, some quantity of a volatile guest (tetrahydrofuran or chloroform), released upon the thermal dissociation of the compounds, was condensed into a side vessel and removed. Therefore the host per guest ratio in the samples of the first series was 1:2 while in the second series it was lower, 1:1.21 and 1:1.9 for THF and $CHCl_3$ compounds, respectively.

The reversibility of the thermal decomposition (in measured temperature area: 17–105°C) of all clathrates was checked and was confirmed by quasi-equilibrium thermogravimetry.

The studied thermal dissociation processes were reversible. However, the reaction rates were very different for the two compounds. The guest equilibrium pressure over $[CuPy_4(NO_3)_2]\cdot 2CHCl_3$ was established in one or two hours, both in the forward and backward direction of the dissociation reaction. In contrast, the stabilization of the guest pressure over $[CuPy_4(NO_3)_2]\cdot 2THF$ required at least 24 h in the forward direction; the reverse reaction required more time and the equilibrium was not attained at low temperatures at all.

Thermal analysis

Thermal stability of the compounds and stoichiometry of the decomposition reactions were studied by the TG technique on a MOM Q-1500-D derivatograph (Hungary). Quasi-equilibrium regime of heating was used in order to investigate the step-by-step character of the thermal dissociation and to determine stable intermediate phases. Standard crucibles (plate, closed and conic) were used as sample holders; the mass of the samples was 150 mg, the mass loss curves were recorded at a rate of 0.4 mg min^{-1} in static air atmosphere. Other details of the technique may be found elsewhere [35].

Kinetics studies were carried out using 50 mg samples of $[CuPy_4(NO_3)_2]\cdot 2THF$ placed in plate-like crucibles. The samples were heated at rate of 2.5, 5 or 10°C min^{-1} in flow of helium 60–120 cm^3 min^{-1}]. We studied only this single compound, $[CuPy_4(NO_3)_2]\cdot 2THF$.

Results and dscussion

In the studied temperature range, the $[CuPy_4(NO_3)_2]\cdot 2G$ compounds (G=THF, $CHCl_3$) decompose in two steps:

$$[CuPy_4(NO_3)_2]\cdot 2G_{\text{solid}}=[CuPy_4(NO_3)_2]_{\text{solid}}+2G_{\text{gas}} \tag{1}$$

$$[CuPy_4(NO_3)_2]_{\text{solid}}=CuPy_3(NO_3)_2]_{\text{solid}}+P_{\text{gas}} \tag{2}$$

Figure 1 shows mass loss curves for the $[CuPy_4(NO_3)_2]\cdot 2THF$ clathrate; decomposition of the chloroform clathrate and studied previously pyridine and benzene clathrates follow the same scheme. First step yields a host complex solid phase $[CuPy_4(NO_3)_2]$. The phase comprises molecular host octahedral complexes similar to those found in the clathrate phase but the crystal packing is different from the clathrate phase [24]. The second step yields a complex with three pyridines, the complex was reported as having molecular structure [36].

Total vapour pressure over studied clathrates is a sum of partial pressures created by guest and pyridine. Therefore, the experimental values directly measured in strain experiment were corrected by subtracting the partial pressure of pyridine contributed by the host [28].

The corrected experimental data on the temperature dependence of the guest vapour pressure over the compounds $[CuPy_4(NO_3)_2]\cdot 2THF$ and $[CuPy_4(NO_3)_2]\cdot 2CHCl_3$ are shown in Fig. 2. For comparison, data on isomorphous pyridine and benzene clathrates are shown in the same figure.

For each system, the results for the two series of experiments coincided within experimental error. In other words, guest pressure over the clathrates does not depend on the host per guest ratio in a studied sample. Therefore, the process (1) is a monovariant equilibrium; it involves two solid phases and the clathrate phase collapses into another, guest-free host phase, as the guest component leaves the clathrate. In other words, the $[CuPy_4(NO_3)_2]{\cdot}2THF$ and $[CuPy_4(NO_3)_2]{\cdot}2CHCl_3$ clathrates are compounds of constant composition.

The data of the two experimental series for each clathrate were combined. The data were approximated by linear equations $\log P=A-B/T$ (P/torr; T/K), with the coefficients A and B refined by least-squares technique. The coefficients are listed in Table 1. Standard changes of enthalpy, entropy and isobaric–isothermal potential calculated therefrom (Table 1) refer to the process (3):

$$1/2[CuPy_4(NO_3)_2]{\cdot}2G_{\text{solid}}=1/2[CuPy_4(NO_3)_2]_{\text{solid}}+G_{\text{gas}} \tag{3}$$

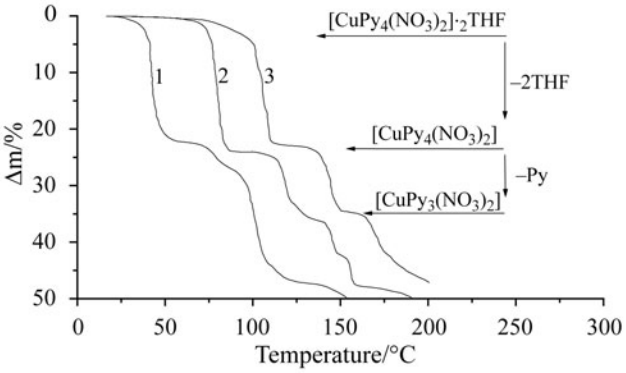

Fig. 1 Mass loss curves for $[CuPy_4(NO_3)_2]{\cdot}2THF$ recorded under quasi-equilibrium conditions. Sample mass: 150 mg; atmosphere: air; q=0.4 mg min^{-1}; sample holders: 1 – plate; 2 – closed and 3 – conic crucibles

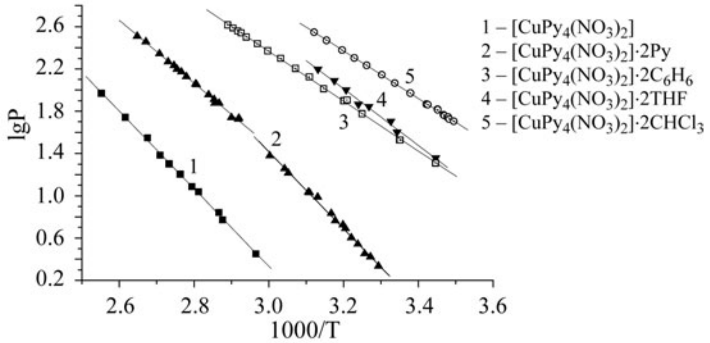

Fig. 2 Temperature dependence of the guest vapour pressure over the $[CuPy_4(NO_3)_2]{\cdot}2G$ clathrates and $[CuPy_4(NO_3)_2]$ host complex. $\log P$–1000/T coordinates (P/torr, T/K)

Table 1 Coefficients for the log$P$=A–B/T equations (P/torr; T/K) and calculated thermodynamic parameters of the clathrate dissociation reaction: $1/2[CuPy_4(NO_3)_2]\cdot 2G_{solid} = 1/2[CuPy_4(NO_3)_2]_{solid} + G_{gas}$

G	T range/K	Number of experimental points	A	B/1000	ΔH^0_{av}*/ kJ mol^{-1}	ΔS^0_{298}/ J mol^{-1} K^{-1}	ΔG^0_{298}/ kJ mol^{-1}	Ref.
Py	304–333	15	13.2(2)	3.90(5)	74.6(9)	197(3)	15.9(5)	[28, 37]
Py	333–378	17	10.43(4)	2.99(2)	57.2(3)	145(9)	14.1(4)	[28, 37]
C_6H_6	290–346	18	9.46(5)	2.36(2)	45.3(3)	126(1)	7.7(5)	[31]
THF	290–320	8	10.5(3)	2.65(8)	51.0(1)	146(6)	7.28(5)	this work
$CHCl_3$	292–320	18	9.55(4)	2.24(1)	42.9(2)	127(1)	4.88(1)	this work

* Average value for studied temperature interval.

Guest vapour pressure in the series of the $[CuPy_4(NO_3)_2]\cdot 2G$ clathrates changes in the following sequence (Table 1 and Fig. 2):

pyridine<benzene<THF<chloroform

The sequence seems to be defined by the volatility of the guest component. Clathrates thermodynamic stability (ΔG^0) changes in the backward direction (Table 1). From these observations we conclude that thermodynamic stability in the series is defined by the volatility of the guest component.

This conclusion is in contrast with our previous work on another series of clathrates, $[MPy_4(NO_3)_2]\cdot 2Py$, where M=Mn, Co, Ni, Cu, Zn, Cd. Most of the $[MPy_4(NO_3)_2]$ host complexes are unstable without guest template (Py), and our studies revealed that relative stability of the clathrates is defined by the strength of coordination bonds in the host complex molecule [28, 37]. The copper complex, $[CuPy_4(NO_3)_2]$, is the only stable host complex in the series and therefore the guest pyridine in $[CuPy_4(NO_3)_2]\cdot 2Py$ can be totally replaced with other guests. The stability of the resulted clathrates, studied in the present work, depends on the guest parameters.

The entropy values (Table 1) are greater for polar guests (dipole moments: benzene, 0D; chloroform, 1.04D; THF, 1.75D; pyridine, 2.22D). Less polar guests are likely to be more disordered in the solid phase that results in both smaller entropy and smaller enthalpy changes upon transition of the guests into the gaseous phase.

The first step of the clathrate dissociation was studied, and the convenient variant of calculation was selected. We used the computer program ‘Netzsch Thermokinetics’ (version 2001.9d) for the processing the thermogravimetric data for $[CuPy_4(NO_3)_2]\cdot 2THF$. Special program module ‘Model free’ allows processing simultaneously several thermogravimetric curves, obtained with different heating rates, without the preliminary information about the kinetic topochemical equations. Only energy activation values can be calculated in such a way. Although Ozawa suggested such approach in 1965 [38], and developed the calculation method later on, it was Vyazovkin who draw attention on the frequent inconstancy of the activation energy during the solid-state reaction and on the clear importance of the direct calculation of the ‘spot’ activation energy values (without the search of the overall topochemical equation) [39–41]. The every value of activation energy is calculated ‘point by point’. Such reactions are the simple ‘moving off’ of the included volatile compounds from the matrix. It is considered that these ‘spot’ values are independent on the conversion degree, but they can decrease or increase under fractional conversion (α) change.

Program ‘ASTM E698 [42] enables to calculate the averaged values of activation energy and preexponential factor according to maximum rate temperatures, and the preexponential factor is calculated conditionally for the first-order reaction). Program ‘Friedman Analysis’ [43] and program ‘Ozawa–Flynn–Wall analysis’ [38, 44] allow calculating only activation energies for every experimental point (in the interval $0.02<\alpha<0.98$).

The same set of experimental data was used for searching the topochemical equation (the selection from 16 equations for chemical reaction on the interface, nucleation, and diffusion). This search utilized an improved differential method of

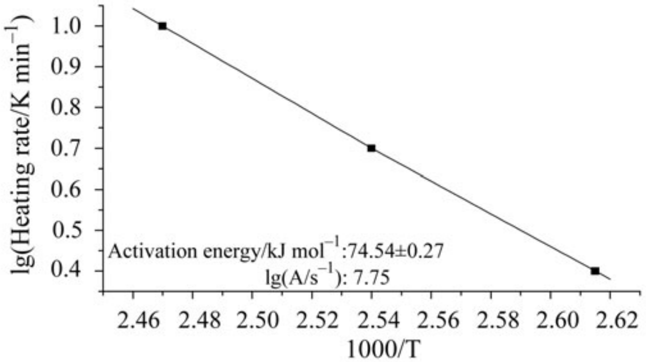

Fig. 3 Kinetics of thermal dissociation of the $[CuPy_4(NO_3)_2]\cdot 2THF$ clathrate. The calculation of the average values of activation energy (*E*) and pre-exponential factor (*A*) by the 'ASTM E698' program

Borchardt–Daniels with multiple linear regression [45]. The choice of the best kinetic description was based on the *F*-test [45].

The best kinetic equation for the dissociation of the $[CuPy_4(NO_3)_2]\cdot 2THF$ clathrate is R3, three-dimensional phase boundary reaction (calculated for the selected region of conversion, $0.40<\alpha<0.98$): $f(\alpha)=(1-\alpha)^{2/3}$, with $E_a=72$ kJ mol^{-1} and $\log A=6.9$. The 'ASTM E698' analysis gives close values of $E_a=74.5$ kJ mol^{-1} and $\log A=7.8$ (Fig. 3). This mechanism is consistent with the conclusion based on the guest vapour experiments that the clathrate decomposition is followed by the formation of a new host phase.

Conclusions

The clathrates of the $[CuPy_4(NO_3)_2]$ host complex decompose in one step to give a new, guest-free, phase of the host complex:

$$[CuPy_4(NO_3)_2]\cdot\ 2G_{\text{solid}}=[CuPy_4(NO_3)_2]_{\text{solid}}+2G_{\text{gas}}$$

Thermal and thermodynamic stability of the $[CuPy_4(NO_3)_2]\cdot\ 2G$ compounds changes in the following sequence: pyridine>benzene>THF>chloroform. The stability is defined by the volatility of the guest component. These conclusions are supported by quantitative thermodynamic and kinetic information obtained in this and our previous work.

The systematic study of supramolecular systems: clathrates and intercalates [46–50] (thermodynamic and kinetic stability in thermal dissociation processes) allows to discuss the difference in the stability of layered and channel (or cage) inclusion compounds [51].

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