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Thermal decomposition of bis(5,7-dichloro-8-quinolinol)-oxovanadium(IV) complexes with pyridines

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Abstract

We describe a kinetic study by differential scanning calorimetry (DSC) of the thermal decomposition under a nitrogen atmosphere of several adducts with pyridine or substituted pyridines of bis(5,7-dichloro-8-quinolinol)oxovanadium(IV), to which the formula assigned is $VO(clox)_2 \cdot B$, where clox = 5,7-dichloro-8-quinolinol and B = pyridine (Py), 3-methylpyridine (3-MP), 4-methylpyridine (4-MP), 3,5-dimethylpyridine (3,5-DMP), 3-aminopyridine (3-AP) or 4-aminopyridine (4-AP).

For the endothermic process of the loss of coordinated base, we calculated activation energies using a new method, and the mechanism of this reaction was also determined. A relationship between activation energies and the properties of the ligands was established.

INTRODUCTION

The determination of kinetic parameters by non-isothermal methods offers interesting advantages over conventional isothermal studies [1]. Only a single sample and fewer data are required, and the kinetics can be calculated over an entire temperature range in a continuous manner.

Nevertheless, the methods usually employed for kinetic analysis [2–9] lead to ambiguous results, especially if the reaction studied follows a diffusion-controlled kinetic law. A disadvantage of the non-isothermal technique is that the reaction mechanism cannot usually be determined, and hence the meaning of the kinetic parameters is uncertain.

In previous papers, we have studied the synthesis, the thermal behaviour and the kinetic parameters, by the procedure of Thomas and Clarke [10], of several vanadium(IV) and molybdenum(IV) complexes with pyridine or substituted pyridines [11–13]. However, the results obtained only have validity in a narrow range of the reaction.

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Recently we have reported a new method for carrying out the kinetic analysis of non-isothermal decomposition reactions of inorganic compounds by means of differential scanning calorimetry (DSC) [14–20].

In this paper, we describe the application of this previously reported method in order to determine the kinetic parameters by which the thermal decomposition process of several adducts with pyridine or substituted pyridines of formula $VO(clox)_2 \cdot B$ (where clox = 5,7-dichloro-8-quinolinol and B = pyridine (Py), 3-methylpyridine (3-MP), 4-methylpyridine (4-MP), 3,5-dimethylpyridine (3,5-DMP), 3-aminopyridine (3-AP) or 4-aminopyridine (4-AP) takes place.

We have determined the mechanism of the process

$$VO(clox)_2 \cdot B(s) \rightarrow VO(clox)_2(s) + B(g)$$

and we have calculated the activation energy for all the adducts synthesized.

A comparison between the activation energies, steric or inductive factors and pK_b values of the coordinated bases has been made, and a relationship between the IR spectra of the compounds and activation energies for the process of the loss of coordinated pyridine has also been determined.

EXPERIMENTAL

Preparation and analyses of compounds

The complex $VO(clox)_2$ and its adducts with pyridine or substituted pyridines were prepared as previously reported [21].

The IR spectra of the residue obtained by thermal decomposition were recorded on a Perkin-Elmer spectrophotometer, model 283, using KBr pellets.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a Mettler HE-20 thermobalance. The following analytical constants were used: heating rate 5°C min^{-1}; TG range, 20 mV; recorder rate, 20 cm h^{-1}; sample mass, 20 mg; reference, Al_2O_3; thermocouple, Pt/Pt–Rh 80%.

The analysis was made in a dynamic nitrogen atmosphere between 25 and 300°C. A platinum pan was used.

Differential scanning calorimetry

DSC was realized on a Mettler TA 3000 system with a Mettler DSC-20 differential scanning calorimeter. The scanning rate used was 5°C min^{-1} and samples of about 5 mg were used, so as to render insignificant the

temperature non-uniformity within the sample. An aluminium pan was used under a dynamic nitrogen atmosphere.

The instrument calibration was checked periodically with standard samples of indium (99.99% purity). Several runs were made.

RESULTS AND DISCUSSION

On the DSC curves of all compounds a first endothermic peak can be identified. On the TG curves the mass loss accompanying this transition corresponds to the loss of the base coordinated to vanadium, the residue being $VO(clox)_2$ in all cases. Table 1 shows the thermogravimetric data.

From the DSC curve of the adduct $VO(clox)_2 \cdot 4\text{-AP}$ we collected the data which appear in Table 2; α is the reacted fraction at time t and $\alpha' = d\alpha/dT$.

Using the most usual mechanisms reported in the literature [1] (see Table 3), and in accordance with our method, we plotted $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/\Delta \ln(1-\alpha)$ vs. $\Delta(1/T)/\Delta \ln(1-\alpha)$. From these seven representations we can calculate the activation energy of the process. Table 4 shows the results for r (correlation coefficient), m (slope), i (intercept value) and E_a (activation energy) obtained for the seven mechanisms.

We can observe that in all cases the plots are straight lines and the correlation coefficients (r) are very near to unity, consistent with the results of Criado et al. [22]. Nevertheless, only when the analysis was performed by the mechanism F1 did the straight line present an intercept value close to zero (0.00105).

TABLE 1

Thermogravimetric data

Compound	T (°C)	$\Delta m/m$		Identified compound
		Calc. (%)	Found (%)	
$VO(clox)_2 \cdot Py$	108–204	13.81	13.73	$VO(clox)_2$
	229–518	81.54	81.24	V_2O_5
$VO(clox)_2 \cdot 3\text{-MP}$	124–183	15.87	16.09	$VO(clox)_2$
	236–539	81.54	81.40	V_2O_5
$VO(clox)_2 \cdot 4\text{-MP}$	74–156	15.87	15.71	$VO(clox)_2$
	208–521	81.54	80.36	V_2O_5
$VO(clox)_2 \cdot 3,5\text{-DMP}$	53–120	17.83	18.09	$VO(clox)_2$
	211–512	81.54	81.19	V_2O_5
$VO(clox)_2 \cdot 3\text{-AP}$	72–129	16.01	15.87	$VO(clox)_2$
	191–530	81.54	82.18	V_2O_5
$VO(clox)_2 \cdot 4\text{-AP}$	100–163	16.01	16.33	$VO(clox)_2$
	200–541	81.54	81.15	V_2O_5

TABLE 2

Values of ΔH, α, T and α' obtained from the DSC curve of the complex $VO(clox)_2 \cdot 4\text{-AP}$

ΔH (mJ)	α	T (°C)	α' (K^{-1})
129.96	0.11324	123.0	0.02614
170.84	0.14886	125.0	0.03403
225.23	0.19626	127.0	0.04636
296.38	0.25826	129.0	0.05672
377.36	0.32882	131.0	0.06215
465.71	0.40581	133.0	0.06757
560.31	0.48825	135.0	0.07201
661.40	0.57633	137.0	0.07645
766.16	0.66762	139.0	0.07645
866.47	0.75502	141.0	0.07053
953.48	0.83084	143.0	0.05524
1021.10	0.88973	145.0	0.04193

Therefore, according to our proposed method, we deduce that the thermal decomposition of the complex $VO(clox)_2 \cdot 4\text{-AP}$ and the loss of 4-aminopyridine take place by the F1 mechanism (random nucleation) with a function $f(\alpha) = (1-\alpha)$ and an activation energy $E_a = 224 \pm 1$ kJ mol^{-1}.

TABLE 3

Kinetic equations

Mechanism (rate-controlling process)	$f(\alpha)$
D1 (one-dimensional diffusion)	$(1/2\alpha)$
D2 (two-dimensional diffusion)	$[-\ln(1-\alpha)]^{-1}$
D3 (three-dimensional diffusion: Jander equation)	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
D4 (three-dimensional diffusion: Ginstling–Brounshtein equation)	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$
F1 (random nucleation)	$(1-\alpha)$
R2 (phase-boundary reaction: cylindrical symmetry)	$2(1-\alpha)^{1/2}$
R3 (phase-boundary reaction: spherical symmetry)	$3(1-\alpha)^{2/3}$

TABLE 4

Results obtained by using the seven mechanisms for the plot of $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/\Delta \ln(1-\alpha)$ vs. $\Delta(1/T)/\Delta \ln(1-\alpha)$ for the complex $VO(clox)_2 \cdot 4\text{-AP}$

Mechanism	r	m	i	E_a (kJ mol^{-1})
D1	−0.99926	−50472.64	1.50371	420 ± 3
D2	−0.99923	−50882.20	1.11145	423 ± 3
D3	−0.99924	−50834.95	0.59910	423 ± 2
D4	−0.99924	−50834.85	0.93243	423 ± 3
F1	−1.00000	−27014.55	0.00105	225 ± 2
R2	−0.99999	−27014.57	0.50105	225 ± 2
R3	−0.99998	−27014.56	0.33439	225 ± 3

TABLE 5

Thermal and kinetic parameters for the complexes $VO(clox)_2 \cdot B$

Compound	Mechanism	ΔH (kJ mol^{-1})	E_a (kJ mol^{-1})	pK_b
$VO(clox)_2 \cdot Py$	F1	21.4±0.5	137±1	8.87
$VO(clox)_2 \cdot 3\text{-MP}$	F1	28.0±0.6	178±2	8.32
$VO(clox)_2 \cdot 4\text{-MP}$	F1	17.6±0.4	98±1	7.98
$VO(clox)_2 \cdot 3,5\text{-DMP}$	D3	40.2±0.9	214±1	7.85
$VO(clox)_2 \cdot 3\text{-AP}$	F1	45.8±0.3	272±2	7.49
$VO(clox)_2 \cdot 4\text{-AP}$	F1	41.7±0.2	225±2	4.88

The results obtained for all the complexes studied in this paper are listed in Table 5.

Using our method, we can assume that the thermal decomposition and the loss of coordinated base of the adducts with pyridine, 3-methylpyridine, 4-methylpyridine, 3-aminopyridine and 4-aminopyridine follow the F1 mechanism (random nucleation), and the D3 mechanism (three-dimensional diffusion) applies to the adduct with 3,5-dimethylpyridine.

If we compare the results, in general, as can be seen from the data in Table 5, the greater the basicity of the base employed, the higher the activation energy for the process of loss of the base. The outstanding exceptions are the 4-MP and 4-AP adducts; these can be attributed to the existence of resonance structures, which has a pronounced effect on the stability of the complex [11,12]. It can be seen that the steric hindrance of 3,5-DMP does not modify the kinetic parameters.

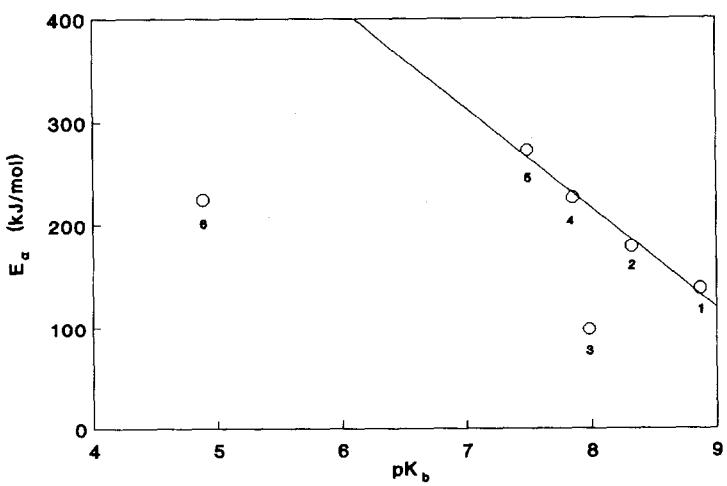

Fig. 1. Activation energy for the decomposition of $VO(clox)_2 \cdot B$ complexes as a function of pK_b. Points 1–6 correspond to complexes of Py, 3-MP, 4-MP, 3,5-DMP, 3-AP and 4-AP respectively.

The plot of pK_b vs. activation energy presented in Fig. 1 shows that, except for the 4-MP and 4-AP adducts, a very satisfactory correlation was obtained. It is obvious from this figure that activation energy is linearly related to the basicity of the ligands.

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