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THERMAL AND KINETIC STUDIES ON THE ADDUCTS WITH PYRIDINES OF BIS(8-QUINOLINOL) OXOVANADIUM(IV)

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ABSTRACT

The kinetic study by differential scanning calorimetry (DSC) of the thermal decomposition under nitrogen atmosphere is described for several adducts with pyridine or substituted pyridines of bis(8-quinolinol) oxovanadium(IV), whose assigned formula is $VO(ox)_2 \cdot B$, where ox ≡ 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).

From the DSC curves, the activation energies and pre-exponential Arrhenius factors, for the endothermic loss of one mole of coordinated base were calculated using a new method, and the mechanism of this reaction was determined. A relationship between the activation energies and the properties of the ligands has also been 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 kinetics 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 kinetics parameters is uncertain.

In other papers, we have studied the synthesis, thermal behaviour and kinetic parameters, using Thomas and Clarke's procedure [10], of several

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vanadium(IV) and molybdenum(IV) complexes with pyridine or substituted pyridines [11–13]. However, the results obtained are only valid over a narrow range of the reaction. We have also reported a new method for the kinetic analysis of non-isothermal decomposition reactions of inorganic compounds by means of differential scanning calorimetry [14–18].

In this paper, this previously reported method is applied in order to determine the kinetics parameters of the thermal decomposition of several adducts with pyridine or substituted pyridines of $VO(ox)_2 \cdot B$, where ox ≡ 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).

The mechanism of the process

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

has been determined and we have calculated the activation energy and the pre-exponential Arrhenius factor for all the adducts synthesised. A comparison between the activation energies, the steric or inductive factors and the pK_b values of the coordinated bases has also been made.

EXPERIMENTAL

Preparation and analyses of the compounds

The complex $VO(ox)_2$ and its adducts with pyridine or substituted pyridines were prepared as previously reported [12].

Infrared spectra of the residues obtained following 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 analytical constants were: heating rate, 2 °C min^{-1}; TG range, 20 mV; record rate, 20 cm h^{-1}, sample mass, 20 mg; reference, Al_2O_3; and thermocouple, Pt/Pt–Rh 80%.

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

Differential scanning calorimetry

Differential scanning calorimetry was carried out on a Mettler TA 3000 system with a Mettler DSC-20 differential scanning calorimeter.

The scanning rate was 2 °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

The DSC curves of all the compounds first show an endothermic peak. On the TG curves the mass loss accompanying this transition corresponds to the loss of the coordinated base to vanadium, the residue being $VO(ox)_2$ in all cases.

Table 1 shows the data from the DSC curve of this transition for the adduct $VO(ox)_2 \cdot Py$, where α is the reacted fraction at time t and $\alpha' = d\alpha/dT$.

Using the mechanisms most commonly reported in the literature [1] (see Table 2), we have plotted $[\Delta\ln \alpha' - \Delta\ln f(\alpha)]/\Delta\ln(1-\alpha)$ versus $\Delta(1/T)/\Delta\ln(1-\alpha)$. From these graphs, the activation energy of the process can be calculated. Table 3 shows the results for r (correlation coefficient), m

TABLE 1

ΔH, α, T and α' obtained from the DSC curve of the complex $VO(ox)_2 \cdot Py$

ΔH (mJ)	α	T (°C)	α' (K^{-1})
136.39	0.11582	98	0.02418
160.54	0.13633	99	0.02654
186.72	0.15856	100	0.02907
216.08	0.18349	101	0.03177
247.32	0.21002	102	0.03464
281.46	0.23901	103	0.03767
318.34	0.27033	104	0.04084
357.82	0.30386	105	0.04415
400.34	0.33997	106	0.04756
447.20	0.37976	107	0.05097
497.10	0.42213	108	0.05436
550.18	0.46721	109	0.05765
607.89	0.51621	110	0.06063
668.20	0.56743	111	0.06326
733.14	0.62257	112	0.06515
801.55	0.68067	113	0.06605
873.44	0.74171	114	0.06544
946.77	0.80398	115	0.06277
1019.70	0.86588	116	0.05713

TABLE 2

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)	$3/[2(1-\alpha)^{1/3}-1]$
F1 (random nucleation)	$(1-\alpha)$
R2 (phase-boundary reaction: cylindrical symmetry)	$2(1-\alpha)^{1/2}$
R3 (phase-boundary reaction: spherical symmetry)	$3(1-\alpha)^{2/3}$

(slope), i (intercept value) and E_a (activation energy) obtained for the seven mechanisms.

We can observe that in all cases the correlation coefficients (r) are very near to unity, consistent with the results of Criado et al. [19]. Nevertheless, only when the analysis was performed with the R_2 mechanism does the straight line have an intercept value close to zero.

Therefore, in accordance with our proposed method, we deduce that the thermal decomposition of the complex VO(ox) · Py and the loss of pyridine, follows an R2 mechanism (phase boundary reaction: cylindrical symmetry) with a function $f(\alpha) = 2(1-\alpha)^{1/2}$, an activation energy $E_a = 120 \pm 2$ kJ mol^{-1} and a pre-exponential Arrhenius factor $A = (3.5 \pm 0.3) \times 10^{13}$ s^{-1}.

The results obtained for the complexes studied in this paper are listed in Table 4.

We can assume that the thermal decomposition and loss of coordinated base of the adducts with pyridine, 4-methylpyridine and 3-aminopyridine

TABLE 3

Results obtained by using the seven mechanisms for the plot of $[\Delta\ln\alpha' - \Delta\ln f(\alpha)]/\Delta\ln(1-\alpha)$ versus $\Delta(1/T)/\Delta\ln(1-\alpha)$ for the complex $VO(ox)_2 \cdot Py$

Mechanism	r	m	i	E_a (kJ mol^{-1})
D1	−0.99987	−36698.16	1.00861	305
D2	−0.99899	−37068.31	0.60737	308
D3	−0.99784	−37025.90	−0.09612	307
D4	−0.99867	−37025.85	0.42945	307
F1	−0.99999	−14466.14	−0.49989	120
R2	−0.99999	−14466.15	0.00011	120
R3	−0.99999	−14466.15	−0.16656	120

TABLE 4

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

Complex	Mechanism	ΔH (kJ mol^{-1})	E_a (kJ mol^{-1})	A (s^{-1})	pK_b
$VO(ox)_2 \cdot$Py	R2	22.3 ± 0.6	120 ± 2	$(3.5 \pm 0.3) \times 10^{13}$	8.87
$VO(ox)_2 \cdot$3-MP	D3	27.2 ± 0.8	164 ± 2	$(3.6 \pm 0.3) \times 10^{20}$	8.32
$VO(ox)_2 \cdot$4-MP	R2	25.6 ± 0.9	90 ± 2	$(7.0 \pm 0.6) \times 10^{9}$	7.98
$VO(ox)_2 \cdot$3,5-DMP	F1	35.9 ± 0.8	207 ± 3	$(1.4 \pm 0.2) \times 10^{27}$	7.85
$VO(ox)_2 \cdot$3-AP	R2	40.8 ± 0.9	239 ± 5	$(7.8 \pm 0.8) \times 10^{32}$	7.49
$VO(ox)_2 \cdot$4-AP	F1	32.5 ± 0.4	210 ± 3	$(2.6 \pm 0.2) \times 10^{27}$	4.88

follow an R2 mechanism, the adducts with 3,5-dimethylpyridine and 4-aminopyridine follow an F1 mechanism (random nucleation) and the adduct with 3-methylpyridine follows a D3 mechanism (three-dimensional diffusion).

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

The plot of pK_b versus 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 the activation energy is linearly related to the basicity of the ligands.

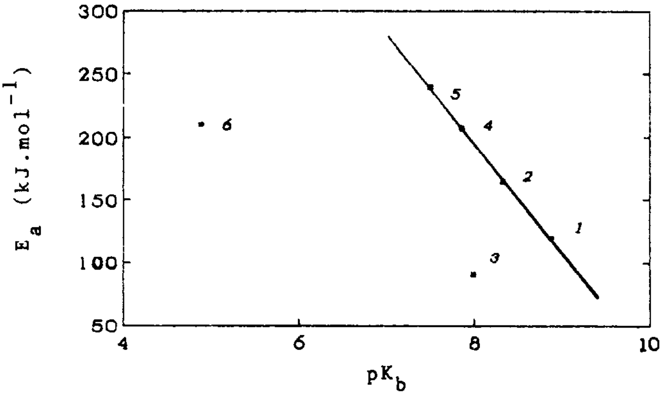

Fig. 1. Activation energy for decomposition of $VO(ox)_2 \cdot B$ complexes as a function of pK_b. Points 1–6 correspond to complexes of Py, 3-MP, 4-MP, 3,5-DMP, 3-AP and 4-AP, respectively.

REFERENCES

1 W.W. Wendlandt, Thermal methods of Analysis, Wiley, New York, 1974.
2 A.E. Nerwkirk, Anal. Chem., 32 (1960) 1558.
3 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
4 A. Jerez, J. Therm. Anal., 26 (1983) 315.
5 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
6 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
7 C.D. Doyle, J. Appl. Polymer Sci., 5 (1961) 283.
8 T.R. Ingraham and P. Marrier, Can. J. Chem. Eng., (1964) 161.
9 B.N.N. Achar, G.W. Brindley and J.H. Sharp, Proc. Int. Clay Conf., Jerusalem, 1 (1966) 67.
10 J.M. Thomas and T.A. Clarke, J. Chem. Soc. A, (1968) 457.
11 R. Lozano, J. Martinez, A. Martinez and A. Doadrio, Polyhedron, 2 (1983) 997.
12 R. Lozano, J. Martinez, J. Román, A. Martinez and A. Doadrio, Polyhedron, 5 (1986) 1341.
13 R. Lozano, J. Román and A. Moragues, Thermochim. Acta, 108 (1986) 1.
14 R. Lozano, J. Román, A. Moragues and J.C. Avilés, Transition Met. Chem., 12 (1987) 289.
15 R. Lozano, J. Román, F. de Jesús, A. Jerez and E. Ramos, Thermochim. Acta, 141 (1989) 261.
16 R. Lozano, J. Román, F. de Jesús, A. Jerez and E. Ramos, Thermochim. Acta, 143 (1989) 93.
17 R. Lozano, J. Martinez and A. Martinez, Eur. J. Sol. State Inorg. Chem., 25 (1988) 565.
18 R. Lozano, J. Martinez, J. Román, A. Martinez and F. de Jesús, Polyhedron, 8 (1989) 2611.
19 J.M. Criado, D. Dollimore and G.R. Heal, Thermochim. Acta, 54 (1982) 159.