Thermochimica Acta, 86 (1985) 295–303
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL STUDIES ON THE ADDUCTS OF BIS(BENZOYLACETONATO)OXOVANADIUM(IV) WITH SUBSTITUTED PYRIDINES

J. MARTINEZ *, A. MARTINEZ and A. DOADRIO

Departamento de Química Inorgánica y Analítica, Facultad de Farmacia, Universidad Complutense de Madrid, Madrid (3) (Spain)

(Received 23 October 1984)

ABSTRACT

Spectroscopic, magnetic and analytical studies on the adducts of bis(benzoylacetonato)oxovanadium(IV) with nitrogen donors have been previously reported. It was observed that the change in the substituent on the pyridine ring was accompanied by changes in the spectral parameters.

Therefore it was of interest to investigate the thermal stability of the adducts with heterocyclic nitrogen donors of different steric requirements. The DTA curves corresponding to the decomposition of the adducts showed only a single endothermic peak. The mass loss accompanying the endothermic transition corresponded, on the TG curve, to the loss of one molecule of the ligand. From the DSC curves, activation energies have been calculated and the relationships between the activation energies and the enthalpies of the processes with the nature of the metal–ligand bond have heen studied.

INTRODUCTION

Thermal analysis techniques have been applied to inorganic complexes for a long time, but these studies have mostly been limited to a determination of the temperature appropriate for drying or ignition for analysis. Recently, more systematic studies have been reported by several workers, and from DSC and DTA curves they report kinetic and thermodynamic data for reactions in the solid state [1–5].

A lot of methods can be found in the literature regarding the study of this process starting with calorimetric curves. Several authors [6–8] have adopted the Thomas and Clarke [9,10] technique indicated for the type of process

$$X_{(s)} \rightarrow Y_{(s)} + Z_{(g)}$$

and activation energies in the linear region of $d\alpha/dt$ vs. $1/T$ have been obtained.

---

* Author for correspondence.

House and Adams [11] used this method to obtain data on activation energy on the loss of ligand in the PdX_2L_2 complex (L = pyridine, or methylpyridine). In this way, Akhavein and House [12] were able to compare the values of the activation energy obtained using Thomas and Clarke's procedure with those obtained using isothermal methods for the decomposition of several solid complexes of silver nitrate with substituted pyridines. A good relationship was found.

In the present work, we report a study of the process of thermal decomposition of $VO(bza)_2$ adducts with amino- and methyl-pyridines. These compounds were previously synthesized and the study was carried out using spectroscopic and magnetic susceptibility techniques by applying the general formula $VOL_2 \cdot B$.

The study of these adducts using DTA and TG techniques allowed the degree of thermal stability of these compounds to be determined in such as way as to observe the loss of one molecule of coordinated base in the first endothermic process.

By means of the study of this first process through DSC, the activation energy and the enthalpy were determined, establishing relationships between the values with the base bonding power and the bonding force with the vanadium atom in the adduct formed, and the position of the functional groups (amino and methyl in the pyridine ring) which produce steric impediment and inductive effects.

EXPERIMENTAL

Preparation of compounds

The bis(benzoylacetonato)oxovanadium(IV) ($VO(bza)_2$) and its adducts with pyridine (Py), 3-methyl-pyridine, (3-MP), 4-methyl-pyridine (4-MP), 3,5-dimethyl-pyridine (3,5-DMP), 3-amino-pyridine (3-AP) and 4-amino-pyridine (4-AP) were prepared following the method described earlier [13].

Materials

Vanadium(IV) oxide, sulphate, benzoylacetone and the substituted pyridines were obtained commercially (Merck) and were used without further purification.

Analytical methods

Elemental analyses were performed with a Perkin-Elmer (model 240-B) instrument. Vanadium was determined by atomic absorption with a Perkin-Elmer (model 430) atomic absorption spectrophotometer after decomposing

TABLE 1

Analytical data

Compound	%Calculated				%Found			
	C	H	N	V	C	H	N	V
$VO(bza)_2$	61.33	4.59	–	13.01	61.29	4.55	–	13.01
$VO(bza)_2 \cdot Py$	63.77	4.88	2.97	10.82	63.65	4.87	2.97	10.80
$VO(bza)_2 \cdot$ 3-MP	64.40	5.16	2.88	10.51	64.12	5.11	2.80	10.24
$VO(bza)_2 \cdot$ 4-MP	64.40	5.16	2.88	10.51	64.54	5.23	2.92	10.68
$VO(bza)_2 \cdot$ 3,5-DMP	64.99	5.41	2.80	10.21	65.10	5.42	2.79	10.24
$VO(bza)_2 \cdot$ 3-AP	61.79	4.94	5.76	10.49	61.49	4.87	5.61	10.45
$VO(bza)_2 \cdot$ 4-AP	61.79	4.94	5.76	10.49	61.64	4.76	5.37	10.38

the complexes with a concentrated HNO_3/H_2SO_4 mixture (1 : 1).

The analytical data for the compounds are shown in Table 1.

Differential thermal analysis and thermogravimetric analysis

Thermal measurements were performed using a Mettler HE 20 thermobalance, with DTA accessory fitted. The analytical constants were: DTA range, 20 mV–0.33 kcal s^{-1}; heating rate, 5°C min^{-1}; TG range, 20 mV; record rate, 20 cm h^{-1}; reference, Al_2O_3; sample mass, 20 mg; thermocouple, Pt/Pt–Rh.

The instrument was calibrated employing indium as standard substance. The analyses were carried out in a dynamic nitrogen atmosphere to 300°C and then in an oxygen atmosphere to 600°C.

Data for the temperatures or thermal transitions and mass loss determinations are shown in Table 2.

TABLE 2

Thermal data for the decomposition of $VO(bza)_2 \cdot B$

Compound	Temp. (°C)	$\Delta m/m$		Process	Identified compound
		(% cal)	(% exp)		
$VO(bza)_2$	240–575	76.74	76.57	Exothermic	V_2O_5
$VO(bza)_2 \cdot Py$	98–170	16.83	16.50	Endothermic	$VO(C_{10}H_9O_2)_2$
	200–595	76.74	77.12	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ 3-MP	80–140	19.22	19.15	Endothermic	$VO(C_{10}H_9O_2)_2$
	190–465	76.74	76.59	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ 4-MP	94–170	19.22	19.27	Endothermic	$VO(C_{10}H_9O_2)_2$
	220–585	76.74	76.64	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ 3,5-DMP	110–190	21.49	21.35	Endothermic	$VO(C_{10}H_9O_2)_2$
	210–595	76.74	76.58	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ 3-AP	140–190	19.38	19.15	Endothermic	$VO(C_{10}H_9O_2)_2$
	230–520	76.74	76.64	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ 4-AP	160–185	19.38	19.27	Endothermic	$VO(C_{10}H_9O_2)_2$
	235–525	76.74	76.78	Exothermic	V_2O_5

TABLE 3

Infrared and kinetic data for $VO(bza)_2 \cdot B$

Compound	$\nu(V{=}O)$ (cm^{-1})	$\nu(V{-}N)$ (cm^{-1})	Temperature (°C) [a]			ΔH (kcal mol^{-1})	Activation energy (kcal mol^{-1})	pK_b
			T_i	T_p	T_f			
$VO(bza)_2$	1000	–	–	–	–	–	–	–
$VO(bza)_2 \cdot Py$	960	330	96.5	124.7	130.5	13.84	25.35	8.87
$VO(bza)_2 \cdot$3-MP	960–952	325	80	124.5	137	16.92	23.20	8.32
$VO(bza)_2 \cdot$4-MP	960	325	94	142.6	150	16.78	24.21	7.98
$VO(bza)_2 \cdot$3,5-DMP	970	338	108	139.8	152	16.30	29.90	7.85
$VO(bza)_2 \cdot$3-AP	938	350	140	172	182	6.11	52.61	7.49
$VO(bza)_2 \cdot$4-AP	937	350	160	180.2	185	7.53	60.54	4.88

[a] T_i and T_f refer to the temperatures at the beginning and end of a reaction, respectively; T_p refers to the peak maxima in the thermograms.

Differential scanning calorimetry

Thermal measurements were made using a Mettler TA 3000 system with a Mettler differential scanning calorimeter (model DSC 20). Samples of about 5 mg were used so as to render the degree of temperature non-uniformity within the sample insignificant. An aluminium pan was used under a dry nitrogen atmosphere. The scanning rate used was 2°C min^{-1}, and the

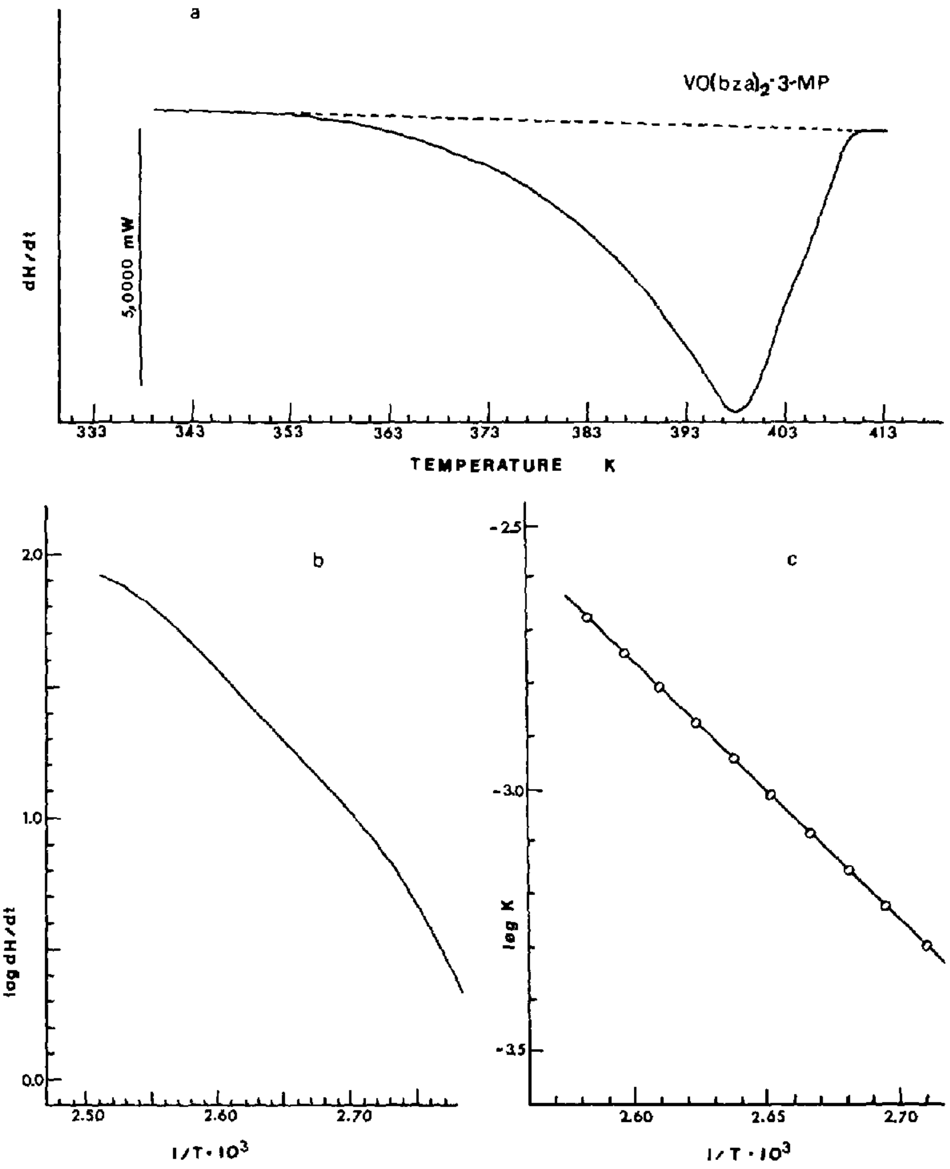

Fig. 1. (a) DSC curve of VO(bza)$_2$·3-MP; (b) Arrhenius plot of log dH/dt vs. $1/T \times 10^3$; (c) Arrhenius plot of log K vs. $1/T \times 10^3$.

instrument calibration was checked periodically with standard samples of indium. In all cases several runs were made and the results are shown in Table 3.

The activation energies were obtained using Thomas and Clarke's procedure. A plot of log dH/dt vs. $1/T$ (Fig. 1b) is obtained from DSC data (Fig. 1a) and on the linear region (Fig. 1c) we can obtain the activation energy using the equation

$$-\log k = -\log(\mathrm{d}H/\mathrm{d}t)\,(1/A) = +\frac{E_A}{2.303RT} - \log C \tag{1}$$

where k = rate constant, A = total area of DSC peak.

When the decomposition proceeds in the linear region over the range of temperature scanned by the calorimeter, the use of eqn. (1) to compute rate constants is justified. Moreover, the activation energy derived from the DSC plot represents the true activation energy for the interfacial reaction.

RESULTS AND DISCUSSION

The DTA curves of all the compounds show a first endothermic peak (or process) between 80 and 195°C; the mass loss accompanying this endothermic transition corresponds, on the TG curve, to the loss of one molecule of base coordinated to vanadium (Fig. 2). Afterwards, series of exothermic processes are produced between 190 and 595°C, corresponding to the decomposition of the complex $VO(bza)_2$, and in all cases the residue was V_2O_5. The process may be schematized as follows

$$VO(bza)_2 \cdot B_{(s)} \xrightarrow{\text{Endo}} VO(bza)_{2(s)} + B_{(g)}$$

$$VO(bza)_{2(s)} \xrightarrow{\text{Exo}} V_2O_{5(s)}$$

For every adduct, the loss of one mole of base occurs in a concrete interval of temperature, after which, once the process of decomposition has been stopped, the residue can be identified by infrared spectroscopy as the complex $VO(bza)_2$. This supports the rupture of the V–N bonding and the loss of one molecule of base as can be seen on the TG curve.

The temperature in which these endothermic transitions (Table 2) take place follow the order: $VO(bza)_2 \cdot$ 3-MP $<$ $VO(bza)_2 \cdot$ 4-MP $\approx$ $VO(bza)_2 \cdot$ Py $<$ $VO(bza)_2 \cdot$ 3,5-DMP $\ll$ $VO(bza)_2 \cdot$ 3-AP $<$ $VO(bza)_2 \cdot$ 4-AP.

It is observed that the initiation temperature in this endothermic process increases as pK_b decreases and therefore as the basicity of the ligand increases. The loss of pyridine occurs at a temperature a little higher than expected which could be due to the absence of substituent in the pyridine ring which would produce steric factors with the phenyl group of benzoylacetone.

The DSC study of the first endothermic process of loss of the base, has allowed the determination of the activation energy by the procedure proposed by Thomas and Clarke from DSC curves (Fig. 1) for solid-state thermal decompositions of type

$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$

or, in this paper

$VO(bza)_2 \cdot B_{(s)} \rightarrow VO(bza)_{2(s)} + B_{(g)}$

The values of activation energy obtained for these compounds may be arranged in the order: $VO(bza)_2 \cdot 3\text{-MP} \lesssim VO(bza)_2 \cdot 4\text{-MP} \lesssim VO(bza)_2 \cdot Py < VO(bza)_2 \cdot 3,5\text{-DMP} \ll VO(bza)_2 \cdot 3\text{-AP} < VO(bza)_2 \cdot 4\text{-AP}$.

This sequence agrees with the value obtained for the initiation temperature of loss of one mole of base and with the basicity of the corresponding pyridine.

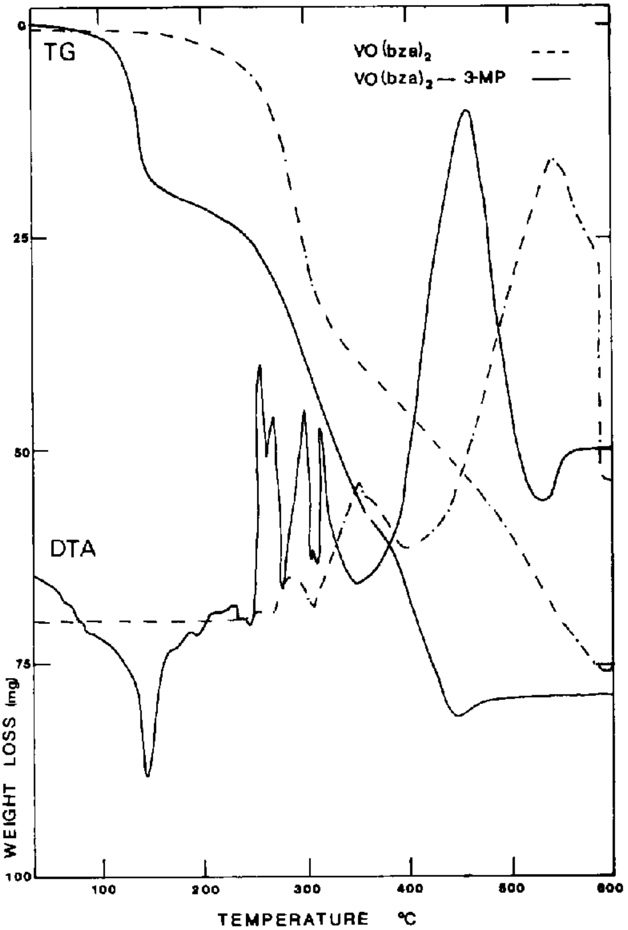

Fig. 2. DTA and TG curves of $VO(bza)_2$ (·–·–·) and $VO(bza)_2 \cdot 3\text{-MP}$ (———).

In the pyridine, 3-methyl and 4-methyl-pyridine adducts the values of activation energy (Table 3) are similar (25.35 kcal mol^{-1} (Py), 23.20 kcal mol^{-1} (3-MP), 24.21 kcal mol^{-1} (4-MP)), as are those of ΔH and the initiation temperature of the endothermic process. This seems to indicate that in these adducts the intensity of the N–V bonding is similar, which concurs with the values obtained from infrared spectroscopy for the frequencies νV–N and νV=O [1].

The initial temperature and the activation energy (29.95 kcal mol^{-1}) values for the adduct with 3,5-dimethyl-pyridine (Table 3) are higher in this compound than those previously analysed though not as much as one would expect from its greater basic character. Moreover, in the infrared spectra of the adduct with 3,5-dimethyl-pyridine, the vibration νV–N appears at a greater frequency (338 cm^{-1}) than in the pyridine, 3-methyl and 4-methyl-pyridine adducts, indicating that the bonding order is higher. The above seems to indicate that the transfer of electronic density from the 3,5-dimethyl-pyridine to the vanadyl ion is partly blocked as a consequence of the steric impediment between its methyl groups and the phenyl groups of benzoylacetone.

The adducts with amino-pyridines present greater activation energy values (52.61 kcal mol^{-1} (3-AP) and 60.54 kcal mol^{-1} (4-AP)) and initial temperatures of all compounds due to the lower values of pK_b of its bases which, combined with the lower νV=O frequency vibrations (938 cm^{-1} (3-AP) and 937 cm^{-1} (4-AP)) and the greater νV–N frequency vibrations (350 cm^{-1}) in these adducts, indicate that the base–metal bonding is greater in these products. The variations in the E_A, T_i, ΔH, νV=O and νV–N values in both these adducts are lower than would be expected from the different pK_b values, which may be due to the existence of a resonance form in the 4-amino-pyridine with a resulting decrease in the ability to transfer electronic density.

Therefore in the adducts with benzoyl-acetone the introduction of phenyl groups into the ligand (bza) produces steric impediments and mesomeric effects in the chelate ring which, in the preparation and stability of the adducts, causes these effects to predominate over the overall basic character of the pyridine used. However it is observed that the amino-pyridines are those in which the bonding to the central atom of the compounds is of greatest intensity, followed by the methyl-pyridines and the 3,5-dimethyl-pyridines.

REFERENCES

1 G. Beech, C.T. Mortimer and E.G. Tyler, J. Chem. Soc. A, (1967) 925.
2 R. Farran and J.E. House, Jr., J. Inorg. Nucl. Chem., 34, (1972) 2219.
3 R.N. Mukherjee, V.S. Vijaya and P.K. Gogoi, Thermochim. Acta, 57 (1982) 387.

4 J.E. House, Jr., Thermochim. Acta, 40 (1980) 225.
5 J. Martínez, R. Lozano, A. Martínez and A. Doadrio, Polymer, 10 (1983) 977.
6 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
7 G.B. Kauffman and G. Beech, Thermochim. Acta, 1 (1970) 99.
8 M.J. Urichek, Instrum. News, 17 (1966) 2.
9 J.M. Thomas and T.A. Clarke, J. Chem. Soc., (1968) 457.
10 J.M. Thomas and T.A. Clarke, J. Chem. Soc., (1969) 2227.
11 J.E. House, Jr. and M.J. Adams, J. Inorg. Nucl. Chem., 34 (1972) 1466.
12 A. Akhavein and J.E. House, Jr., J. Inorg. Nucl. Chem., 32 (1970) 1479.
13 J. Martínez, R. Lozano, A. Martínez and A. Doadrio, An. Quim., 80 (1984) 271.