

THERMAL AND STRUCTURAL STUDIES ON THE ADDUCTS OF BIS(ACETYLACETONATE) OXOVANADIUM(IV) WITH SUBSTITUTED PYRIDINES

J. MARTÍNEZ *, A. MARTÍNEZ and A. DOADRIO

Departamento de Química Inorgánica y Analítica, Facultad de Farmacia, Universidad Complutense de Madrid, Madrid 28 040 (Spain)

(Received 10 December 1984)

ABSTRACT

A series of $\text{VO}(\text{aca})_2$ adducts have been prepared and characterized. Studies of the structural and thermal properties of these compounds have been carried out using infrared spectroscopy, differential scanning calorimetry, magnetic susceptibility, thermogravimetric measurements and analytical data.

The study of these adducts using DSC and TG techniques allowed us to determine the degree of thermal stability of these compounds and to observe the loss of one mole of coordinate base in the first endothermic process.

By means of the study of the first process through DSC techniques, the activation energy and the enthalpy were calculated, establishing relationships between the $\text{p}K_b$ values and the bonding force with the vanadium atom in the adducts formed.

Therefore, good relationships have been established between the values obtained from infrared spectroscopy for the vibration $\nu(\text{V}=\text{O})$ and the activation energy values.

INTRODUCTION

In this paper we report a structural study of the adducts of bis(acetylacetonate) oxovanadium(IV) with substituted pyridines, to which we assign the general formula $\text{VO}(\text{aca})_2 \cdot \text{B}$ (B = pyridine (Py), 3-methylpyridine (3MP), 4-methylpyridine (4MP), 3,5-dimethylpyridine (3,5DMP), 3-aminepyridine (3AP), 4-aminepyridine (4AP)). However, the principal objective is to establish a relationship between the basic character of the pyridines and the intensity of their bonding to the vanadium atom in the adduct formed, with the $\text{p}K_b$ values and with the position of the functional groups, amino and methyl, in the pyridine ring. This study has been realized by infrared spectroscopy, showing a decrease in the $\nu(\text{V}=\text{O})$ values, and by means of the activation energy values calculated from DSC curves. Therefore, we have

* Author for correspondence.

determined the enthalpy of the first endothermic process by differential scanning calorimetry.

EXPERIMENTAL

Preparation of compounds

Vanadylacetonate was prepared by literature methods [1].

The adducts were prepared by dissolving 1 g (3.74 mM) of the VO(aca)₂ complex in 2 ml of pyridine or substituted pyridine, if the base is liquid (Py, 3MP, 4MP and 3,5DMP), and in a ethanolic solution of the base if it is a solid (3AP, 4AP). This mixture was heated for 15 min, and a green solid was formed after 24 h at room temperature. This solid was filtered in vacuo, washed with a water and ethanol mixture (1 : 1) and dried over P₂O₅.

All adducts obtained were green, stable, soluble in organic solvents and insoluble in water.

Materials

The acetylacetonate (aca = CH₃-CO-CH₂-CO-CH₃) and the organic bases were Merck commercial products. The solvents used to prepare the complexes were Carlo Erba or Merck.

Analytical procedures

Elemental analyses were performed with a Perkin-Elmer model 240B. Vanadium was determined by atomic absorption with a Perkin-Elmer model 430 atomic absorption spectrophotometer after decomposing the compounds with a concentrated HNO₃ and H₂SO₄ mixture (1 : 1) [2].

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

TABLE 1
Analytical data

	% Calculated				% Found			
	C	H	N	V	C	H	N	V
VO(aca) ₂	45.28	5.28	—	19.24	45.37	5.18	—	19.19
VO(aca) ₂ ·Py	52.32	5.52	4.06	14.82	52.39	5.47	4.14	14.70
VO(aca) ₂ ·3MP	53.63	5.86	3.91	14.24	53.48	5.79	3.87	14.30
VO(aca) ₂ ·4MP	53.63	5.86	3.91	14.24	53.75	5.67	3.94	14.27
VO(aca) ₂ ·3,5DMP	54.83	6.18	3.76	13.70	54.79	6.27	3.92	13.60
VO(aca) ₂ ·3AP	50.13	5.57	7.79	14.20	50.28	5.49	7.87	14.25
VO(aca) ₂ ·4AP	50.13	5.57	7.79	14.20	50.25	5.42	7.74	14.18

TABLE 2

Magnetic properties

	T (°C)	I (A)	$\chi \times 10^6$ (cgs)	$\chi_M \times 10^6$ (cgs)	$\chi'_M \times 10^6$	μ (BM)
VO(aca) ₂	20	2.0	3.95495	1048	1164	1.66
VO(aca) ₂ ·Py	20	2.0	3.19742	1100	1297	1.75
VO(aca) ₂ ·3MP	20	2.0	2.97358	1065	1274	1.73
VO(aca) ₂ ·4MP	20	2.0	2.89549	1037	1245	1.71
VO(aca) ₂ ·3,5DMP	20	2.0	2.59437	965	1186	1.67
VO(aca) ₂ ·3AP	20	2.0	2.79487	1003	1206	1.68
VO(aca) ₂ ·4AP	20	2.0	2.81737	1011	1214	1.69

Magnetic susceptibility

Magnetic susceptibilities were measured by the Gouy [3] method at room temperature on a Mettler H-51 AR balance and a type C Oxford electromagnet. Molar susceptibilities have been corrected for the diamagnetism of the constituent molecules [4,5]. The magnetic moments were calculated according to the formula $\mu = 2.84 (\chi'_M T)^{0.5}$ BM, where χ'_M is the corrected molar susceptibility. The values of magnetic moments are given in Table 2.

Infrared spectra

The IR spectra were recorded on a Perkin-Elmer recording spectrophotometer (model 283). The samples were run as KBr pellets. The IR absorption peaks for the compounds prepared in this study are listed in Table 3.

Thermogravimetric analysis

Thermogravimetric measurements were performed using a Mettler HE 20 thermobalance. The analytical constants were: heating rate, 5°C min⁻¹; TG

TABLE 3

Infrared spectra

	$\nu(\text{V=O})$	$\nu_a(\text{V-O})$	$\delta(\text{O-V-O})$	$\nu_s(\text{V-O})$	$\nu(\text{C=C}) + \nu(\text{C=O})$	$\nu(\text{C-O-V})$
aca	—	—	—	—	1740–1620	—
VO(aca) ₂	1000	610	428	368	1530	1375–1360
VO(aca) ₂ ·Py	995	603	423	365	1550–1530	1374–1357
VO(aca) ₂ ·3MP	968	600	420	358	1560–1530	1380
VO(aca) ₂ ·4MP	974	610	428	369	1570–1540	1385
VO(aca) ₂ ·3,5DMP	952	583	428	343	1575	1375
VO(aca) ₂ ·3AP	958	600	418	360	1570–1530	1385
VO(aca) ₂ ·4AP	950	590	416	347–330	1575–1535	1390

range, 20 mV; record rate, 20 cm h⁻¹; reference, Al₂O₃; sample mass, 20 mg; thermocouple, Pt/Pt-Rh.

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

Data for the temperatures of thermal transitions and mass loss determinations are shown in Table 4.

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 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 instrument calibration was checked periodically with standard samples of indium. In all cases several runs were made and the results are shown in Table 5.

The activation energies were calculated using Thomas and Clarke's procedure [6]. A plot of log dH/dt versus 1/T is obtained from the DSC data and on the linear region we can obtain the activation energy using the equation

$$-\log K = -\log(dH/dt)(1/A) = + \frac{E_a}{2.303RT} - \log C$$

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

TABLE 4

Thermal data for decomposition of VO(aca)₂·B

Compound	T (°C)	$\Delta m/m$		Process	Identified compound
		(% calc)	(% exp)		
VO(aca) ₂	250–555	65.66	65.47	Exothermic	V ₂ O ₅
VO(aca) ₂ ·Py	70–124	22.84	22.37	Endothermic	VO(C ₅ H ₈ O ₂) ₂
	255–540	65.66	65.35	Exothermic	V ₂ O ₅
VO(aca) ₂ ·3MP	65–106	25.43	25.18	Endothermic	VO(C ₅ H ₈ O ₂) ₂
	245–535	65.66	65.84	Exothermic	V ₂ O ₅
VO(aca) ₂ ·4MP	72–128	25.43	25.37	Endothermic	VO(C ₅ H ₈ O ₂) ₂
	250–545	65.66	65.84	Exothermic	V ₂ O ₅
VO(aca) ₂ ·3,5DMP	80–140	28.80	28.24	Endothermic	VO(C ₅ H ₈ O ₂) ₂
	240–550	65.66	65.18	Exothermic	V ₂ O ₅
VO(aca) ₂ ·3AP	100–178	26.05	25.87	Endothermic	VO(C ₅ H ₈ O ₂) ₂
	230–540	65.66	65.27	Exothermic	V ₂ O ₅
VO(aca) ₂ ·4AP	102–205	26.05	26.24	Endothermic	VO(C ₅ H ₈ O ₂) ₂
	240–545	65.66	65.70	Exothermic	V ₂ O ₅

TABLE 5

Infrared and kinetic data for VO(aca)₂·B

Compound	$\nu(\text{V=O})$ (cm^{-1})	Temperature ($^{\circ}\text{C}$) ^a			ΔH (kcal mol^{-1})	E_a ^b (kcal mol^{-1})	$\text{p}K_b$
		T_i	T_p	T_f			
VO(aca) ₂	1000	—	—	—	—	—	—
VO(aca) ₂ ·Py	975	64	111.1	124	13.5	15.70	8.87
VO(aca) ₂ ·3MP	968	58	92.6	104.5	10.25	24.60	8.32
VO(aca) ₂ ·4MP	974	68	116.5	127	15.29	18.83	7.98
VO(aca) ₂ ·3,5DMP	952	73	120.8	134.8	17.37	20.79	7.85
VO(aca) ₂ ·3AP	958	100	157.7	179	20.65	17.56	7.49
VO(aca) ₂ ·4AP	960	102	185	205	11.28	15.80	4.88

^a T_i = initial temperature, T_p = peak temperature, T_f = end temperature.^b E_a = activation energy.

RESULTS AND DISCUSSION

According to the results of the analytical data the stoichiometry of the complexes obtained is 2:1 ligand–metal, and 1:1 base–complex for the adducts. The magnetic moments calculated (1.66–1.75 BM) show that all the compounds are monomer species of vanadium(IV).

The IR spectra of all the compounds studied show an intense band at 1575–1530 cm^{-1} [7,8], which we assign to the combined vibrational stretching mode of the C=C and C=O bonds. This band can also be described as a combination of the vibrational stretching modes of the C–O–V and C–C bonds; the former corresponds to the ligand coordinated to the metal and the latter to the chelate ring formed. We attribute a very strong band in the 1390–1357 cm^{-1} region to the C–O–V vibrational mode, which confirms the formation of a vanadium chelate [9].

If we compare the IR spectra of the complex with the IR spectra of the adducts, we observe that the former displaces the band of the V=O terminal bond to a higher frequency (1000 cm^{-1}) than that for the adducts (975–952 cm^{-1}).

This difference can be attributed to the electronic donation of the pyridine to the vanadium (N → V) which increases the electron density in the metal d orbitals and consequently the $p_{\pi} \rightarrow d_{\pi}$ donation from oxygen atom to vanadium is expected to be reduced to an extent which depends upon the donor ability of the base. As a result there will be a lowering of the V=O bond strength, and hence $\nu(\text{V=O})$.

In the IR spectra of the adducts obtained with pyridine, 3MP and 4MP give similar values for $\nu(\text{V=O})$, which agrees with the $\text{p}K_b$ values that are similar in all cases. Therefore, the same effect is observed when comparing the adducts with 3AP and 4AP (958 and 960 cm^{-1} , respectively), in spite of their different $\text{p}K_b$ values. This can be due to the tautomeric possibility of the 4AP to form imine.

In the majority of the adducts, the $\nu_a(\text{V-O})$, $\nu_s(\text{V-O})$ and $\delta(\text{O-V-O})$ appear to be displaced to lower frequencies than in the complex, which indicates that in the adducts the ligand-metal bond is weakened because of the electronic donation from the base to the vanadium atom.

The DSC curves of all the compounds $\text{VO}(\text{aca})_2 \cdot \text{B}$ show a first endothermic process between 65 and 205°C; the mass loss accompanying this endothermic transition corresponds, on the TG curve, to the loss of one molecule of base coordinated to vanadium.

In order to establish the degree of thermal stability the initial temperature of the loss of base has been taken as reference [10]. In this way the thermal stability increases in the order: $\text{VO}(\text{aca})_2\text{Py} > \text{VO}(\text{aca})_2\text{3MP} < \text{VO}(\text{aca})_2\text{4MP} < \text{VO}(\text{aca})_2\text{3,5DMP} < \text{VO}(\text{aca})_2\text{3AP} < \text{VO}(\text{aca})_2\text{4AP}$.

We observe that as the $\text{p}K_b$ value of the base decreases, the initiation temperature of the first endothermic process increases. Therefore, the adduct with pyridine presents a higher initiation temperature than expected. This effect may be due to the greater bond order ($\text{N} \rightarrow \text{V}$), as we have also observed in the IR spectra.

We have studied the kinetics in the solid state of the process corresponding to the loss of the base by DSC.

If we compare the E_a values calculated for the adducts with 3MP ($E_a = 24.6 \text{ kcal mol}^{-1}$) with those obtained for the V=O bond by IR spectroscopy, a relationship is observed. The lower value of E_a and the greater value of $\nu(\text{V=O})$ for the adduct with 4MP indicates a lower bonding between the base and the vanadium atom, which can be attributed to the existence of resonance forms which do not occur when the methyl group is in the 3 position.

The adduct obtained with 3,5DMP presents an E_a value greater than the pyridine adduct, which is in agreement with the $\nu(\text{V=O})$ and $\text{p}K_b$ values.

In the adducts with aminepyridines we can also observe greater values of E_a in relation to the values obtained for the pyridine adduct which agree with the values for the $\nu(\text{V=O})$ vibrations (958 (3AP), 960 (4AP) and 975 cm^{-1} (Py)).

From the E_a values we observe that in the adduct of the $\text{VO}(\text{aca})_2$ complex with monosubstituted pyridines, the change of substituent from position 3 to 4 weakens the base-metal bonding. Also, the base-metal bonding is stronger in the adduct with 3,5DMP than in the other bases.

The above seems to indicate that on the strength of the V-N bonding in those adducts, the substituent in the 3 position of the pyridine ring does not produce steric impediments, probably due to the absence of voluminous groups in the acetylacetonate. Hence, substituents in the pyridine ring which influence the capacity to transfer electronic density and the possibility of resonance or tautomerism when the substituents are in the 4 position are very important in these adducts.

The values obtained for the enthalpy of the first endothermic process do

not show a clear relationship with the basicity of the pyridines with respect to the higher or lower intensity of the metal–base bonding because another factor affects these enthalpies [11,12] that we were not able to evaluate with the numerical formula used.

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