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THERMAL STUDIES ON MOLYBDENUM(IV) DIALKYL DITHIOCARBAMATE ADDUCTS WITH PYRIDINE

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ABSTRACT

Spectroscopic, magnetic and analytical studies on the adducts of several molybdenum(IV) dialkyl dithiocarbamate complexes with pyridine have been previously reported. The formula which most closely fits the analyses is $Mo_2(dtc)_4 \cdot Py_2$ (where dtc = di-ethyl, di-n-propyl, di-isopropyl, di-isobutyl and *N*-methyl-cyclohexyl dithiocarbamates).

The study of these adducts using DSC and TG techniques allowed us to determine the degree of thermal stability of these compounds. The DSC curves corresponding to the decomposition of the adducts showed only a single endothermic peak. The mass loss accompanying the endothermic transition corresponded to the loss of two molecules of pyridine with a residue of $Mo_2(dtc)_4$. From the DSC curves, activation energies have been calculated.

INTRODUCTION

We have previously reported [1–3] the synthesis and characterization of pyridine adducts with dialkyl dithiocarbamate molybdenum(IV) complexes. We assign the general formula: $Mo_2(dtc)_4 \cdot Py_2$ (dtc = di-ethyl, di-n-propyl, di-isopropyl, di-isobutyl and *N*-methyl-cyclohexyl dithiocarbamates).

The use of thermal methods of analysis to study the bonding and structure of coordination compounds has increased greatly in the last few years [4]. Recently, more systematic studies have been reported and from DSC and TG curves the workers report kinetic and thermodynamic data for reactions in the solid state [5–9].

Several papers show the correlation between the thermal stability of transition metal complexes with pyridine and substituted pyridines, or copper(II) sulphate with ethylenediamine, 1,2-propanediamine and 1,3-propanediamine, and the ligand basicity and steric factors [10–15].

In the present paper we report a study of the process of thermal

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TABLE 1

Thermal data for decomposition of $Mo_2(dtc)_4Py_2$

Compound	Temp. (°C)	$\Delta m/m$ (%)		Process	Identified compound
		calc.	exp.		
Mo_2(di-ethyl dtc)$_4 \cdot Py_2$	101.5–125	16.77	18.02	Endothermic	Mo_2(di-ethyl dtc)$_4$
	263.0–650	52.66	52.47	Exothermic	MoO_3
Mo_3(di-n-propyl dtc)$_4 \cdot Py_2$	130.5–153	14.99	15.12	Endothermic	Mo_2(di-n-propyl dtc)$_4$
	254.0–680	57.69	58.01	Exothermic	MoO_3
Mo_2(di-isopropyl dtc)$_4 \cdot Py_2$	125.5–160	14.99	14.76	Endothermic	Mo_2(di-isopropyl dtc)$_4$
	294.0–635	57.69	57.91	Exothermic	MoO_3
Mo_2(di-isobutyl dtc)$_4 \cdot Py_2$	127.0–151	13.55	13.62	Endothermic	Mo_2(di-isobutyl dtc)$_4$
	275.0–671	61.76	61.94	Exothermic	MoO_3
Mo_2(*N*-methyl-cyclohexyl dtc)$_4 \cdot Py_2$	118.5–209	14.29	14.07	Endothermic	Mo_2(*N*-methyl-cyclohexyl dtc)$_4$
	251.0–637	59.68	59.73	Exothermic	MoO_3

decomposition on the adducts of molybdenum(IV) dialkyl dithiocarbamates with pyridine, using DSC and TG techniques, and we also determine the relationship between the thermal parameters associated with the decomposition and the steric factors of the alkyl dithiocarbamate groups.

EXPERIMENTAL

Preparation and analysis of compounds

Molybdenum(IV) dialkyl dithiocarbamate complexes and their adducts with pyridine were obtained following methods described previously [1–3].

Elemental and molybdenum analyses performed with a Perkin-Elmer 240-B analyser and a Perkin-Elmer 430 atomic absorption spectrophotometer, respectively, show results which are concordant with the formula $Mo_2(dtc)_4 \cdot Py_2$.

Thermogravimetric analysis and differential scanning calorimetry

Thermogravimetric measurements were performed using a Mettler HE-20 thermobalance. The constants were: heating rate, 2°C min^{-1}; TG range, 10 mV; chart speed, 20 cm h^{-1}; sample mass, 10 mg; reference, Al_2O_3; thermocouple, Pt/Pt–Rh.

The analyses were made in a dynamic atmosphere to 250°C and then in an air atmosphere to 1000°C. A platinum pan was used.

Differential scanning calorimetry was performed using a Mettler TA 3000 system with a differential scanning calorimeter (Mettler DSC-20). The scanning rate used was 2°C min^{-1} and samples of about 5 mg were used so as to render the degree of temperature non-uniformity within the sample insignificant.

TABLE 2

Kinetic data for $Mo_2(dtc)_4 \cdot Py_2$ complexes

Compound	Temperature (°C) [a]			ΔH (kcal mol^{-1})	Range of α	Activation energy (kcal mol^{-1})
	T_i	T_p	T_c			
Mo_2(di-ethyl dtc)$_4 \cdot Py_2$	101.5	111.4	125	28.34	0.018–0.140	80.71
Mo_2(di-n-propyl dtc)$_4 \cdot Py_2$	130.5	139.4	153	10.68	0.030–0.201	87.20
Mo_2(di-isopropyl dtc)$_4 \cdot Py_2$	125.5	138.9	160	8.81	0.003–0.090	126.24
Mo_2(di-isobutyl dtc)$_4 \cdot Py_2$	127	136.6	151	2.99	0.011–0.072	135.13
Mo_2(N-methyl-cyclohexyl dtc)$_4 \cdot Py_2$	118.5	161	209	33.39	0.006–0.033	37.21

[a] T_i = initial temperature; T_p = peak temperature; T_c = end temperature.

Aluminium pans were used under a dynamic nitrogen atmosphere. The instrument calibration was checked periodically with standard samples of indium (99.99% purity). Several runs were made in all cases.

Table 1 shows thermal transition temperatures and mass loss determination data.

Kinetic data for $Mo_2(dtc)_4 \cdot Py_2$ adducts are shown in Table 2.

RESULTS AND DISCUSSION

The objectives of the present paper were to determine the nature of the thermal decomposition for a series of adducts of $Mo_2(dtc)_4$ with pyridine and to investigate the relationship between the steric factors of the alkyl dithiocarbamate groups and the thermal parameters.

The analytical data show that all the adducts contain two molecules of pyridine. The formula which we ascribe is $Mo_2(dtc)_4 \cdot Py_2$.

The DSC curves of all the compounds show a first endothermic peak between 101.5 and 209°C; the mass loss accompanying this endothermic transition corresponds, on the TG curves, to the loss of two molecules of pyridine coordinated to molybdenum. The residue is $Mo_2(dtc)_4$ in all cases.

Afterwards, a series of exothermic processes are produced between 250 and 620°C, corresponding to the decomposition of the $Mo_2(dtc)_4$ complexes, and in all cases the residue was MoO_3. The process may be schematized as follows:

$$Mo_2(dtc)_4 \cdot Py_2(s) \rightarrow Mo_2(dtc)_4\,(s) + 2\ Py\ (g)\ (endo)$$

$$Mo_2(dtc)_4 \rightarrow 2\ MoO_3\ (exo)$$

For every adduct, the loss of two molecules of pyridine occurs in a concrete interval of temperature after which, once the process of decomposition has stopped, the residue can be identified by infrared spectroscopy, elemental and molybdenum analyses, as the complex $Mo_2(dtc)_4$.

The DSC study of the first endothermic process involving the loss of pyridine has allowed the determination of the activation energy by the method proposed by Thomas and Clarke [16] from the DSC curves for solid-state thermal decompositions of the type

$$A\ (solid) \rightarrow B\ (solid) + C\ (gas)$$

A plot of $\log(\mathrm{d}H/\mathrm{d}T)$ vs. $1/T$ (Fig. 1), obtained from DSC data for the Mo_2(di-ethyl dtc)$_4 \cdot Py_2$ complex, was indeed found to be linear for $\alpha =$ 0.018–0.14 (see Table 2 for other complexes).

When the decomposition proceeds in the linear region over the range of temperatures scanned by a calorimeter, the use of the following equation

$$-\log k = -\log(\mathrm{d}H/\mathrm{d}T)(1/A) = \frac{E_a}{2.303RT} - \log C \qquad (1)$$

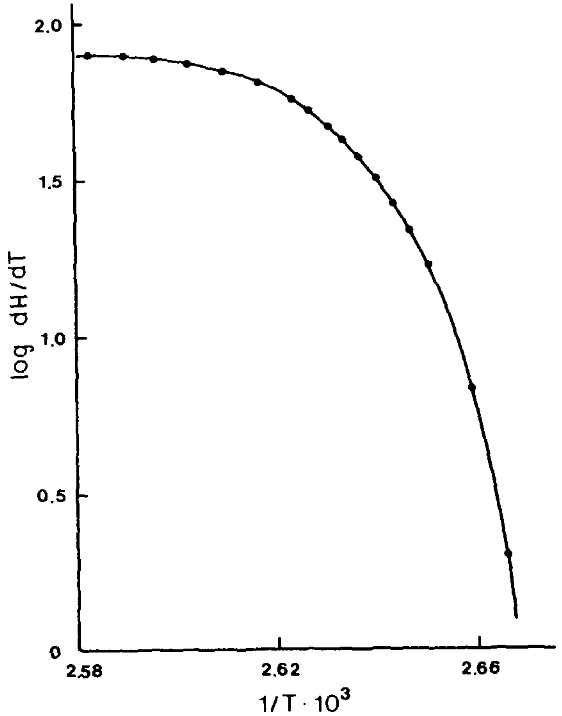

Fig. 1. Arrhenius plot of log(dH/dT) vs. 1/T for the Mo_2(di-ethyl dtc)$_4$·Py_2 complex .

(where k = rate constant; A = total area of the DSC peak) to compute the rate constants is justified. Moreover, the activation energy derived from Arrhenius plots represents the true activation energy for the interfacial reaction. Figure 2 shows the Arrhenius plot constructed from DSC data using eqn. (1) for Mo_2(di-ethyl dtc)$_4$ · Py_2.

The values of activation energy obtained for these compounds may be arranged in the order: Mo_2(N-methyl-cyclohexyl dtc)$_4$ · Py_2 < Mo_2(di-ethyl dtc)$_4$ · Py_2 < Mo_2(di-n-propyl dtc)$_4$ · Py_2 < Mo_2(di-isopropyl dtc)$_4$ · Py_2 < Mo_2(di-isobutyl dtc)$_4$ · Py_2.

If we compare the E_a values for the complexes in which the substituent groups of the dithiocarbamate are linear, we can observe that the greater the steric effects of the substituent the lower activation energy value for the decomposition of the complexes.

The complex Mo_2(N-methyl-cyclohexyl dtc)$_4$ · Py_2, presents the lowest value of the activation energy. The reason for this behaviour may be the existence of two different conformations for the substituent cyclohexyl, and consequently the steric impediments exercised by the radical cyclohexyl are lower than expected.

The values obtained for the enthalpy of the first endothermic process may be arranged in the order: Mo_2(N-methyl-cyclohexyl dtc)$_4$ · Py_2 > Mo_2(di-

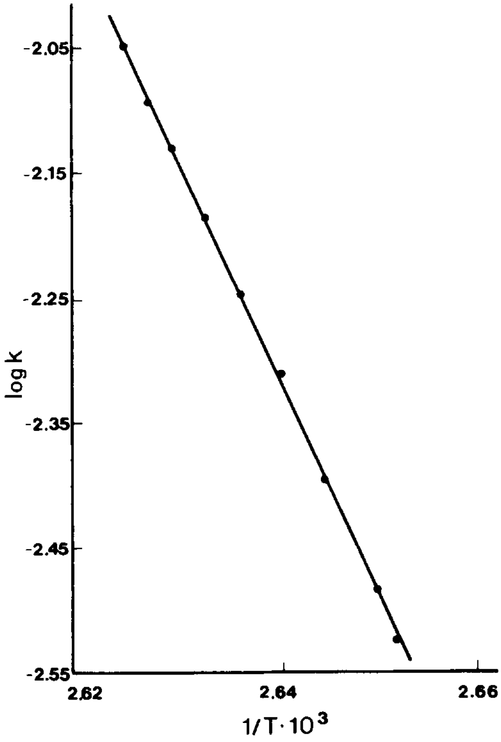

Fig. 2. Arrhenius plot constructed from DSC data using eqn. (1) for the Mo_2(di-ethyl dtc)$_4$·Py_2 complex.

ethyl dtc)$_4$ · Py_2 > Mo_2(di-n-propyl dtc)$_4$ · Py_2 > Mo_2(di-isopropyl dtc)$_4$ · Py_2 > Mo_2(di-isobutyl dtc)$_4$ · Py_2. This order is opposite to that observed for the activation energy values.

We can assume that the greater enthalpy value and the lower value of activation energy indicate a greater bonding between the pyridines and the molybdenum atoms in the complexes.

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