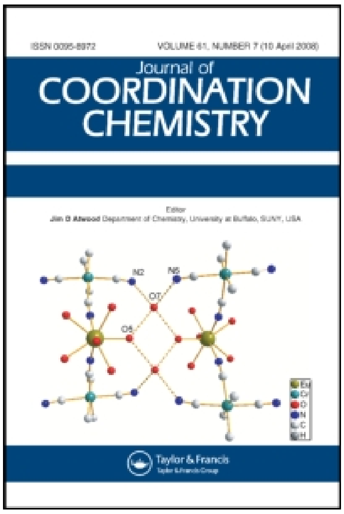

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THERMAL DECOMPOSITION OF METAL COMPLEXES. VIII. MIXED COMPLEXES OF DIVALENT TRANSITION METALS WITH α-NITROKETONES

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The thermal behaviour of mixed complexes containing transition metals, α-nitroketones and pyridine or ethanol was investigated by thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The values of the activation energies and the enthalpies for the dissociation processes have been calculated in high vacuum and isothermal conditions. Comments are made on the obtained heats and correlations with structural characteristics are looked for.

INTRODUCTION

Recently the complexing ability of α-nitroketones has been studied in detail.[1–7] The experimental results suggest that nitroketones resemble β-diketones in their coordinating properties. The nitro group is generally a poor ligand unless it is conjugated to a carbonyl group. Then it shows an appreciable enhancement of its coordinating power.

Previous structural investigations on some transition metal complexes containing α-nitroketones[1–7] show that the necessary conditions for a correct comparison of their thermoanalytical behaviour are satisfied, in particular, these complexes are isomorphous; thus an equal contribution from lattice energy is expected and the different values of the activation energies or the enthalpies can be ascribed only to bonding characteristics.[8–12] Therefore, the thermal behaviour of the complexes $M(na)_2L_2$ (M = Mn, Co, Ni; L = py or EtOH), $M(1n2b)_2py_2$ (M = Fe, Co, Ni), $M(\omega\text{-nap})_2L_2$ (M = Mn, Co, Ni; L = py or EtOH; M = Fe, L = py) were studied to elucidate the decomposition mechanism of these mixed complexes containing 2-nitroacetone (na), 1-nitrobutan-2one (1n2b) or 2-nitracetophenone (ω-nap) and pyridine or ethanol as ligands. These mixed complexes show a six-coordinate octahedral or pseudooctahedral arrangement in their adducts with pyridine or ethanol and in their simple parent complexes (through the formation of polymeric species), as it was stated on the basis of X-ray data, magnetic moments and electronic spectra.[1–7] The influence of the substituents in the equatorial ligands and of the axial ligands on the decomposition mechanism and on the values of the activation energies and the enthalpies of dissociation will be evaluated in comparison with magnetic and spectral characteristics.

EXPERIMENTAL

Preparation of ligands and complexes

2-Nitroacetophenone was prepared as reported by Long and Troutman;[13] 2-nitroacetone and 1-nitrobutan-2-one were synthesized according to Hurd and Nilson.[14] The metal complexes ML_2py_2 and $ML_2(EtOH)_2$ (L = α-nitroketone) were obtained according to the procedure reported by Ercolani et al.[2,3,15] The new compounds $Mn(na)_2(EtOH)_2$, $Mn(na)_2py_2$, $Fe(1n2b)_2py_2$ were prepared using a general procedure suggested by Attanasio et al.;[15] the pertinent analytical data are: $Mn(na)_2(EtOH)_2$ (Found: C, 34.01%; H, 5.50%; N, 8.20%. Calc.: C, 34.18%; H, 5.70%; N, 7.97%); $Mn(na)_2py_2$ (Found: C, 46.60%; H, 4.20%; N, 13.51%. Calc.: C, 46.03%; H, 4.32%; N, 13.43%); $Fe(1n2b)_2py_2$ (Found: C, 49.71%; H, 4.71%; N, 12.15%. Calc.: C, 48.42%; H, 4.95%; N, 12.57%).

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†Presented in part at the first European Symposium on Thermal Analysis, Salford (1976).

Thermal analyses and DSC measurements

The simultaneous TG, DTG and DTA were performed with a Mettler thermoanalyzer in a dynamic nitrogen atmosphere (10 lh^{-1}), under reduced pressure (5×10^{-2} mm Hg) and high vacuum (2×10^{-6} mm Hg). The heating rates were 0.5, 1, 2, 4°min^{-1}. A Mettler model TD3 crucible holder, 0.3 ml platinum microcrucible and thermally inactive Al_2O_3 as reference material were used. DSC measurements were carried out with a Perkin Elmer differential scanning calorimeter model DSC–1B. The samples were covered by a thin layer of graphite powder which was also placed in the reference pans, in order to eliminate differences in emissivities between samples and reference.[16] These measurements were performed in a dynamic nitrogen atmosphere at a flow rate of 1 lh^{-1} and a heating rate of 2°min^{-1}.

From the DTA and TG curves the values of Ea^* and ΔHd were obtained. The "activation energy" ($Kcalmol^{-1}$) of the dissociation reactions was calculated through the relation:

$$\log\frac{k_2}{k_1} = \frac{Ea^*}{2.3\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The ΔHd were graphically determined using Indium as standard material. The average deviations are ± 6% in Ea^* and ± 1% in ΔHd.

Mass spectral measurements

A Balzer mass spectrometer model QMG 311 was used to analyze the evolved gases.

RESULTS AND DISCUSSION

The TG curves of the ML_2py_2 complexes show in a dynamic nitrogen atmosphere only one step and the overall reaction may be written as:

$$ML_2py_2\ (s) \longrightarrow MO\ (s) + \text{gaseous products.}$$

However, in the temperature range over which continuous weight losses were observed the DTA curves showed two peaks, a small endothermic peak followed by a large exothermic one. As an example, the curves for the thermal decomposition of $Ni(1n2b)_2py_2$ are presented in Figure 1. The endothermic DTA peak is more pronounced in the DSC curve with a sample diluted with graphite (Figure 2). Probably the endothermic peak is associated with the initial and partial release of the two neutral ligands. When the complexes were thermally decomposed in high vacuum at a heating rate of 0.5°min^{-1}, the TG curves were indicative of a two step reaction (Figure 3). The simultaneous gas analysis confirmed that the first weight loss is caused by the release of the two pyridine molecules and the second by the decomposition of the α-nitroketones to carbon dioxide, nitrogen oxides and other products.

In high vacuum under isothermal conditions at the temperature at which the expulsion of pyridine begins, pyridine is quantitatively released producing the complexes $[ML_2]_n$, which remain as residue.

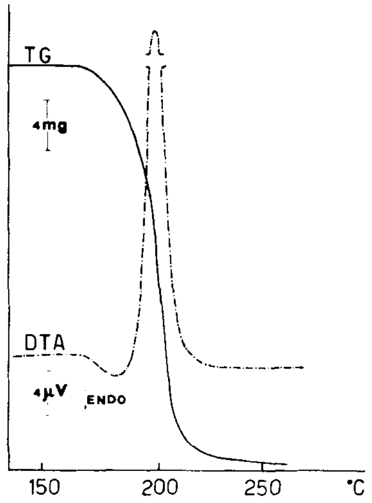

FIGURE 1 Thermoanalytical curves of $Ni(1n2b)_2py_2$ in a dynamic atmosphere using a heating rate of 4°min^{-1}.

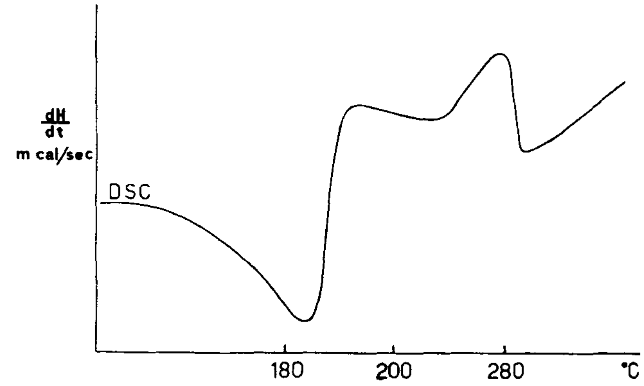

FIGURE 2 DSC analysis of $Ni(1n2b)_2py_2$ diluted with graphite at a heating rate of 2°min^{-1}.

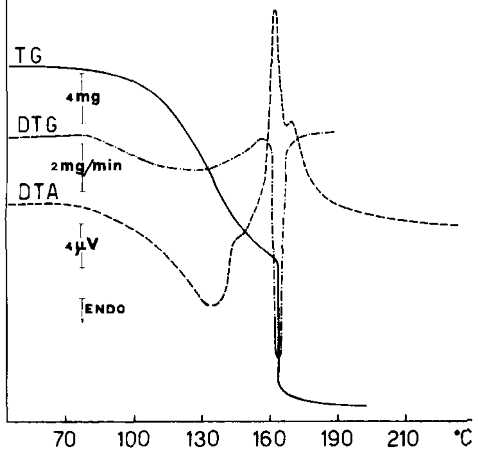

FIGURE 3 Thermoanalytical curves of $Co(na)_2py_2$ at 2×10^{-6} mm Hg and a heating rate of $0.5^{\circ}min^{-1}$.

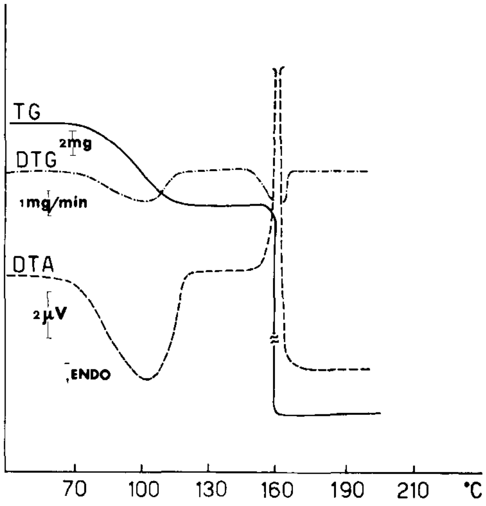

FIGURE 4 Thermoanalytical curves of $Co(\omega\text{-nap})_2(EtOH)_2$ at 2×10^{-6} mm Hg and a heating rate of $0.5^{\circ}min^{-1}$.

The decomposition of the complexes occurs in two steps:

$$n\,ML_2py_2\,(s) \longrightarrow [ML_2]_n\,(s) + 2n\,py\,(g)$$

$$[ML_2]_n\,(s) \longrightarrow n\,MO\,(s) + \text{gaseous products}$$

All the TG curves of the complexes $ML_2(EtOH)_2$ (Figure 4) in a dynamic nitrogen atmosphere and under high vacuum prove that the two ethanol molecules are expelled first. The thus formed complexes $[ML_2]_n$ decomposed later, in the same way as did the simple complexes obtained by the decomposition of ML_2py_2 (they are similar in their thermoanalytical pattern). Hence, a general reaction mechanism, involving first the release of the base and second the decomposition of the $[ML_2]_n$ species is proposed. This behaviour indicates that the aromatic or aliphatic substituents of the α-nitroketone molecule and the axial ligands do not play a determinant role in the reaction mechanism. DTA curves in a dynamic nitrogen atmosphere are characterized by a large and broad peak, whereas a sharp peak appears under vacuum. A possible explanation of this fact is that the vacuum makes the evolution of gaseous products (EtOH or py) just released by the complexes easier; therefore, the thermal dissociation reaction of these complexes is probably characterized by a rate-determining step, originated by a superficial adsorption of the gaseous products.

We have determined the *Ea** and the heat of decomposition for the reaction:

$$n\,ML_2py_2\,(s) \longrightarrow [ML_2]_n\,(s) + 2n\,py\,(g).$$

Because the heats of sublimation of simple and mixed complexes are not known, it was not possible to determine the gas-phase enthalpy changes for the above-mentioned reaction. However, assuming the differences between the enthalpies of sublimation of the mixed and simple complexes remain constant, the ΔH values of the various heterogeneous decomposition reactions can be compared. The *Ea** and ΔHd values for the isothermal decompositions are reported in Tables I and II.

The absence of exothermic effects after the release of the neutral ligands allows us to assert that the polymeric species $[ML_2]_n$ must be simultaneously with the loss of the axial ligand from the mixed complex. It is difficult to evaluate the influence of the polymerization process upon the decomposition reaction and hence, to compare the *Ea** or ΔHd values obtained for different complexes.

TABLE I
"Activation Energies" ($Kcalmol^{-1}$) in high vacuum under isothermal conditions for the thermal decomposition.

$n\,ML_2py_2\,(s) \longrightarrow [ML_2]_n\,(s) + 2n\,py\,(g).$

L	Mn	Fe	Co	Ni
na	36	–	23	34
ln2b	–	30	33	40
ω-nap	25	32	40	26

TABLE II
Enthalpy changes ($Kcalmol^{-1}$) in high vacuum under isothermal conditions for the thermal decompositions.

$$n\,ML_2py_2\,(s) \longrightarrow [ML_2]_n\,(s) + 2n\,py\,(g).$$

L	Mn	Fe	Co	Ni
na	39	–	19	26
ln2b	–	28	31	32
ω-nap	24	31	37	25

Previous report on these complexes based on their spectroscopic and magnetic characteristics stated that the different ligand field acting on the metal ion as a function of the nature of the substituents attached to the α-nitroketone, is not such as to be revealed by significant variations in the energy of electronic transitions.[1-7]

Our data are not in agreement with these conclusions because *Ea** and Δ*Hd* values are clearly dependent on the equatorial ligand (ω-nap, na, ln2b); a noteworthy difference was particularly observed in the case of the mixed complexes containing Co(II) and Ni(II). In order to explain these differences, structural features cannot be invoked (e.g. a change from a trans-axial structure to a cis-axial undergone by the complex at high temperature before the decomposition), since these possibilities are excluded by our experimental data; neither phase transition using DSC or DTA techniques, nor colour changes by microscopic analysis using a Koffler apparatus were observed before the decomposition. Moreover, on the basis of a careful examination of the electronic spectra of $[CoL_2]_n$, $[NiL_2]_n$ and $[MnL_2]_n$ in solution and in the solid state, differences in the structures of the polymeric products obtained after the release of the neutral ligand molecules can be excluded; furthermore a difference in the coordination of the oxygen atoms in the axial positions of the polymeric species can be excluded by taking into account their magnetic properties.[3]

The only factor that can be responsible for the differences found in *Ea** and Δ*Hd* values among the series of these complexes, is the degree of polymerization in the cobalt, manganese and nickel complexes. The behaviour of similar acetylacetonate complexes supports this simple explanation. The thermal decomposition of some mixed complexes with Mn(II), Fe(II), Ni(II) and Co(II), acetylacetone and pyridine has been extensively studied.[17] The authors found the thermal stability to vary in the order $MnL'_2py_2 < FeL'_2py_2 < CoL'_2py_2 < NiL'_2py_2$ (L' = acetylacetonate), using as comparison parameter the temperature at which the DTG peak begins to rise from the baseline. The same trend of stability was also found for the complexes studied in this paper by using the same parameter instead of the *Ea**; however, this comparison is of limited value because the starting temperature of decomposition is so influenced by experimental factors (as heating rate, atmosphere, sample holder, etc.) that no significant correlation with chemical properties can be made.

REFERENCES

1. M. Bonamico, I. Collamati, C. Ercolani, G. Dessy and D. J. Machin, *Chem. Comm.*, 654 (1967).
2. I. Collamati, C. Ercolani and D. J. Machin, *J. Chem. Soc.(A)*, 1537 (1969).
3. I. Collamati and C. Ercolani, *J. Chem. Soc.(A)*, 1542 (1969).
4. D. Attanasio, I. Collamati and C. Ercolani, *J. Chem. Soc.(A)*, 2516 (1971).
5. I. Collamati and C. Ercolani, *J. Chem. Soc.(A)*, 2522 (1971).
6. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc. Dalton*, 2477 (1972).
7. D. Attanasio, I. Collamati and C. Ercolani, *J. Chem. Soc. Dalton*, 1319 (1974).
8. R. P. Bonomo, S. Gurrieri, S. Musumeci, E. Rizzarelli and G. Siracusa, *Thermochim. Acta*, **9**, 373 (1974); **10**, 119 (1974).
9. S. Gurrieri, R. Maggiore, S. Musumeci and G. Siracusa, *Thermochim. Acta.*, **11**, 73 (1975).
10. S. Gurrieri, A. Seminara, G. Siracusa and A. Cassol, *Thermochim. Acta.*, **11**, 433 (1975).
11. A. Seminara, S. Gurrieri, G. Siracusa and A. Cassol, *Thermochim. Acta.*, **12**, 173 (1975).
12. R. P. Bonomo, G. Bruno, E. Rizzarelli, A. Seminara and G. Siracusa, *Thermochim. Acta.*, **18**, 207 (1977).
13. L. M. Long and H. O. Troutman, *J. Amer. Chem. Soc.*, **71**, 2469 (1949).
14. C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, **20**, 927 (1955).
15. D. Attanasio, I. Collamati and C. Ercolani, *J. Chem. Soc. Dalton*, 772 (1972).
16. G. G. T. Guarini, R. Spinnici and D. Donati, *J. Thermal Anal.*, **6**, 405 (1974).
17. D. G. Batir, V. T. Balan and G. N. Marchenko, *Izv. Akad. Nauk. Mold. SSR*, **1**, 61 (1973).