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VIBRATIONAL AND THERMAL BEHAVIOUR OF NICOTINIUM DICHROMATE

C M PALOPOLI, S B ETCHEVERRY and E J BARAN *

Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata 1900-La Plata (Argentina)

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ABSTRACT

The infrared and Raman spectra of nicotinium dichromate $(C_6H_6O_2N)_2Cr_2O_7$ were recorded and discussed The most remarkable result of this analysis is the apparent existence of anions with linear Cr–O–Cr bridges in this crystal lattice The thermal behaviour was investigated by means of TG and DTA measurements The pyrolysis is very complex and resembles in certain aspects that of $(NH_4)_2Cr_2O_7$ Cr_2O_3 is obtained as the only final solid residue

INTRODUCTION

The preparation of 3-carboxypiridinium dichromate $(C_6H_6O_2N)_2Cr_2O_7$ (nicotinium dichromate, NDC) and its use as a very efficient reagent for the oxidation of alcohols into carbonyl compounds have been described recently [1,2] It is interesting to obtain a deeper insight into the general physicochemical properties of this compound In this paper, we report details of its vibrational-spectroscopic and thermal behaviour

EXPERIMENTAL

NDC was prepared by reaction of cold (0–5 °C) aqueous solutions of CrO_3 and nicotinic acid in a 2 1 molar ratio and subsequent addition of cold acetone to precipitate the substance as a fine microcrystalline orange powder The product was filtered off and washed with acetone and dichloromethane until the filtrate became colourless [1,2]

Infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer using the KBr pellet technique Raman spectra were also obtained

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* Author to whom correspondence should be addressed

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on KBr pellets, using a Spex-Ramalog 1403 double monochromator spectrometer, equipped with a SCAMP data processor The 514 5 nm line of an Ar-ion laser was used for excitation

Thermogravimetric and differential thermal analyses were carried out simultaneously on a Rigaku thermoanalyser (type YLDG/CN 8002 L2) using Pt/Pt(Rh) thermoelements and working under a constant flow of N_2 (0 4 l min^{-1}) Al_2O_3 was used as a DTA standard The heating rate was 5 °C min^{-1} and the sample weight ranged between 6 and 8 mg The use of higher heating rates and/or sample amounts usually caused the material to project out of the sample holders due to the violence of the initial degradation step

RESULTS AND DISCUSSION

Vibrational spectrum

The IR bands related to the $C_6H_6O_2N^+$ cation show only slight modifications in relation to those of the pure nicotinic acid. On the other hand, those related to the internal vibrations of the $Cr_2O_7^{2-}$ anion are very interesting.

Figure 1 shows a part of the IR spectrum of $(C_6H_6O_2N)_2Cr_2O_7$ in which most of the characteristic vibrations of the anion can be clearly identified The stretching vibrations show a certain resemblance to those found in simple inorganic dichromates, such as $K_2Cr_2O_7$ [3–5] and $Cs_2Cr_2O_7$ [6], although they are more defined and less broadened. This behaviour is characteristic of oxoanions associated with bulky organic cations [7–9] and is essentially related to the screening effect of such cations, which diminishes

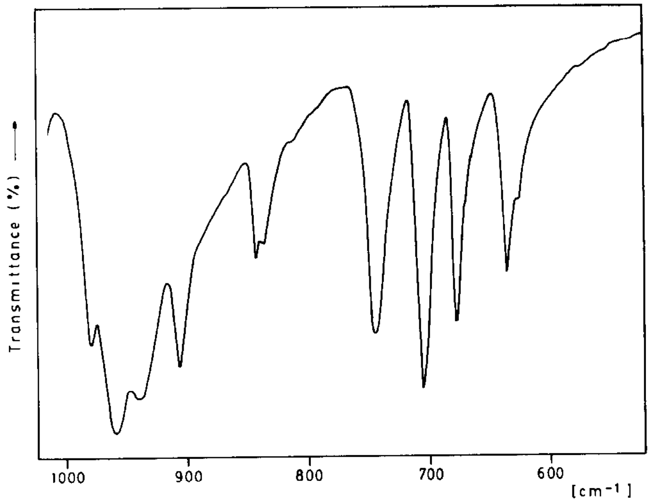

Fig 1 Infrared spectrum of $(C_6H_6O_2N)_2Cr_2O_7$ between 1000 and 525 cm^{-1}

TABLE 1

Proposed assignment for the internal vibrations of the $Cr_2O_7^{2-}$ anion in NDC (values in cm^{-1})

Infrared	Raman	Assignment
980, 960, 940	957 w	$\nu_{as}(CrO_3)$
915	907 vs	$\nu_s(CrO_3)$
840 [a]	–	$\nu_{as}(CrOCr)$
–	341 w	$\nu_s(CrOCr)$ (?)
360 m	377 w	$\delta(CrO_3)$

[a] Partially overlapped with a cation band vs, very strong, s, strong, m, medium, w, weak

to a great extent the interactions and couplings between the anions in the crystal lattice

It is also very interesting to note the absence of IR bands assignable to the symmetric Cr–O–Cr bridge stretching vibration This behaviour suggests the presence of a linear or practically linear bridge, a novel situation because no other crystalline dichromate with this structural peculiarity has been described so far

The Raman spectrum is much simpler than the IR spectrum It only shows lines related to the anion vibrations, those of the cations are very weak and diffuse The assignment of the internal vibrations of the $Cr_2O_7^{2-}$ anion is shown in Table 1

The assignment of the antisymmetric stretching is difficult because in the IR regions in which it is expected, the organic cation also has strong bands, and this mode is usually very weak in the Raman effect [3–6] On the other hand, in X_2O_7 systems with linear X–O–X bridges, this stretching may lie at higher frequencies than the $\nu_{as}(XO_3)$ modes (as in the thortveitite-type diarsenates [10,11], disilicates, digermanates and diphosphates [12,13]) or keep its position at lower frequencies than all the stretching modes of the terminal XO_3 groups (as in the divanadates [14,15])

To clarify this aspect we have made some approximate model calculations for the triatomic Cr–O–Cr system, using the force constants obtained for $K_2Cr_2O_7$ [5] and a standard set of equations [16], and analysing the dependence of both stretching vibrations from the bridge angle This calculation supported the assignment given in Table 1

The assignment of terminal deformation and torsional modes is also difficult because in the low frequency region of the IR spectrum, the organic cation also has a great number of bands. As indicated in Table 1, only one of the $\delta(CrO_3)$ modes could be identified with certainty (at 360 cm^{-1})

Thermal behaviour

Nicotinium dichromate melts with decomposition at around 215 °C [1,2] The thermal decomposition occurred explosively between 210 an 230 °C, when large samples were heated

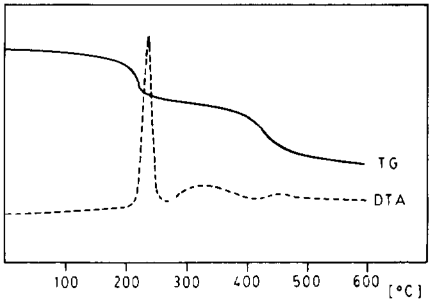

Fig 2 A typical TG and DTA plot for $(C_6H_6O_2N)_2Cr_2O_7$

Typical DTA and TG plots, recorded with a small quantity of sample and a slow heating rate, are shown in Fig 2 As it can be seen, the pyrolysis occurs at least, in two steps Small weight losses can be observed even at low temperatures, but the first clear and strong step begins at 216°C and is associated with the very strong and sharp exothermic peak ($T_{max} = 228°C$) in the DTA diagram In this first step a mass loss between 20 and 25% could usually be observed This would be consistent with an oxidative-decarboxylation, according to

$$(C_6H_6O_2N)_2Cr_2O_7 \rightarrow [Cr_2O_5\ \ 2C_5H_5N] + H_2O + 2CO_2 + \tfrac{1}{2}O_2 \tag{1}$$

a process with a theoretical weight loss of 26 7%

The IR spectra of the intermediate phase, collected after interruption of the heating at 350–380°C are usually poorly defined although some of the typical pyridine bands are observable

The subsequent TG step is related to a further degradation of this intermediate chromium(V) species During this last process, pyridine could be slowly released and/or suffer another oxidative degradation During this stage of the thermolysis, no clear DTA signals can be observed, although two very broad and badly defined features at 330 and 445°C can be seen

Better analysis and characterization of all the pyrolysis intermediates is very difficult, due to the violence of the reaction when larger samples were manipulated However, the final product could be identified unambiguously as Cr_2O_3

$$[Cr_2O_5\ \ 2C_5H_5N] \rightarrow Cr_2O_3 + 2C_5H_5N + O_2 \tag{2}$$

completing a total weight loss of 67 3%, which is in good agreement with the experimental values usually observed during the thermolysis experiments

It is evident that the degradation of NDC resembles in some aspects that of $(NH_4)_2Cr_2O_7$ [17] Also in this case the reaction occurs explosively and an intermediate Cr(V) oxidic species, which finally generates Cr_2O_3 as the ultimate degradation residue, is stabilized

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REFERENCES

1 C López, A González, F P Cossio and C Palomo, Synth Commun , 15 (1985) 1197
2 F Roldán, A González and C Palomo, Carbohydr Res , 149 (1986) C1
3 M S Mathur, C A Frenzel and E B Bradley, J Mol Struct , 2 (1986) 429
4 R L Carter and C E Bricker, Spectrosc Lett , 2 (1969) 247
5 R Mattes, Z Anorg Allg Chem , 382 (1971) 163
6 R L Carter and C E Bricker, Spectrosc Lett , 2 (1969) 321
7 A Muller and W Rittner, Spectrochim Acta Part A, 23 (1967) 1831
8 E J Baran, Z Anorg Allg Chem , 382 (1971) 80
9 A Muller, E J Baran and R O Carter, Struct Bonding, 26 (1976) 81
10 I L Botto, E J Baran, P J Aymonino, J C Pedregosa and G F Puelles, Monatsh Chem , 106 (1975) 1559
11 M A Juri, G F Puelles and J C Pedregosa, An Asoc Quím Argent , 69 (1981) 339
12 A N Lazarev, Vibrational Spectra and Structure of Silicates, Consultant Bureau, New York, 1972
13 P Tarte, M J Pottier and A M Próces, Spectrochim Acta 29 Part A, (1973) 1017
14 P Schwendt and D Joniaková, Chem Zvesti, 29 (1975) 381
15 E J Baran, J Mol Struct , 48 (1978) 441
16 E J Baran, I L Botto, J C Pedregosa and P J Aymonino, Monatsh Chem , 109 (1978) 41
17 C H Bamford and C F H Tipper (Eds), Comprehensive Chemical Kinetics, Vol 22 (Reactions in the Solid State), Elsevier, Amsterdam, 1980, p 205