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Note

Thermal behaviour of isonicotinium dichromate

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Abstract

The thermal behaviour of isonicotinium dichromate, $(C_6H_6O_2N)_2Cr_2O_7$, was investigated by means of TG and DTA measurements, working in oxygen or nitrogen atmospheres. The results were compared with those of the corresponding nicotinium salt. The enthalpy values of the main processes were also determined.

INTRODUCTION

Nicotinium dichromate (NDC) and isonicotinium dichromate (INDC) are described as mild, efficient oxidation agents of organic substrates. They oxidise alcohols to carbonyl compounds, hydroquinones to quinones and mercaptans to disulphides [1,2].

Recently, we have investigated the vibrational and thermal behaviour of nicotinium dichromate [3]. In order to extend our knowledge on the thermal properties of these oxidants, we have now investigated isonicotinium dichromate.

EXPERIMENTAL

INDC was prepared by the reaction of cold aqueous solutions of CrO_3 and isonicotinic acid in a 2 : 1 molar ratio, with 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].

TG measurements were carried out with a Perkin-Elmer TGS 2 thermobalance and the differential thermal analyses with a Perkin-Elmer DTA-1700 instrument. Al_2O_3 was used as a DTA standard; the heating rate was $10\,^\circ C\ min^{-1}$ and the sample weight ranged between 1 and 3 mg.

Infrared spectra were recorded with a Perkin-Elmer 783 spectrophotometer using the KBr pellet technique.

RESULTS AND DISCUSSION

Although the reported value for the melting point of INDC is 250–253° C [1,2], the thermal decomposition begins around 215° C and the DTA trace shows a small exothermic peak centred at 233–234° C in both nitrogen and oxygen atmospheres.

Typical TG plots, in the two atmospheres, are shown in Fig. 1. As can be seen, the thermolysis rate is strongly dependent on the atmosphere.

In both cases, the pyrolysis occurs in at least two steps. In both atmospheres the first step, which begins, as stated above, at 215° C, extends up to around 350° C and involves a weight loss of around 25%. It is related with the small exothermic DTA signal centred at approx. 233° C. In this first step, an oxidative-decarboxylation may occur

$$(C_6H_6O_2N)_2Cr_2O_7 \rightarrow [Cr_2O_5 \cdot 2C_5H_5N] + H_2O + CO_2 + 0.5O_2 \qquad (1)$$

This is in good agreement with the theoretical weight loss of 26.7%.

The spectroscopic characteristics of the intermediate phase are identical to those of the product collected after the first degradation step of NDC [3].

The subsequent TG step is related to the further degradation of this intermediate

$$[Cr_2O_5 \cdot 2C_5H_5N] \rightarrow Cr_2O_3 + 2C_5H_5N + O_2 \qquad (2)$$

giving a total weight loss of 67.3%, in good agreement with the experimentally found values.

The presence of Cr_2O_3 as the unique final solid residue was confirmed unambiguously by IR spectroscopy.

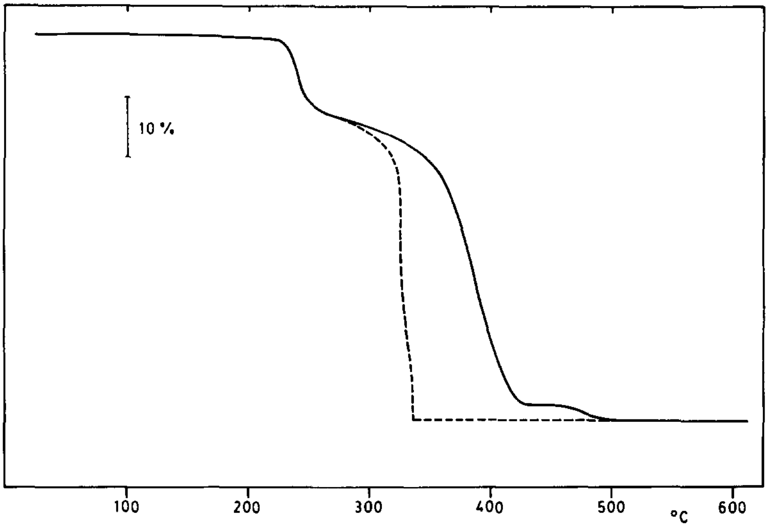

Fig. 1. TG traces of the thermal decomposition of INDC in N_2 (———) and O_2 (- - - - -).

During this second degradation step, no clear DTA signals were observed when working under nitrogen atmosphere. However, in oxygen a very strong exothermal signal was observed at 338 ° C.

A comparison of the two TG traces of Fig. 1 also shows clear differences. In oxygen, the first step extends up to 325 ° C followed immediately by a very fast degradation of the intermediate, the full process being practically complete at 340 ° C. In a nitrogen atmosphere, however, it occurs much more slowly, covering a wider temperature range and concluding just beyond 500 ° C.

It is probable that under nitrogen the degradation of the intermediate occurs through a slow release of pyridine, according to eqn. (2) above, whereas in oxygen a more violent reaction probably takes place, accelerating the decomposition of the proposed chromium(V) intermediate species.

Finally, a thorough analysis of the DTA data also shows differences in the enthalpy values with respect to the atmospheres used during the measurements.

In N_2, the first step (DTA signal at 233° C) has a ΔH value of -49.04 kcal mol^{-1} whereas in O_2 (DTA signal at 234° C) this value is -65.98 kcal mol^{-1}. These differences show that although the main process takes place at the same temperature in each case, it probably occurs through a different mechanism. The second strong DTA signal, only observed in O_2 (338 ° C), has a ΔH change of -1418.5 kcal mol^{-1}.

To conclude, this study has shown that INDC and NDC have very similar thermal behaviours. It also extends our previous results, showing that the process depends strongly on the atmosphere used and gives an insight into the enthalpy changes associated with the degradation.

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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 C.M. Palopoli, S.B. Etcheverry and E.J. Baran, Thermochim. Acta, 131 (1988) 273.