Thermochimica Acta, 111 (1987) 21–26
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF SOME ADAMANTANE DERIVATIVES

SALMAN R. SALMAN

Chemistry Department, College of Science, University of Baghdad, Jadirija, Baghdad (Iraq)

ELHAM Z. SAID and KAFAA F. ABAS

Petrolum Research Center, Scientific Research Council, P.O. Box 10039 Baghdad (Iraq)

(Received 9 May 1986)

ABSTRACT

The differential thermal analysis (DTA) of several substituted adamantanes was investigated. X-ray diffraction, proton NMR, IR absorption and DTA of 1-hydroxyadamantane prove that the extra peak at 369.16 K was due to a phase transition. The thermodynamic data for such a transition were calculated.

INTRODUCTION

Adamantane phase transition at atmospheric pressure was studied and was found to undergo a phase transition under pressure from a disordered face-centered cubic structure to ordered body-centered tetragonal structure [1]. Hara et al. [2–5] studied the pressure induced phase transition of several substituted adamantanes. On the other hand, little attention was given to the thermal behaviour of adamantane and its derivatives at atmospheric pressure [6]. In this work an interesting observation was noticed during the thermal investigation of 1-hydroxyadamantane at atmospheric pressure. Thus the aim of this paper is to study the phase transition of 1-hydroxyadamantane and to calculate the thermodynamic data that characterize the phase transition, such data are useful in determining solid → solid transformations in which order → disorder effects are predominant.

EXPERIMENTAL

Adamantane and its derviatives (Fluka) were used without further purification. Non-isothermal DTA measurements were carried out on a Heraeus TA-500 thermal analyser under nitrogen atmosphere with a flow rate of 10 l h^{-1} using a special purpose cell. The heating rate was 10°C min^{-1}.

0040-6031/87/$03.50

Aluminium oxide was used as a reference. The experimental error was ±3°C.

The proton NMR spectra were run on a Varian FT 80A machine operating at 80 MHz. The samples were run as solutions in $CDCl_3$ with TMS as internal reference.

The X-ray diffraction spectra were run on a Philips diffractometer and the recording conditions were 50 kV, 20 mA, with a chart speed of 2 cm min^{-1}, goniometer speed was 2° min^{-1}.

IR measurements were made on a Pye-Unicam SP3-300 spectrometer. Samples were KBr discs, scan time being 3 min. All measurements were made at 25°C.

RESULTS AND DISCUSSION

The differential thermal analysis curves of adamantane and its derivatives are presented in Figs. 1 and 2. The sublimation temperature of adamantane, adamantanone, aminoadamantane, 1-adamantyl-acetamide, 1-hydroxyadamantane were 496, 536, 410, 418 and 529 K, respectively.

From these figures it appears that only 1-hydroxyadamantane gives an extra endothermic peak at 369.16 K. The nature of this peak was investigated using the following techniques.

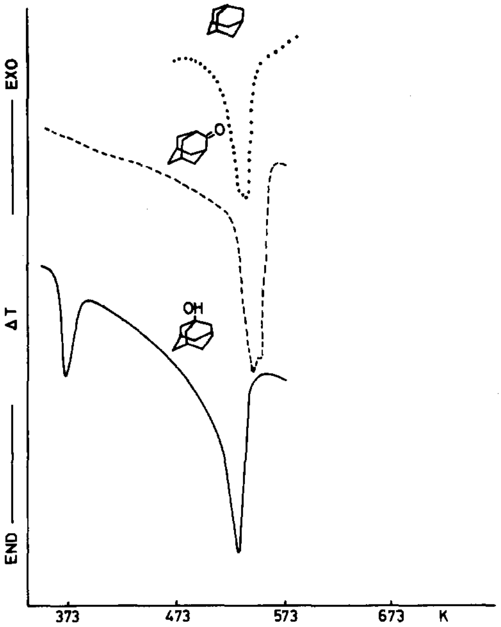

Fig. 1. DTA curves of some adamantane derivatives in a nitrogen atmosphere.

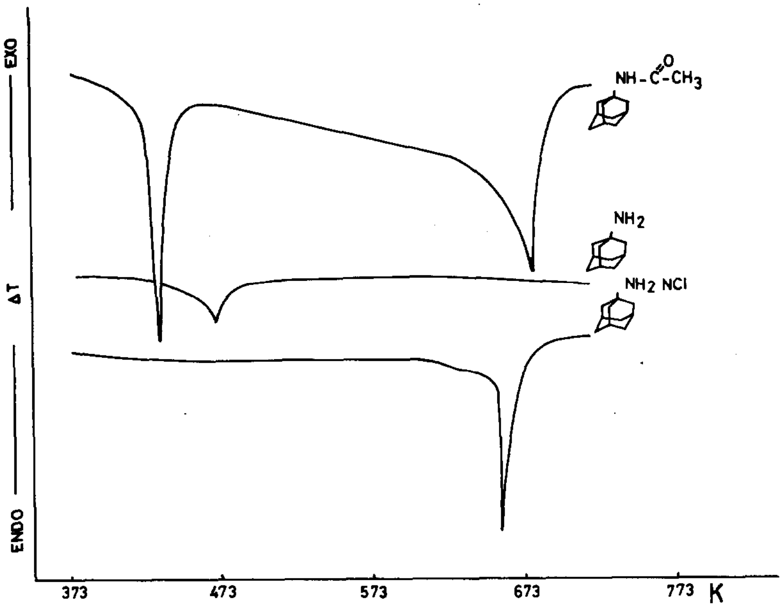

Fig. 2. DTA curves of some adamantane derivatives in a nitrogen atmosphere.

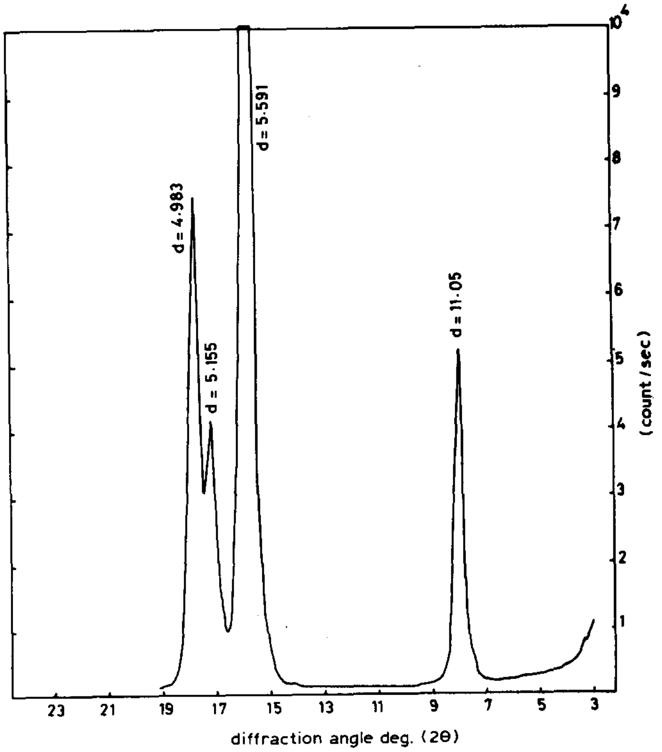

Fig. 3. X-ray spectrum of 1-hydroxyadamantane.

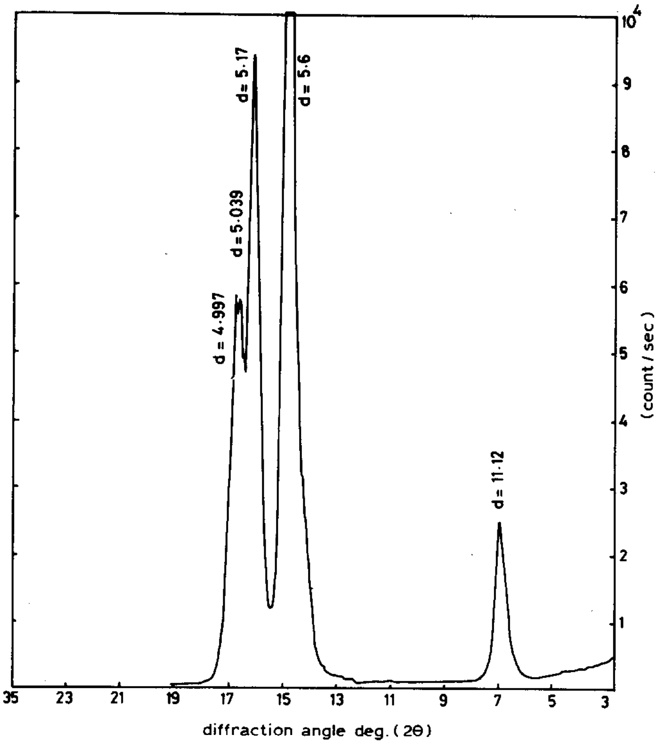

Fig. 4. X-ray spectrum of 1-hydroxyadamantane after heating up to 373.16 K.

(1) The X-ray diffraction was recorded for 1-hydroxyadamantane below 369.16 K and then higher than this temperature (Figs. 3 and 4); the solid residue which was collected above 369.16 K was used again to run the DTA curve. The residues obtained for the solid residue of 1-hydroxyadamantane were similar to those obtained for the original compound.

(2) The proton NMR spectra for 1-hydroxyadamantane in deuterated chloroform were obtained before and after the transition at 369.16 K; no difference was observed for the two recorded proton NMR spectra.

(3) The IR spectra of 1-hydroxyadamantane (KBr disc) recorded before and after the transition at 369.16 K were identical.

(4) The cooling curve of this endothermic peak gave an exothermic peak (Fig. 5). X-ray diffraction in conjunction with DTA was used with several compounds to determine whether a peak on the DTA curve represented a change in the crystalline structure [7,8]. IR and proton NMR [9,10] could also reveal changes which occur in the structure and were used by Chesnokov et al. [11] and Yabe [12] to determine the crystalline phase transition. DTA were used to study polymorphous transformations in drugs [13]. In this paper, X-ray diffraction, proton NMR spectra, IR-spectra and DTA curves of 1-hydroxyadamantane indicate that the absorption at 369.16 K is

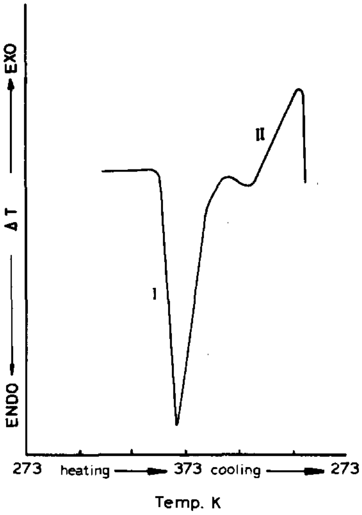

Fig. 5. The first transition peak of 1-hydroxyadamantane; (I) upon heating, (II) upon cooling.

TABLE 1

Thermodynamic properties of some adamantane derivatives

Compound	T_1 (K)	T_2 (K)	H (kJ mol^{-1})	S (J mol^{-1} K^{-1})
Adamantane	–	496.16	7.80	15.75 (16.25) [a]
Adamantanone	–	536.16	8.01	14.95
1-Adamantyl-acetamide	–	418.16	19.78	47.18
Adamantane amine	–	410.16	16.59	40.49
1-Hydroxyadamantane	369.16	529.16	9.63	18.25

[a] Ref. 6.

due to an ordered → disordered solid → solid phase transition. This transition is reversible (Fig. 5) and associated with a heat change of 2.5 kJ mol^{-1}.

The thermodynamic properties of the adamantane and its derivatives were calculated according to the method given by David [14] and the data are listed in Table 1. The result for 1-hydroxyadamantane was higher than other adamantane derivatives and this might be due to the existance of the solid → solid transition phase.

ACKNOWLEDGEMENT

The authors wish to thank Mr. F.M.J. Ali for his helpful assistance for X-ray measurements and Prof. F. Jasim for reading this paper.

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