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# THERMAL BEHAVIOUR OF 2-HYDROXYADAMANTANE

SALMAN R. SALMAN *
*Chemistry Department, College of Science, University of Baghdad, Jadiriyah, Baghdad (Iraq)*

KAFAA F. ABAS
*Petroleum Research Centre, Scientific Research Council, P.O. Box 10039, Baghdad (Iraq)*
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## ABSTRACT

Differential thermal analysis (DTA) of 2-hydroxyadamantane was performed. X-ray diffraction, $^{13}C$ NMR and DTA results for 2-hydroxyadamantane indicate that the two peaks which appear in the DTA curve at 326.16 and 391.16 K are due to phase transitions. The thermodynamic data for the two transitions were calculated and compared with those for 1-hydroxyadamantane.

## INTRODUCTION

IR, $^1H$ NMR [1–4], X-ray diffraction and DTA [5–7] have been used to study the crystalline phase transition of several compounds. Studies of the phase transition of adamantane under pressure [8–12] have revealed a change from a disordered f.c.c. structure to an ordered body-centred tetragonal structure. Little work has been done on the thermal behaviour of adamantane [13] and its derivatives at atmospheric pressure. In a previous communication, Salman et al. [14] noted that the DTA curve of 1-hydroxyadamantane was different from that of adamantane and its derivatives, and that there was an extra peak which was due to a phase transition.

In this paper, we extend our investigation to 2-hydroxyadamantane.

## EXPERIMENTAL

2-Hydroxyadamantane (Aldrich) was used without further purification. The X-ray diffraction analyses were run on a Phillips diffractometer under recording conditions of 50 KV, 20 mA, with a chart speed of 2 cm $m^{-1}$, and

* To whom correspondence should be addressed.

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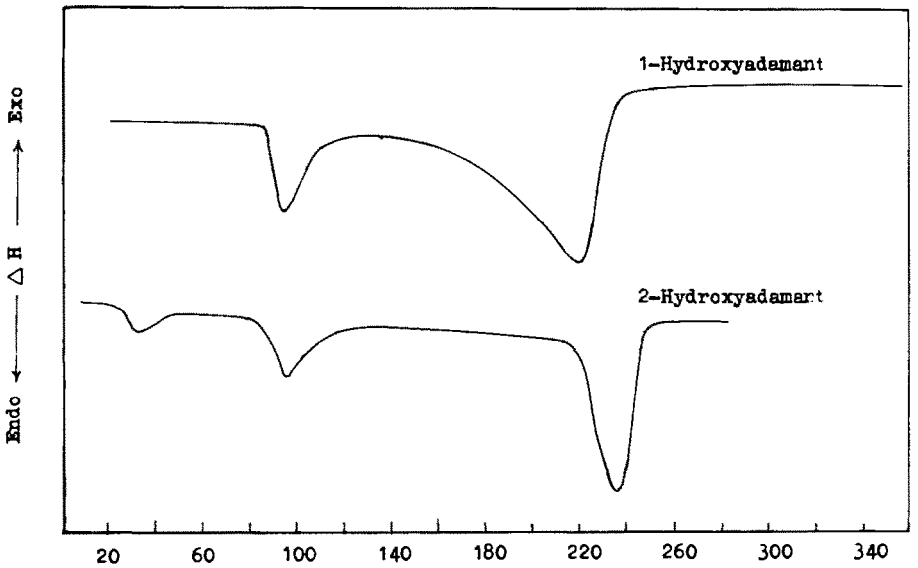


Fig. 1. DTA curves of 1-hydroxyadamantane and 2-hydroxyadamantane.

a goniometer speed of 2° $min^{-1}$. The $^1H$ NMR analyses 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.

Thermal analysis was performed in a nitrogen atmosphere with a flow rate of 10 l $h^{-1}$, using a special purpose cell. The heating rate was 10 °C $min^{-1}$. Aluminium oxide was used as a reference. The experimental error was within the limit of ±3 °C.

## RESULTS AND DISCUSSION

The DTA curves for 1-hydroxyadamantane and 2-hydroxyadamantane are presented in Fig. 1. The sublimation temperatures of 1-hydroxyadamantane and 2-hydroxyadamantane were 529.16 and 516.16 K respectively. In our previous communication [14] we showed that only 1-hydroxyadamantane gives an extra endothermic peak at 369.16 K.

Figure 1 indicates that 2-hydroxyadamantane has two extra peaks: one which is very small, at 325.16 K, and a second at 391.15 K. The natures of these peaks were investigated using various techniques:

(1) There was no difference between $^1H$ NMR spectra taken in $CDCl_3$ before and after the second transition.
(2) X-ray diffraction was recorded for the original 2-hydroxyadamantane before heating (Fig. 2a), and after heating up to 395 K (Fig. 2b). These spectra reveal some change in the crystal structure of 2-hydroxyadamantane both before and after heating.

(3) The DTA curve for the solid residue, which was collected at 395 K and cooled, is similar to that shown in Fig. 1. This indicates that the two transitions are reversible.
(4) The $^{13}C$ spectra of solid 2-hydroxyadamantane at different temperatures support the occurrence of these two transitions [15].

All the above results indicate that the absorption at 391.16 K is due to an ordered → disordered solid phase transition. The thermodynamic properties of 2-hydroxyadamantane were calculated according to the method given by David [16] and the data compared with those obtained for 1-hydroxyadamantane (Table 1). It can be seen that the heat change associated with the first transition was very small (0.3 kJ $mol^{-1}$), while that associated with the second transition was 3.74 kJ $mol^{-1}$.

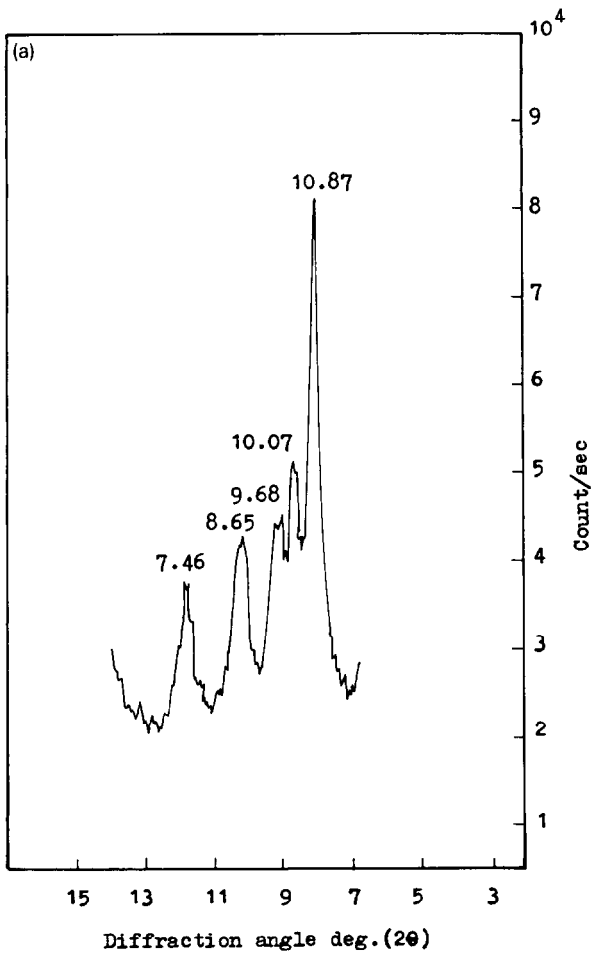


Fig. 2. a, X-ray spectrum of 2-hydroxyadamantane. b, X-ray spectrum of 2-hydroxyadamantane after heating up to 395 K.

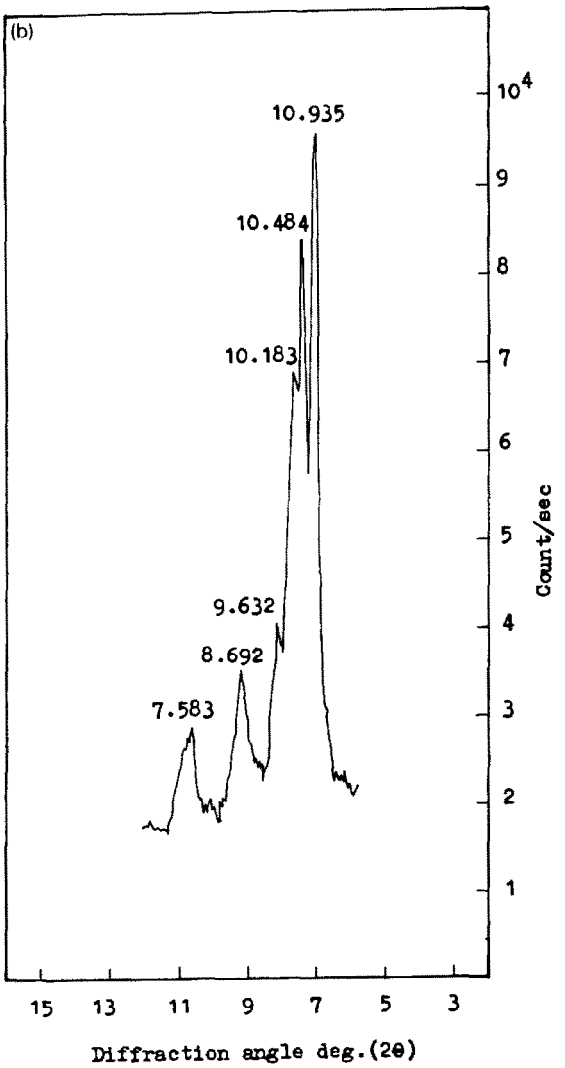


Fig. 2 (continued).

TABLE 1

Thermodynamic properties of 1-hydroxyadamantane (1-HA) and 2-hydroxyadamantane (2-HA)

| $T$ (K) | | | $H$ (kJ mol$^{-1}$) | | | $S$ (J mol$^{-1}$ K$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | 1-HA | 2-HA | | 1-HA | 2-HA | | 1-HA | 2-HA |
| $T_1$ | | 325.16 | $H_1$ | – | 0.30 | $S_1$ | – | 0.92 |
| $T_2$ | 369.16 | 391.16 | $H_2$ | 2.50 | 3.74 | $S_2$ | 6.77 | 9.56 |
| $T_3$ | 529.16 | 516.16 | $H_3$ | 7.13 | 7.75 | $S_3$ | 13.25 | 15.02 |

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