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# THERMAL BEHAVIOUR OF 2-HYDROXYADAMANTANE

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## ABSTRACT

Differential thermal analysis (DTA) of 2-hydroxyadamantane has been carried out; the results, with those of X-Ray diffraction, and $^{13}C$ NMR spectroscopy prove that the two peaks at 326.16 and 391.16 K are due to a phase transition. The thermodynamic properties of the two transitions are calculated and compared with those of 1-hydroxyadamantane.

## INTRODUCTION

Infrared and $^{1}H$ NMR spectroscopy [1–4], X-ray diffraction and DTA [5–7] have been used to study the crystalline phase transition of several compounds. The adamantane phase transition has been studied under pressure [8–12] and found to be a change from a disordered face-centred cubic structure to an ordered body-centred tetragonal structure.

Little work has been done on the thermal behaviour of adamantane [13] and its derivative at atmospheric pressure. In a previous communication Salman et al. [14] noticed that the DTA of 1-hydroxyadamantane was different from adamantane and its derivatives and that there was an extra peak which was due to a phase transition. In this paper, we extended our investigation to 2-hydroxyadamantane.

## EXPERIMENTAL

2-Hydroxyadamantane (Aldrich) was used without further purification. The X-ray diffraction patterns were run on a Philips diffractometer and the

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recording conditions were 50 kV, 20 mA with a chart speed of 2 cm $min^{-1}$ and goniometer speed of 2° $min^{-1}$. The $^1H$ 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.

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

## RESULTS AND DISCUSSION

The DTA curves of 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 paper [14] we show that only 1-hydroxyadamantane gives an extra endothermic peak at 369.16 K.

Figure 1 indicates that 2-hydroxyadamantane has two extra peaks; the first, which is very small, at 325.16 K, and the second at 391.15 K. The nature of these peaks was investigated using the following techniques:

(1) $^1H$ NMR spectra in $CDCl_3$ before and after the second transition reveal no difference.

(2) The X-ray diffraction was recorded for the original 2-hydroxyadamantane before heating (Fig. 2a) and after heating to 395 K (Fig. 2b). These figures reveal some change in the crystal structure of 2-hydroxyadamantane before and after heating.

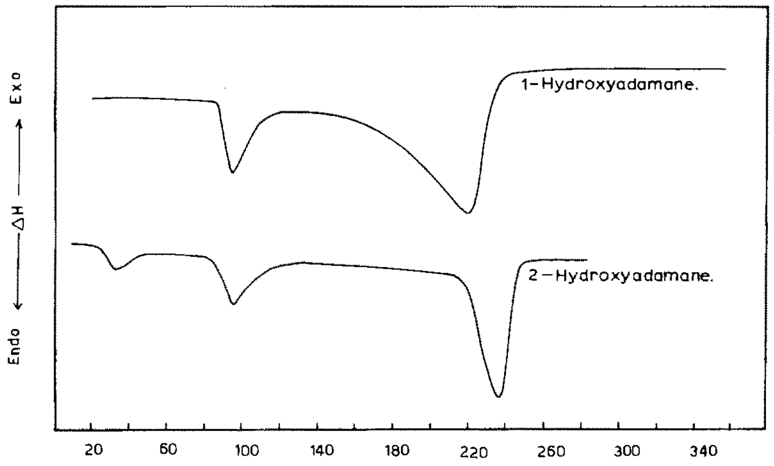

Fig. 1. DTA curves of 1-hydroxyadamantane and 2-hydroxyadamantane.

TABLE 1

Thermodynamic properties of 1-hydroxyadamantane and 2-hydroxyadamantane

| | Temperature (K) | | | Enthalpy (kJ mol$^{-1}$) | | | Entropy (J mol$^{-1}$ K$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_1$ | $T_2$ | $T_3$ [a] | $H_1$ | $H_2$ | $H_3$ | $S_1$ | $S_2$ | $S_3$ |
| 1-Hydroxyadamantane | – | 369.16 | 529.16 | – | 2.50 | 7.13 | – | 6.77 | 13.25 |
| 2-Hydroxyadamantane | 325.16 | 391.16 | 516.16 | 0.30 | 3.74 | 7.75 | 0.92 | 9.56 | 15.02 |

[a] Sublimation temperature.

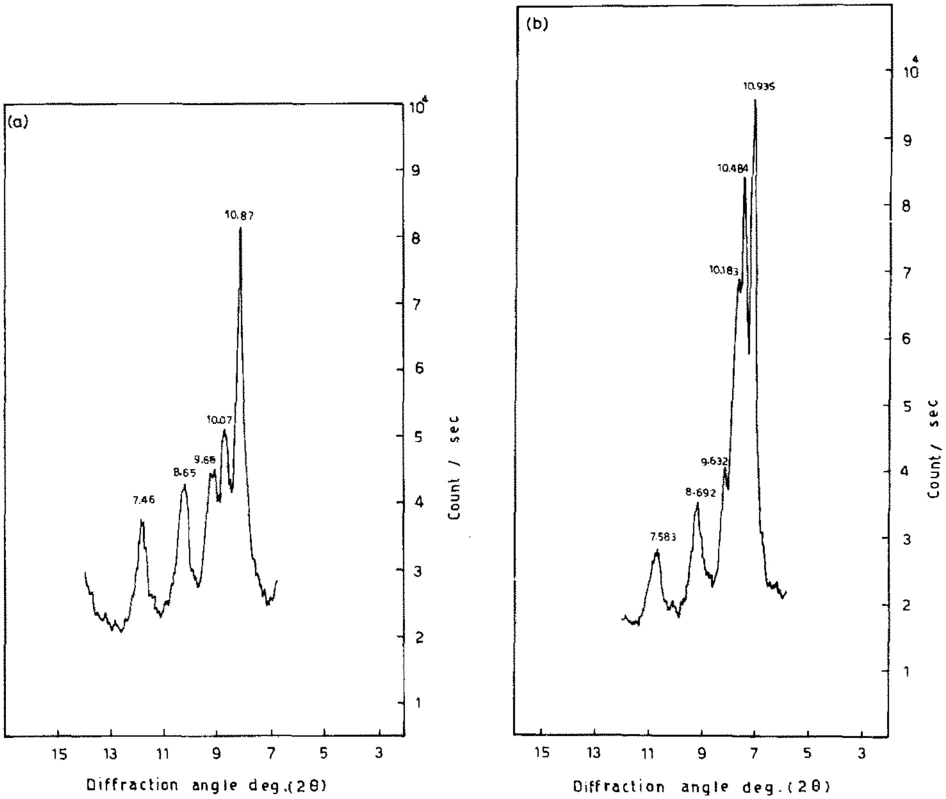

Fig. 2. (a) X-Ray spectrum of 2-hydroxyadamantane. (b) X-Ray spectrum of 2-hydroxyadamantane after heating to 395 K.

(3) The solid residue which was collected at 395 K was cooled and the DTA for this residue was similar to that shown in Fig. 1. This indicates that the two transitions are reversible.

(4) The $^{13}C$ NMR spectra of solid 2-hydroxyadamantane at different temperatures support the presence of these two transitions [15].

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

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## REFERENCES

1 R.M. Silverstein, C.G. Bassler and T.G. Morril, Spectrometric Identification of Organic Compounds, Wiley, London, 1974.
2 L.M. Jackman and S. Sternshell, Application of NMR Spectroscopy in Organic Chemistry, Pergamon Press, Oxford, 1969.
3 R.C. Mackenzie, Differential Thermal Analysis, Vol. 1, Academic Press, London, 1970, p. 630.
4 R.C. Mackenzie, Differential Thermal Analysis, Vol. 1, Academic Press, London, 1970, p. 631.
5 H.L. Spier and K.G. Van Senden, Steroids, 6 (1975) 871.
6 T. Sakuri and M. Yabe, J. Phys. Soc. Jpn., 13 (1958) 5.
7 R.C. Mackenzie, Differential Thermal Analysis, Vol 1, Academic Press, London, 1970, p. 456.
8 T. Ito, Acta Crystallogr., Sect. B, 29 (1973) 369.
9 K. Hara, G. Schuster and H.G. Drickamer, Chem. Phys. Lett., 47 (1977) 462.
10 K. Hara, J. Osugi, I. Taniguchi and K. Suzuki, High Temp. High Press., 12 (1980) 221.
11 K. Hara, Y. Katou, J. Taniguchi and K. Suzuki, Chem. Lett., (1980) 803.
12 K. Hara, Y. Katou and J. Osogi, Bull. Chem. Soc. Jpn., 54 (1981) 687.
13 S.S. Chang and E.F. Westrum, Jr., J. Phys. Chem., (1960) 1546.
14 S.R. Salman, E.Z. Said and K.F. Abas, Thermochim. Acta, 111 (1987) 21.
15 S.R. Salman and J.C. Lindon, unpublished results.
16 D.J. David, Anal. Chem., 36 (1964) 2162.