

THERMOANALYTICAL CHARACTERIZATION OF 1,3-DIMETHYLURACIL AND MALONAMIDE CRYSTALS *

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ABSTRACT

DSC measurements showed that 1,3-dimethyluracil crystals prepared by vacuum sublimation or recrystallization from various solutions were in most cases in a stable phase (cr2) at 300 K. When heated, the stable crystals did not transform to the high temperature stable phase (cr1). The superheated crystals melted at 394 K; this liquid then underwent a monotropic transformation to phase cr1, which finally melted at 398 K. A melt-crystallized sample (phase cr1) did not readily transform into phase cr2 on cooling, whereas crystals in phase cr1 formed by the above-mentioned monotropic transformation from the liquid state transformed readily into phase cr2 at 380 K on cooling. DSC measurements on malonamide crystals indicated the occurrence of a high and a low temperature stable phase (cr1 and cr2, respectively) and a metastable phase (cr3) formed by melt-crystallization. Phase cr1 supercooled on cooling. Schematic Gibbs energy and enthalpy diagrams are given for both compounds.

INTRODUCTION

Recently, standard enthalpies of formation for acetylurea and trimethyl isocyanurate in crystalline and gaseous states have been determined by combustion and sublimation calorimetric methods [1], and atomization enthalpies of aliphatic compounds with alternately adjacent carbonyl groups and nitrogen atoms, including the above compounds, have been analysed theoretically [2]. A similar study was carried out on 1,3-dimethyluracil and malonamide together with trimethyl cyanurate [3]. DSC measurements were performed to characterize the phases of the crystals, and also to determine the purity of the samples which were used in the calorimetric measurements of ref. 3. In this paper, details of the DSC study for the characterization of the crystals are described.

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EXPERIMENTAL

A DuPont 990 Thermal Analysis System and a Shimadzu DT-30 thermal analyser, each incorporating a DSC module, were used for the DSC measurements. The samples were enclosed in a sealed aluminium pan. The heating rate was 1 K min^{-1} in the melting region.

1,3-Dimethyluracil was purified by recrystallization from various solutions, followed by vacuum sublimation. Malonamide (Tokyo Kasei, G.R.) was purified by recrystallization from aqueous solution (twice), followed by vacuum sublimation.

RESULTS AND DISCUSSION

1,3-Dimethyluracil

Typical patterns of DSC curves in the melting region (above 394 K) for the samples heated from 300 K are shown in Fig. 1. Pattern A was observed irrespective of the final treatment (sublimation, melt-crystallization, or recrystallization from acetone, benzene, ethanol, carbon tetrachloride or aqueous solution). Pattern B was observed for melt-crystallized samples and also for samples obtained by recrystallization from ethanol or benzene solution. The molar enthalpy changes of the peaks at 398 K in patterns A and B are equal ($\Delta H_1 = 14.6 \pm 0.5 \text{ kJ mol}^{-1}$). The shape of peaks below 397 K in patterns A and B was not reproducible. However, the net molar enthalpy change of the lower temperature peaks in pattern A and that of the lower temperature peak in pattern B are constant and equal ($\Delta H_2 = 3.9 \pm 0.2 \text{ kJ mol}^{-1}$). Pattern C was observed less frequently, occurring only for samples obtained by recrystallization from acetone or benzene solution. Pattern D was observed quite often for samples obtained by melt-crystallization, and also for the sample obtained by recrystallization from ethanol solution. The molar enthalpy change of pattern D is equal to that of the higher temperature peak in patterns A and B. The sum of ΔH_1 and ΔH_2 is equal to the molar enthalpy change of pattern C ($\Delta H_3 = 18.4 \pm 0.5 \text{ kJ mol}^{-1}$).

From these enthalpy changes, it can be deduced that the peak at 394 K in pattern C and the peaks at 398 K in patterns A, B and D are the melting peaks of crystals in different phases. It can also be deduced that the phases at 300 K of crystals showing patterns A, B or C are identical, and that the phases just below 398 K in patterns A and B are the same as that which appears in pattern D. The latter phase is denoted by cr1 and the former by cr2.

At 394 K or 398 K, $\Delta G = 0$ and $\Delta_{\text{fus}} S = \Delta_{\text{fus}} H / T_{\text{fus}}$ between the relevant crystal phase and the liquid phase. The entropy change at 394 K ($46.7 \text{ J K}^{-1} \text{ mol}^{-1}$) is larger than that at 398 K ($36.7 \text{ J K}^{-1} \text{ mol}^{-1}$). Since $(\partial G / \partial T)_p =$

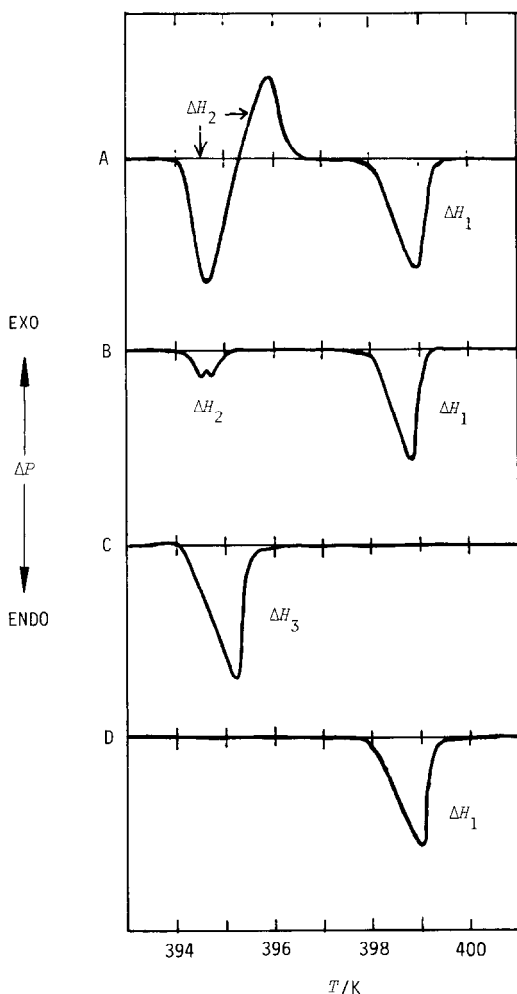


Fig. 1. Typical DSC heating curves of 1,3-dimethyluracil in the melting region. A, B, C and D denote the four patterns. Heating rate: 1 K min^{-1} .

$-S$, $\Delta_{\text{fus}}S = -\Delta(\partial G/\partial T)_p$ at $T = T_{\text{fus}}$. Hence, $\Delta(\partial G/\partial T)_p$ at 394 K is numerically higher than that at 398 K. This shows that the Gibbs energy curve of phase cr2 crosses that of the liquid phase at 394 K with an angle larger than that of phase cr1 at 398 K in the heating direction. It implies that the Gibbs energy curve of phase cr1 will probably cross that of phase cr2 at a lower temperature.

To examine the above thermodynamic reasoning, a series of measurements were conducted for a sample that showed pattern B. The results are presented in Fig. 2. When the crystal was heated up to 396 K and then cooled down to 300 K (run 1), an exothermic peak was observed at 380 K, with the molar enthalpy change being numerically equal to ΔH_2 . When the

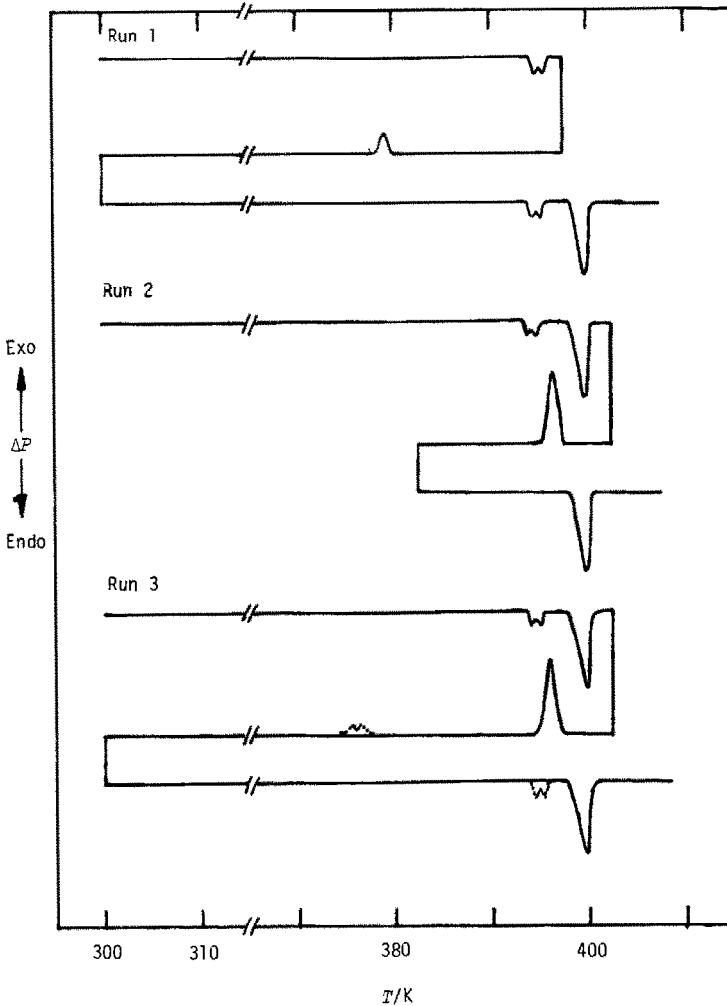


Fig. 2. DSC curves of samples of 1,3-dimethyluracil with various thermal histories. In run 3, when an exothermic peak (dotted curve) was observed at or below 380 K on cooling, an endothermic peak (dotted curve) was observed at 394 K on subsequent heating.

resulting crystal was heated again, pattern B was observed in the melting region. When a melt-crystallized sample was cooled to 383 K and then again heated (run 2), or when it was cooled to 300 K (no transition occurred at 380 K) and heated soon afterwards (run 3), no peaks were observed below 398 K in the melting region. Furthermore, the molar enthalpy changes for the recrystallization from the melt in runs 2 and 3 were each numerically equal to ΔH_1 . It is clear that phases cr1 and cr2 are in equilibrium at 380 K, but the phase transition did not take place in the heating direction, and also did not readily take place for the melt-crystallized crystal in the cooling direction, in each case owing to kinetic reasons. Cooling of the melt-crystallized

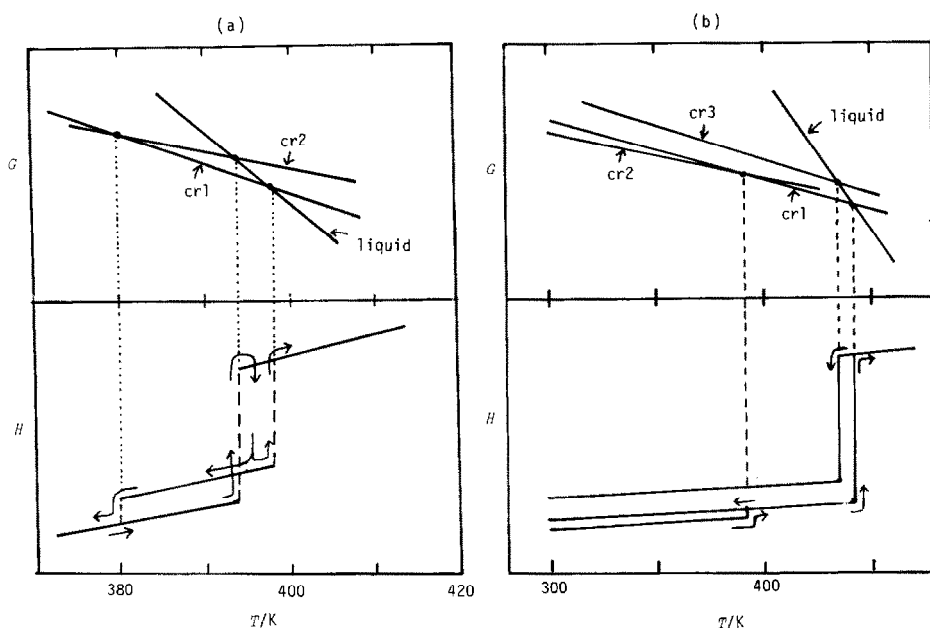


Fig. 3. Schematic Gibbs energy and enthalpy curves of (a) 1,3-dimethyluracil and (b) malonamide.

crystal to about 90 K can be used to actuate the transition from cr1 to cr2.

From these observations, Gibbs energy curves and enthalpy curves were deduced, as shown schematically in Fig. 3. Phases cr2 and cr1 are the stable phases in the regions 300–380 K and 380–398 K, respectively. On heating from 300 K, the crystal does not transform to phase cr1 at 380 K. Therefore, the crystal is in a metastable state between 380 and 394 K, which is the superheated low temperature stable phase. The metastable crystal melts at 394 K, and the resulting liquid transforms monotropically into the high temperature stable phase (phase cr1), which finally melts at 398 K. This is illustrated by arrows in Fig. 3. Poor reproducibility of the shape of lower temperature peaks in patterns A and B and an exothermic peak in pattern A are in accord with this diagram. Pattern A in Fig. 1 corresponds to this behaviour. When melting of the metastable crystal and monotropic transformation of the liquid into phase cr1 occur simultaneously, net enthalpy change will be recorded as shown in pattern B. Pattern C will be observed in cases where, for some reason, monotropic recrystallization of the liquid to cr1 does not occur at 396 K. Pattern D will be observed when the sample is in the supercooled phase cr1 at 300 K.

Malonamide

Malonamide crystals prepared by the method used here, which included vacuum sublimation, showed a small and broad endothermic peak ($\Delta H = 1.9$

kJ mol^{-1}) at 393 K, and a melting peak ($\Delta H = 35.8 \text{ kJ mol}^{-1}$) at 443 K, on heating. A crystal heated above 393 K did not show the lower temperature peak on subsequent heating. Since the final treatment of the sample was vacuum sublimation, evaporation of water used as a solvent of recrystallization can be excluded as a possible cause of the peak. A melt-crystallized sample showed a melting peak ($\Delta H = 29.8 \text{ kJ mol}^{-1}$) at 435 K on heating. These findings suggest that: (1) the crystal obtained by sublimation is in a stable phase (cr2) at 300 K; (2) the crystal heated above 393 K was brought to a meta-stable phase at 300 K, which was formed by supercooling of the high temperature stable phase (cr1) on subsequent cooling; and (3) another meta-stable phase (cr3) was formed by crystallization from the melt. Gibbs energy and enthalpy curves are shown schematically in Fig. 3.

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