ENTHALPIES AND ENTROPIES OF MELTING FROM DIFFERENTIAL SCANNING CALORIMETRY AND FREEZING POINT DEPRESSIONS: UREA, METHYLUREA, 1,1-DIMETHYLUREA, 1,3-DIMETHYLUREA, TETRAMETHYLUREA, AND THIOUREA

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ABSTRACT

The following enthalpies of melting have been determined with a differential scanning calorimeter: urea, 3.22 kcal mole^{-1}; 1,3-dimethylurea, 2.97 kcal mole^{-1}; methylurea, 3.34 kcal mole^{-1}; 1,1-dimethylurea, 5.49 kcal mole^{-1}; thiourea, 3.30 kcal mole^{-1}. Freezing point depression measurements have led to the following enthalpies of melting: benzoic acid, 4.29 kcal mole^{-1}; urea, 3.30 kcal mole^{-1}; 1,3-dimethylurea, 3.11 kcal mole^{-1}; tetramethylurea, 3.37 kcal mole^{-1}. The results above lead to the following entropies of melting: urea, 8.00 cal deg^{-1} mole^{-1}; methylurea, 8.90 cal deg^{-1} mole^{-1}; 1,1-dimethylurea, 12.06 cal deg^{-1} mole^{-1}; 1,3-dimethylurea, 7.95 cal deg^{-1} mole^{-1}; tetramethylurea, 12.39 cal deg^{-1} mole^{-1}; thiourea, 7.28 cal deg^{-1} mole^{-1}.

INTRODUCTION

We have undertaken measurements leading to the enthalpy of melting of urea and some derivatives of urea because of specific interests in these compounds and also as a means of gaining some understanding of accuracy and reliability of results obtained by way of the relatively new technique of differential scanning calorimetry as compared to cryoscopic measurements.

Miller and Ditmar[1] have determined the solubility of urea in water from 70°C to the melting point (132.7°C) of urea and have calculated $\Delta H = 3470$ cal mole^{-1} for the enthalpy of melting of urea. Other solubility data (phase equilibria) from Howells[2] for urea–inorganic salt systems lead us to $\Delta H \cong 3.0$ kcal mole^{-1} for melting of urea. Although it is difficult to estimate uncertainties to be associated with either of these values, the uncertainty in the latter value is surely greater than the difference

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between the two values. Solubility data[3] for various binary systems involving thiourea indicate $\Delta H \cong 3.5$ (large uncertainty) kcal mole^{-1} for melting of thiourea. Further measurements are clearly needed in order to select ΔH of melting values for urea and several derivatives of urea.

Differential scanning calorimetry offers two important attractions: (*i*) very small samples can be used and (*ii*) measurements can be made rapidly so that effects of thermal decomposition may be much smaller than in other methods. On the other hand, there are legitimate questions about stability of calibration, temperature variation of calibration, and general accuracy of these instruments that have become readily available only in the last few years. In order to obtain data for several compounds of interest and to gain experience that might lead to answers to these questions, we have made both differential scanning calorimetry measurements and freezing point depression measurements on similar samples of urea and to compare ΔH of melting values from these two sources. These same techniques have also been applied to determination of enthalpies of melting for some derivatives of urea.

EXPERIMENTAL

Our calorimetric measurements were made on a Perkin–Elmer Differential Scanning Calorimeter, DSC-1, with output recorded on a Leeds and Northrup Speedomax Model G. An A. Ott Type 16 planimeter was used in measuring areas under recorded curves. All calorimetric samples were weighed with a Model M-10 Cahn Electrobalance.

The DSC-1 was calibrated by running melting curves with benzoic acid and metallic indium, for which enthalpies of melting are reliably known[4,5], and for which melting temperatures are above and below that of urea. A series of fifteen measurements with benzoic acid led to 0.03008 in.^{2} mcal^{-1} for the calibration factor. A similar series with indium led to 0.03001 in.^{2} mcal^{-1}.

The cryoscopic apparatus consisted of a 25-mm Pyrex sample tube supported inside a larger Pyrex tube that was suspended in a one-quart Dewar Flask. The inner tube was partially closed with a cork containing holes for an electrically operated reciprocating glass stirrer and the probe from a Hewlett Packard 280 1A Quartz Crystal Thermometer.

Two different samples of urea were used with similar results throughout. Mann Analysed Urea (Ultrapure M.A. No. 9200) was used without further purification. Reagent grade urea was purified according to the method of Stokes[6].

Reagent grade thiourea was recrystallized from distilled water and then washed with cold ethanol followed by cold ether.

Tetramethylurea (Aldrich) was purified by two fractional freezings.

Both methylurea (Eastman) and 1,1-dimethylurea (K & K Laboratories) were purified by crystallization from absolute alcohol, followed by washing with cold chloroform and cold ether.

Samples of 1,3-dimethylurea (Aldrich and Eastman) were purified in two ways.

(*i*) A warm, slightly turbid solution of the original material in absolute ethanol was filtered and then chilled in an ice bath. The resulting crystals were collected on a fritted glass filter and washed with cold ethanol followed by cold ether. (*ii*) The compound was crystallized from ethyl acetate with resulting crystals being washed with cold ethyl acetate and cold ethanol. After these crystals were dried by suction on a filter, they were recrystallized from chloroform and washed with cold chloroform, cold ethanol, and cold ether.

RESULTS

As a means of testing accuracy of enthalpies of melting derived from our cryoscopic measurements we first carried out such measurements with camphor and anthracene as solutes in benzoic acid. Results of these measurements led to $\Delta H = 4.29$ kcal mole^{-1} (average deviation $= 0.06$ kcal mole^{-1}) for the enthalpy of melting of benzoic acid. This result agrees well with the "standard" $\Delta H = 4.30$ kcal mole^{-1} from calorimetric measurements[5].

Urea. — Twenty-one measurements on urea were made with the DSC-1, with ΔH values for melting ranging from 3162 to 3288 cal mole^{-1}. The average of all values was $\Delta H = 3224$ cal mole^{-1} (average deviation $= 32$ cal mole^{-1}). We estimate that the *total* uncertainty is about twice the average deviation and write $\Delta H = (3.22 \pm 0.06)$ kcal mole^{-1} as the "best" value for the enthalpy of melting of urea as determined by differential scanning calorimetry.

A total of twelve freezing point depression measurements were made on urea with thiourea, sodium chloride, sodium acetate, and tetramethylammonium bromide as solutes in urea. All results led to an average $\Delta H = 3.35$ kcal mole^{-1} (average deviation $= 0.15$ kcal mole^{-1}) for the enthalpy of melting of urea. In calculating ΔH values from the data we have taken the van't Hoff $i = 1$ for thiourea and $i = 2$ for the salts. Because non-ideal solution behavior of the salts would have the effect of making calculated ΔH values too large, we have given extra weight to the results of four experiments with thiourea (average $\Delta H = 3.21$ with average deviation $= 0.05$ kcal mole^{-1}) in obtaining $\Delta H = 3.30 \pm 0.10$ kcal mole^{-1} as the "best" enthalpy of fusion from our cryoscopic measurements. (Here it should be noted that there was no evidence of solid solution formation in the urea–thiourea system.)

On the basis of our results reported above, we take $\Delta H = 3.25$ kcal mole^{-1} for the enthalpy of melting of urea.

1,3-Dimethylurea. — Sixteen calorimetric runs led to $\Delta H = 2.97$ kcal mole^{-1} (average deviation $= 0.03$ kcal mole^{-1}) for the enthalpy of melting. Six freezing point depression measurements with thiourea and aniline as solutes led to $\Delta H = 3.11$ kcal mole^{-1} (average deviation $= 0.03$ kcal mole^{-1}). We choose $\Delta H = 3.02$ kcal mole^{-1} as the enthalpy of melting of 1,3-dimethylurea.

Methylurea. — Twelve calorimetric runs led to $\Delta H = 3.34$ kcal mole^{-1} (average deviation $= 0.02$ kcal mole^{-1}) for the enthalpy of melting of methylurea.

1,1-Dimethylurea. — Eight calorimetric runs led to $\Delta H = 5.49$ kcal mole^{-1}

(average deviation = 0.03 kcal mole^{-1}) for the enthalpy of melting of 1,1-dimethylurea.

Tetramethylurea. — Seven freezing point depression measurements with aniline and *m*-cresol as solutes led to $\Delta H = 3.37$ kcal mole^{-1} (average deviation = 0.02 kcal mole^{-1}) for the enthalpy of melting of tetramethylurea.

Thiourea. — Five calorimetric runs led to $\Delta H = 3.30$ kcal mole^{-1} (average deviation = 0.02 kcal mole^{-1}) for the enthalpy of melting of thiourea.

Results of all of our measurements are summarized in Table I, where we also report entropies of melting calculated as $\Delta S_m = \Delta H_m / T_m$.

TABLE I

ENTHALPIES AND ENTROPIES OF MELTING

Substance	ΔH_m (kcal mole^{-1})	ΔS_m (cal deg^{-1} mole^{-1})
Urea	3.25	8.00
Methylurea	3.34	8.90
1,1-Dimethylurea	5.49	12.06
1,3-Dimethylurea	3.02	7.95
Tetramethylurea	3.37	12.39
Thiourea	3.30	7.28

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