

A DSC, TG, IR study of the thermal decomposition of some alkyl- and aryl-ureas

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Abstract

The melting, vaporization and thermal decomposition of monoethyl-, 1,3-diethyl-, mono-phenyl-, 1,3-diphenyl-urea were investigated by means of TGA and DSC measurements together with evolved products analysis by I.R. spectrometry. I.R. spectra allowed to identify isocyanate, amine and trimer among the compounds coming from the thermal treatment. DSC data seem to indicate hydrogen bonds are determinant for the enthalpy of vaporization of these derivatives of urea.

Keywords: Alkyl-, aryl-ureas; Decomposition; Vaporization

The course of the thermal decomposition of urea derivatives has not well characterized, despite the fact that these compounds are of relevant interest in industry, agriculture and medicine [1, 2].

In a previous paper we have reported on the thermal analysis of urea and thiourea [3], and now we have extended the investigation to mono- and di-substituted alkyl- and aryl-ureas.

1. Experimental

Calorimetric measurements were performed on a Mettler differential scanning calorimeter model DSC 20. Weight loss studies were determined using a Mettler thermogravimetric analyzer model TG 50. The I.R. spectroscopic analysis of the

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volatile decomposition products were made with a Perkin-Elmer IR spectrometer (1760X) in carbon tetrachloride solution. Separation and identification of the volatile, insoluble compounds were also made with a gas chromatograph (Perkin-Elmer model GC 8420).

The alkyl-, aryl- ureas were commercial high purity grade. They were further purified by several successive crystallizations from ethyl acetate solution.

Each calorimetric and thermogravimetric run was repeated at least five times to check reproducibility. In DSC and TGA a heating rate of 10 min^{-1} was adopted and argon was used as the purge gas.

2. Results and discussion

2.1. Alkyl ureas

Figs. 1a-d show the DSC and TG curves of melting, evaporation and decomposition of the mono- and di-ethylureas (hereafter cited as MEU and 1, 3-DEU). The more significant parameters deduced from the curves (enthalpy and entropy of melting, enthalpy of vaporization and decomposition) are collected in Table 1. The weight loss before and during melting of these ureas was less than 1% and therefore decomposition in this range of temperature was excluded.

Several attempts have been made to correlate enthalpy and entropy of fusion with the chemical structure of molecules, but no definite conclusion has been drawn [4, 5]. An alternative procedure which compares the thermodynamic quantities of the state transitions with the decomposition process is suggested.

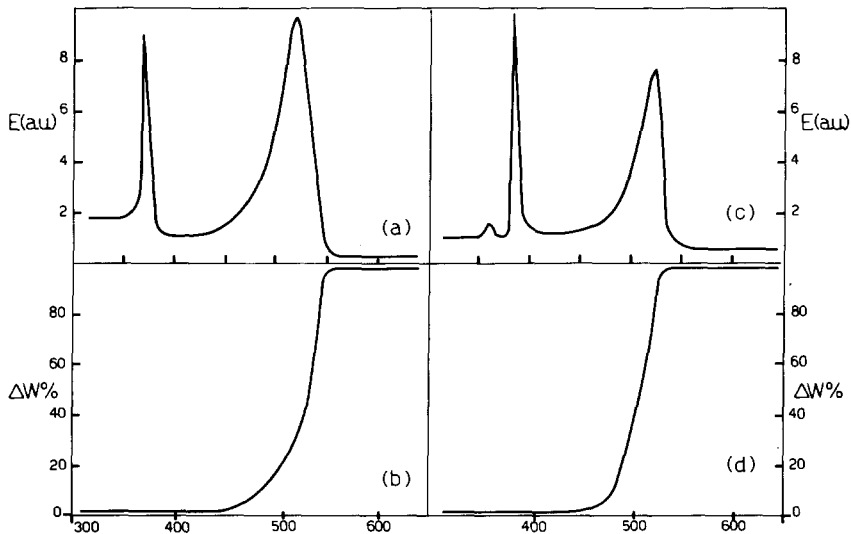


Fig. 1. DSC and TGA curves of MEU (a, b) and of DEU (c, d) melting, vaporization and decomposition.

Table 1

Enthalpy (ΔH_m) and entropy (ΔS_m) of melting, and enthalpy of vaporization and of decomposition ($\Delta H_{\text{vap,dec}}$) for some alkyl and aryl ureas

Compound	$\Delta H_m/(\text{kJ mol}^{-1})$	$\Delta S_m/(\text{u.e.})$	$\Delta H_{\text{vap,dec}}/(\text{kJ mol}^{-1})$
Ethyl urea	13.9 ± 0.2	4.56	44.3 ± 2.0
1,3-Diethyl urea	$2.8 \pm 0.3^a, 14.2 \pm 0.2$	4.09	114.3 ± 2.0
Phenyl urea	23.8 ± 0.2	6.85	122.2 ± 2.0
1,3-Diphenyl urea	37.7 ± 0.2	8.87	101.1 ± 2.0

^a Enthalpy change of a solid-solid transition.

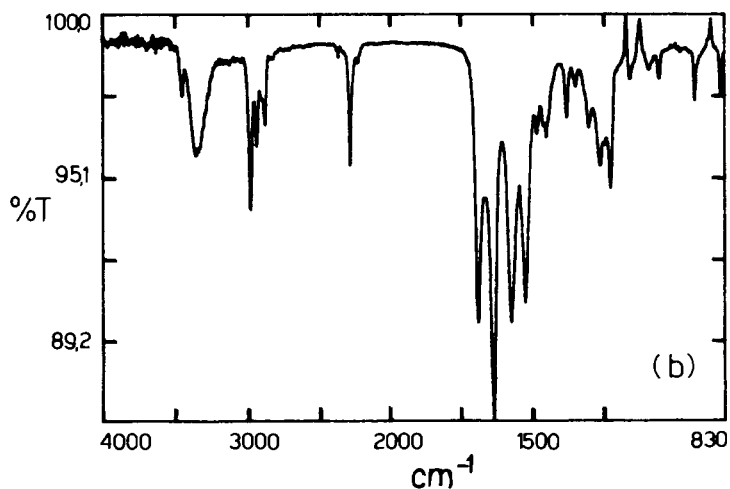
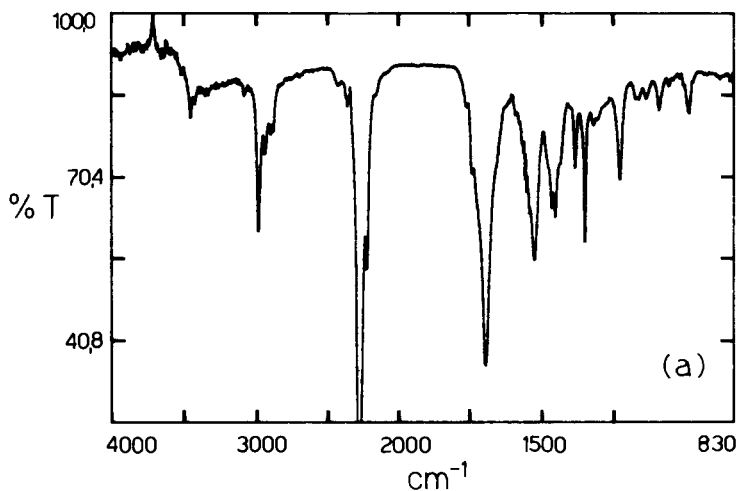
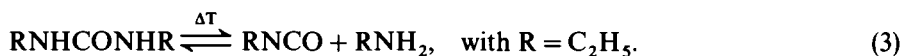


Fig. 2. I.R. spectra of the thermal decomposition products of MEU (a) and of DEU (b), in carbon tetrachloride solution.

The IR spectra of the decomposition products of MEU and 1,3-DEU are shown in Fig. 2a,b. Beside the frequencies associated with urea (1693, 1523, 1165 cm^{-1}) for MEU, (1636, 1573, 1263 cm^{-1}) for 1,3-DEU, bands typical of isocyanate group (the asymmetric stretching, 2278 cm^{-1} ; the symmetric one, 1381 cm^{-1}) are present. The presence of ethylamine and isocyanic acid was also confirmed by a GC assay. Accordingly, the main steps in the thermal decomposition of MEU would appear to be:



while for 1,3-DEU the main step is:



However for both alkyl-ureas another reaction is present which gives a small but detectable contribution to the decomposition products. This is a polymerization reaction and the spectra shown in Fig. 2 contains a band typical of the trimer of ethyl-isocyanate (1750 cm^{-1}) [6]; it is well known that isocyanate readily forms trimers under catalyst action [7], but it seems to be the first time such compound has been obtained from an alkyl-urea. The overall heats detected ($\Delta H_{\text{vap.,dec}}$ of Table 1) is an average from all the various processes (vaporization, decomposition, polymerization) which are developing after melting.

In particular, with MEU, the relative low value of $\Delta H_{\text{vap.,dec.}}$, appears to be an average of the following: i) this compound is not much associated in the liquid state (relative high value of the entropy of melting), so less energy is required to break the hydrogen and van der Waals bonds; ii) the reaction enthalpy concerning the step (1), as deduced from the heat of formation of each compound given in literature [8, 9], is small ($\Delta H_1 = +64 \text{ kJ mol}^{-1}$), while the enthalpy concerning the step (2) ($\Delta H_2 = +145 \text{ kJ mol}^{-1}$) is comparable with the one of step (3) ($\Delta H_3 = +150 \text{ kJ mol}^{-1}$); iii) the endothermic contributions of the above cited steps are somehow compensated by the exothermic polymerization process. With 1,3-DEU, the feature of the NH stretching bands in the solid state indicates a prevalence of the trans rotamer, which is usually connected with a strong self association [10]; in agreement with such an interpretation we have a higher sublimation enthalpy for 1,3-DEU, than for MEU, and the occurrence of a solid–solid transition with an enthalpy value typical of a first order phase transition [11]. This allotropism should correspond to the transition from a more to a less symmetrical rotor. But the hydrogen and the van der Waals bonds are so important for 1,3-DEU, that some association remains also in the melt (relative low value of ΔS_m). In short, the higher value of $\Delta H_{\text{vap.,dec.}}$ of DEU in comparison with that of MEU is coming from the greater contribution of the endothermic terms (hydrogen bonds breaking, decomposition steps) as compared with the exothermic one (polymerization).

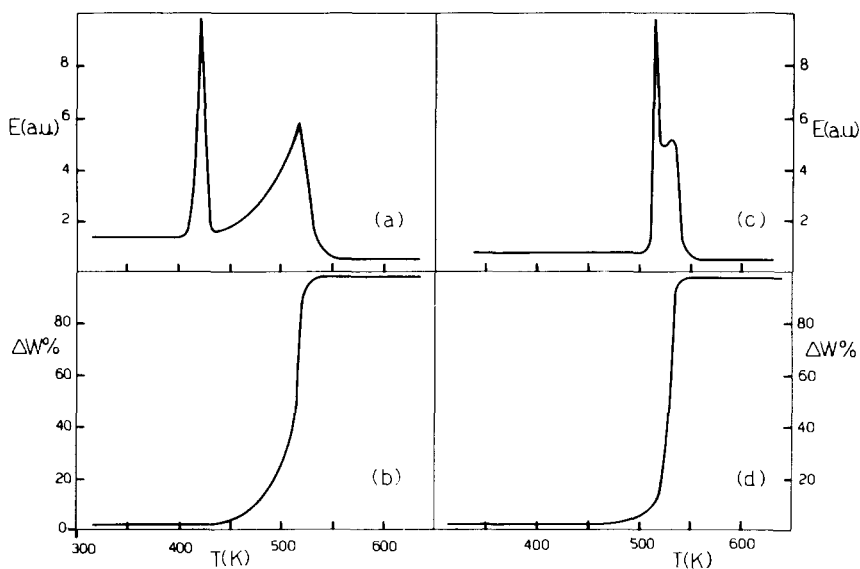


Fig. 3. DSC and TGA curves of MPhU (a, b) and of DPhU (c, d) melting, vaporization and decomposition.

2.2. Aryl ureas

In Fig. 3 a-d the DSC and TG curves of melting, evaporation and decomposition of the mono- and diphenyl-urea (hereby cited as MPhU and 1,3-DPhU) are given.

With these ureas the opposite occurs to that of the alkyl derivatives, the enthalpy value ($\Delta H_{\text{vap,dec}}$) of mono- is higher than that of the di-substituted compound (see Table 1), even if the same processes (hydrogen bonds breaking, vaporization, polymerization) develop beyond the melting point.

In Fig. 4a the IR spectra of the decomposition products of MPhU are shown. Bands characteristic of MPhU ($1703, 1533, 1247 \text{ cm}^{-1}$), of aniline ($3475, 3320, 1619, 1275 \text{ cm}^{-1}$), of phenylisocyanate (2275 cm^{-1}), of isocyanate trimer (1718 cm^{-1}) are present, similarly with 1,3-DPhU ($1646, 1533, 1230 \text{ cm}^{-1}$). The decomposition reactions that occur on heating in the melt phase are similar to those proposed for alkylureas, step (1) and (2) with $R = \text{C}_6\text{H}_5$; furthermore we have



and the trimer formation.

In Fig. 4b we have the IR spectra of the products obtained from heating of 1,3-DPhU; one can distinguish the strong bands of DPhU (1730 cm^{-1}), those due to aniline, phenylisocyanate, and isocyanate trimer. The decomposition that occurs is like (3) with $R = \text{C}_6\text{H}_5$.

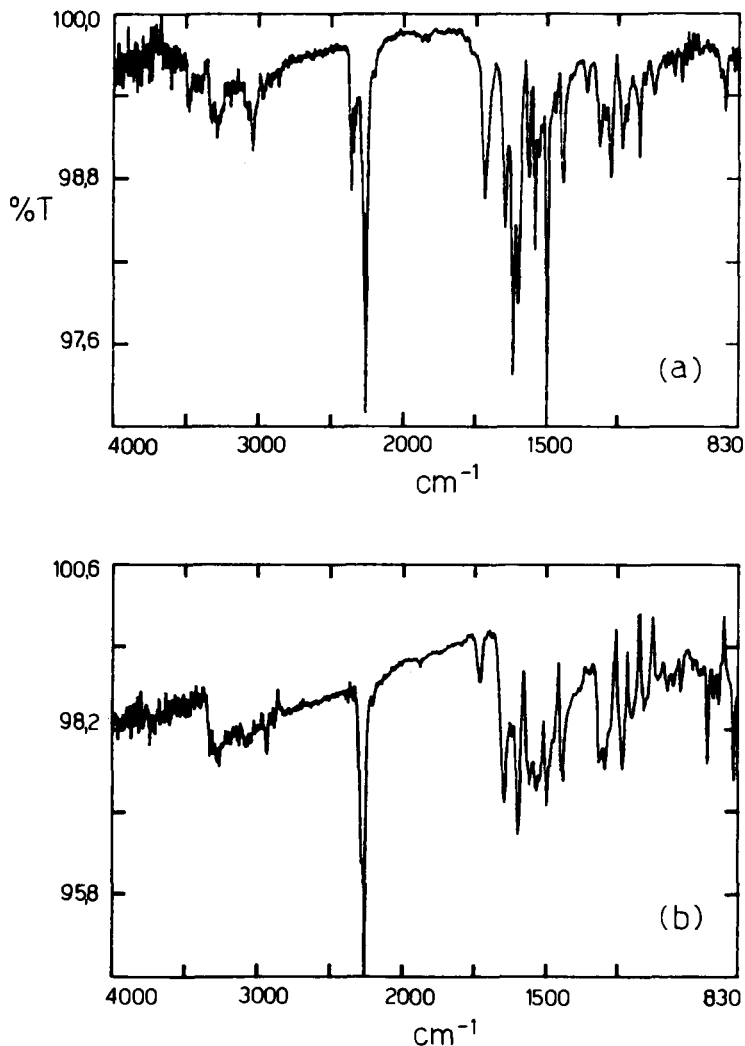


Fig. 4. I.R. spectra of the thermal decomposition products of MPhU (a) and of DPhU (b), in tetrachloride solution.

3. Conclusion

In trying to explain the difference in the thermal decomposition of aryl-ureas we suggest the following: i) MPhU is more associated in the melt than 1,3-DPhU (lower value of ΔS_m); in agreement with this hypothesis we remember that the IR spectra of CCl_4 solutions of 1,3-DPhU show the prevailing of *cis*-rotamer, which is usually connected to non relevant association of a secondary amide [12]; ii) as concerns the decomposition, the reaction enthalpy (ΔH_4) for step (1) with $\text{R} = \text{C}_6\text{H}_5$ is -107 kJ

mol^{-1} ; for step (2), $\Delta H_5 = +13 \text{ kJ mol}^{-1}$; for step [4] $\Delta H_6 = +22 \text{ kJ mol}^{-1}$; overall we should have a decomposition value of -72 kJ mol^{-1} for MPhU. For DPhU (step (3)) we should have $\Delta H_8 = -139 \text{ kJ mol}^{-1}$. Therefore we come to the surprising conclusion that the decomposition steps give an overall exothermic term but this is higher in the case of DPhU.

So the endothermic contribution (hydrogen bonds breaking) is greater for MPhU than for DPhU, the reverse is true for the exothermic terms: finally the algebraic sum of all these terms gives heat that just in a qualitative sense are consistent with the experimental values of Table 1.

So we have shown, comparing IR, TG and DSC analysis data, that the magnitude of amide hydrogen bonds seems to be determinant both for the entropy of fusion and for the enthalpy of vaporization of some alkyl-, aryl-ureas.

The question is complicated by the decomposition which sets up in competition with vaporization and which may follow different steps.

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