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A study of the thermal decomposition of urea, of related compounds and thiourea using DSC and TG–EGA

Luigi Stradella * and Massimo Argentero

Dipartimento di Chimica inorganica, Chimica fisica e Chimica dei materiali, Via P. Giuria 9, 10125 Turin (Italy)

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Abstract

The thermal decomposition of urea, of related compounds and of thiourea was investigated by means of TGA and DSC measurements together with evolved gas analysis (EGA), achieved by connecting an FTIR spectrometer to the outlet of the thermobalance. Biuret, ammelide and cyanuric acid were identified as intermediate compounds from their thermograms and IR spectra. An inexplicable exothermic phenomenon was detected during the decomposition of thiourea.

INTRODUCTION

Urea, thiourea and some of their substituted and derivative compounds are well-known chemicals that are of great importance in several fields of application [1–3]. However, the course of the thermal decomposition of these compounds is unclear [4–6]. In this paper, we report a TGA–DSC combined study on the thermal behaviour of urea, thiourea, biuret and cyanuric acid, together with an IR investigation of the volatiles evolved and of the solid residue formed during the decomposition process.

EXPERIMENTAL

The calorimetric measurements were performed with a Mettler DSC 20 differential scanning calorimeter; for the determination of the weight losses, a Mettler TG 50 thermogravimetric analyser was used.

The TG–IR analysis of the volatile products evolved during the decomposition and of the solid residues remaining at different sample temperatures was obtained by connecting a thermogravimetric analyser to an FTIR spectrometer (Perkin-Elmer, Mod. 1760-X).

Commercial purity urea, biuret and cyanuric acid samples were purified

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* Corresponding author.

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by successive crystallization processes. Thiourea was recrystallized from a water–methanol mixture and then washed with cold ethanol and cold ether.

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

RESULTS AND DISCUSSION

The enthalpies of melting and of decomposition of the investigated compounds, as obtained from the DSC curves, are given in Table 1.

TABLE 1

Enthalpy of fusion $\Delta_f H$ and of decomposition $\Delta_d H$ of urea, its related compounds, and thiourea

Substance	$\Delta_f H$ (kJ mol^{-1})	$\Delta_d H_1$ (J g^{-1})	$\Delta_d H_2$ (J g^{-1})	$\Delta_d H_3$ (kJ mol^{-1})
Urea	14.1 ± 0.1	172 [a]	41 [a]	166.0 ± 2.0
Biuret	28.8 ± 0.3	630 [a]	150 [a]	167.9 ± 2.0
Cyanuric acid				168.8 ± 2.0
Thiourea	16.0 ± 0.2	458 [a]	192 [a]	

[a] Computed from the initial weight of the sample.

Urea

It is well known that the DSC curve of urea shows four endothermic effects, the first of which is due to its melting [4]. Four net changes were observed in our DSC curve (not given here for simplicity), but it must be recalled that some authors report another endothermic effect before melting [7, 8]. Our TGA curve for urea shows three steps: the first 408–493 K with 69% weight loss, corresponds to the formation of biuret; the second (497–530 K) with 13.3% weight loss corresponds to the formation of cyanuric acid, to the decomposition of urea to ammonia and cyanic acid, and to the production of a small amount of ammelide [9]; the third (580–645 K) with 17.5% weight loss corresponds to the decomposition of cyanuric acid.

The enthalpy of fusion obtained (see Table 1) is smaller than the value reported in a recent compilation [10]: this discrepancy cannot be explained, either by assuming a spurious effect [11, 12] because we always used fresh sample, or by hypothesizing the initiation of decomposition. In fact, the weight loss was less than 1% at 423 K, while the melting process in the DSC curve is complete at 418 K.

The other heats given in Table 1 and relating to the decomposition of urea, will be discussed below in the section describing biuret.

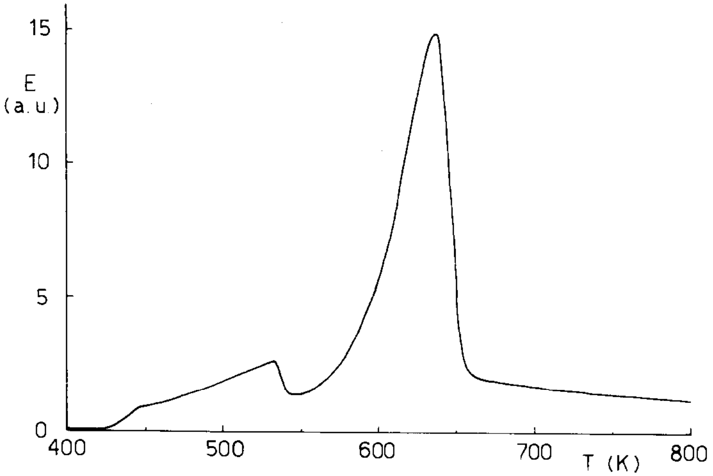


Fig. 1. FTIR integrated spectrum of the gas evolved from the thermobalance as a function of sample temperature.

Figure 1 shows an example of a TG/FTIR study. The curve was obtained by integrating the total IR signal from the volatiles evolved as a function of temperature. We observe an acceptable agreement between this type of thermogram and the classical DSC and TG decomposition curves for urea.

The IR analytical spectra of the volatiles evolved between 433 and 633 K are shown in Figs. 2 and 3. Figure 2(a) shows the typical group frequencies (2250, 2280, 3530 cm^{-1}) of cyanic acid [13], the typical bands of NH_3 [14] and the bands of CO_2 [15].

The absorption bands of Fig. 2(a) were measured at 433 K, the temperature at which the decomposition process becomes measurable. This temperature, however, is somewhat different from that given by other authors [4, 5], but the discrepancy may be due to different geometry in the TG apparatus.

The ammonia produced mainly derives from the decomposition of urea and from the reaction of biuret, whose presence was confirmed by IR analysis of the residue at this stage of the decomposition (see Fig. 4 and related discussion below). Ammonia may also be produced from the reaction

$$HNCO + H_2O \rightleftharpoons CO_2 + NH_3 \qquad (1)$$

which also accounts for the appearance of carbon dioxide. No CO was detected in the gas phase, as was reported in ref. 5. We suggest that the origin of the water for this reaction, in addition to the hypothesis given in ref. 4, may be a side reaction of ammonia with the enolic form of urea or of analogous keto compounds to produce guanidine, which may lead to ammelide [6]. Another possibility is the reaction of cyanic acid with biuret

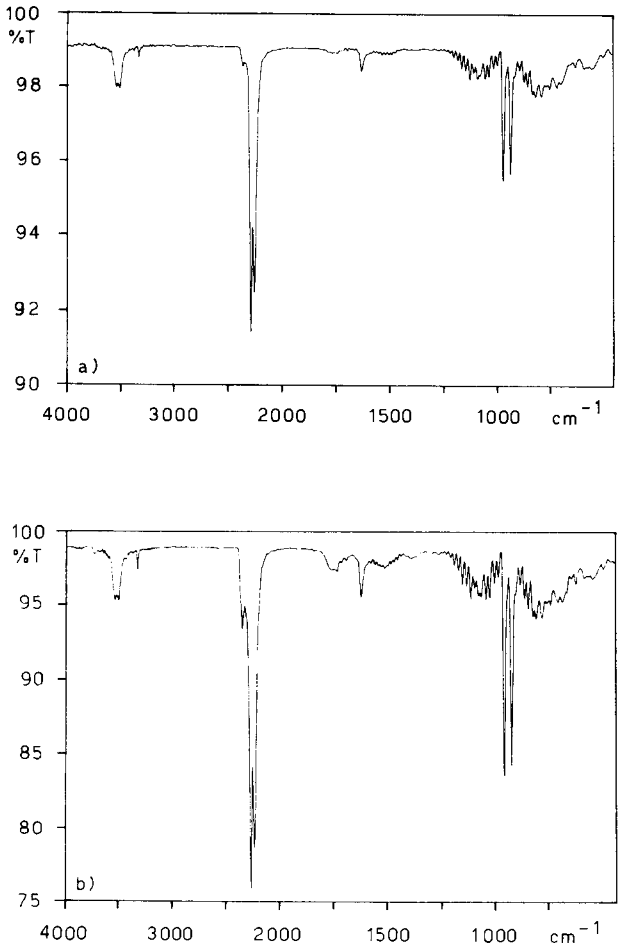


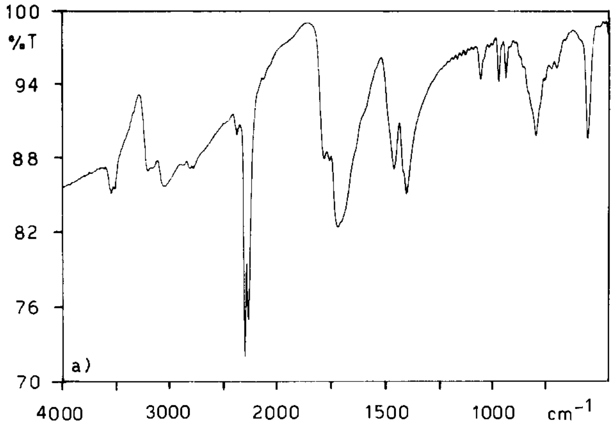
Fig. 2. IR spectra of the gaseous products at different sample temperatures: (a) 433 K; (b) 518 K.

to give ammelide and water [9]. One must, however, assume that all these reactions are quantitative, because at 433 K and at other temperatures, no water was detected in the gaseous phase.

At 518 K, (Fig. 2b), cyanic acid and ammonia are still being evolved but the increase of the absorption intensity appears greater for the latter than for the former: this observation is in qualitative agreement with the fact that the decomposition of biuret produces cyanic acid and ammonia, while the polymerization to cyanuric acid consumes cyanic acid.

Figure 4 shows the IR spectra of the solid residue obtained at different temperatures (493, 513, 533 K) for the typical absorption bands of biuret, ammelide and cyanic acid.

The evolution of these bands as a function of temperature may be interpreted with reference to the main chemical processes occurring: (i) the



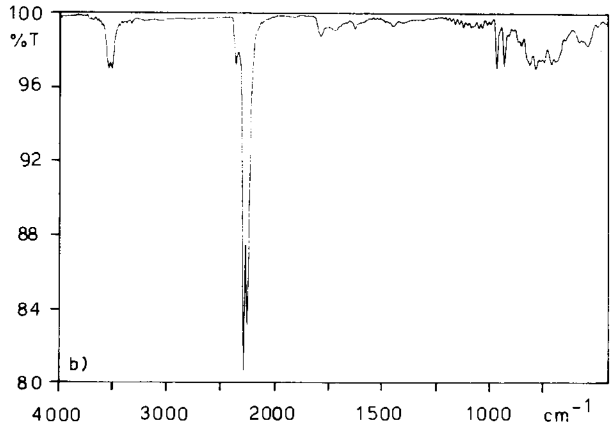


Fig. 3. IR spectra of the gaseous products at different sample temperatures: (a) 603 K; (b) 633 K.

decomposition of biuret, whose band (1081 cm^{-1}) decreases monotonically; (ii) the reaction of biuret and cyanic acid to give ammelide (1073 cm^{-1}), whose concentration increases up to 523 K, after which ammelide becomes unstable and its decomposition products predominate; (iii) the formation of cyanuric acid (1053 cm^{-1}) from 490 K, becoming the only stable species up to 620 K.

At 603 K, Fig. 3(a), the IR spectrum shows bands typical of sublimated cyanuric acid (1778, 1703, 1053, 764 cm^{-1}) [16] and those of its decomposition products. NH_3 and CO_2 are still present, probably as products of reaction (1).

At 633 K, Fig. 3(b), the rate of depolymerization of cyanuric acid becomes greater than the sublimation rate and only bands of cyanic acid, which continues to react partly according to reaction (1), are observed. The

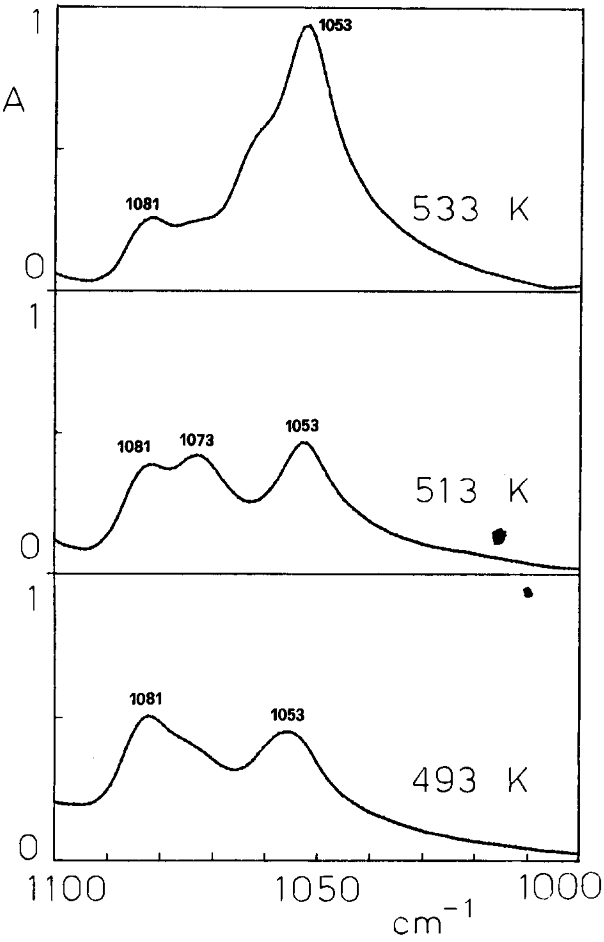


Fig. 4. Evolution of the IR absorption bands of biuret (1081 cm^{-1}), ammelide (1073 cm^{-1}) and cyanuric acid (1053 cm^{-1}) at different sample temperatures.

TGA data corroborate the scheme deduced from the IR spectral data, see below.

Biuret and cyanuric acid

TGA–EGA and DSC studies were performed on pure biuret and pure cyanuric acid to confirm the results described above. From the data presented in Fig. 5(a) and (b) and in Table 1, we can deduce the following:

(i) Biuret melts at 466.6 K, absorbing 28.8 kJ mol^{-1}, without noticeable decomposition (the average weight loss when fusion is complete is less than 1%).

(ii) The second endothermic effect is centred at 513.1 K, with a heat value of 630 J g^{-1} ($\Delta_d H_1$).

(iii) The third endotherm at 530.2 K, heat value 150 J g^{-1} ($\Delta_d H_2$), seems to

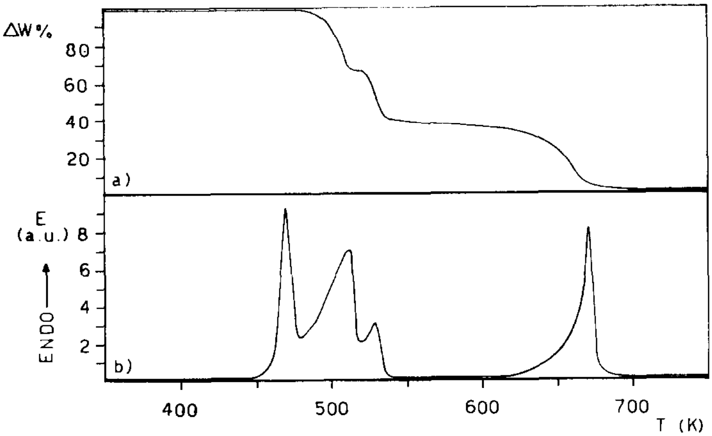


Fig. 5. TGA (a) and DSC (b) curves for the thermal decomposition of biuret.

correspond to the decomposition of biuret to cyanic acid and ammonia, and to the formation of cyanuric acid and small amounts of ammelide. These processes are overlapping but the formation of cyanuric acid seems to become prevalent at higher temperature, as might be deduced from the fact that the second weight loss is smaller than the expected according to the stoichiometry of these reactions. Some of the IR analyses agree with this interpretation (see Fig. 4 and related discussion). The same heats of decomposition, $\Delta_d H_1$, $\Delta_d H_2$, $\Delta_d H_3$ (within an experimental error of 5%), have been deduced for urea as well as for biuret, remembering that less than one sixth of the former is converted into the latter.

(iv) The fourth endothermic effect corresponds to the final decomposition of cyanuric acid with no solid residue; this is in disagreement with the results of other authors [5]. This also occurs with pure cyanuric acid, Fig. 6(a). From a comparison of the energy associated with this peak

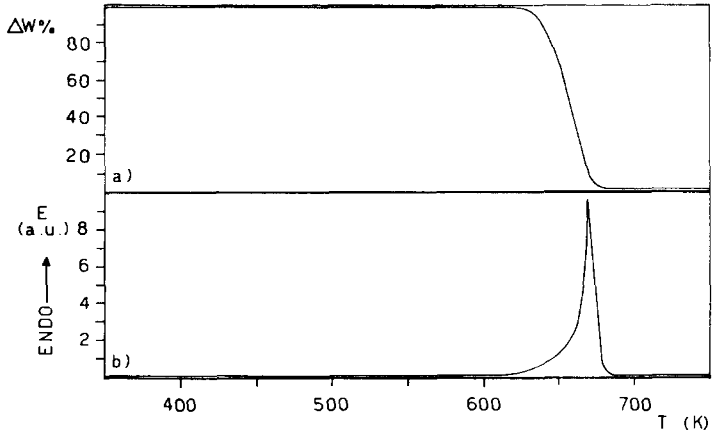


Fig. 6. TGA (a) and DSC (b) curves for the thermal decomposition of cyanuric acid.

with that obtained from pure cyanuric acid, Figs. 5(b) and 6(b), one may deduce that about 50% of the biuret has converted to cyanuric acid and then decomposed. The TGA data also agree with this hypothesis, within experimental error. Furthermore, the molar heat of decomposition of cyanuric acid remains constant in the series of related compounds, Table 1.

Incidentally, these data suggest that it is possible to determine the composition of urea–biuret mixtures from a TGA or DSC analysis, keeping the experimental conditions strictly unchanged [17].

Thiourea

Figure 7(a) and (b) show the TGA and DSC curves of thiourea. The enthalpy of melting, measured over five runs, has an average value of 16.0 ± 0.2 kJ mol^{-1} with a weight loss of 0.6%. This value for the enthalpy of fusion is significantly higher than that reported in the literature [18]. On heating thiourea beyond its melting point, the decomposition processes begin with a net weight loss. Two overlapping exotherms are present along with a very sharp exotherm. Above 600 K a further endotherm is present. The nature of these is obscure (isomerization of some intermediates or intramolecular redox reactions may take place). A yellow residue was obtained at 750 K. Unfortunately, some of the FTIR spectra of the volatile products and of the solid residue could not be interpreted.

In conclusion, we consider that the coupling of an FTIR spectrometer with a TGA apparatus makes an important contribution to the identification of stable intermediates and volatile products in thermal decomposition studies.

However, further IR data are needed to interpret the decomposition of

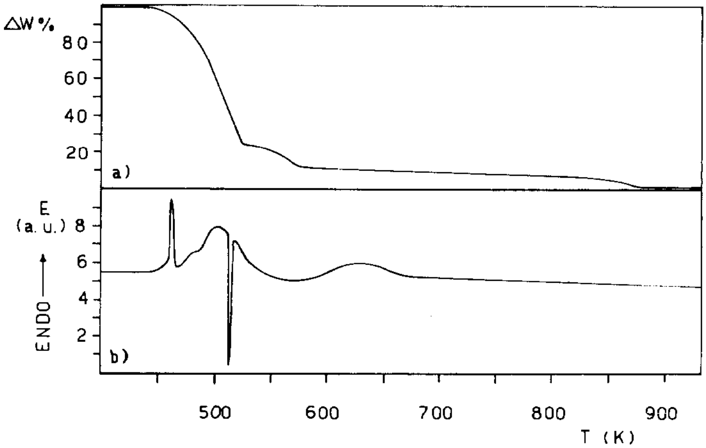


Fig. 7. TGA (a) and DSC (b) curves for the thermal decomposition of thiourea.

thiourea and analogous systems because current spectral data do not allow an unequivocable assignment of the absorption bands.

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