

Thermal decomposition (pyrolysis) of urea in an open reaction vessel

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Abstract

A study was done of the thermal decomposition of urea under open reaction vessel conditions by thermogravimetric analysis (TGA), high performance liquid chromatography (HPLC), Fourier transform-infrared (FT-IR), and an ammonium ion-selective electrode (ISE). Both evolved gases and urea residue were analyzed, and profiles of substances present versus temperature are given. Major reaction intermediates are also identified. Plausible reaction schemes based on product distribution in relation to temperature are proposed. Our data indicate that at temperatures in excess of 190 °C, cyanuric acid (CYA), ammeline and ammeline are produced primarily from biuret. Biuret itself is a result of prior reaction of cyanic acid, HNCO, with intact urea. Cyanic acid is primarily a result of urea decomposition at temperatures in excess of 152 °C. CYA and ammeline first appear at approximately 175 °C, but the reaction rate is very slow. At temperatures in excess of 193 °C, alternate reactions involving the decomposition of biuret substantially increases reaction rates. Several parallel processes compete for the production of products. Production of CYA, ammeline and ammeline appears complete at 250 °C, after which sublimation and eventual decomposition of products occurs.

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1. Introduction

The thermal decomposition (pyrolysis) of urea to produce cyanuric acid (CYA: 2,4,6-trihydroxy-1,3,5-triazine) was discovered by Wöhler approximately 175 years ago [1]. Details of the reaction mechanism have been studied for many years and recently a plausible temperature dependent reaction scheme, based primarily on product distribution, has been proposed [2]. It is apparent that this reaction proceeds by a very complex and diverse pathway. For example, it is known that the primary decomposition products exhibit high reactivity and undergo a series of secondary reactions. Reaction conditions such as temperature, heating time, closed or open reaction vessel, atmosphere make-up and pressure, have all been shown to affect the outcome of this reaction process in terms of total product distribution and intermediates observed [2–15]. Pyrolysis of urea is not

just a topic of academic concern. The industrial production of CYA from urea is a widely used process and one that has been practiced for several decades. Industrial interest in CYA is based on its widespread use as a precursor for the production of disinfectants, sanitizers, bleaches and herbicides [16]. In addition, ammonia generated from urea decomposition is currently being considered by the diesel engine industry in an effort to develop a selective NO_x catalytic reduction process (to nitrogen and water) for engine exhaust. There is present, continuing, and growing interest in the details of this reaction and its associated mechanism.

Stradella and Argentero [12] recently published a study on the thermal decomposition of urea and related compounds with TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) measurements, together with EGA (evolved gas analysis). Chen and Isa [13], and Carp [15] published related studies using simultaneous TGA, DTA, and MS (mass spectroscopy). These studies focus on the decomposition of urea under purge gas (Ar, He or air) conditions. Tracking of residue species and accounting for the production of by-products such as ammeline

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and ammelide and accompanying synthetic details, were not included in these reports. In this study, an analysis of urea decomposition under open reaction vessel conditions utilizing TGA, high performance liquid chromatography (HPLC), Fourier transform-infra red (FT-IR), and an ammonium ion-selective electrode (ISE), is reported. Both evolved gases and urea residue were analyzed and profiles of substances present versus temperature are given. Major reaction intermediates are identified. Although others are considered, plausible reaction schemes based on product distribution in relation to temperature, favoring those with observable intermediates, are proposed.

2. Experimental

Urea was obtained from Aldrich Chemical Co., Milwaukee, WI (99% pure, ACS reagent grade), and used without further purification. Biuret was obtained from Fisher Scientific Co., Pittsburgh, PA (99.9% pure, ACS reagent grade) and also used without further purification. CYA, ammelide, ammeline, and melamine were obtained from OxyChem's industrial process and purified in-house.

Urea residue in an open reaction vessel was obtained by heating 3.0 g samples of urea in a 10 mL Pyrex™ beaker on a sand bath until the desired temperature was reached. The sample was then quickly cooled to room temperature in a water bath and the residue collected.

Chromatographic analyses of urea residues were conducted with HPLC methods previously described in the literature [2]. Samples were analyzed for the presence of urea, biuret, CYA, ammelide, ammeline and melamine. An HPLC Mass Table (Table 1) and an HPLC Mass Plot (Fig. 1) were constructed from the data obtained.

Thermogravimetric analysis (TGA) and measurements of mass losses (and the 1st derivative) versus temperature were determined using a Hi-Res TGA 2950 Thermogravimetric Analyzer under N₂ (g) purge. The “high resolution” option was routinely used. Typically, 30–50 mg of sample was placed on a Pt pan and heated at 10 °C min⁻¹. Urea “critical temperatures”, defined as those temperatures corresponding to plateau regions, points of rapidly changing mass, or where phase changes are known to occur (melting points, etc.), were identified from the TGA data plot (Fig. 2).

Table 1
HPLC Mass Table (urea pyrolysis) open reaction vessel^a

Temperature (°C)	Mass (g)	Urea (g)	Biuret (g)	CYA (g)	Ammelide (g)	Ammeline (g)	Melamine (g)	Total % recovery
133	100.0	98.7	1.0	–	–	–	–	99.7
190	80.0	60.5	20.0	0.6	0.5	–	–	102.0
225	33.0	6.0	4.6	15.6	6.1	0.9	–	100.5
250	29.0	0.3	0.2	19.9	7.7	1.3	0.058	101.4
275	28.0	0.5	0.3	18.9	7.5	1.3	0.056	102.3
320	20.0	–	–	12.1	4.9	1.1	0.044	90.7
350	5.0	–	–	3.1	1.0	0.5	0.100	94.0

^a These data were calculated based on the results obtained from HPLC analysis assuming 100.0 g of urea initially present.

Table 2

Urea pyrolysis residue analysis; ammonium ion (NH₄⁺) analysis with an ion-selective electrode^a

Temperature (°C)	Concentration of NH ₄ ⁺ ion (ppm)
133	70
190	380
225	2600
250	260
275	150
325	120
350	90

^a Results in ppm are based upon the mass of the original sample.

Table 3

Urea pyrolysis off-gas; ammonium ion (NH₄⁺) analysis with an ion-selective electrode^a

Temperature range (°C)	Concentration of NH ₄ ⁺ ion (ppm)
Room temperature to 133	210
133–210	11900
210–225	8500
225–255	1210
255–350	5200
350–400	450

^a Results in ppm are based upon the mass of the original sample.

Ammonium ion [NH₄⁺] analysis of both urea residue and pyrolysis off-gases were accomplished using an ammonium ISE (Orion, Beverly, MA). Typically for urea residues, a 1% aqueous solution was made and analyzed. Resultant concentration versus temperature data are collected in Table 2. Urea pyrolysis off-gases were generated by placing a 3.0 g sample of urea in a three-neck round bottom flask fitted with a thermometer, a thermal watch device, a N₂ (g) purge, and an NH₃ (g) scrubber (gas trap) consisting of 50.0 mL of 12.0 M HCl. As the urea sample was heated, the gases that evolved between the desired “critical temperature” points were allowed to pass through the scrubber and collected. Ammonium ion analysis was conducted on diluted scrubber solutions. Results are collected in Table 3.

FT-IR spectra of the urea melt were collected using the Applied Systems Inc. (ASI) REACT-1000 system (ASI SensIR Technologies, Danbury, CT), fitted with a sili-con (Si) probe. A spectrum was acquired every 2 min as

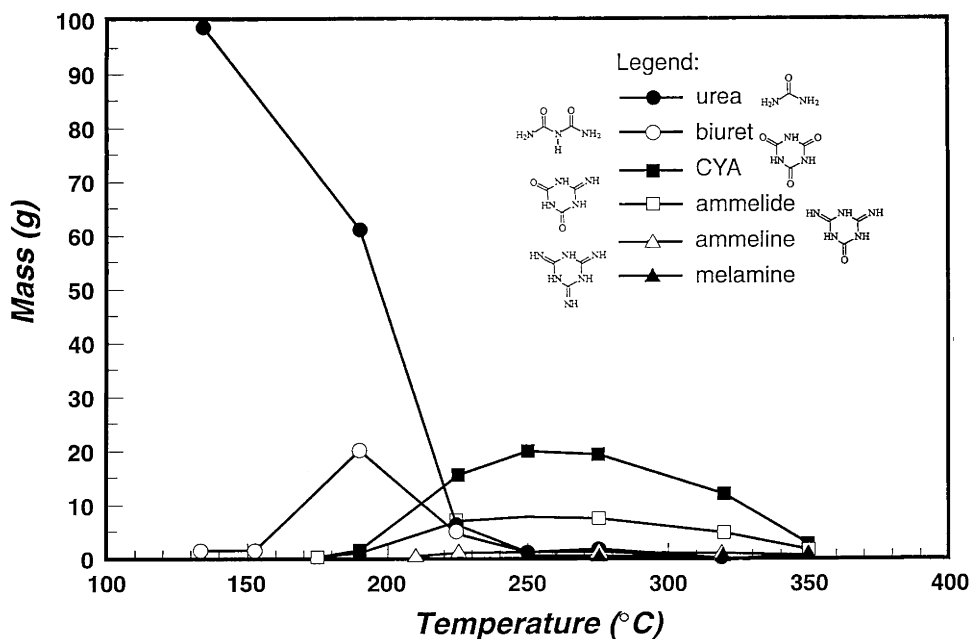


Fig. 1. HPLC Mass Plot: urea pyrolysis reaction (assume 100.0 g of urea initially).

“critical temperature” points, between 133 and 225 °C, were ramped to and held with the aid of an Omega thermocouple (Fig. 3). Qualitative analysis was performed using the REACT-1000 soft-ware package supplied by ASI. Analy-

sis of urea pyrolysis off-gases were conducted by placing a 1.0 g sample of urea into a glass vial and inserting into a tube furnace fitted with a N₂ (g) purge and gas collection adapter. The urea sample was heated to the desired

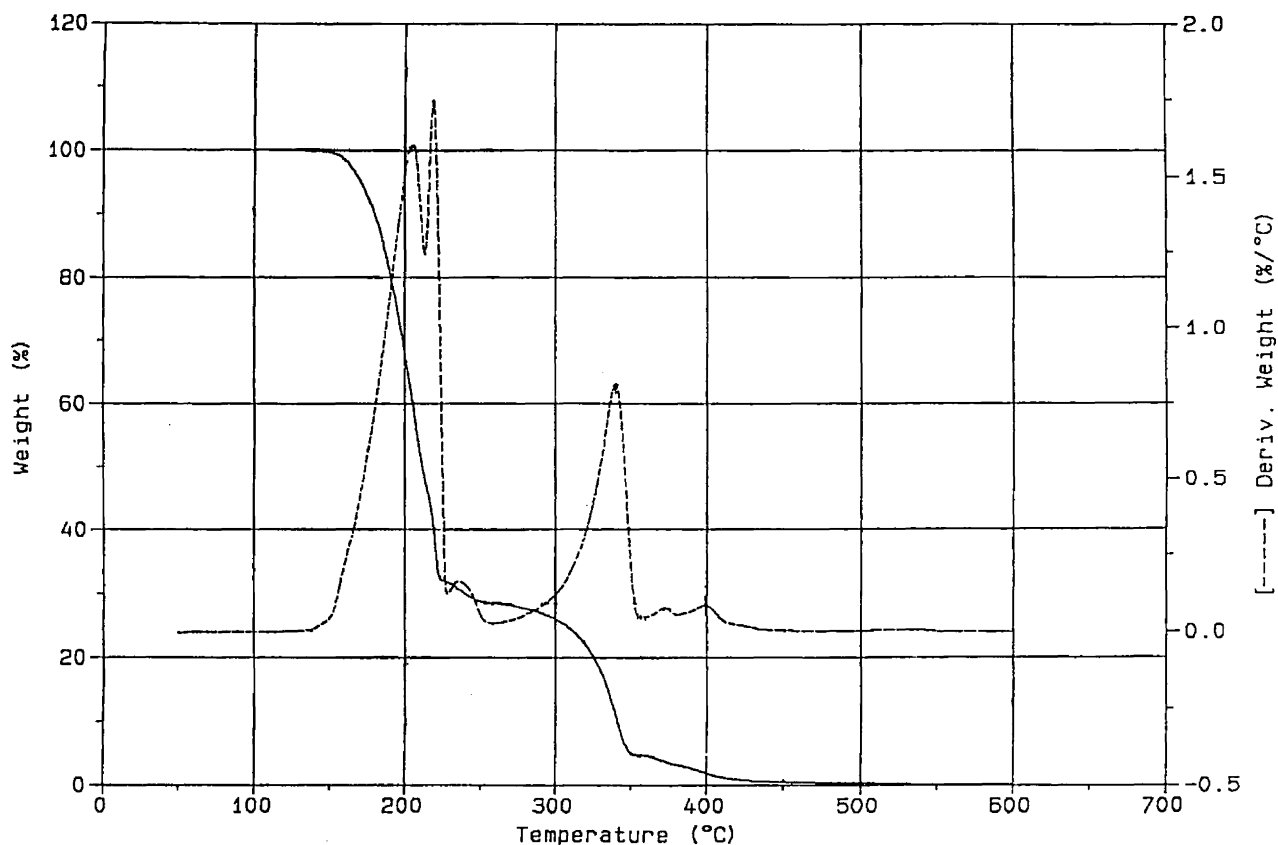


Fig. 2. TGA: urea pyrolysis reaction.

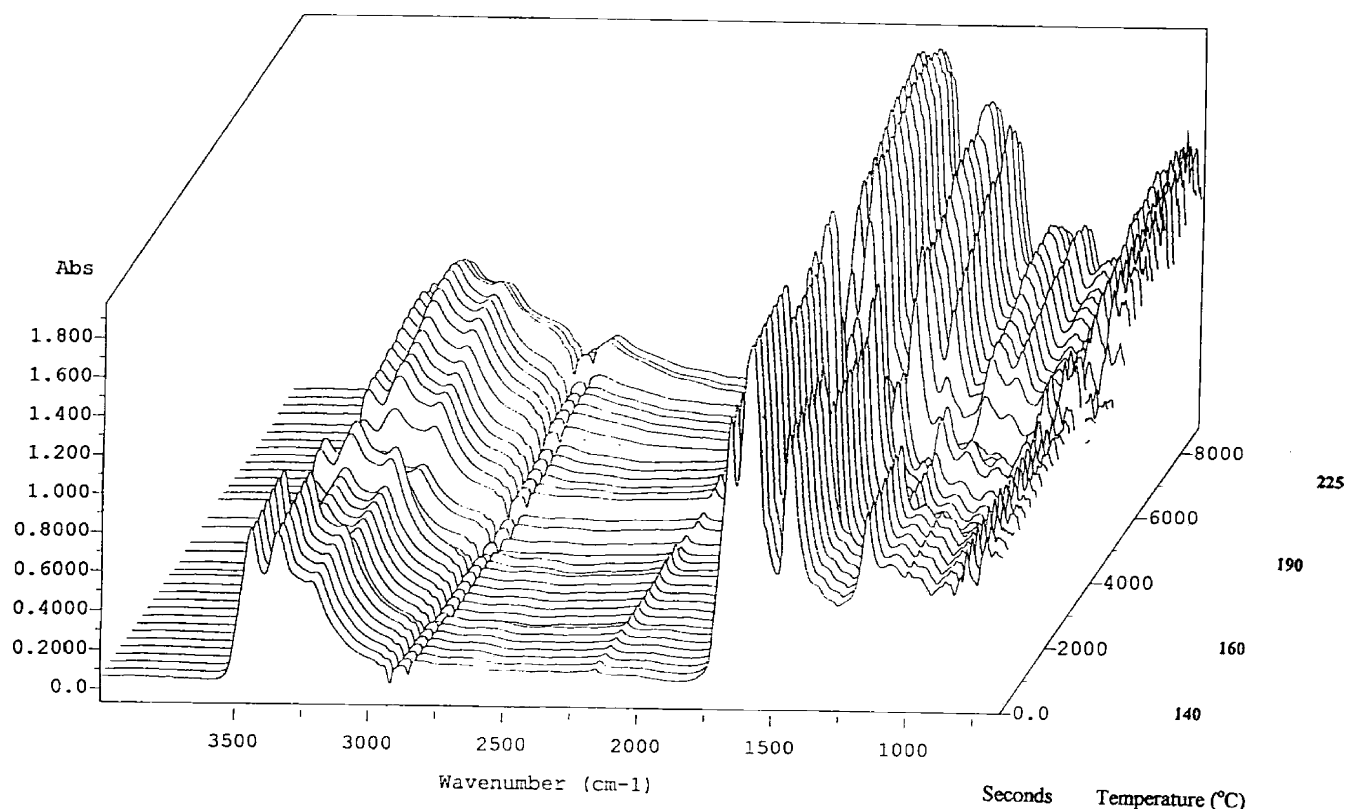


Fig. 3. FT-IR Si-probe spectra: urea pyrolysis reaction.

“critical temperature” and held there for several minutes with the aid of a thermal watch device. Evolved gases were subsequently swept into an IR gas cell fitted with NaCl windows. FT-IR spectra of urea off-gases were obtained with a Nicolet 20 SXB Spectrometer (Nicolet, Madison, WI). Condensed materials adhering to the surface of the gas collection adapter were collected and subjected to melting point determination with a 510 Melting Point apparatus (Brinkmann Instruments, Inc., Westbury, NY), and HPLC analysis using methods previously referenced in this section.

3. Results and discussion

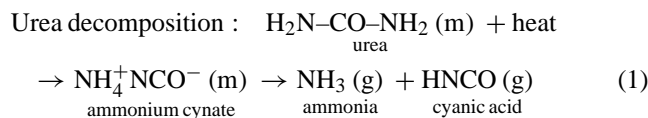
3.1. Process overview

The TGA of urea measured with a heating rate of $10^{\circ}\text{C min}^{-1}$ under N_2 (g) purge between 50 and 600°C is given in Fig. 2. Three major stages of mass loss are observed and calculated to be approximately 72, 24, and 4%. The pyrolysis reaction of urea in an open reaction vessel can be divided into four major “reaction” regions. “Reaction” regions are dominated by different chemical processes associated with the mass loss stages observed in the TGA. What follows is a detailed description of the chemical process in each of the urea pyrolysis “reaction” regions.

3.2. First “reaction” region (room temperature to 190°C)

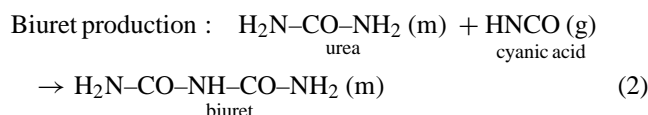
Little significant mass loss (0.01%) is observed when heating urea in an open reaction vessel from room temperature to its melting point 133°C . HPLC analysis of the residue at the melting point, gives 98.7% urea and 1.0% biuret (Table 1). The biuret present at this point primarily represents contamination in the original sample. Only a small relative amount of $[\text{NH}_4^+]$ ion is observed in both the residue and off-gas analysis (Tables 2 and 3) and a very small $[\text{NCO}^-]$ absorption peak at 2156 cm^{-1} is noted in the FT-IR spectra (Si-probe) of the melt (Fig. 3). These observations are consistent with a very small amount of urea decomposition and vaporization. Recently, Chen and Isa [13] have also observed only a small mass change prior to urea’s melting point, which is consistent with our data.

Mass loss begins in earnest at approximately 140°C as observed from the TGA (Fig. 2). The loss observed between 140 and 152°C , is associated primarily with urea vaporization. (Condensed material adhering to the surface walls of the gas collection adapter (see Section 2), in this temperature range was identified as urea from melting point and HPLC determinations.) A more significant mass loss is observed between approximately 152 and 160°C and proceeds via two processes; continued urea vaporization and decomposition [9].

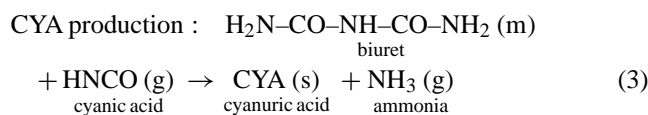


At 152 °C decomposition begins [4], Eq. (1), accompanied by vigorous gas evolution from the melt. Above 152 °C the decomposition rate of urea increases rapidly. At 160 °C, the FT-IR Si-probe spectra of the melt, indicates an increase in intensity of the [NCO⁻] peak from that observed at 140 °C (Fig. 3). The FT-IR spectrum of gases evolved at 160 °C indicates the strong presence of NH₃ (g) (peaks at 3333, 965 and 930 cm⁻¹), but little discernible HNCO (g). Stradella and Argentero [12] have, however, observed HNCO (g) in the evolved gases at this temperature. Chen and Isa [13], and Carp [15] have also identified evidence of HNCO (g) production in their studies. That the ammonium cyanate salt, [NH₄⁺NCO⁻], is formed as an intermediate in Eq. (1) has recently been confirmed by Carp [15]. These data are all consistent with urea's initial decomposition to [NH₄⁺NCO⁻], which itself decomposes resulting in the evolution of NH₃ (g) and HNCO (g).

A product of urea decomposition, HNCO, begins to react with intact urea to produce biuret at approximately 160 °C, Eq. (2).¹ This is supported by an increase in the intensity of a peak unique to biuret at 1324 cm⁻¹, in the FT-IR Si-probe spectra (Fig. 3).



Between 160 and 190 °C urea continues to vaporize and decompose and HNCO, continues to react with intact urea to produce biuret. However, complications also begin to enter the system in this temperature range. A small amount of HNCO can now begin to react with biuret [10], Eq. (3), or itself, Eq. (4), to produce CYA, or with urea, Eq. (5), to produce ammelide. From the FT-IR Si-probe data, it appears that the production of both CYA and ammelide commence simultaneously at approximately 175 °C. This is supported by an increase in the intensity of respective peaks unique to CYA at 1058 cm⁻¹, and ammelide, at 977 cm⁻¹, in the FT-IR Si-probe spectra (Fig. 3).

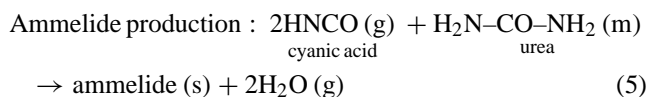


via Eq. (4) is a reasonable candidate and one that has been known experimentally for many years. Herzberg and Reid

[17] have observed that if HNCO (g) exceeds a critical vapor pressure,

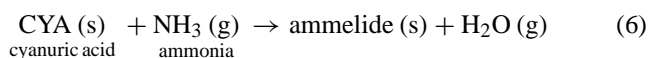


spontaneous and rapid polymerization to CYA can occur. This critical vapor pressure can be quite low, especially in the presence of a metal surface.² Another potential route to CYA involves the cyclicization of triuret (H₂N-CO-NH-CO-NH-CO-NH₂) with the evolution of NH₃ [3]. Chen and Isa [13] identify the existence of urea trimer under TGA conditions. However, since no triuret is observed in these studies, its existence under open reaction vessel conditions is questionable.

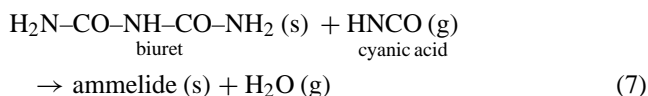


The intermediate for Eq. (5) could be either biuret, via Eq. (2), or dicyanic acid (H₂N₂C₂O₂). Biuret is observed in the reaction sequence and if it also serves as an intermediate to ammelide, Eq. (5) is then very similar in essence to that represented in Eq. (7). Dicyanic acid would be very unstable at these temperatures and if behaving as the intermediate, would not be expected to accumulate to a significant extent. However, since not a hint of dicyanic acid was detected in this study, its contribution to ammelide production is questionable under the reaction conditions imposed.

The conceptually simplest route to ammelide involves the direct reaction of CYA with available NH₃ (amination), Eq. (6). This is a seeming logical path but one that has been determined to occur only under conditions of high pressure [18] or temperatures above 300 °C [19]. In the industrial preparation of CYA using a kiln, less ammelide is in general,



produced when NH₃ is removed from the system. Although this would seem consistent with Eq. (6), the situation is likely more reflective of the different environmental aspects of laboratory versus industrial preparation of CYA, where temperature gradients in the kiln may produce conditions favorable to the production of ammelide in this fashion. A more likely laboratory route is one that parallels the formation of CYA, that is, the direct reaction of biuret with HNCO, Eq. (7), but with the formation of ammelide [20,21]. Other possible routes to ammelide have been suggested, however, they



¹ The actual reaction to form biuret likely involves the interaction of urea with [NCO⁻] in the melt [11]. The form of the equation used here is for convenience, and will be used throughout this document. However, it should be realized that reactions in the melt involving HNCO are likely to proceed via [NCO⁻] interaction.

² Under TGA conditions, or with the use of a purge gas, this route is expected to be somewhat curtailed. However, Eq. (4) may be significant in the industrial preparation of CYA where metal kilns are often used.

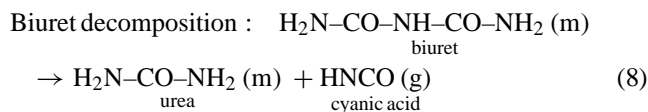
typically require the presence of a precursor such as amidated bi- or triuret, guanidine [10], or cyanamide [19]. These proposed precursor species are stable in this “reaction” region and if present, evidence of their existence would be expected. Our HPLC data give no indication any exist in measurable amounts in the residue (see Table 1; note approximately 100% recoveries at these temperatures), nor are any detected in the FT-IR data.

Under the conditions imposed, the reaction scheme most likely to produce ammelide, Eq. (7), operates in parallel to the one most likely to produce CYA, Eq. (3). Both products are produced at about the same overall rate, and begin to appear at approximately the same temperature (175 °C). This suggests the reactions producing them share common reactants, (i.e. biuret and HNCO) and possess similar activation energies. In addition, since relatively small amounts of CYA and ammelide are observed in the residue (Table 1), whatever route adapted, reaction rates are rather sluggish for their production in this temperature range.

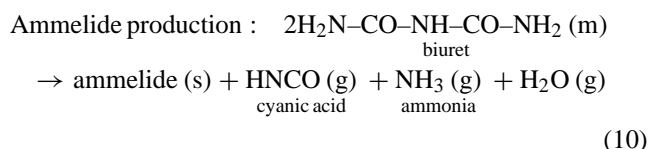
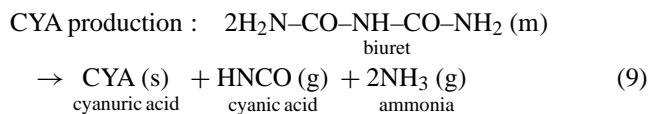
Up to 190 °C, the net mass loss for the system is predominately the result of urea decomposition. By this same temperature, urea mass has decreased by 38.2%, biuret mass has increased by 19.0% and has reached a maximum according to HPLC analysis (Table 1). The FT-IR of evolved gases is dominated by NH₃ due primarily to the continual and increased decomposition rate of urea. Peaks in the 2100–2300 cm⁻¹ region indicate the presence of HNCO, or of volatile salts of HNCO³ such as ammonium cyanate, [NH₄⁺NCO⁻], or hydronium cyanate, [H₃O⁺NCO⁻] [22]. Continued build up of [NH₄⁺NCO⁻] in the melt is indicated by both the FT-IR Si-probe data (Fig. 3), and the [NH₄⁺] ion analysis of the residue (Table 2). However, although building, the amount of [NH₄⁺] ion in the residue (380 ppm) is still not significantly large. These data indicate that much of the NH₃ formed escapes the system without further reaction and that HNCO has either reacted to produce biuret, CYA, or ammelide, or escaped the system in the vapor form. In addition, the vaporization of volatile HNCO salts, has just begun.

3.3. Second “reaction” region (between 190 and 250 °C)

As temperature exceeds 190 °C, alternate reaction sequences begin to dominate the process. At approximately 193 °C, the increased evolution of gases from the urea melt reflects the beginning of biuret decomposition (biuret melts with decomposition at 193 °C), Eq. (8). A corresponding mass maximum for biuret (Table 1), and 1st derivative peak in the urea TGA near this temperature are observed (Fig. 2). However, the gas evolution rate increase is not only the result of biuret and continuing urea decomposition.



(The urea produced by biuret decomposition in Eq. (8), is unstable in this “reaction” region and will itself decompose further to HNCO (g) and NH₃ (g), Eq. (1)). It also results from gas producing, auto-condensation reactions associated with biuret decomposition, Eqs. (9) and (10), to produce CYA and ammelide.



Although Eqs. (3), (4) and (9) all contribute to the production of CYA, Eq. (3) is expected to predominate at lower temperatures [9] (first “reaction” region), Eqs. (4) and (9) become more competitive at higher temperatures (second “reaction” region) where biuret begins to decompose. It is also expected that Eq. (4) will begin to play an increased role in CYA production if, or when, critical vapor pressure is achieved [17]. A similar situation exists with respect to the production of ammelide. Eq. (7) is expected to predominate at lower temperatures (first “reaction” region), Eq. (10) above 193 °C (second “reaction” region). However, only small amounts of CYA and ammelide are observed prior to the decomposition temperature of biuret. At this point the production rate for both CYA and ammelide increase rapidly. The close relationship between the onset of biuret decomposition and increased production rates suggests that both CYA and ammelide are produced largely from biuret and in parallel fashion within the second “reaction” region [8]. In addition, Eqs. (9) and (10) involve stoichiometric larger amounts of gaseous products than reaction candidates previously considered. The large increase in gas evolution physically observed in the urea melt above 193 °C and the large amount of [NH₄⁺] detected (11,900 ppm) in the pyrolysis off-gas analysis between 133 and 210 °C (Table 3) are consistent with both continued urea and biuret decomposition and the production of CYA and ammelide by kinetically faster mechanisms. TGA and DTA data collected on biuret itself indicates ready transformation to CYA upon heating [8,23]. Stradella and Argentero [12] estimate that about 50% of biuret is converted to CYA. At temperatures exceeding the melting point of biuret, conversion to CYA most probably involves Eqs. (4) and (9). At lower temperatures an alternative reaction path, be it minor, is one reminiscent of the production of CYA from urea and involves the initial decomposition of biuret to urea and HNCO.

³ In our studies, unequivocal identification of the HNCO salts cannot be made at this temperature due to poor resolution in this region of the FT-IR spectrum.

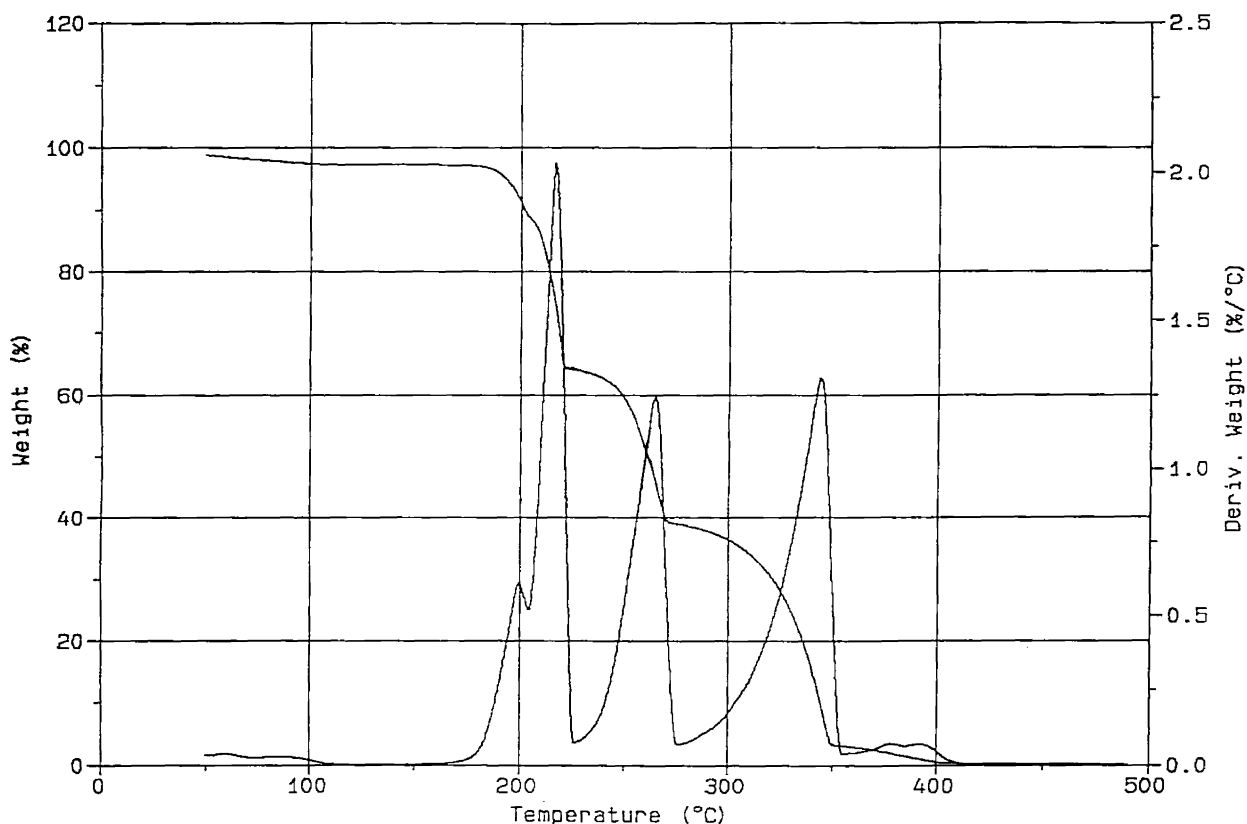
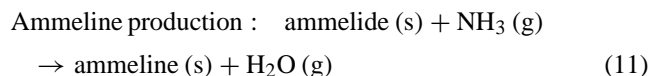


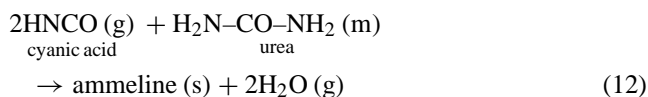
Fig. 4. TGA: biuret pyrolysis reaction.

(Although the melting point of biuret is 193 °C, our TGA analysis indicates mass loss prior to this temperature (Fig. 4). These data are consistent with other investigators including Nelson et al. [8,23]). Biuret decomposition is followed by reaction of intact biuret with HNCO to produce CYA as in the urea process.

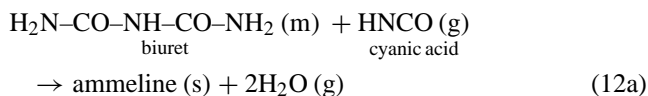
The beginning of ammeline production is also observed in the second “reaction” region as noted by its detection in the HPLC analysis of the residue at 250 °C (Table 1). Although CYA and ammeline are most likely produced via parallel processes, ammeline could be produced either by amination of ammeline, Eq. (11), or as suggested by Haeffele et al. [20], by the direct reaction between HNCO and remaining urea, Eq. (12), or some modification thereof. No other species is detected in our analysis that could serve as a precursor to ammeline. However, at all temperatures up to 350 °C, the mass amounts of ammeline exceed ammeline in the residue (Table 1). Although this is not proof of a linear process, it has been used as supporting evidence [24]. As previously mentioned, however, amination reactions are only likely to occur at elevated pressures [18] or temperatures [19]. The intermediate for Eq. (12) is most likely biuret.



or



If this occurs, Eq. (12) can be written in the following combined form assuming the previous occurrence of Eq. (2). This is a very likely scenario.⁴



The evolution of gases begins to visibly slow as a white precipitate forms at temperatures exceeding 210 °C. Conversion of the melt into a “sticky” solid matrix is complete at 225 °C, and CYA becomes the major component of the residue. Analysis of trapped off-gases for [NH₄⁺] ion collected between 210 and 225 °C, gives 8500 ppm (Table 3). This is an indication that decomposition of urea and biuret

⁴ Eq. (12a) is very similar to Eqs. (3) and (7). The latter two reactions are relatively slow and most likely continue to be so even at elevated temperatures. Eq. (12a) is probably even slower than either Eq. (3) or Eq. (7) at all temperatures, and is likely the reason ammeline is not observed until this point. (Biuret + HNCO reaction rates: Eq. (3) producing CYA > Eq. (7) producing ammeline > Eq. (12a) producing ammeline.)

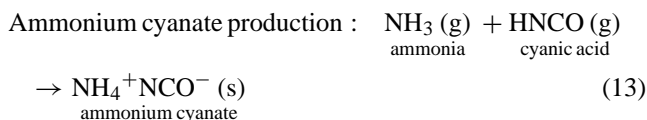
Table 4
HPLC Mass Table (biuret pyrolysis)^a

Temperature (°C)	Mass (g)	Biuret (g)	CYA (g)	Ammelide (g)	Ammeline (g)	Melamine (g)	Total (%) recovery
225	65.0	28.6	34.5	2.86	0.26	–	101.8
260	51.0	6.63	40.8	3.83	0.36	–	101.2
275	39.0	0.08	35.5	3.47	0.35	–	101.0

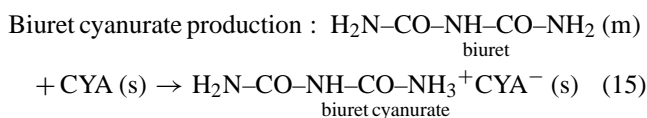
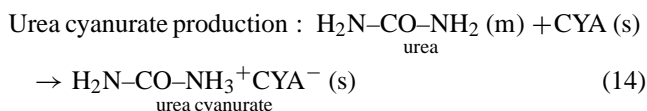
^a These data were calculated based on the results obtained from HPLC and TGA analysis assuming 100.0 g of urea initially present.

continue in this temperature range. The continued production of CYA and ammelide, Eqs. (9) and (10), are also expected to contribute to the NH₃ (g) production as well.

Analysis for [NH₄⁺] ion gives a maximum in the residue at 225 °C. This represents a substantial increase from the value observed at 190 °C (Table 2). Accumulation of [NH₄⁺] is a direct consequence of system precipitation. As the urea melt is transformed into a solid matrix, the rate at which NH₃ (g) and HNCO (g) can diffuse from the system is diminished. These species are either trapped in the solid matrix, or interact with each other, Eq. (13), and exist in the residue in ionic form. The fact that ionic formation occurs is supported by the [NH₄⁺] analysis of the residue from these studies, and by the MS data collected by Carp [15]. Just as decomposition species are “tied up” in ionic form



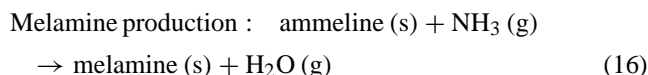
in the matrix,⁵ it is also likely that the remaining urea and biuret are likewise converted to ionic cyanurates via interaction with CYA, Eqs. (14) and (15).



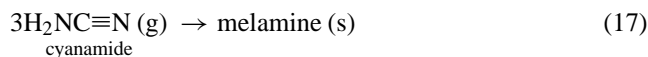
The narrow plateau region observed near 225 °C in the urea TGA corresponds very well to a more demonstrable one exhibited by biuret at approximately the same temperature (Figs. 2 and 4, respectively). In the biuret system, the residue is primarily composed of biuret and CYA, with lesser amounts of ammelide and ammeline (Table 4). Since all the product species are thermally stable at 225 °C, a plateau region is observed in both the urea and biuret TGA at this temperature. FT-IR data collected on the off-gases resulting from the urea residue at this temperature illustrates that gaseous emissions have greatly decreased. Only a small

amount of NH₃ (g), HNCO (g) and HNCO salt species are emitted from the residue matrix. Emission therefore continues, but at a much reduced rate [12].

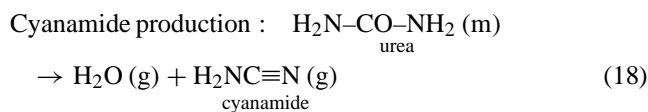
Melamine is positively identified for the first time at 250 °C⁶ (Table 1). This represents a departure from the temperature and level at which this product is first observed under TGA conditions (350 °C, and in substantially smaller amounts) [2]. The direct ammination of ammeline, Eq. (16), is one possible route to melamine. Once again, although this may be the simplest conceptual route, it is one likely only to be observed at



elevated pressures [18] or temperatures [19]. However, open reaction vessel conditions as applied here may produce localized temperature conditions favoring this process to a limited extent. Another possibility is cyanamide (H₂NC≡N) trimerization [10], Eq. (17). Although cyanamide has not been isolated from urea decomposition under normal



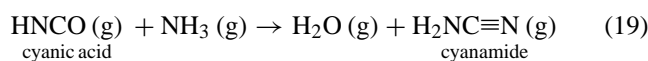
pressure [11], it could be produced via an alternate decomposition route associated with urea dehydration, Eq. (18), or by ammination of cyanic acid [10], possibly within the solid matrix, Eqs. (19) and (19a), and behave as a very reactive intermediate at these temperatures. The small amounts of melamine observed may be reflective of small



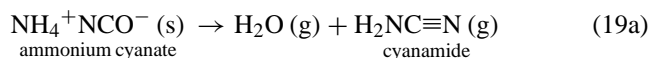
⁶ This is somewhat of an anomaly since melamine is reported to melt with accompanying sublimation below 250 °C. It is therefore necessary to assume that if melamine forms, it sublimates simultaneously as it is being produced. The sublimation of melamine may therefore also contribute to the mass loss observed between 225 and 250 °C in the TGA (Fig. 2). Accumulation of measurable amounts of melamine, result from production that is kinetically faster than sublimation. It should also be noted that melamine is observed at 250, 275, and 350 °C, but not at 320 °C (Table 1). This would suggest different mechanisms for its production in different temperature ranges. At lower temperatures (below 300 °C), Eq. (17), or some other unidentified reaction, results in production of melamine. At higher temperatures, Eq. (16) is expected to predominate.

⁵ Eq. (13) is in essence the reverse of the latter portion of Eq. (1).

or



or



amounts of cyanamide produced. Mixed trimerization of cyanamide and cyanic acid has been suggested to be responsible for the production of CYA, ammelide, ammeline and melamine [10] at relatively low temperatures. However, a question of appropriate concentration arises. Under the conditions used here, cyanamide is not detected in the FT-IR of the melt nor the off-gases (absorbance at 2268 and 1504 cm^{-1} are characteristic of $\text{H}_2\text{NC}\equiv\text{N}$), and it is difficult to explain the relatively large amounts of CYA, ammelide and ammeline produced without at least the hint of cyanamide detection. In any event, production of melamine is slow and only very small amounts of it are produced.

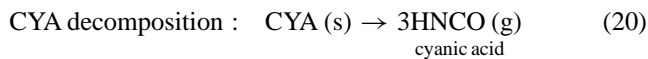
A relatively small mass loss is noted in the urea TGA between 225 and 250 °C (Fig. 2) even though the mass amounts of CYA, ammelide and ammeline continue to increase and reach a maximum at 250 °C (Fig. 1; Table 1). Sources of this small mass loss may be attributed to continuation of urea and biuret decomposition, reactions producing CYA, ammelide and ammeline, and their associated gaseous by-products, and sublimation or decomposition of HNCO salts, cyanurates [25], and possibly melamine. Analysis of trapped off-gases for $[\text{NH}_4^+]$ ion indicates a smaller amount of NH_3 (g) escapes in the 225–255 °C temperature range, than in the former (Table 3). This is consistent with the small amount of urea and biuret left in the residue and the reduced emission rates. That $[\text{NH}_4^+]$ salts are significantly lost from the matrix is confirmed by the 10-fold difference in $[\text{NH}_4^+]$ ion residue concentration going from 225 to 250 °C (Table 2). The FT-IR of emitted gases at 250 °C supports this as evidence of HNCO related species are detected in the 2100–2300 cm^{-1} region of the FT-IR. (A small peak corresponding to HNCO at approximately 2276 cm^{-1} is observed [17], along with peaks at 2200 and 2162 cm^{-1} that have been associated with $[\text{NH}_4^+\text{NCO}^-]$ and $[\text{H}_3\text{O}^+\text{NCO}^-]$, respectively [22].)

At 250 °C, remaining amounts of urea and biuret have been depleted to minor constituent levels and the “sticky” appearance of the solid matrix has disappeared; the solidification of the matrix is complete at this point.

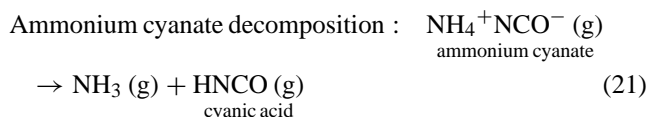
3.4. Third “reaction” region (between 250 and 360 °C)

At 250 °C, only CYA, ammelide and ammeline exist in appreciable amounts. In addition, since all major constituent species in the solid matrix are for the most part thermally stable at this temperature, another plateau region is observed in the urea TGA. These conditions persist to approximately 260 °C, after which the system begins to experience a large mass loss (Fig. 2). As temperature is increased, CYA begins

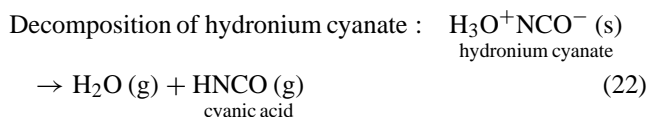
to lose mass (Fig. 5) via sublimation with a small amount of decomposition, Eq. (20), and is responsible for most of the mass loss between 250 and 275 °C [16]. (It should be noted that Eq. (20) is just the reverse of Eq. (4).) In this temperature range, TGA data indicate that ammelide and ammeline also begin to slowly lose mass (Figs. 6 and 7). Indeed,



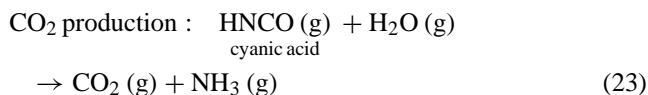
small mass losses are detected for melamine and ammelide. However, ammeline shows no mass loss (Table 1). Mass data for urea and biuret at 275 °C indicate a slight increase from 250 °C levels. This could be an artifact of the analytical method, or reflective of available cyanic acid reacting to produce small amounts of each, followed by matrix trapping. The FT-IR of gaseous material collected at 275 °C is also much different from that observed at 250 °C. Although ammonia peaks are still present, a substantial amount of water (peak at 3747 cm^{-1}), and peaks associated with $[\text{NH}_4^+\text{NCO}^-]$, $[\text{H}_3\text{O}^+\text{NCO}^-]$ and HNCO are observed to have increased in intensity. A large CO_2 peak (2361 cm^{-1}) is also observed. In addition, analysis for $[\text{NH}_4^+]$ ion in the residue has decreased to 150 ppm (Table 2). The NH_3 (g) peaks in the FT-IR partially result from decomposition of residual urea and biuret, and ammonium cyanate, Eq. (21). (It should be noted that Eq. (21) is just the reverse of Eq. (13).) Eqs. (20)–(22) can be used to explain the increase in



HNCO [22] observed in the FT-IR and the continued reduction in the amount of $[\text{NH}_4^+]$ ion observed in the residue. The presence of water is likely a consequence of several water producing reactions, especially those associated with the production of ammelide, ammeline and melamine (see Section 3.2). Water can react with HNCO to produce $[\text{H}_3\text{O}^+\text{NCO}^-]$, which can become trapped in the solid matrix. Subsequent decomposition, Eq. (22), in this “reaction” region would result in water observed in the FT-IR [22]:



The relatively large CO_2 peak observed in the FT-IR can be explained by reaction of water with available HNCO, Eq. (23). Water can be produced from several reactions [13,22]



previously mentioned and released from the matrix via Eq. (22), which also acts as a source of HNCO. Other

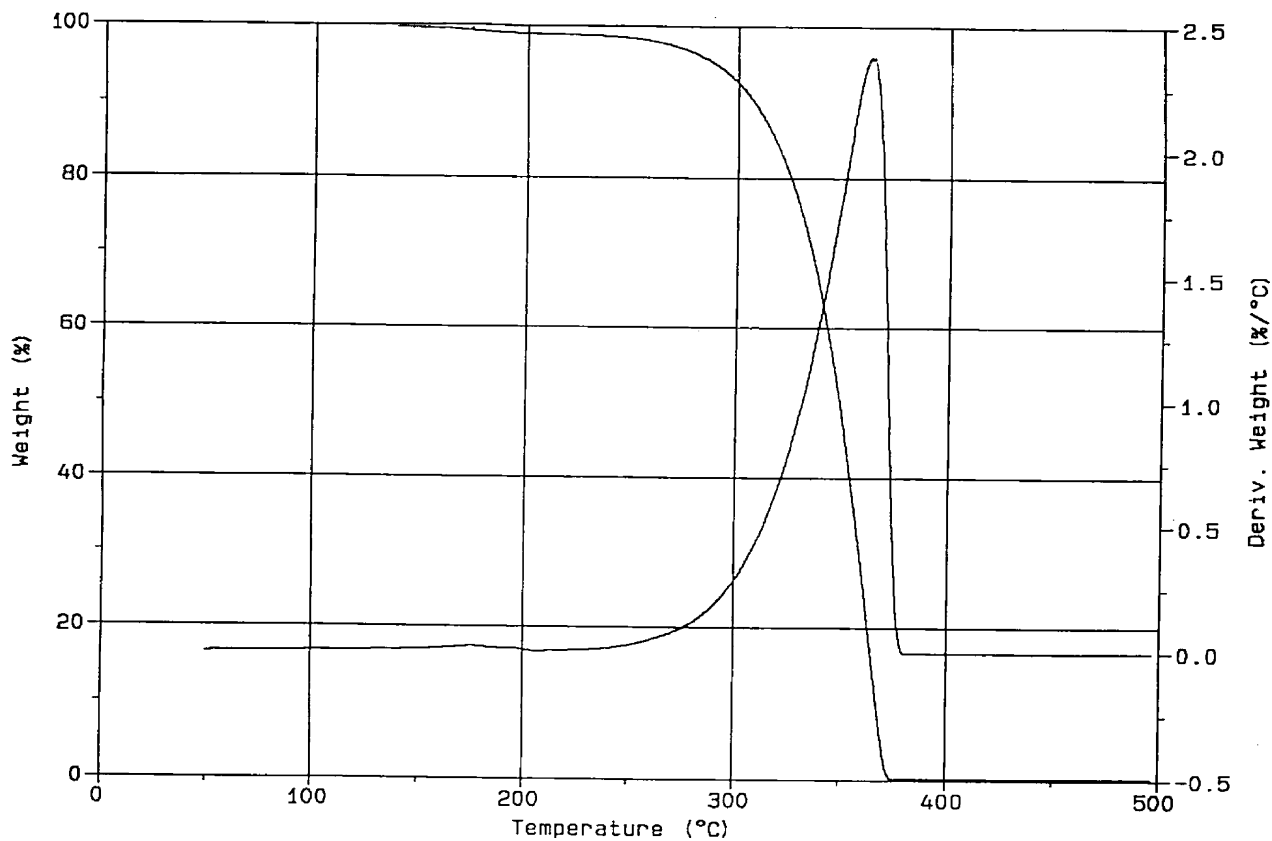


Fig. 5. TGA: CYA pyrolysis reaction.

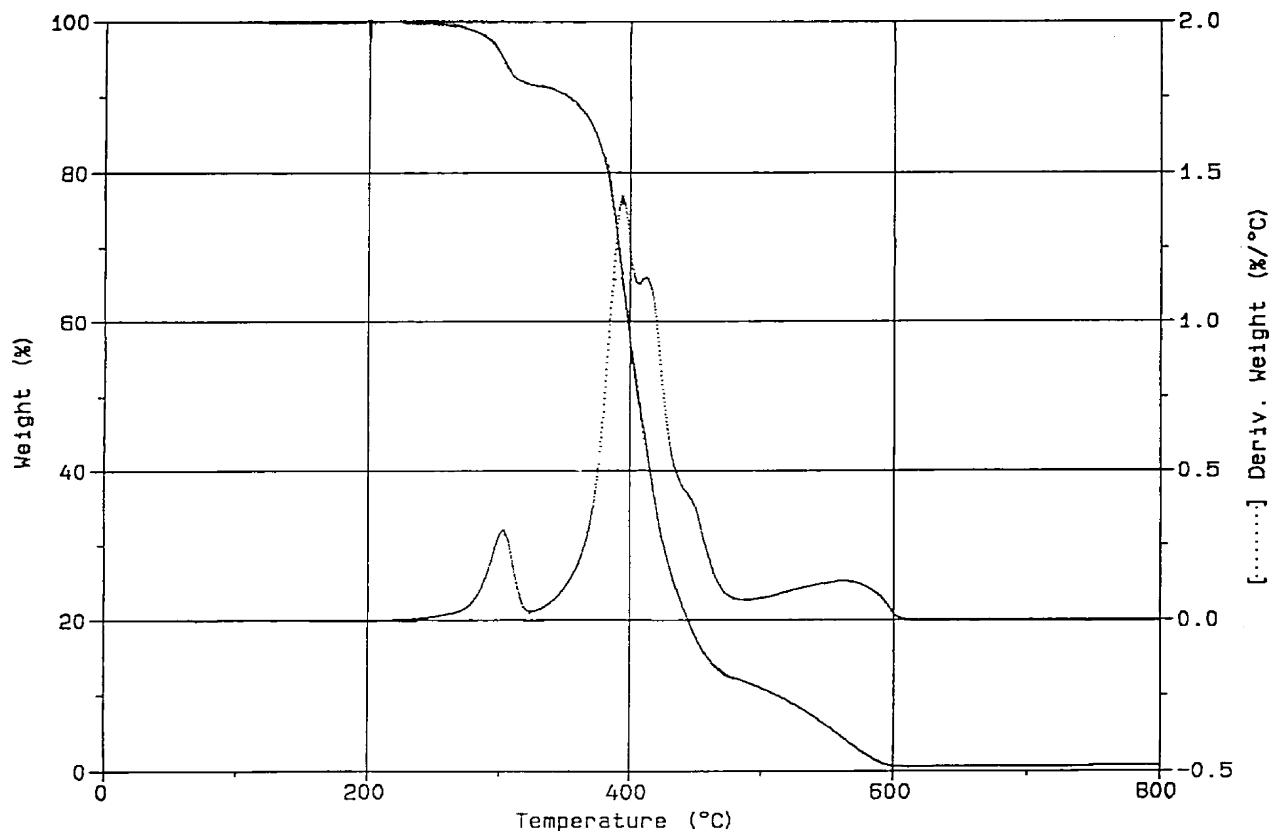


Fig. 6. TGA: ammelide pyrolysis reaction.

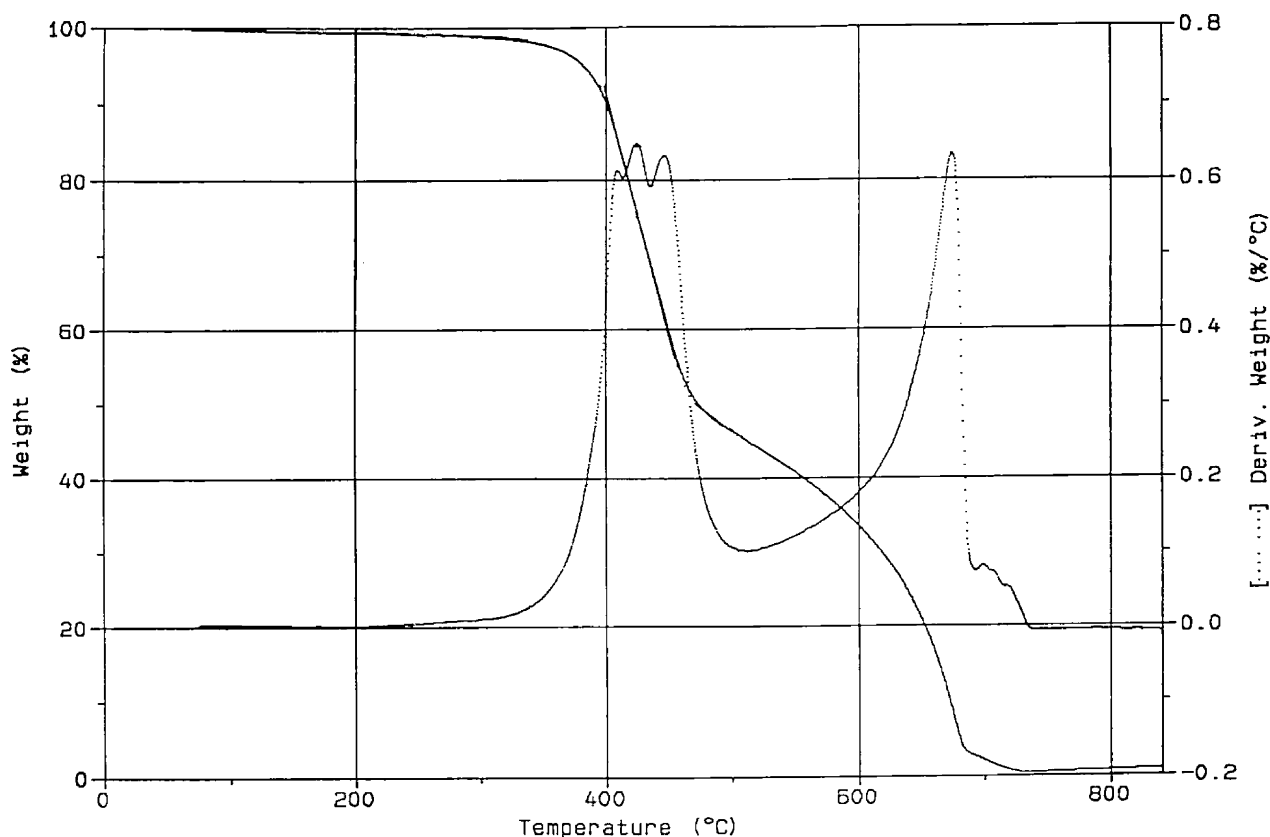


Fig. 7. TGA: ammeline pyrolysis reaction.

sources of HNCO include Eqs. (20) and (21). Production of CO₂ would also be expected to contribute to the NH₃ peaks observed in the FT-IR at 275 °C.

At temperatures greater than 275 °C, CYA and ammelide continue, and ammeline begins to show a mass loss. At 320 °C urea, biuret and melamine are no longer detectable (Table 1). CYA decomposition begins in earnest between 320 and 330 °C, Eq. (20), ammeline and ammelide begin to sublime at 310 and 340 °C, respectively.⁷ Analyses of off-gases collected between 255 and 350 °C indicate a substantial amount of NH₃ (g) emitted from the system (Table 3). FT-IR of residue off-gases at 325 °C indicates the presence of water, CO₂, and HNCO. Ammonia is also detected but in somewhat diminished proportion. Analysis for [NH₄⁺] ion in the residue (Table 2) at 325 °C continues to show a decrease (120 ppm). These data are all consistent with a continuation of the reaction processes mentioned in this section.

At 350 °C, HPLC data (Table 1) indicates CYA has significantly decomposed and ammelide and ammeline continue to sublime. A small amount of melamine reappears. This may be an artifact or the result of the direct ammoniation of remaining ammeline [19], Eq. (16). The FT-IR data on

residue off-gases at this temperature exhibit a large doublet in the [NCO⁻] region (peaks at 2282 and 2256 cm⁻¹) with only the slightest hint of NH₃ remaining. This is an indication that only a small amount of [NH₄⁺] ion remains in the residue. The off-gas data is supported by direct residue analysis (Table 2). At this point, most of the [NH₄⁺NCO⁻] has either sublimed or decomposed and other sources of NH₃ have been depleted. Due to limited mass amounts, rates of decomposition and sublimation have substantially subsided resulting in a small net mass loss and the corresponding observed plateau region in the urea TGA between 350 and 360 °C (Fig. 2).

3.5. Fourth “reaction” region (above 360 °C)

Between 360 and 450 °C, a gradual mass loss is noted in the urea system (Fig. 2). This is reflective of continued decomposition of residual CYA, which is complete between 375 and 380 °C (Fig. 5), and ammelide and ammeline sublimation and decomposition. Ammelide melts with decomposition prior to 410 °C; ammeline melts with decomposition at 435 °C. Ammelide is not completely eliminated from the system until temperatures in excess of 600 °C are achieved (Fig. 6); ammeline requires temperatures in excess of 700 °C (Fig. 7). Melon has been mentioned in the literature [8] as the final pyrolysis product of urea. This has not been confirmed in this study.

⁷ Literature data give sublimation temperatures for ammelide and ammeline at 350 and 310 °C, respectively. However, data obtained from condensation materials indicate that ammelide begins to sublime prior to 340 °C.

4. Summary and conclusion

In the first “reaction” region, room temperature to 190 °C, mass loss is largely associated with urea decomposition. Biuret, a product of urea decomposition, reaches a mass maximum and the kinetically slow synthesis of the more complex reaction products, CYA and ammelide, begins. In the second “reaction” region, 190–250 °C, urea continues, and biuret begins, to decompose. The production rate of CYA and ammelide, increases dramatically and two new products, ammeline and melamine, appear in smaller amounts. The close relationship between the onset of biuret decomposition and increased production rates for both CYA and ammelide suggests that they are produced largely from biuret, and in parallel fashion within the second “reaction” region. All products reach mass maxima and then begin to lose mass via sublimation or decomposition. The third “reaction” region, 250–360 °C, is dominated by continued sublimation and decomposition of the remaining products. In the fourth “reaction” region final decomposition and elimination of remaining products occurs.

Much work still needs to be accomplished to gain a more complete understanding of this complex pyrolysis reaction and the effect of changing parameters. More detailed temperature versus product distribution analysis would aid in a more precise determination of when and where mass changes occur, and in the determination of appropriate reaction mechanisms. Finally, the intricate and undoubtedly complex kinetics associated with this pyrolysis reaction largely remains a mystery and a challenge to investigators.

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