FORMATION OF THE MAIN GAS COMPOUNDS DURING THERMAL ANALYSIS AND PYROLYSIS
Betaine and betaine monohydrate

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Abstract

The thermochemical behaviour of betaine and betaine monohydrate was investigated under two degradation conditions. Betaine was heated up to 700ºC at 10ºC min^{-1} in air and nitrogen flows and the evolved gas was analysed with the combined TG-FTRIR system. The evolved gas from betaine pyrolysis at 350 and 400ºC was analysed by gas chromatography using mass-selective detection (Py-GC/MSD). In addition, the electron impact mass spectra of betaine and betaine monohydrate were measured.

Esterification is one of the most important pyrolytic processes involving beta- ines. Even glycine betaine can change to dimethylglycine methyl ester via intermolecular transalkylation by heating. Trimethylamine, CO_2, and glycine esters were the main degradation products. Small amounts of ester type compounds evolved both in pyrolysis and with TG-FTIR. The monohydrate lost water between 35 and 260ºC while the main decomposition took place at 245–360ºC. The residual carbon burnt in air to CO_2 up to a temperature 570ºC.

Keywords: betaine, betaine monohydrate, degradation, EGA, pyrolysis, thermal analysis, trimethyl ammonium acetate, trimethyl glycine

Introduction

Betaine (trimethyl glycine) compounds are important as complex lipids and transmethylating agents in biological systems. Interest in betaines has increased during recent years, as they are clear involved in the regulation of osmotic pressure by microbes, plants and animals [1–4]. Betaines can be used in fermentation, animal food, and cosmetic and medical products [3–4]. Betaine exists widely in nature, and in plants it is most abundant in sugar beet.

The crystal structure and the IR spectrum of anhydrous betaine (trimethyl ammonium acetate, trimethyl glycine), crystallised from ethanol, and betaine monohydrate, crystallised from water, have been determined [5–7]. Betaine exists as

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a neutral zwitterion: three methyl groups bound to the nitrogen atom gain a positive charge and the carbonyl oxygen atom a negative charge. Therefore we later write the molecular form of betaine as $(CH_3)_3^+NCH_2COO^-$ instead of $(CH_3)_3N+CH_2COO^-$, which is misleading from the standpoint of the charge distribution [7]. The local Cs symmetry of the betaine molecule is a part of the result of weak electronic interaction, and internal hydrogen bonds.

The fragmentation found in electron impact (EI) mass spectrometry (MS), thermal analysis (TA) and pyrolysis is similar in that rupture takes place at weak bonds. The mass spectra consist of a series o competitive and consecutive unimolecular fragmentations in conjunction with thermal decomposition. With EI, the ion produced is formed with a specific amount of internal energy, which is independently conserved in all subsequent dissociations. With TA, the molecules are continuously energised by heat and deactivated by the evolution of gas compounds. From this it follows that the distribution of this energy can be described in relation to temperature. Because a rise in temperature increases the movements of atoms in a molecule, the temperature coefficients of the crystallised compound and their changes at different temperatures can be applied as indicators of thermal decomposition processes [8]. Since the basis of the changes with EI and TA are different, the fragmentation does not necessary follow the same pathway. Moreover, additions of fragments can follow the basic fragmentation. The conditions governing are different in MS, TA and pyrolysis.

In general, betaine is a stable compound, easily soluble in water and biologically active. A number of organic nitrogen compounds form inflammable and poisonous decomposition products. Because of wide use of betaine in a variety of applications, it is important to know the risk involved is handling it. Therefore the thermal behaviour and degradation by pyrolysis of betaine was investigated.

Experimental

Anhydrous betaine and betaine monohydrate

The anhydrous betaine and betaine monohydrate were produced by Finnfeeds Finland, and the purity of the compounds was 99.5 and 100.0% (HPLC on dry basis), respectively.

The anhydrous betaine was recrystallized from ethanol by dissolving the compound in hot ethanol and then slow cooling the solution by stirring. The recrystallized product was preserved at room temperature in a desiccator over phosphorus pentoxide. Moreover, to confirm the samples, both reagents were recrystallized. The phase structures of the resulting samples were the same as those for the samples produced by Finnfeeds Finland.

TG-FTIR experiments

Simultaneous TG and FTIR curves were recorded with Perkin–Elmer equipment using the following configuration:

TG: PE TGA7, TAC7/DX, PC J&M Pentium, HP LaserJet IIIP or Xerox Phaser 1235 PS, PE Pyris^{TM} Software for Windows.

FTIR: PE System 2000 FT-IR, PC J&M Pentium, HP LaserJet IIIP or Xerox Phaser 1235 PS, TR-IR software for system 2000 Ver. 1.00 or TimeBase (V1.0).

TG was coupled to FTIR by a heated transfer line and a heated 10 cm^3 gas cell was used in FTIR.

TG measurements were carried out in Pt pans in a current of air and nitrogen, with a flow rate of 80 mL min^{-1}. The sample masses were 9–18 mg, the heating rate 10ºC min^{-1} and the temperature range varied from 25–700ºC. The evolved gas from the TG was analysed by FTIR. The temperature of the transfer line and the gas cell was adjusted to 200ºC. Scanning and data collection parameters were: resolution, 8 or 4 cm^{-1}; scan speed, 0.2 cm s^{-1}; detector DTGS; background scans, 8; scans per slice, 16; interval between slices, 0.0 min. The measured absorbance data were displayed as a stacked plot, infrared spectra at selected time points and window TG curves for the main degradation compounds. The purge gases were dried air and nitrogen. All together seven measurements were performed by TG-FTIR: one betaine monohydrate measurement in air and one in nitrogen, and three anhydrous betaine measurements in nitrogen and two in air.

For the presentation of the FTIR spectra and the identification of the evolved gases, the Perkin–Elmer TRIR (Time-Resolved Infrared Spectra) or Spectrum TimeBase (V1.0), Spectrum and search programs were used. The search program uses PSU (possible structure units), a select enhanced EPA vapour Phase Database (code: 4602) and the reference database of Pure Organic Compounds (code: 4050) of BIO-RAD (Sadtler). Additionally, the Socrates Infrared Characteristic Group Frequencies Tables and Charts, Second Edition of BIO-RAD, Sadtler Division, and the Aldrich Library of FTIR Spectra, Vapour Phase were also used. The frequency values of peaks given below in parenthesis were taken from these FTIR databases, if the references are not given separately.

Pyrolysis experiments

About 2 mg of betaine was pyrolyzed in a quartz tube (3.0 cm×1.0 mm i.d.) at temperatures of 350 and 400ºC using a CDS Pyroprobe 1000 heated filament pyrolyzer coupled to an HP (Hewlett Packard) 5890 II gas chromatograph (interface temperature, 350ºC), which in turn was interfaced to an HP 5970 mass-selective detector. To calculate the mass loss for betaine at different temperatures the quartz tube was weighed before and after each measurement.

An HP-1 fused-silica capillary GC column (25 m×0.32 mm; film thickness, 0.17 µm) was employed. The temperature program began with 2 min at 30ºC, then heating at 10ºC m s^{-1} to an end temperature and finally holding for 15 min at the end temperature. Helium as the carrier gas, and a split/splitless capillary injection port, operating in the split mode, were used. The peak areas on the total ion current (TIC) pyrogram were used as such without any mutual response factors when calculating the relative composition of the pyrolysis products.

The interpretation of the mass spectra obtained by Py-GC/MSD was based both on an automatic library search (NBS REV_F/HP 9000 series 310) and on fragmentation data.

Mass spectra

The mass spectrometer used in this work was a VG AutoSpec. The mass spectra of betaines were obtained by the direct insertion technique where the injector temperature was 280°C. The mass spectra were obtained by electron impact (EI) ionisation at an electron beam energy of 70 eV.

Results and discussion

Thermal analysis

At first betaine monohydrate lost water in two steps. The solid crystal sample lost water faster than melted betaine monohydrate. The melting peak measured by DSC was 94.4°C, at a heating rate of 10°C min^{-1}.The total amount of water measured by TG was 13.2±0.5% over the temperature range 25–263°C, and the calculated mass% was 13.33%. The peak value of the DTG curve was 88°C, which was almost the same as the onset value of the DSC curve.

The main decomposition of monohydrate and anhydrous betaine is rapid and only elemental carbon remains. The initial and final temperatures, loss in mass and residuals of anhydrous betaine and monohydrate in the nitrogen and air atmospheres are listed in Table 1. In air, degradation ended at a lower temperature than in nitrogen. Anhydrous betaine easily absorbs a small amount of water during storage or during sample preparation. Therefore the initial temperature varied between 242 and 256°C on the five measurements. The initial temperature of the main degradation for the monohydrate was higher than the initial temperature for the anhydrous form. Even a small amount of water seems to stabilise the structure, thus allowing betaine to stand more heat. The residue was one per cent greater in the air flow (3.5%) than in the nitrogen flow (2.5%). We found three peaks in the DTG curves for anhydrous betaine while the monohydrate showed only one in the main degradation. All the residual carbon burnt slowly in air up to a temperature 570°C.

Table 1 The TG data of main decomposition steps of anhydrous betaine (*A*) and betaine monohydrate (*M*) in air and in nitrogen, heating rate 10 C min^{-1}

Compound	Atmosphere	Number of measurements	t_i/ C	t_f/ C	Mass loss/%	Residue/%
A	nitrogen	3	245±3	343±2	97.6±0.2	2.4±0.2
A	air	2	252±4	323±7	96.6±0.5	3.4±0.4
M	nitrogen	1	257	361	84.2	2.5
M	air	1	261	329	83.1	3.6

FTIR results

The detected peaks of the RMS (= the root-mean-square) or GS (= Gram Schmidt)) intensity profiles of the total evolved gases used in the FTIR experiments paralleled the TG curves very well, as shown in Fig. 1. Figure 2 presents the stacked plot diagrams of anhydrous betaine in air and in nitrogen. Figure 3 shows the separated gas
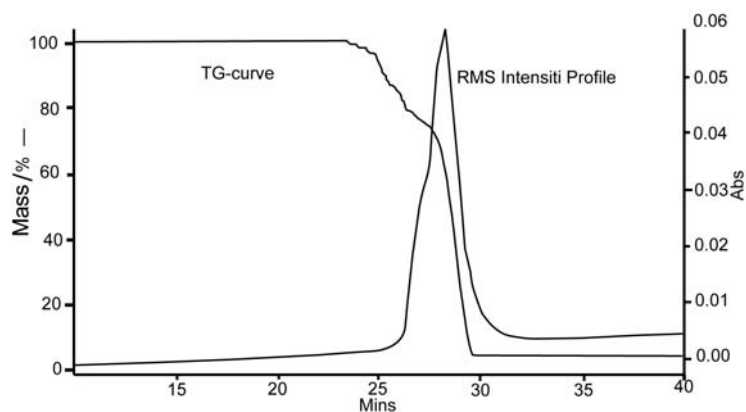

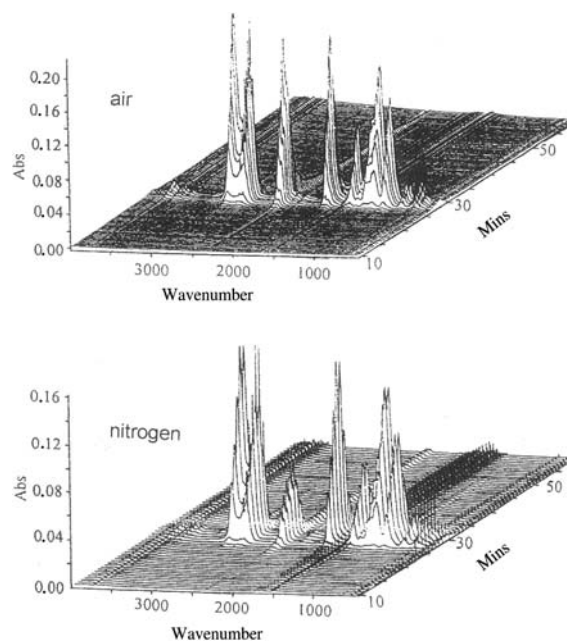**Fig. 1** TG curve and RMS intensity profile measured in air

Fig. 2 Stacked plot pictures of betaine in air and in nitrogen

spectra of anhydrous betaine in air after 25.1 min (276ºC), 27.2 min (297ºC), 28.5 min (310ºC), 29.7 min (322ºC) and 31.0 min (335ºC).

CO_2, and $(CH_3)_3N$ were easy to recognise. CO_2 showed strong absorption peaks of 2361 cm^{-1} (2362 stretching) and 2330 cm^{-1} (2332 stretching), weak deformation peaks of 720 cm^{-1} (720) and 669 cm^{-1} (668), and weak overtones of 3732 cm^{-1} (3735) and 3594 cm^{-1} (3599). $(CH_3)_3N$ absorbs at 2963cm^{-1} vs (2962 CH-stretching), 2824 cm^{-1} vs (2824 CH-stretching), 2776 cm^{-1} vs (2776 CH-stretching), 1457 cm^{-1} m (1462 CH_3-bending), 1270 cm^{-1} m (1270 CH_3-rocking), 1174 cm^{-1} bvs (1181 CH_3-rocking), 1057 cm^{-1} s (1043 CN-stretching), and 823 cm^{-1} m (824 CN-stretching) [9]. Here vs means very strong, m is medium peak intensity, and bvs is a broad very strong peak.
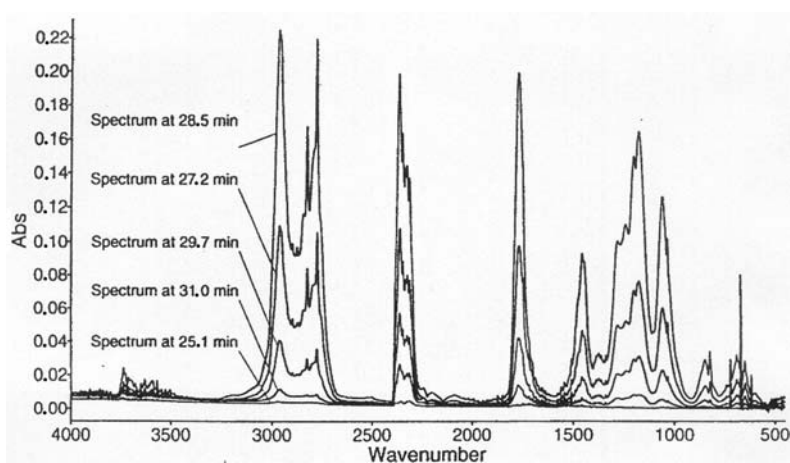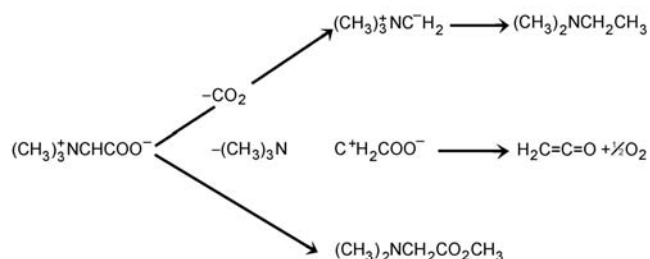

Fig. 3 FTIR spectra of evolved gas products of betaine in air

Two near peaks at 1780 and 1762 cm^{-1} or a single peak at 1765 cm^{-1} showed carbonyl compounds. N,N-dimethylglycine alkylesters corresponded best to the measured spectra of carbonyl compounds. In addition, dicarboxylic alkyl esters as dimethyl malonic ester or dimethyl succinic ester showed good fit with the difference spectrum of the measured and database spectrum of trimethyl amine. Obviously, esterification is one of the most important pyrolytic processes involving betaines. Water vapour showed many weak absorption bands arising from the rotation-vibration frequencies of the gas state at 3990–3500 and 1900–1300 cm^{-1}. The weak peaks at 2180 and 2114 cm^{-1} show CO.

The evolved gas curves of $(CH)_3N$, CO_2, CO, H_2O, and carbonyl esters as dimethylglycine esters and alkyl dicarboxylate in air are shown in Fig. 3. Degradation began in all cases as decarboxylation, producing CO_2, and was followed by a Stevens rearrangement to produce ethyldimethylamine, $(CH_3)_2NCH_2CH_3$. On the other hand, the evolved trimethylamine and carbonyl alkylesters followed soon after the appearance of CO_2. On the basis of this experiment it is clear that degradation begins with two different splittings, and with esterification, as the following scheme shows:

$$(CH_3)_3^+ NC^- H_2 \longrightarrow (CH_3)_2 NCH_2 CH_3$$

$$-CO_2$$

$$(CH_3)_3^+ NCHCOO^- \Big\langle \quad -(CH_3)_3 N \quad C^+ H_2 COO^- \longrightarrow H_2 C=C=O + \tfrac{1}{2} O_2$$

$$(CH_3)_2 NCH_2 CO_2 CH_3$$

Clearly, the degradation products of the trimethyl glycine and the dimethyl glycine methyl ester of betaine are partially different and as a group numerous. $C^+ H_2 CO_2^-$ and $(CH_3)_3^+ NC^- H_2$ are reactive forms, which, when added to each other, also to betaine, give rise to dimethylglycine and other esters. It is possible that $C^+ H_2 COO^-$ might change into ketene, $H_2 C=C=O$; however, this was not found in the IR spectra. The specific value (2153 cm^{-1}) for ketene was absent [10, 11]. However it is possible that ketene was decomposed by other compounds, and although even contamination of the surface can cause decomposition [10]. The change in the carbonyl peak in the evolved gas spectra followed the change in the trimethylamine peak. The removal of trimethylamine started in the evolved gas as a result of reactions from secondary addition giving rise to glycine and dicarboxylic acid alkyl esters. The evolved gas spectra show minor amounts of water and carbon monoxide.

When we compared the TG curves in air to those in nitrogen we observed minor differences. This was also true of the evolved gas analysis. More carbon dioxide and more water were formed in air than in nitrogen. This means that evolved hydrocarbons burned partially in air, forming water and carbon dioxide. A slight amount of water was also formed in nitrogen, which is possible, if the amount of elemental oxygen in the carbonyl group had been reduced.
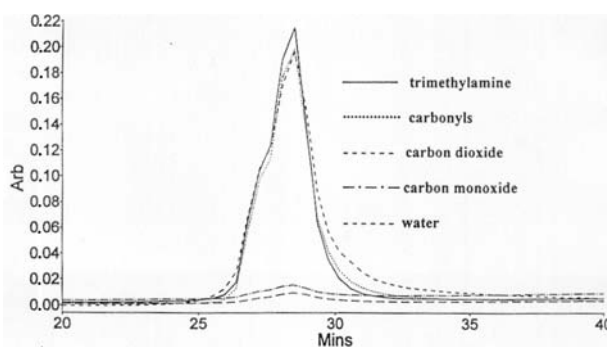

Fig. 4 Decomposition products of betaine in air. The profiles of water at 3592 cm^{-1}, trimethylamine at 2777 cm^{-1}, carbon dioxide at 2361 cm^{-1}, carbon monoxide at 2192 cm^{-1}, and carbonyls (glycine esters) at 1764 cm^{-1} are presented as a function of time

Mass spectroscopy

The full-scan EI mass spectrum for anhydrous betaine is presented in Fig. 5. According to Undheim and Lærum [12], the betaine spectrum shows the gas phase molecule to be an intermolecular transalkylated ester (*m/e* 117):

$$(CH_3)_3{}^+N\,CH_2COO^- \quad (CH_3)_2NCH_2COOCH_3$$
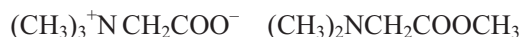
One of the main degradation products is trimethylamine. The major peaks in the spectrum of trimethylamine should be at *m/e* 59 (45%) $[(CH_3)_3N]^+$, 58 (100%) $[C_3H_8N]^+$, and 42 (42%) $[C_2H_4N]^+$ [12, 13]. The dimethylglycine ester does not give the molecular peak for trimethylamine. In Fig. 5 relative intensities are at *m/e* 59 (31%), 58 (100%) and 42 (54%). Thus the spectrum in Fig. 5 contains fragmentation of both the trimethylglycine and dimethylglycine methylesters. The relative height of peak *m/e* 42 can be explained by $[C_2H_4N]^+$ and by the presence of the ketene fragment $[C_2H_2O]^+$.

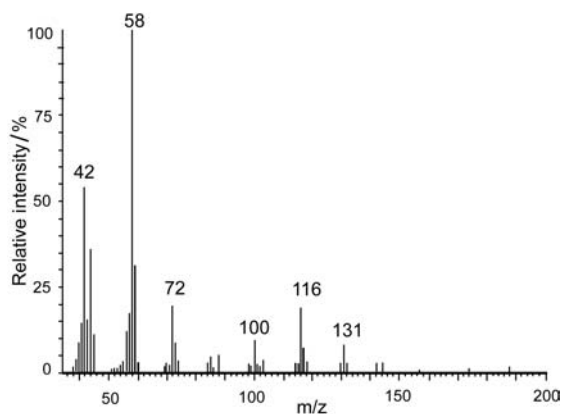**Fig. 5** The mass spectrum of betaine

The other dominant peaks are at the *m/e* values 117 ($[(CH_3)_3NCH_2CO_2]^+$ or $[(CH_3)_2NCH_2CO_2CH_3]^+$), 116 ($[(CH_3)_3NCHCO_2]^+$), 100 ($[(CH_3)_3NCHCO]^+$), 73 ($[(CH_3)_2NCH_2CH_3]^+$ or $[H_2COCOCH_3]^+$), 72 ($[(CH_3)_2NCH_2CH_2]^+$), 45 ($[HCO_2]^+$), and 44 ($[CO_2]^+$ or $[(CH_3)_2N]^+$). In addition to these, low intensity fragments were found at *m/e* 103, 88, 85 and 74.

The relative intensities of some peaks changed notably, if the spectrum was recorded during the first part of the TIC (total ion current) peak or later. The peaks at *m/e* 116, 100, 72, 45, 44 and 42 decreased and those at *m/e* 117, 74 and 73 increased. The former are mainly fragment peaks of the molecular ion of betaine and the latter fragment peaks of the molecular ion of the esterified betaine.

Low intensity fragment peaks were found beyond the molecular ion peak at *m/e* 118, 131, 132, 142, 144, 157, 174, 175 and 188 [13]. These ion peaks are the result of additions between decomposition fragments and betaine. Because mass spectral reactions are unimolecular, the additions have to take place before EI ionization of

betaine. These fragments mainly have their origin in the esterification of betaine and thermal degradation products.

The mass spectra of betaine monohydrate were found to be very similar to those of anhydrous betaine.

Pyrolysis

The main degradation products found in the full scan total ion current chromatogram (TIC) from the GC-MS analysis of the betaine measured at 350 ºC are listed in Table 2. Besides these, several weak peaks were observed in the chromatogram, such as at 16.38 min (*m/e* 125), 20.86 min (*m/e* 189), 24.22 min (*m/e* 173) and 31.78 min (*m/e* 196) min. The greatest m/e peak in the mass spectra is shown in parenthesis. These compounds were not identified. In the mass spectra they gave only low m/e values; hence their molecules could not be determined. Chromatogram peaks at 19.24 and 19.64 min in the mass spectra gave molecular ion peaks at *m/e* 175, but their mass spectra were different. The same situation was found with the chromatogram peaks at 20.21 (*m/e* 189) and 20.86 min, respectively.

Wood and Collacott in FD (field desorption) MS obtained *m/e* 132 $[M+CH_3]^+$ ion by transfer of methyl from the quaternary ammonium of one molecule to the carboxylate of another molecule [14]. $(CH_3)_3^+ NCH_2CO_2CH_3$ easily forms an intermediate ion pair and moves slower in the GC column than a neutral molecule of the same molecular mass. The group $(CH_3)_3^+ N$ on the other hand gives up a methyl group or is broken off as a whole. In our case, on the basis of the library search, *m/e* 132 (8.28 min) was the methyl ester of acetoxyacetic acid.

The peak *m/e* 131 existed in both EI MS and py-GC/MSD. The thermal decomposition product $(CH_3)_3^+ NC^- H_2$ of betaine might also undergo displacement of trimethylamine:

$$(CH_3)_3^+ NC^- H_2 + (CH_3)_3^+ NCH_2CO_2^- \rightarrow (CH_3)_3 N + (CH_3)_3^+ NCH_2CH_2CO_2^-$$
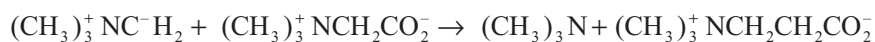
The latter product is not stable at higher temperatures and can undergo esterification to $(CH_3)_2NCH_2CH_2CO_2CH_3$ (*m/e* 131) or decomposition via Hoffman elimination to acrylic acid [15]. The highest fragmentation peak in the mass spectrum of this compound was *m/e* 72, which corresponds to the molecular ion peak of acrylic acid.

Comparative study between MS, TA and pyrolysis

The degradation of anhydrous betaine and betaine monohydrate was determined by three different methods. The degradation of betaine took place in the gas phase in MS as well as in py-GC/MSD and in a crystalline or partially liquid state in TG-FTIR. The evolved gases were mainly of the same types. However, the different methods yielded varying amounts of products. Full-scan EI mass spectra in the direct inlet showed the main fragments to be light decomposition fragments of betaine. On the other hand py-GC/MSD gave plenty of secondary addition products. TG-FTIR clarified the relative amounts of the degradation compounds as a function of temperature

and gave information about the beginning of decomposition. Whereas py-GC/MSD made it possible to recognise many carbonyl esters, with TG-FTIR these overlapped with the peaks of the carbonyl and other functional groups. With TG-FTIR it was not possible to reliably identify a single compound in a mixture of many carbonyl compounds.

Table 2 The main decomposition product of betadine in pyrolisis from TIC (total ion chromatogram) by py–GC/MSD

Time/ min	Molecular ion peak m/z		Compounds
0.33	44	$[M-73]^+$	CO_2
1.41	59	$[M-58]^+$	$(CH_3)_3N$
2.76	90	$[17+(M-59)]^+$	$HOCH_2CO_2CH_3$
4.04	101	$[M-16]^+$	$(CH_3)_2NCH_2C(O)CH_3$
5.65	117	$[M]^+$	$(CH_3)_2NCH_2CO_2CH_3$
7.27	131	$[M+14]^+$	$(CH_3)_2NCH_2CH_2CO_2CH_3$
8.28	132	$[(M-44)+(M-58)]^+$	$CH_3CO_2CH_2CO_2CH_3$
12.70	144	$[(M-45)+(M-45)]^+$	$CH_3CO_2(CH)_2CO_2CH_3$
19.24	175	$[(M-15)+(M-44)]^+$	$(CH_3)_2NCH_2CO_2CH_2CO_2CH_3$
19.64	175	$[M+(M-59)]^+$	$(CH_3)_3^+NCH_2CO_2CH_2CO_2^-$
20.21	189	$[M+(M-44)]^+$	$(CH_3)_3^+NCH_2CO_2CH_2CH_2N(CH_3)_2$
30.87	233	$[M+(M-1)]^+$	$(CH_3)_3^+NCH_2CO_2CH_2N(CH_3)_2CH_2CO_2$

Table 3 Degradation compounds of anhydrous betaine by TG-FTIR, mass and pyrolysis mass

TG-FTIR nitrogen	TG-FTIR air	m/e	MS compounds	m/e	Pyrolysis-mass compounds
Carbonyls	CO_2	58	$(CH_3)_2NCH_2/CH_2CO_2$	117	$(CH_3)_2NCH_2CO_2CH_3$
$(CH_3)_3N$	Carbonyls	42	CH_2CO/C_2H_4N	59	$(CH_3)_3N$
CO_2	$(CH_3)_3N$	44	CO_2	175	$(CH_3)_2NCH_2CO_2CH_2CO_2$
H_2O	H_2O	59	$(CH_3)_3N$	175	$(CH_3)_3+NCH_2CO_2CH_2CO_2^-$
CO	CO	72	$(CH_3)_2NCH_2CH_2$	44	CO_2
		116	$(CH_3)_3NCHCO_2$	189	$(CH_3)_3+NCH_2CO_2(CH_2)_2N(CH_3)_2$

Although fragments over the betaine molecular ion (m/e=117) existed in MS, their amounts were minute compared to those of light fragments. The situation was different with TA and particularly with py-GC/MSD. The addition compounds of thermal degradation fragments were numerous and extensive in TA and py-GC/MSD. This is under-

standable, since some of the light fragments were reactive and, especially in pyrolysis, were present for long enough and in sufficient concentrations.

Table 3 shows the main degradation products of anhydrous betaine. The order is based on the area of the curves in TG-FTIR, their mass spectra intensity values and their abundance in of the pyrolysis mass chromatograms.

Water and carbon monoxide were not determined by MS and py-GC/MSD, and were hardly visible in TG-FTIR compared to the total gas products.

Trimethylamine is highly poisonous and easily inflammable gas, which evolved in the degradation of betaine. It formed in large quantities during degradation. Ketene existed only in fragments in the mass spectra. According to the TG curve, pure betaine starts to decompose at temperature higher than 245°C and yielding a poisonous and inflammable gas mixture. If betaine is present in a mixture, interactions with other components may influence the reactions.

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