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COMPARATIVE EVOLVED GAS ANALYSES ON THERMAL DEGRADATION OF THIOUREA BY COUPLED TG-FTIR AND TG/DTA-MS INSTRUMENTS

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Identification and monitoring of gaseous species released during thermal decomposition of pure thiourea, $(NH_2)_2C{=}S$ in argon, helium and air atmosphere have been carried out by both online coupled TG-FTIR and simultaneous TG/DTA-MS apparatuses manufactured by TA Instruments (USA). In both inert atmospheres and air between 182 and 240°C the main gaseous products of thiourea are ammonia (NH_3) and carbon disulfide (CS_2), whilst in flowing air sulphur dioxide (SO_2) and carbonyl sulphide (COS) as gas phase oxidation products of CS_2, and in addition hydrogen cyanide (HCN) also occur, which are detected by both FTIR spectroscopic and mass spectrometric EGA methods. Some evolution of isothiocyanic acid (HNCS) and cyanamide (NH_2CN) vapours have also observed mainly by EGA-FTIR, and largely depending on the experimental conditions. HNCS is hardly identified by mass spectrometry. Any evolution of H_2S has not been detected at any stage of thiourea degradation by either of the two methods. The exothermic heat effect of gas phase oxidation process of CS_2 partially compensates the endothermicity of the corresponding degradation step producing CS_2.

Keywords: *coupled TG/DTA-EGA-MS, coupled TG-EGA-FTIR, EGA, simultaneous TG/DTA, thiourea*

Introduction

Variety of solid degradation products in thermolysis of thiourea drew a considerable attention already in the past concerning the complexity of reactions that may take place in the melt of urea's sulphur analogue, including its isomerization to ammonium thiocyanate [1]. Mysterious, disappearing or wandering exothermic heat effect [2–4] was observed by DTA at various temperatures (above the melting point of thiourea), what probably depended on the circumstances of the measurements and is still unexplained. The gaseous degradation products seem also to be known for a long time from work of Krall [5], who mentioned H_2S, NH_3, CS_2 and HNCS. However a recent TG-FTIR study [4] has been failing in unequivocal interpretation of the obtained IR spectra of evolved gaseous mixtures from thiourea. A more recent similar study [6] carried out in flowing nitrogen still contains some uncertainties in identification of rare gaseous species evolved.

Repeated attempts for use of thiourea solutions together with various metal salts in spray pyrolysis deposition (SPD) of semiconducting metal sulfide thin films for purposes of solar cell fabrication [7–13] require a deeper insight into the composition and composition changes of the gaseous mixture released during an SPD process using thiourea, especially from point of view of technological and environmental aspects. In order to model various SPD processes through thermal decomposition of their single-source thiourea-metal precursor complexes, we have carried out recently a TG-FTIR study on dichlorobis(thiourea) cadmium(II), $Cd(tu)_2Cl_2$ (*tu*=thiourea) in 10% O_2/He atmosphere and identified additionally SO_2, COS, and HCN gases and cyanamide (H_2NCN) vapour, as well [14], anyhow H_2S was not detected. During decomposition of $Cu(tu)Cl{\cdot}0.5H_2O$ studied also in similar way, a huge amount of HCl was released and a different evolution pattern of the other gases was observed [15]. Significant differences were also observed in the evolution dynamics of gases from $SnCl_2(tu)$ and $Sn_2Cl_4(tu)_5{\cdot}2H_2O$ complexes being poor and rich in thiourea, respectively, as followed by online coupled TG-FTIR and TG/DTA-MS evolved gas analytical (EGA) techniques [16, 17]. Combined EGA-MS and EGA-FTIR studies on dichlorobis(thiourea)zinc(II), $Zn(tu)_2Cl_2$ have shown strong similarities of gas evolutions [18, 19] in comparison with the cadmium analogue [14].

In order to elucidate the basic reactions of thermal degradation of thiourea itself in inert and oxidative atmosphere, excluding the effects of metal salts, here

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we present our study on identification and tracing of evolving gaseous species from pure thiourea using both online coupled FTIR spectrometric gas cell and quadrupole mass spectrometer as detectors connected to furnaces of thermal balances (TG-FTIR and TG/DTA-MS, respectively). The components of released gaseous mixtures have been monitored and identified mostly on the basis of their FTIR and MS reference spectra available on world-wide web in the public spectrum libraries of NIST and EPA [20]. Evolution curves obtained in flowing argon, helium and air by both EGA methods are compared in details. This study has also aimed, beyond the comparisons on the composition of the elaborated gaseous multi-component mixtures and the evolution courses of the individual gas components in inert and oxidative media, even a trial on the tracing abilities and limitations of the two EGA systems.

Experimental

Material

Thiourea (Fluka Chemika 88810, p.a.>99%) was used without any further purification.

Methods

EGA by coupled TG-FTIR

A TGA 2050 Thermogravimetric Analyzer (TA Instruments, USA) with a heating rate of 10°C min^{-1}, purge gas (Ar, He and air) with flow rate of 130 mL min^{-1}, (and an extra 20 mL min^{-1} argon as a balance purge) and sample sizes between 15–25 mg in open Pt crucible were used. Gaseous species evolved from thiourea were led to FTIR gas cell of a BioRad TGA/IR Accessory Unit equipped with cooled DTGS detector through a heated stainless steal transfer line (l=90 cm, d=4 mm) kept at T=180°C. FTIR spectra (650–4000 cm^{-1}) were collected in every 30 s after accumulation of 29 interferograms by a BioRad Excalibur Series FTS 3000 spectrometer using Win IR Pro 2.7 FTIR (BioRad) data collection and evaluation software.

EGA by coupled TG/DTA-MS

An STD 2960 Simultaneous TG/DTA apparatus (TA Instruments, USA), heating rate of 10°C min^{-1}, purge gas (Ar, He and air) with a flow rate of 130 mL min^{-1}, sample sizes between 5–10 mg, pure α-Al_2O_3 as reference material and open Pt crucible was used. Mixture of gaseous species could reach a

Table 1 Wavenumbers of the most intense characteristic IR absorption bands and literature references of whole spectra of possible gaseous species

FTIR data Gas or vapour	The most intense absorption band $\tilde{\nu}/\text{cm}^{-1}$	2nd intense absorption band $\tilde{\nu}/\text{cm}^{-1}$	3rd (and 4th) intense absorption band $\tilde{\nu}/\text{cm}^{-1}$	Literature references of the whole spectrum
NH_3 ammonia	966, 932 (2×Q)	1627 (Q)	3335 (Q)	[20, 21]
CS_2 (S=C=S) carbon disulfide	1490–1550 (PR)	2170–2200 (PR)	–	[20]
$H_2N–C≡N$ cyanamide	2266 (PR)	1621 (PR)	3400–3600 (PR)	[22]
HN=C=S isothiocyanic acid	1974 (PR)	3546, 3524 (PR)	995 (PR)	[23, 24]
HN=C=O (iso)cyanic acid	2274 (PR)	3531 (PR)	1327 (PR)	[24]
HCN hydrogen cyanide	714 (PQR)	3250–3350 (PR)	1350–1450 (PR) (2800 Q)	[20, 21]
SO_2 sulfur dioxide	1300–1400 (PR)	1150 (PR)	2500 (Q)	[21]
COS (O=C=S) carboxyl sulfide	2063 (PR)	–	–	[20, 25, 26]
H_2S	1200–1400	2703	–	[20, 21, 27]
H_2O	1300–2100 (rotational lines)	3500–4100 (rotational lines)	–	[20]
CO_2	2300–2400 (PR)	670 (PQR)	3550–3760 (2×PR)	[20, 21]

Q – a sharp band, PR – two connected broad wings of absorption band, PQR – both PR-wings and sharp Q band(s) in between them

ThermoStar GDS 300 (Balzers Instruments) quadrupole mass spectrometer equipped with Chaneltron detector, though a heated 100% methyl deactivated fused silica capillary tubing kept at T=200°C. Data collection was carried out with QuadStar 422v60 software in multiple ion detection mode (MID) monitoring 64 channels ranging between m/z=15–78. Measuring time was ca. 0.5 s for a channel, resulting in time of measuring cycles of ca. 30 s.

FTIR and MS identification of various gaseous species

Reference data on wavenumbers of characteristic IR absorption bands and of whole spectra of possible gaseous species are collected in Table 1, while reference data on MS fragmentation spectra of possible gaseous species are collected in Table 2.

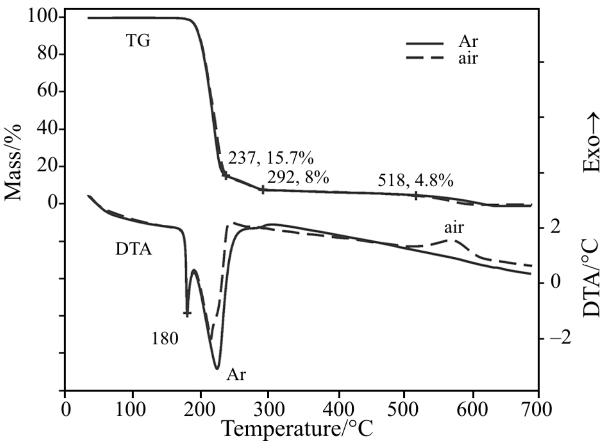

Fig. 1 Simultaneous TG/DTA curves of thiourea in argon and air (sample masses: 5.88 and 6.50 mg, respectively; heating rate: 10°C min^{-1}

Results and discussion

Simultaneous TG/DTA curves of thiourea in argon and air atmosphere

Although the TG curves of thiourea obtained both in Ar and air atmosphere are strikingly similar (Fig. 1), the DTA curves of the same sample size shows some significant differences. The main endothermic degradation process takes place right after the melting of the compound at 180°C in both cases. Nevertheless, the amount of heat required by the degradation in air seems to be significantly less than in argon. We suppose that an exothermic oxidation process also takes place around 220–240°C in the gas phase mixture of the self-generated gases and air above the sample. The heat of oxidation may compensate partially the endothermicity of degradation processes of the solid phase. This kind of change in the feature of the overall heat effect was much more pronounced in comparison when thiourea was measured in pure O_2 and pure N_2 [31]. We consider some exothermic gas phase reactions of volatile decomposition products with oxygen to be responsible for the phenomenon. See more facts and details later in the sub-chapter on. Comparative EGA of thiourea **(1)** in flowing air atmosphere by online TG-EGA-FTIR and TG/DTA-EGA-MS methods.

The mysterious, disappearing or wandering exothermic heat effects [2–4] observed earlier by DTA methods, in static air with self-generated atmosphere at various temperatures above the melting point of thiourea, are considered by us as explicitly occurring exothermic effects largely depending on the sample sizes and actual non-purged conditions of the measurements.

The exothermic heat effect in air between 500 and 600°C is explained by air oxidation of the residual solid phase(s).

Table 2 Data of the first five most intense peaks (m/z and relative intensity/% separated by slash) of MS reference spectra

MS (m/z)/%	1st peak	2nd peak	3rd peak	4th peak	5th peak	References
NH_3	17/100	16/80	15/7	14/2	18/0.4	[20]
CS_2	76/100	44/16	32/14	78/8	38/5	[20]
SO_2	64/100	48/49	32/11	16/5	66/5	[20]
COS	60/100	32/58	28/14	44/8	62/4	[20]
HCN	27/100	26/17	12/4	28/1.7	13/1.7	[20]
H_2O	18/100	17/22	16/3	19/0.5	20/0.3	[20]
CO_2	44/100	28/6	16/5	22/2	45/1	[20]
H_2S	34/100	32/44	33/42	36/4	35/3	[20]
HNCS	59/100	32/50	44/20	27/18	26/9	[28, 29]
H_2NCN	42/100	28/20	41/16	43/11	27/5	[20, 30]

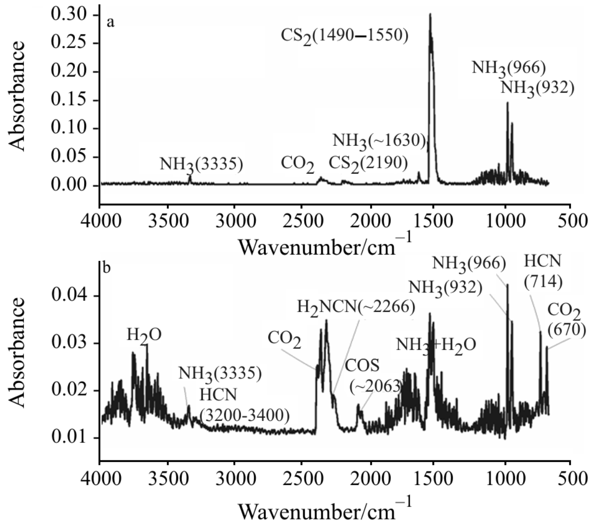

Fig. 2 FTIR spectra of gaseous mixtures observed above thiourea in argon at a – 230°C and b – 630°C measured by the online TG-FTIR system (initial sample mass: 14.96 mg, heating rate: 10°C min^{-1})

Comparative EGA of thiourea in argon atmosphere by online TG-EGA-FTIR and TG/DTA-EGA-MS methods

The main gaseous products of thiourea in pure Ar atmosphere between 182 and 330°C are found by TG-FTIR to be carbon disulfide (CS_2) and ammonia (NH_3) (Fig. 2, top spectrum) indicating decomposition of neighboring thiourea molecules in the melt:

$$2SC(NH_2)_{2(l)} = CS_{2(g)} + 2NH_{3(g)} + H_2NCN_{(l)} \quad (1)$$

Evolution of other gaseous species as cyanamide (H_2NCN), hydrogen cyanide (HCN), carbon dioxide (CO_2), and carbonyl sulfide (COS) are observed only at temperatures higher than 500°C (Fig. 2, bottom spectrum). Whilst in TG/DTA-MS experiment, cyanamide formation has been detected already from 200°C (Fig. 3). The vapor of cyanamide probably condensed and polymerized on the windows of the FTIR gas cell, and being responsible for strange changes is the baselines of FTIR spectra, and some

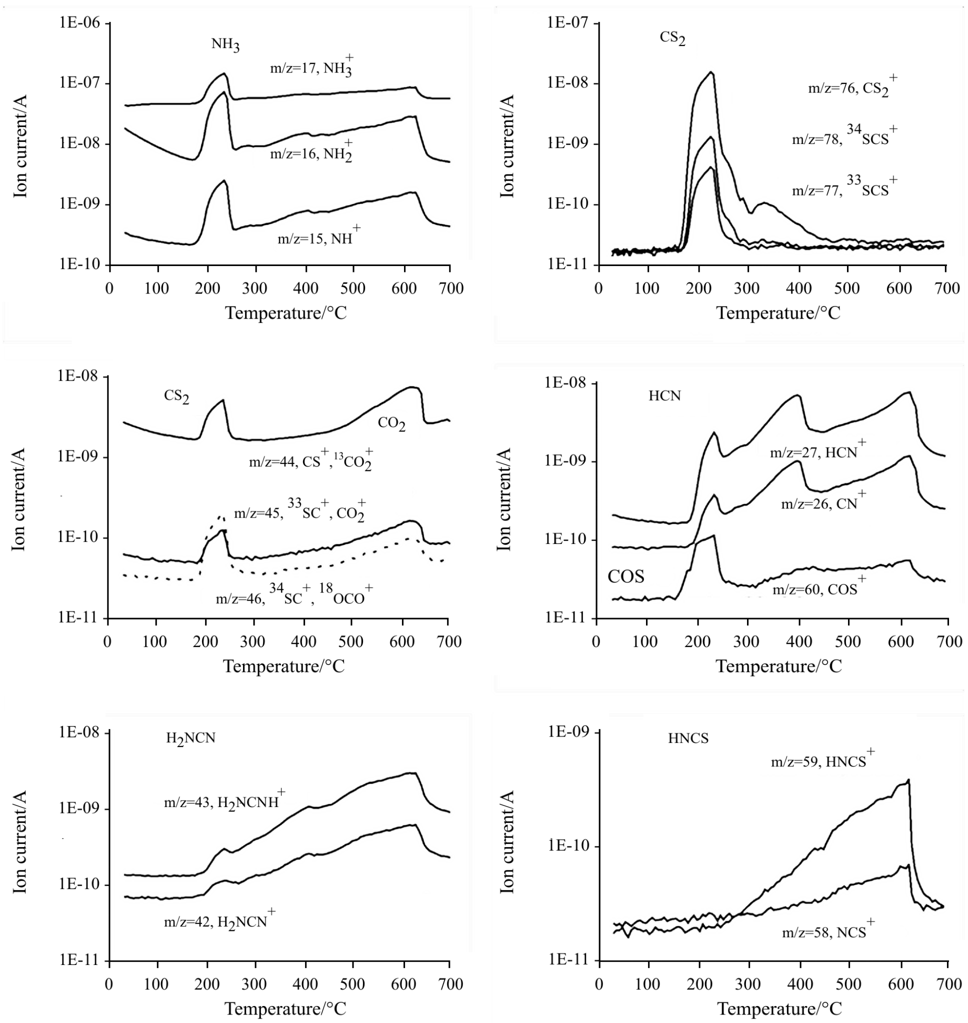

Fig. 3 Ion current *vs.* temperature curves of ion fragments of identified gases evolved from thiourea, measured in argon by online TG/DTA-MS (initial sample mass: 5.88 mg, heating rate: 10°C min^{-1})

broad absorption bands not identifiable as gaseous products.

A recent TG-EGA-FTIR study [6] on thiourea in N_2, have reported, beyond CS_2 and NH_3 an occurrence of HNCS as main products, identifying it with absorption bands at around 2070 cm^{-1}. Anyhow, COS has IR-bands centred at 2073 cm^{-1}, while absorption bands of HNCS can be centred at 1974 cm^{-1} (Table 1).

Anyhow, according to the TG/DTA-MS measurement in argon, beyond ammonia and carbon disulfide a small amount of HCN, COS, and H_2NCN have also been detected already in the first decomposition steps (Fig. 3). Along with the increasing temperature gradually isothiocyanic acid (HNCS) and CO_2 have also occurred. The characteristic fragments of these species, m/z=76, 78, 77, and 38 for CS_2, m/z=17, 16, and 15 for NH_3, m/z=27, and 26 for HCN, m/z=60, 62, 61, and 30 for COS, m/z=59, and 58 for HNCS, and m/z=43 and 42 for H_2NCN (Table 2) are in accordance with the overall mass spectrum of thiourea available in the public NIST reference database [20].

The sources of oxygen to formation of COS and CO_2 species can be the surroundings of the open measuring systems, certain lever of oxygen impurities in the inert Ar and He purge gases used, or a minute amount of urea as partial hydrolysis product may be formed during crystallization of thiourea.

EGA of thiourea in helium atmospheres by online coupled TG-EGA-FTIR

An early occurrence of HCN and HNCS has been detected in pure He by the online coupled TG-FTIR instrument, as well (Fig. 4). In this case cyanamide (H_2NCN) evolution has not been detected below 350°C. It has occurred in substantial amount above 450°C together with CO_2. Because of the high similarities in IR spectra of cyanamide [22] and (iso)cyanic acid (HNCO) [24] and of the unwanted source of oxygen mentioned above, there is a small possibility of high temperature formation of (iso)cyanic acid accompanied with carbon dioxide, as well.

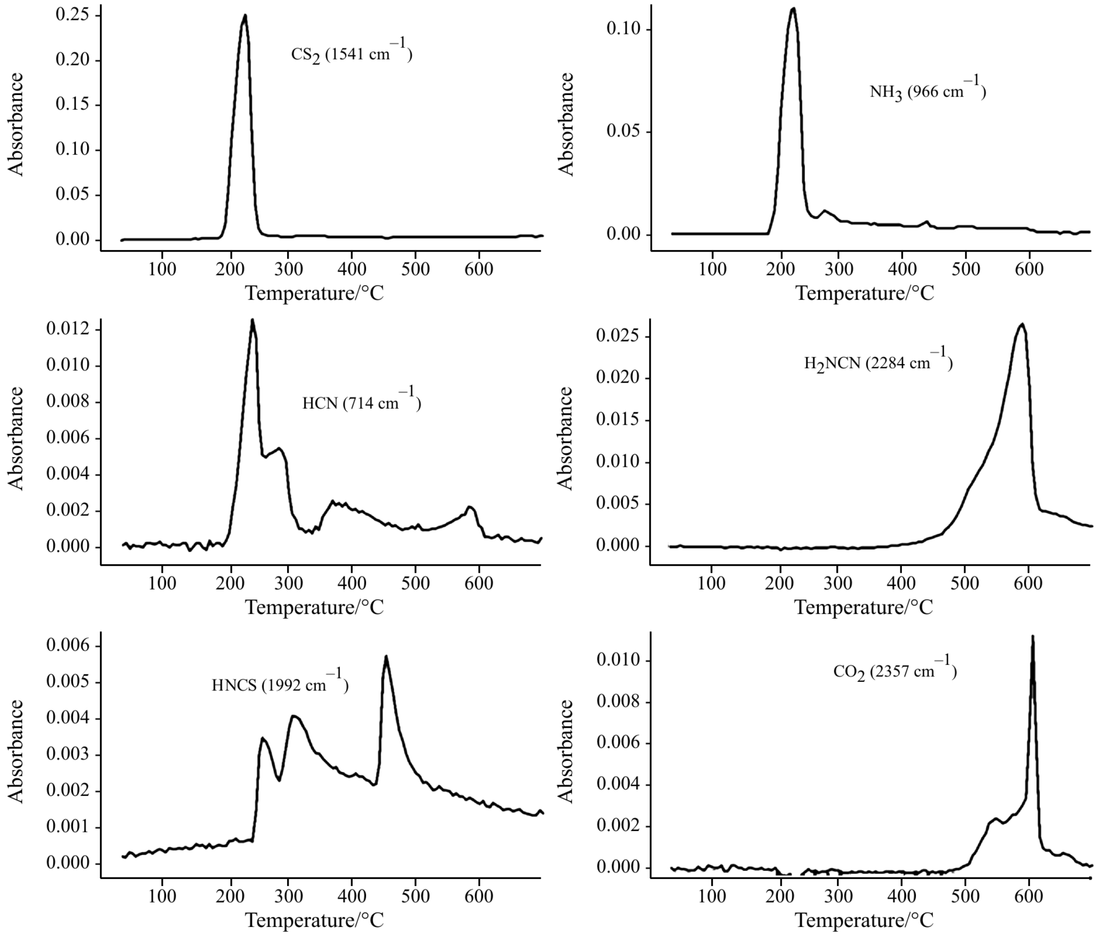

Fig. 4 Absorbance *vs.* temperature curves of identified gaseous species evolved thiourea in He measured by online TG-FTIR system (initial sample mass: 16.84 mg, heating rate: 10°C min^{-1})

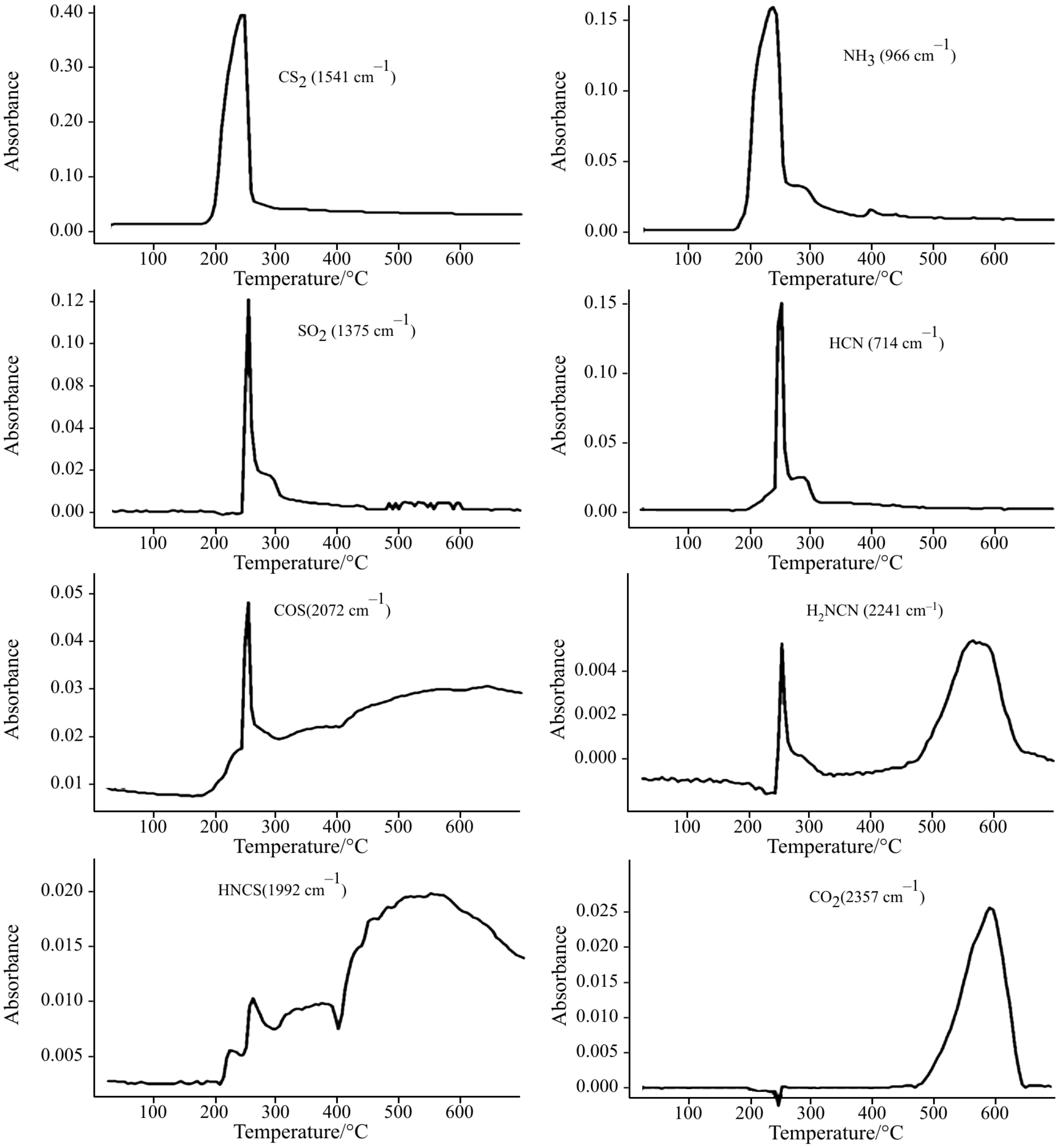

Fig. 5 Absorbance *vs.* temperature curves of identified gaseous species evolved thiourea in air measured by online TG-FTIR system (initial sample mass: 22.16 mg, heating rate: 10°C min^{-1})

Comparative EGA of thiourea in flowing air atmosphere by online TG-EGA-FTIR and TG/DTA-EGA-MS methods

The EGA-FTIR evolution curves of the identified gaseous species in air as absorbance *vs.* temperature are shown in Fig. 5, while EGA-MS evolution curves as ion currents of characteristic mass fragments are in Fig. 6.

The main gaseous products of thiourea in flowing air atmosphere between 182 and 240°C are again carbon disulfide (CS_2) and ammonia (NH_3) observed by both TG-FTIR (Fig. 7, top spectrum) and TG/DTA-MS, as well.

At around 240°C an exothermic oxidation of CS_2 vapor may occur as proven by a sudden decrease of the CS_2 vapor concentration and sharp increase that of both sulfur dioxide (SO_2) and carbonyl sulfide (COS) at the same time (Fig. 7, lower spectrum), and formulated as follows:

$$CS_{2(g)} + 1.5O_{2(g)} = SO_{2(g)} + COS_{(g)} \qquad (2)$$

The heat of this gas phase oxidation is considered as an exothermic contribution to the endothermic decomposition processes of the condensed phase (observed by DTA) and resulting also in a very intense evolution of hydrogen cyanide (HCN) and occurrence of isothiocyanic acid (HNCS) and cyanamide (H_2NCN) observed above 240°C (Fig. 7, lower spectrum).

The exothermic effect in the range of 500–650°C corresponds to the ignition of the final residues resulting in mainly CO_2. No SO_2 formation has been detected in this temperature range by either of the EGA methods..

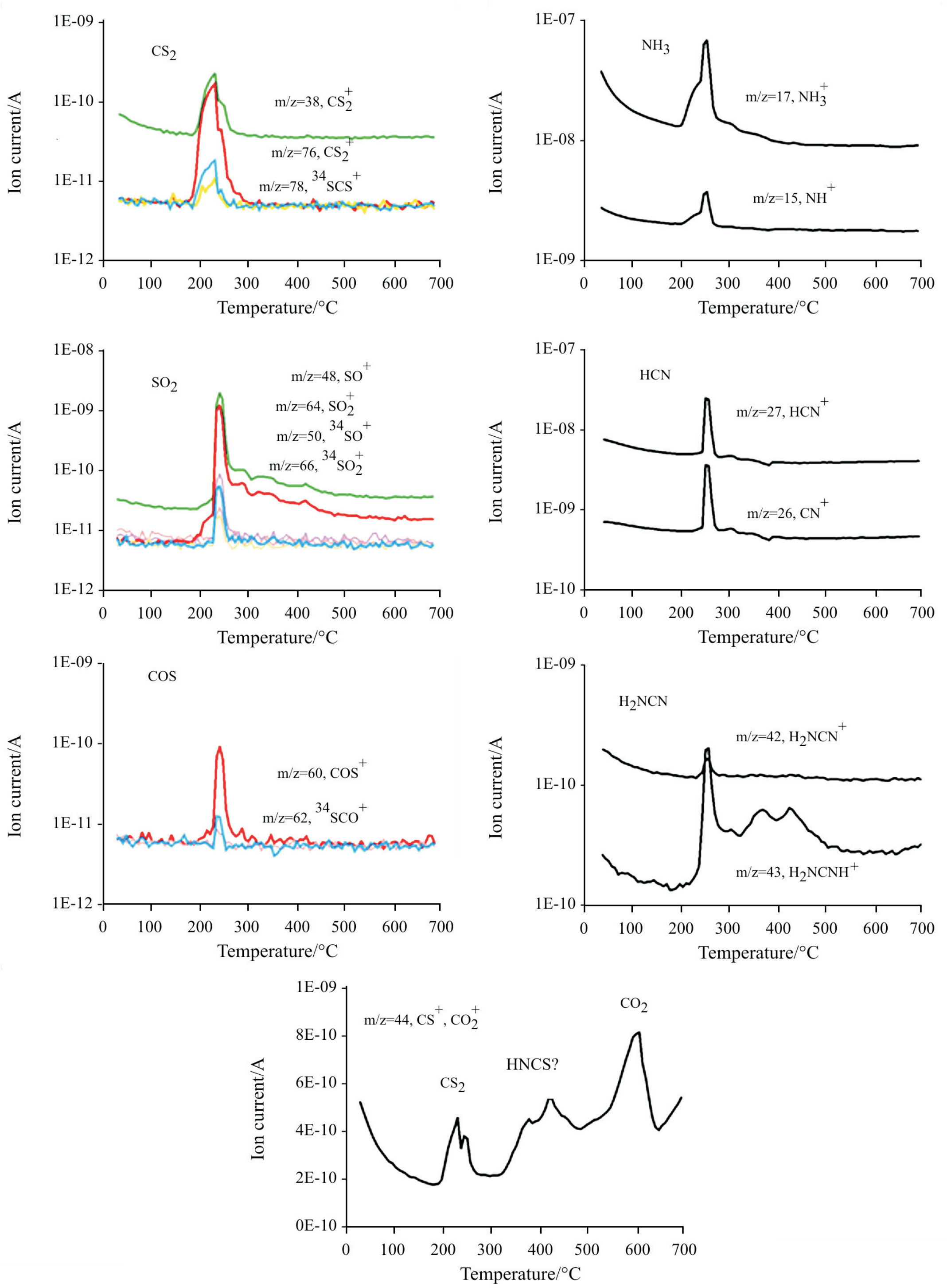

Fig. 6 Absolute ion current *vs.* temperature curves of ion fragments of identified gases evolved from thiourea, measured in air by online TG/DTA-MS (the placement lever of annotations follows the order of absolute maxima of peak height in case of fragments of CS_2, SO_2 and COS) (initial sample mass: 8.41 mg, heating rate: 10°C min^{-1})

Conclusions

Evolved gases have been identified and monitored during the thermal degradation of thiourea by both online coupled quadrupole mass spectrometer (EGA-MS) and FTIR gas cell (EGA-FTIR). In both inert atmospheres and air between 182 and 240°C the main gaseous products of thiourea are ammonia (NH_3) and carbon disulfide (CS_2). In air a sudden change in the composition of gas phase has been observed at 240°C, which is corresponding to a gas phase oxidation of CS_2 into SO_2 and COS. The exo-

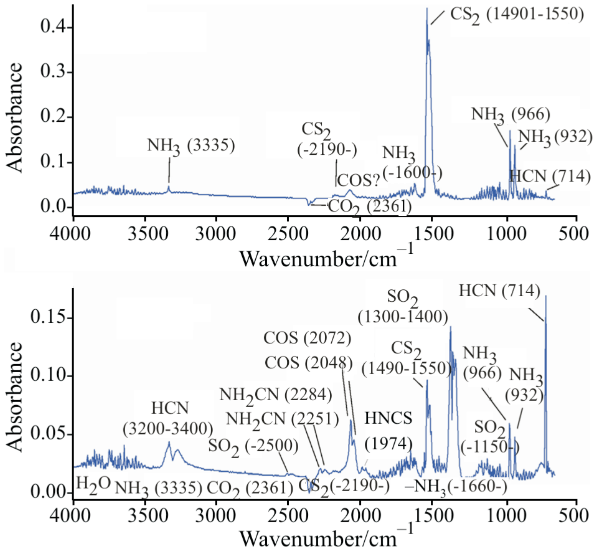

Fig. 7 FTIR spectra of gaseous mixtures observed above thiourea in air at 240 (top spectrum) and 250°C (bottom spectrum) measured by the online TG-FTIR system (initial sample mass: 22.16 mg, heating rate: 10°C min^{-1})

thermic heat effect of this oxidation process partially compensates the endothermicity of decomposition process as well. The main gas components, NH_3, CS_2, SO_2, COS, and HCN as inorganic gases are unambiguously identified by both of the EGA techniques, while the molecular ion of HNCS could not be really observed by MS. The NH_2CN and HNCS vapors which have been identified mainly by their main characteristic IR-absorption bands have caused disturbing condensations on the optics of the FTIR cell.

Nevertheless, evolved gas studies on individual thiourea complexes are still also needed to avoid even nowadays occurring assumptions, like stepwise thermal elimination of thiourea molecules from complexes containing multiple thiourea ligands [32] based on evaluation of single TG experiments, only.

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