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EVOLVED GAS ANALYSIS OF DICHLOROBIS(THIOUREA)ZINC(II) BY COUPLED TG-FTIR AND TG/DTA-MS TECHNIQUES

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Abstract

Identification and monitoring of gaseous species released during thermal decomposition of the title compound **1**, $Zn(tu)_2Cl_2$, (*tu*=thiourea, $(NH_2)_2C{=}S$) have been carried out in flowing air atmosphere up to 800°C by both online coupled TG-EGA-FTIR and simultaneous TG/DTA-EGA-MS. The first gaseous products of **1**, between 200 and 240°C, are carbon disulfide (CS_2) and ammonia (NH_3). At 240°C, an exothermic oxidation of CS_2 vapors occurs resulting in a sudden release of sulphur dioxide (SO_2) and carbonyl sulphide (COS). An intense evolution of hydrogen cyanide (HCN) and beginning of the evolution of cyanamide (H_2NCN) and isothiocyanic acid (HNCS) are also observed just above 240°C. Probably because of condensation and/or polymerization of cyanamide vapors on the windows and mirrors of the FTIR gas cell optics, some strange baseline shape changes are also occurring above 330°C. Above 500°C the oxidation process of organic residues appears to accelerate which is indicated by the increasing concentration of CO_2, while above 600°C zinc sulfide starts to oxidize resulting in the evolution of SO_2. All species identified by FTIR gas cell were also confirmed by mass spectrometry, except for HNCS.

Keywords: coupled TG/DTA-EGA-MS, coupled TG-EGA-FTIR, evolved gas analysis, simultaneous TG/DTA, thiourea, zinc(II) chloride

Introduction

Attempts to use thiourea solutions together with various metal salts in chemical spray pyrolysis (CSP) deposition of semiconducting metal sulfide thin films for purposes of alternative solar cell fabrication [1–4] require in order to succeed a deeper insight into the composition and compositional changes of gaseous mixtures released during a CSP process based on thiourea, especially from the technological and environmental points of view. For modelling of various CSP processes for CdS through controlled thermal de-

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composition of single-source thiourea-metal precursor complexes, we have recently carried out TG-FTIR studies of $Cd(tu)_2Cl_2$ in a 10% O_2/He atmosphere and identified beyond NH_3, CS_2, and HNCS, also SO_2, COS, and HCN gases and cyanamide (NH_2CN) vapour [5], however, H_2S has remained undetected. During the decomposition of $Cu(tu)Cl{\cdot}0.5H_2O$, studied in a similar way, a considerable amount of HCl was released and also a completely different evolution pattern of the other gases was observed [6]. Comparative studies on the evolved gases during thermal decomposition of $Sn(tu)Cl_2$ and $Sn_2(tu)_5Cl_4{\cdot}2H_2O$ compounds, poor and rich in thiourea, respectively, have been carried out in air by online coupled TG/DTA-MS and TG-FTIR systems [7, 8].

As single-source precursor compound for spray pyrolysis deposition of ZnS, $Zn(tu)_2Cl_2$ (tu = thiourea) has also been recently characterized by us, besides inert atmosphere also in static and flowing air, by simultaneous TG/DTA techniques, together with *ex situ* XRD and FTIR spectroscopy [9, 10]. Here we would like to report in more detail our results on evolved gas analysis of $Zn(tu)_2Cl_2$ (1) as obtained first by TG-FTIR [10] and then complemented by TG/DTA-MS observations.

Experimental

*Preparation of dichlorobis(thiourea)zinc(II) $Zn_2(tu)_2Cl_2$ (**1**)*

Title compound **1** was prepared and characterized by the literature methods [9, 10]. Its FTIR spectra were measured in FT-IR 550 (Jasco, Tokyo, Japan), Excalibur Series FTS 3000 (Biorad/Digilab, Krefeld, Germany), and Perkin Elmer System 2000 (PerkinElmer, Boston, MA, USA) spectrophotometers in KBr pellets between 650 and 4000 cm^{-1} while the XRD patterns were registered on Rint-1100 (Rigaku, Tokyo, Japan), and HZG-4 (FPM-Zeiss, Jena, Germany) X-ray diffractometers using Ni-filtered CuK_α radiation.

EGA by online coupled TG-FTIR

A TGA 2050 Thermogravimetric Analyzer (TA Instruments Inc., New Castle, DE, USA) with a heating rate of 10°C min^{-1}, an air flow rate of 130 mL min^{-1}, (plus an extra 20 mL min^{-1} argon as a balance purge) and sample sizes between 20–30 mg in open Pt crucible were used. Gaseous species evolved from **1** were led into FTIR gas cell of a BioRad/Digilab TGA/IR Accessory Unit equipped with cooled DTGS detector through a heated stainless steel transfer line (l = 50 cm, d = 4 mm) kept at T = 180°C. FTIR spectra (650–4000 cm^{-1}) were collected every 30 s after accumulation of 29 interferograms by a BioRad/Digilab Excalibur Series FTS 3000 spectrometer using Win IR Pro 2.7 FTIR (BioRad/Digilab) data collection and evaluation software.

EGA by online coupled TG/DTA-MS

An STD 2960 Simultaneous DTA-TGA apparatus (TA Instruments Inc.), a heating rate of 10°C min^{-1}, an air flow rate of 130 mL min^{-1}, sample sizes between 10–15 mg, high-purity α-Al_2O_3 as reference material and an open Pt crucible were employed. Mixture of gaseous species evolved could reach a ThermoStar GDS 200 (Balzers Instruments, Brügg, Switzerland) quadrupole mass spectrometer equipped with channeltron detector through a heated 100% methyl deactivated fused silica capillary tubing kept at $T = 200°\text{C}$. Data collection was carried out with QuadStar 422v60 software in Multiple Ion Detection (MID) mode monitoring 64 channels ranging between $m/z = 15–78$. Measuring time was ca. 0.5 s for each channel, resulting in measuring cycles of ca. 32 s duration.

FTIR spectroscopic and mass spectrometric identification of various gaseous species

The components of gaseous mixtures were monitored and identified mostly on the basis of their FTIR and MS reference spectra available on world-wide web in the public domain spectral libraries of NIST and EPA [11].

Results and discussion

*Simultaneous TG/DTA curves of $Zn(tu)_2Cl_2$ (**1**)*

On the TG curve of **1** (Fig. 1), two main mass loss steps are visible. The rate of mass loss during the first step (210–430°C) is relatively high but in the second one (430–700°C) relatively low. The overall mass loss measured up to 790°C (81.4%) is much higher than expected (the theoretical mass loss value corresponding to ZnS or ZnO is only 66.2 or 71.8%, respectively), indicating a release of some volatile zinc species in the high temperature regime (e.g. $ZnCl_2$ whose melting point is 283°C [12]). Similar losses of zinc species from **1** has been observed earlier as well [9, 10]. It should be noted that differences in experimental conditions (sample size, instrument geometry, etc.) cause differences in observed mass losses and thermal effects, as seen in Tables 1 and 2 of [10].

The decomposition starts right after the observed endothermic melting at 159.4°C (*mp*. of **1** is 160°C [10]), while in the temperature ranges 220–310, 500–600 and 600–700°C distinct exothermic heat effects are observed (Fig. 1). We also note that there is a sudden change at 220°C from an endothermic to an exothermic heat effect. DTA peaks centred at 240 and 679°C are highly exothermic while the peak at 545°C represents a much weaker effect .

*Comparative online evolved gas analyses of $Zn(tu)Cl_2$ (**1**)in air by TG/DTA-EGA-MS and TG-EGA-FTIR*

The EGA-FTIR evolution curves of the identified gaseous species recorded as absorbance *vs*. temperature are shown in Fig. 2, while the EGA-MS evolution curves as ion currents of characteristic mass fragments are presented in Fig. 3.

The first gaseous decomposition products between 200 and 240°C are carbon disulfide (CS_2) and ammonia (NH_3) (Fig. 4, upper spectrum), indicating the decomposition of adjacent thiourea ligands in the melt of **1**:

$$2SC(NH_2)_{2(l)} = CS_{2(g)} + 2NH_{3(g)} + NH_2CN_{(l,g)} \qquad (1)$$

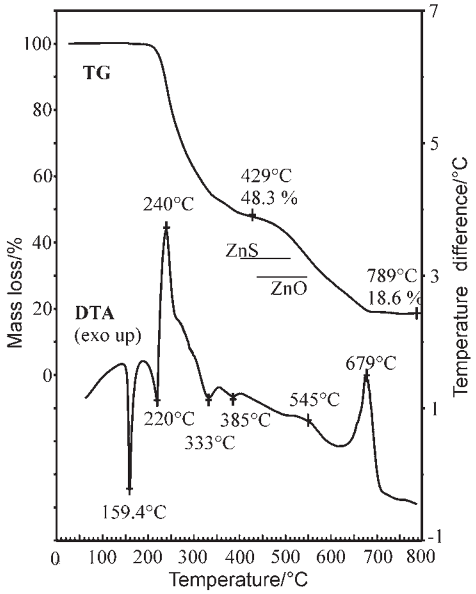

Fig. 1 Simultaneous TG/DTA curves of $Zn(tu)_2Cl_2$ (**1**) in air flow of 130 mL min^{-1} (heating rate 10°C min^{-1}, initial mass 10.48 mg). Theoretical mass levels of ZnS and ZnO are indicated

At 240°C, an exothermic oxidation of CS_2 vapor occurs, which is observed as a sudden decrease in the CS_2 vapor concentration and a sharp increase in that of both sulfur dioxide (SO_2) and carbonyl sulfide (COS) at the same time (Fig. 4, lower spectrum), and formulated as follows:

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

The heat of this reaction may contribute to the intense evolution of hydrogen cyanide (HCN) resulting also in the occurrence of isothiocyanic acid (HNCS) and cyanamide (NH_2CN), both observed above 240°C (Fig. 4, lower spectrum).

Possible reactions in the melt of complex **1** leading simultaneously to cyanamide formation may originate from the processes involving the metal sulfide formation (Eq. 3) and the molten ligand decomposition (Eq. 1):

$$Zn^{2+} + SC(NH_2)_2 = ZnS_{(s)} + NH_2CN_{(l,g)} + 2H^+ \quad (3)$$

Unfortunately, cyanamide vapors cause condensation and/or polymerization on the windows and mirrors of the IR gas cell, as judged from strange baseline shape changes and unidentified broad bands.

The proton formation indicated in Eq. (3) probably catalytically promotes the subsequent HCN and HNCS formation processes of Eqs (4) and (5), explaining the occurrence of HCN and HNCS among the evolved cases.

$$SC(NH_2)_{2(l)} + H^+ = NH_{3(g)} + H^+ + HCN_{(g)} + 1/8S_{8(l)} \quad (4)$$

$$SC(NH_2)_{2(l)} + H^+ = NH_{3(g)} + H^+ + HNCS_{(l,g)} \qquad (5)$$

Between 330 and 500°C the evolution of HNCS becomes a constant feature together with that of NH_3 and COS. The kinetics of HNCS release seem to be sensitive to small changes in the experimental conditions. However, HNCS is definitely formed according to the FTIR gas spectra but unfortunately the molecular ions of HNCS could not be confirmed by MS.

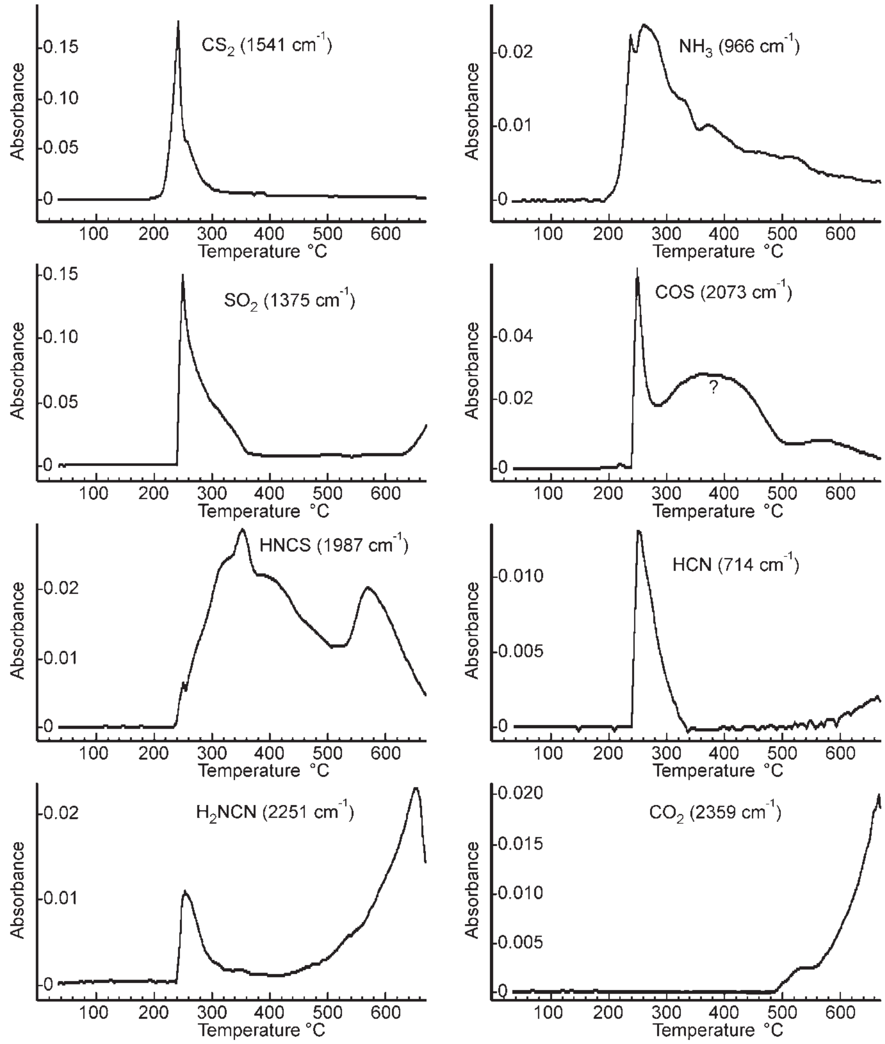

Fig. 2 Absorbance *vs.* temperature curves of the identified gaseous species evolved from $Zn_2(tu)_2Cl_2$ (**1**) as measured in air by online TG-FTIR system (heating rate 10°C min^{-1}, initial mass 24.10 mg)

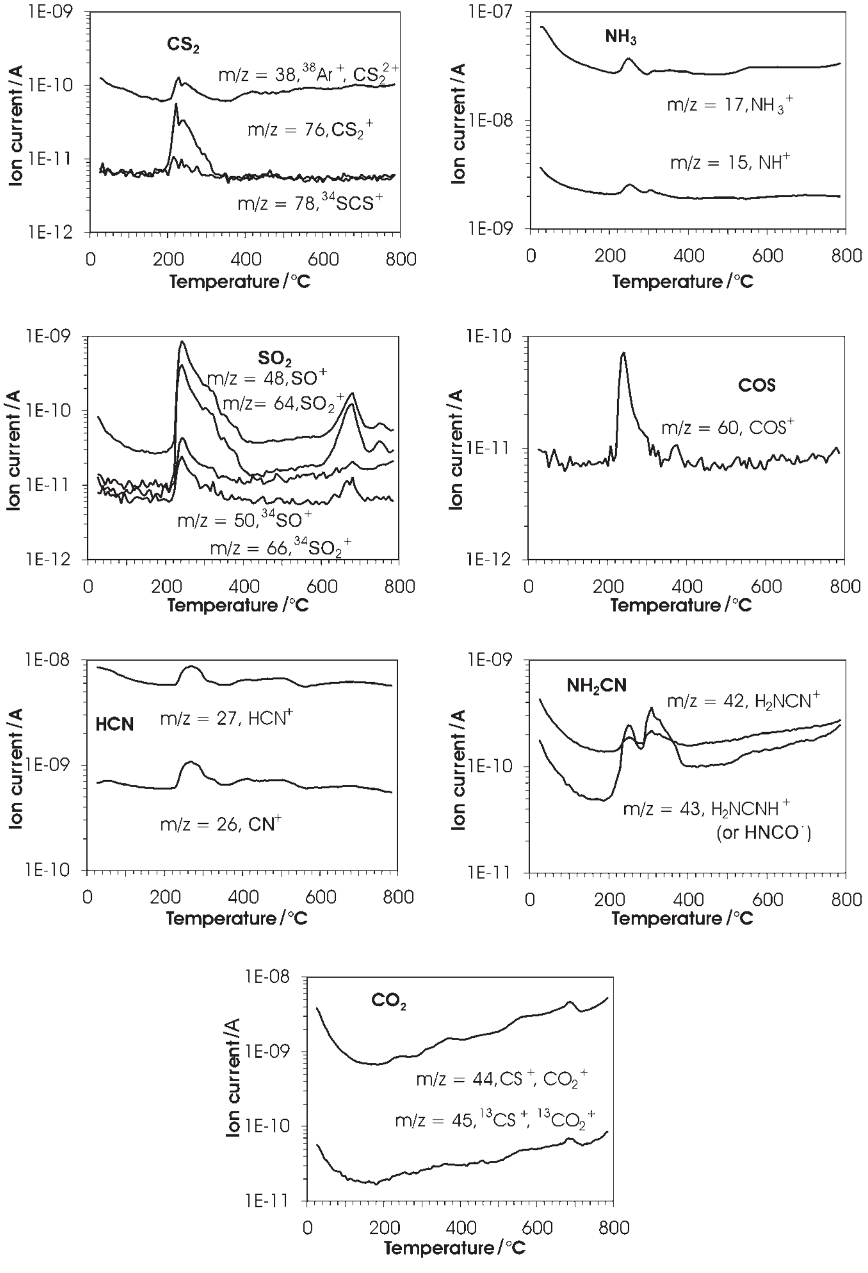

Fig. 3 Ion current *vs.* temperature curves of ion fragments in the identified gases evolved from Zn(tu)$_2$Cl$_2$, (**1**) as measured in air by online TG/DTA-MS (heating rate 10°C min^{-1}, initial mass 10.48 mg)

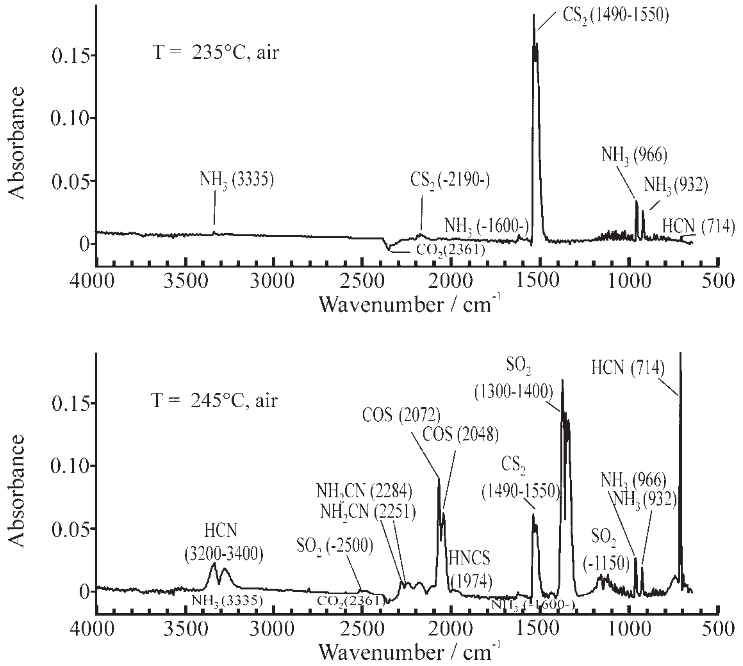

Fig. 4 FTIR spectra of gaseous mixtures observed before and during the oxidation of CS$_2$ above Zn$_2$(tu)$_2$Cl$_2$ (**1**) in air at 235°C (top) and 245°C (bottom) as observed in the online TG-FTIR system (heating rate 10°C min^{-1}, initial mass 24.10 mg)

Above 500°C the air oxidation processes seem to accelerate which is indicated by the increased evolution of both SO$_2$ and CO$_2$. Resulting from exothermic heat balance, the CO$_2$ is formed from the solid organic residues containing carbon, while SO$_2$ is formed above 600°C probably through oxidative processes involving zinc sulfides and/or solid residues containing sulfur:

$$\mathrm{ZnS_{(s)} + 1.5O_{2(g)} = ZnO_{(s)} + SO_{2(g)}} \tag{6}$$

No definite concentrations of hydrogen sulfide (H$_2$S), hydrogen chloride (HCl) nor ZnCl$_2$ could be observed by either one of our measuring systems.

Both EGA-FTIR and EGA-MS analysis of **1** in air show the same complexity of thermal decomposition as was observed earlier in the case of Cd(tu)$_2$Cl$_2$ [5]. All gases, except for HCl, are also among the decomposition products of **1**, and all evolution curves of the gaseous species are found quite similar to those of the analogous Cd compound, as reported in our earlier EGA-FTIR study [5].

Conclusions

Eight gaseous components were detected in the gas mixtures evolving from the decomposing Zn(tu)$_2$Cl$_2$ (**1**) when heating it in flowing air up to 800°C. The gas evolution was identified and monitored by both online coupled quadrupole mass spectrometer (EGA-MS) and FTIR gas cell (EGA-FTIR). A sudden change in the composition of gas phase was observed at 240°C which corresponds to a gas phase oxidation of CS_2 to SO_2 and COS. The main inorganic gaseous components, viz. NH_3, CS_2, SO_2, COS and HCN, were unambiguously identified by both of the EGA techniques, while the molecular ion of HNCS could not be observed by MS. The NH_2CN and HNCS vapours, which were identified mainly by their characteristic IR absorption bands, caused disturbing condensations on the optics of the FTIR cell.

In spite of some loss of zinc at elevated temperatures, **1** appears to be a suitable single-source precursor for processing of ZnS thin films by spray pyrolysis [10, 13]. Thermoanalytical studies especially by coupled techniques appear highly valuable in developing such processes [14].

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