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THERMAL ANALYSIS OF THIONE COMPOUNDS
I. The thermal behaviour of thiourea and N-methylthioureas*

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The thermal behavior of thiourea (Tu), N-methylthiourea (MeTu), N, N'-dimethylthiourea (Me_2Tu) and N, N, N', N'-tetramethylthiourea (Me_4Tu) was investigated by means of conventional thermal analysis in O_2 and N_2 and IR spectroscopy of the residues on heating in air at various temperatures.

At ordinary pressure, the compounds are thermally stable up to the melting points. After melting, they show high vapor pressure, combustion in O_2 atmosphere and isomerization to ammonium thiocyanate, with the exception of Me_4Tu.

Keywords: complexes, thione compounds

Introduction

Thiourea and related compounds interact with many substances and numerous complexes have been prepared and investigated in solution chemistry [1–5]. Owing to the simultaneous presence of both acceptors and donor sites, liquid thioureas probably exhibit good solvating properties toward many classes of materials.

Before undertaking systematic DSC studies on solubility phenomena in such a category of liquid thiocarbonyls, the thermal behaviour is investigated both to ob-

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tain a basis for the proper selection of the materials and for the correct interpretation of the heating curves of the mixtures.

In spite of literature reports on the thermal analysis investigations of thiourea-metal ion complexes, publications on the thermal behaviour of these individual materials are very scarce [6–9].

Experimental

Materials

Thiourea and N-substituted thioureas were commercial products (Aldrich) used without further purification (purity: Tu > 99%, MeTu > 97%, Me_2Tu > 99%, Me_4Tu > 98%).

Thermal analysis

The measurements were carried out in a dynamic O_2 or N_2 atmosphere with TSG-2 and DSC-7 Perkin-Elmer apparatus connected to a Data Station, at a flow rate of 50 ml/min and a heating rate of 10 deg·min^{-1}. Temperature and heat flux calibrations were performed with the standard calibration device. The specimens were contained in standard open (without lid) platinum crucibles. The calibration device and crucibles were supplied with the instruments.

IR spectroscopy

The infrared spectra of the residues on heating in air were recorded with a Perkin-Elmer FT 1600 spectrometer in Nujol emulsion and in NaCl or CsI disks. The primary materials (0.5–1 g) were heated in oven in open air porcelain crucibles at the lowest selected temperature and maintained under isothermal conditions for 2–3 minutes. A small amount was withdrawn from the heated sample to record the IR spectrum and the residue was heated up to the next selected temperature.

The temperatures were selected on the basis of the results of TG and DSC plots.

Results and discussion

Thiourea (Tu)

TG

Horizontal layouts in both investigated atmospheres from room temperature up to 175°C. Total weight loss in two (in O_2) or three (in N_2) steps. The percentage weight loss for the first step is greater in N_2 atmosphere. The DTG minimum procedural temperatures are different (incoherent) in the two atmospheres.

DSC

Only complessively endothermal events. Coherent maximum procedural temperature (180°C), but incoherent entahlpy changes for melting in the two atmospheres. Large endothermal heat flux immediately following the melting peak and spread over a large temperature range with incoherent maximum procedural temperatures and enthalpy changes (lower peak temperature and more exothermal enthalpy change in O_2).

IR spectra

– Original sample: Three equally intense medium bands at 3370, 3270 and 3170 cm^{-1} (ν-NH_2) [10], a strong band at 1610 cm^{-1} (S–NH_2). Bands at 1415, 1080, 725 and 630 cm^{-1} ascribed to composite vibrations of the 'thioureide group', =N–C = S [10].

– Residue at 180°C. External appearance: faint-yellow liquid smelling of pungent sulphur compounds. IR spectrum with three uniformly decreasing bands at 3420, 3316 and 3210 cm^{-1}. A very intense single band at 2052 cm^{-1} and bands at 1600, 1097 and 725 cm^{-1}.

– Residue at 200°C (see residue at 180°C).

– Residue at 250°C. External appearance: yellow in color and waxy solidity. IR spectrum with two large bands at 3395 and 3210 cm^{-1}. The band at 2052 cm^{-1} turns into a doublet of equally intense bands at 2070 and 2052 cm^{-1}. A strong band at 1660 cm^{-1} with a shoulder at 1609 cm^{-1}, two weak bands at 1521 and 789 and a very weak band at 626 cm^{-1}.

– Residue at 300°C. External appearance: yellow solid IR spectrum substantially identical to the previous one.

N-methylthiourea (MeTu)

TG

TG curves similar in shape to those for Tu: no weight change from room temperature up to 150°C, but subsequent total weight loss in three sharp steps in both atmospheres. The percentage weight loss for the first step is greater in N_2. DTG minimum procedural temperatures incoherent in the two atmospheres.

DSC

General features similar to the layout for Tu, except for the peak temperatures and enthalpy changes. Second endothermal event after melting. Incoherent maximum procedural temperatures and enthalpy changes in the two atmospheres in the same way as for Tu (lower maximum procedural temperatures and more exothermal enthalpy change in O_2).

IR spectra

– Original sample: Two large bands at 3250 and 3170 cm^{-1}. Several medium-intensity bands between 1700 and 500 cm^{-1}.

– Residue at 130°C. The bands between 3500 and 3000 cm^{-1} become sharper. Medium-intensity bands recorded at 2894, 2691, 1490 and 1256 cm^{-1}.

– Residue at 170°C. External appearance: waxy white. IR spectrum with a very intense band at 2052 cm^{-1} and a weak band at 1042 cm^{-1}.

N, N'-dimethylthiourea (Me_2Tu)

TG

Horizontal layouts from room temperature up to 125°C followed by total weight loss in three steps in O_2 and in a single (?) step in N_2. In N_2, greater weight loss for the first step and also greater in comparison with the corresponding value for Tu or MeTu. Incoherent DTG minimum procedural temperatures in the two atmospheres.

DSC

Endo-flux for melting coherent in both atmospheres. After melting, endothermic heat flux which becomes exothermal at higher temperatures. Coherent peak temperatures in O_2 and N_2.

IR spectra

– Original sample: As for MeTu. IR spectrum of Me_2Tu with large absorptions between 3500 and 3000 cm^{-1} and a sequence of medium-intensity bands between 1600 and 500 cm^{-1}.

– Residues at 80°, 130°, 200° and 230°C: IR spectra identical to that of the original sample.

– Residue at 250°C. Bands at 2052 cm^{-1} (strong), 1640 cm^{-1}, 1575 cm^{-1} (strong) and 1142 cm^{-1} (medium).

N, N, N'N'-tetramethylthiourea (Me_4Tu)

TG

No weight loss up to 60°C, followed by total loss in a single (!?) step. In the two atmospheres, the layouts are practically superimposed. Almost coherent minimum procedural temperatures.

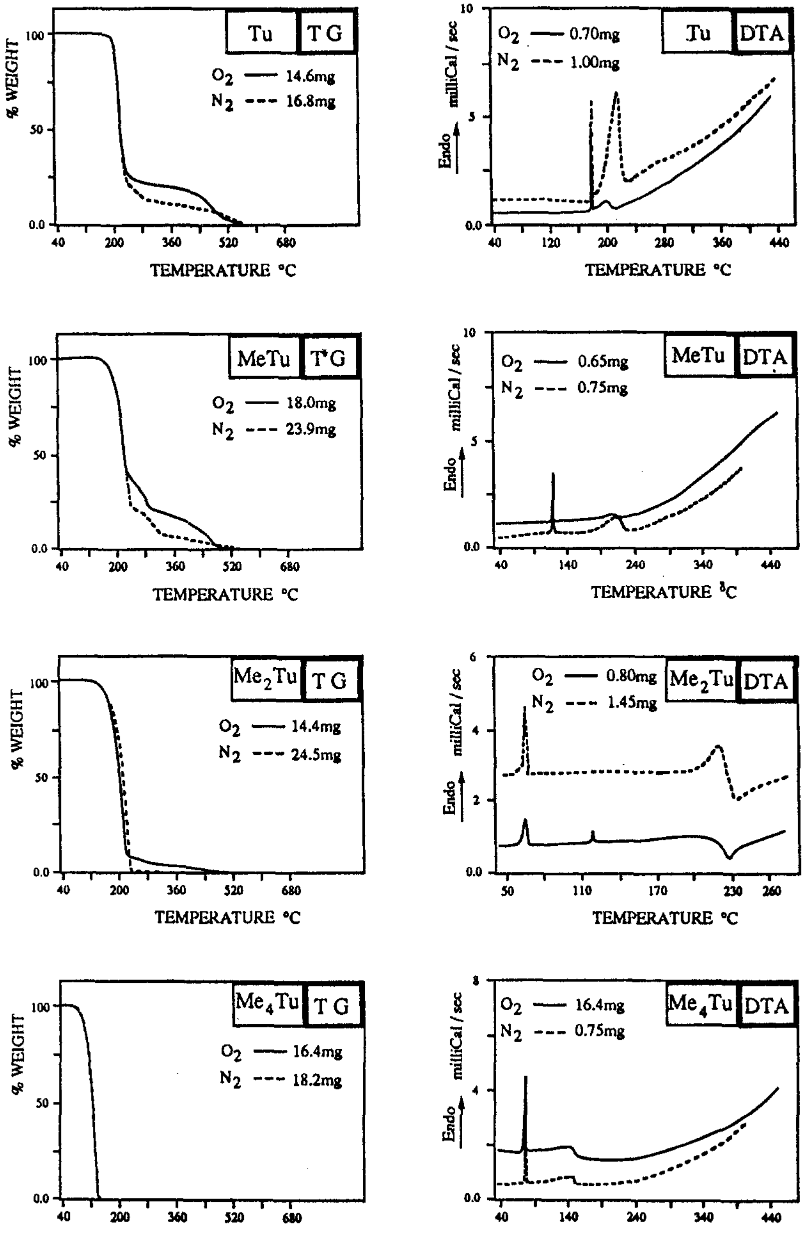

Fig. 1 TG and DSC curves for thiourea and N-methylthioureas in dynamic O_2 and N_2 atmospheres

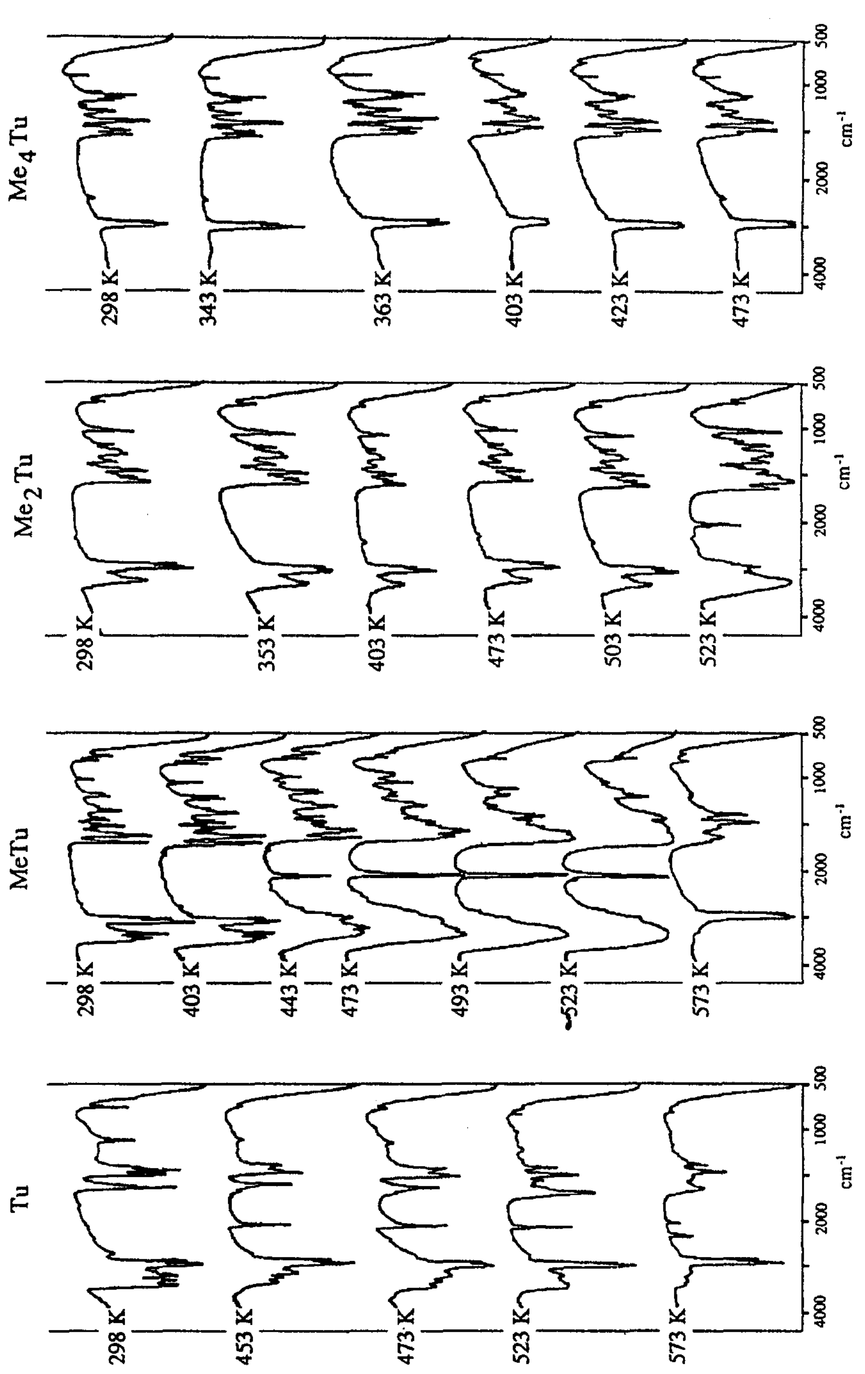

Fig. 2 Selected IR spectra of the residues of thiourea and N-methylthioureas on heating in air at various temperatures

DSC

Layout similar in shape to that for Me_2Tu: endothermic peak for melting and evident exothermal heat flux at higher temperatures.

IR spectra

– Original sample: Medium-intensity bands within the range 1700–500 cm^{-1}.

– Residues at 90°, 130°, 150° and 200°C: IR spectra identical to that of the original sample. Starting from the residue at 130°C, differences only in the intensity of the band at 1508 cm^{-1}.

Thermal analysis curves and IR spectra are reported in Figs 1 and 2, respectively. Table 1 refers to the results deduced from the thermal analysis diagrams.

The investigated compounds are stable on heating up to the melting points. In the liquid state, they undergo chemical changes and total weight loss.

On the basis of the features of the thermogravimetric layouts, they can be classified in two different groups:

a) The first group, constitued by Tu, MeTu and Me_2Tu, is characterized by the total weight loss occurring in two or three stages.

b) The second group, constituted by Me_4Tu, is characterized by a single-stage total weight loss.

In all cases, locally increasing endothermic fluxes correspond to the thermogravimetric negative steps.

From stoichiometric considerations on the percentage weight losses and from the general shapes of the DSC diagrams in O_2 and N_2 atmospheres, high vapor pressure and partial combustion of the samples in oxidizing atmosphere must be inferred. Higher temperatures are induced locally by the combustion of part of the sample, and the reaction rates of the chemical changes in progress are increased. In such a way, the higher percentages of the solid residues in O_2 can be accounted for.

The absorption band at 2052 cm^{-1}, which occurs in a wavelength range free from absorption, is diagnostic for the reaction product. The absorptions can be ascribed to the presence of thiocyanate [11] in the residue. The presence is confirmed by the $FeCl_3$ test and by the absorption at 1660 cm^{-1}. The test for cyanide failed.

The presence of ammonium in the heating residues was evidenced by chemical tests and confirmed by the absorption bands between 3500 and 3000 cm^{-1}.

The formation of thiocyanate was not found in the Me_4Tu residues.

Table 1 Thermogravimetry and differential scanning calorimetry data on the thermal behavior of thiourea and N-methylthioureas in O_2 and N_2 atmospheres. Owing to the shapes of the thermogravimetric layouts, the percentage weight losses are approximate

	Thermogravimetry					
Compound	O_2 atm.			N_2 atm.		
	T /°C*	$-\Delta W$ / %	Step	T / °C	$-\Delta W$ / %	Step
Tu	210	~ 80	single	210	~ 89	two
	455	~ 15	two	535	~ 1	single
MeTu	203	~ 60	single	206	~ 80	single
	285	~ 19	single	301	~ 15	single
	nd	~ 21	single	nd	~ 5	single
Me_2Tu	197	~ 91	single	210	~ 99	single
	nd	~ 5	single	nd	~ 1	single
Me_4Tu	120	100	single	125	100	single

	Differential scanning calorimetry					
Compound	O_2 atm.			N_2 atm.		
	T / °C	ΔH /J·g^{-1}	ΔH /kJ·mol^{-1}	T / °C	ΔH /J·g^{-1}	ΔH /kJ·mol^{-1}
Tu	180	145.3	11.0	181	196.8	15
	202	199.7	15.2	217	1997	152.0
MeTu	120	180.4	16.2	120	180	16.3
	208	171.7	15.9	214	659	59.4
Me_2Tu	66	87.7	9.17	66	109	11.4
	nd	nd	nd	nd	nd	nd
Me_4Tu	78	151.6	20.01	78	138.2	18.2
	nd	nd	nd	nd	nd	nd

nd = not determined

Conclusions

The investigated thioureas are thermally stable when solid. In the liquid state, they show

(i) high vapor pressure,

(ii) partial combustion in O_2 atmosphere,

(iii) isomerization to ammonium thiocyanate.

Ammonium thiocyanate is formed at about 200°C and is observed only for incompletely substituted thioureas. Me_4Tu does not produce thiocyanate in the residue.

Partial combustion in O_2 produces the differences in behavior in the two atmospheres.

The data recorded in N_2 can be considered reliable values for the enthalpy change for melting.

The influence of the substituent is mainly reflected in the melting points, rather then in the enthalpy changes for fusion. It must be concluded that, in comparison with the behavior of Tu, the substituents introduce favorable entropy elements for melting, probably connected with the more pronounced loss of structure in the liquid phase on substitution of the hydrogen atoms of Tu.

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Zusammenfassung — Mittels herkömmlicher Thermoanalyse in O_2 und N_2 sowie IR-Spektroskopie der Rückstände des Erhitzens an Luft auf verschiedene Temperaturen wurde das thermische Verhalten von Thioharnstoff (Tu), N-Methylthioharnstoff (MeTu), N,N-Dimethylthioharnstoff (Me_2Tu) und N,N,N',N'-Tetramethylthioharnstoff (Me_4Tu) untersucht.

Bei Normaldruck sind die Verbindungen bis zu den Schmelzpunkten thermisch stabil. Nach dem Schmelzen weisen sie einen hohen Dampfdruck auf, verbrennen in O_2-Atmosphäre und isomerisieren mit Ausnahme von Me_4Tu zu Ammoniumthiocyanat.