

KINETIC STUDY OF THE THERMAL DECOMPOSITION
OF HETEROCYCLIC THIOL COMPLEXES
UNDER NON-ISOTHERMAL CONDITIONS

K. N. JOHRI, N. K. KAUSHIK and K. A. VENUGOPALAN

Department of Chemistry, University of Delhi, Delhi-110007, India

(Received December 3, 1975)

The thermal decomposition in the solid-phase has been studied by thermogravimetric (TG) and differential thermal analysis (DTA) techniques for a number of heterocyclic thiol complexes. The method of Coats and Redfern was used to study the kinetics of the thermal decomposition process. The enthalpy changes and activation energies for the decomposition have been calculated.

In recent years, the chelate complexes with the sulphur-donor ligands have been extensively studied as one of the most interesting topics in the field of coordination chemistry and many reports have been well documented on the properties and reactivities of such complexes.

In earlier papers from Johri et al. [1-3], the thermogravimetric (TG) studies of potassium thiocarbonate (PTC) reagent and some metal thiocarbonates and sulphides obtained with PTC have been studied under dynamic temperature conditions, with a view to confirm the purity of the precipitated products and the correct temperature ranges for the resulting products to attain constant weight, thereby affording gravimetric evaluations of the metal ions.

This communication reports on extensive thermoanalytical investigations that have been undertaken on complex compounds involving the two heterocyclic thiol ligands: 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBI). These have been widely used as organic reagents for inorganic ions notably for the gravimetric [4-6], amperometric [7] and spectrophotometric [8, 9] determinations.

Only preliminary studies on the thermal behaviour of some of the complexes have been studied by Duval [10], with a view to investigate analytical procedures for determining suitable and stable weighing forms and the limits of the horizontal stretch between which the complexes have the assigned formulae. Bera et al. [11], have reported the thermal decomposition studies of these ligands.

The present work includes the kinetics of the thermal decomposition of the complexes under dynamic temperature conditions both by thermogravimetric (TG) and differential thermal analysis (DTA) techniques. Derivation of the kinetic parameters has been performed by means of Coats and Redfern's integral method [12], assuming a rate law of the type

$$\frac{d\alpha}{dT} = k(1 - \alpha)^n \quad (1)$$

and an Arrhenius equation of the type

$$k = Z \cdot e^{-E/RT} \quad (2)$$

to be valid, where “ α ” stands for the fraction transformed, “ n ” for the reaction order, k for the rate constant and “ E ” for the activation energy. The graph of

$$\log \frac{1 - (1 - \alpha)^{1-n}}{(1-n)T^2} \text{ vs. } \frac{1}{T}$$

gave a straight line of slope $-E/2.303R$ for the correct value of “ n ” ($n \neq 1$). The following apparent reaction orders were tried: $n = 0, 1/3, 1/2, 2/3$ and 2 . For $n = 1$, the plot of

$$\log \left[-\log \frac{(1 - \alpha)}{T^2} \right] \text{ vs. } \frac{1}{T}$$

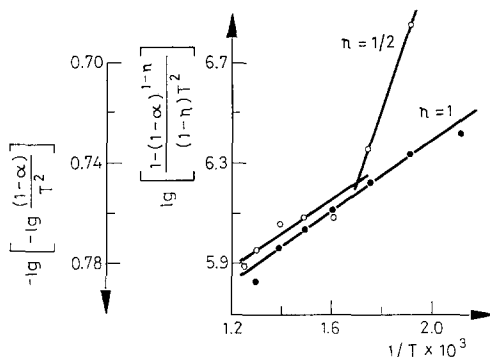


Fig. 1. Determination of activation parameters for the thermal decomposition of bismuth mercaptobenzothiazole $\text{Bi}(\text{MBT})_3$

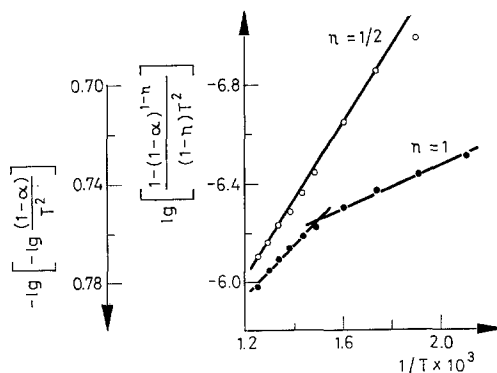


Fig. 2. Determination of activation parameters for the thermal decomposition of cadmium mercaptobenzimidazole, $\text{Cd}(\text{OH})(\text{MBI})\text{NH}_3$

Table 1
Kinetic parameters for the thermal decomposition of complexes

Complex	Order of reaction <i>n</i>	Activation energy <i>E</i> , cals/mole ⁻¹	<i>T</i> _{max.} , °C	<i>K</i> , Kcal cm ⁻²	<i>H</i> , Kcal mole ⁻¹
Cu(MBT) ₂	1	651.8	360	0.0935	107.8
Ag(MBT)	—	—	300	0.0720	24.5
Zn ₂ (OH)(MBT) ₃	1	338.8	340	0.0855	31.6
Cd(NH ₃) ₂ (MBT) ₂	1	390.4	342	0.0870	194.4
			405		
Hg(MBT) ₂	—	—	192	0.0328	9.4
Co ₂ (MBT) ₃	1	429.9	345	0.0880	60.7
Ni(MBT) ₂	1	366.1	314	0.0770	17.9
Tl(MBT)	1	347.4	307	0.0745	20.8
Pb(MBT) ₂	—	—	—	—	—
Bi(MBT) ₃	1	390.1	284	0.0660	56.0
Th(MBT) ₄	1	314.2	185	0.0300	28.1
Cu(OH)(MBI)	1/2	6949.0	222(+)	0.0438	9.4
Ag(MBI)	—	—	124	0.0080	1.9
Cd(OH)(MBI)NH ₃	1/2	6998.0	365	0.0955	32.5
Hg(OH)(MBI)	1	540.8	295	0.0710	9.1
Co(OH)(MBI)	1	217.7	133	0.0112	3.8
Pb(OH)(MBI)	1	472.4	399(+)	0.1080	83.9
Te(MBI).SO ₄	1	290.7	268	0.0602	146.0
AgNO ₃	—	—	225	0.0438	3.01
NaNO ₃	—	—	324	0.0806	3.76
C ₆ H ₅ COOH	—	—	135	0.0128	4.14

(+) Exothermic decomposition temperature

gave a straight line of slope $-E/2.303R$ (Figs 1, 2). Coats and Redfern's method allows a good linearization and gave excellent straight lines even under extreme conditions [13]. However, the first few points (initial 2 to 5 per cent of the decomposition reaction) did not fall on the line. This is expected, since the decomposition of solids is known to disobey first-order kinetics in the initial stages [14]. The apparent reaction order ensuring the best linearity of the Coats–Redfern plot and the activation energy values have been tabulated (Table 1).

The enthalpy changes have been estimated by comparing the area of each peak on the DTA curves with that for a number of standard substances. The area of the peak on the DTA curve, *A*, and the enthalpy change (ΔH , Kcal/mole) are related by the expression [15]

$$\Delta H = \frac{KA}{N_0} \quad (3)$$

where “*K*” is a constant, “*N*₀” is the initial number of moles of the specimen.

The areas were obtained by integration of the peaks by the use of tracing paper and a semi-micro balance.

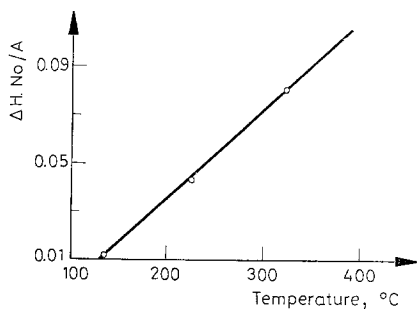


Fig. 3. Calibration curve for temperature dependence of K

Table 2

Summary of thermal stability data (Temperature in °C)

Complex	DTA		TG
	Decomposition peak	Decomposition endotherm	Decomposition range
Cu(MBT) ₂	360	300–387	265–475
Ag(MBT)	300	269–306	—
Zn ₂ (OH)(MBT) ₃	340	324–350	245–695
Cd(NH ₃) ₂ (MBT) ₂	342, 405	222–426	250–580
Hg(MBT) ₂	192	159–202	—
Co ₂ (MBT) ₃	345	300–361	245–610
Ni(MBT) ₂	314	298–320	270–615
Tl(MBT)	307	292–314	275–515
Pb(MBT) ₂ **	—	—	—
Bi(MBT) ₃	284	263–294	210–550
Th(MBT) ₄	185, 340	83–363	40–*
Cu(OH)(MBI)	222(+)	150–240	200–585
Ag(MBI)	124	82–207	—
Cd(OH)(MBI)NH ₃	365	300–390	180–540
Hg(OH)(MBI)	295	282–298	295–710
Co(OH)(MBI)	133	79–180	140–550
Pb(OH)(MBI)	399(+)	300–445	340–445
Te(MBI)·SO ₄	268	204–288	105–610
AgNO ₃	225	210–234	—
NaNO ₃	324	222–330	—
C ₆ H ₅ COOH	135	124–137	—

* The curve slopes downward continuously

** Curves not recorded owing to explosive nature of the complex

(+) Exothermic decomposition temperature

The constant “ K ” is a characteristic of the instrumentation employed, which varies with the change in temperature and its value must be arrived at by employing suitable standards. The value of “ K ” should be determined as closely as possible to the temperature of the experimental measurements to be made on unknowns.

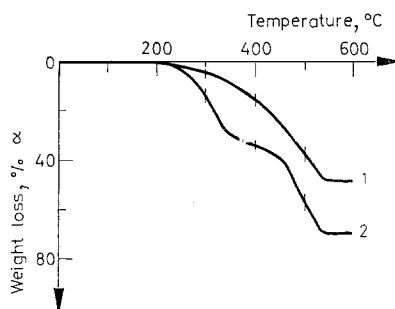


Fig. 4. TG curves of (1) cadmium mercaptobenzimidazole, $\text{Cd}(\text{OH})(\text{MBI})\text{NH}_3$ and bismuth mercaptobenzothiazole, $\text{Bi}(\text{MBT})_3$

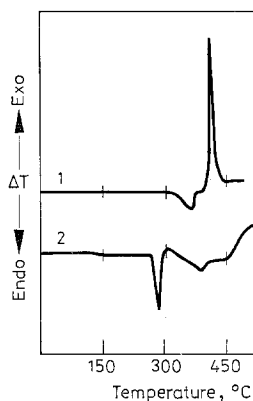


Fig. 5. DTA curves of (1) cadmium mercaptobenzimidazole, $\text{Cd}(\text{OH})(\text{MBI})\text{NH}_3$ and (2) bismuth mercaptobenzothiazole, $\text{Bi}(\text{MBT})_3$

To determine the nature of the temperature dependence of K , we used the following standard materials: Silver nitrate, sodium nitrate and benzoic acid (ΔH and T_{max} values are tabulated, Table 1). The calibration curve (Fig. 3) used in the calculations was obtained by plotting the values of $\frac{\Delta H \cdot N_0}{A}$ against T_{max} .

The values of ΔH for the metal complexes studied are given in the Table 1.

Owing to large number of TG and DTA curves obtained, only representative curves are shown in the Figs (4, 5). A summary of the thermal stability data is given in Table 2. The curve for each complex has been discussed briefly correlating

Table 3
Preparatory methods for complexes

No.	Complex	Colour	Starting metal salt	Reference
1.	Cu(MBT) ₂	Pale orange yellow	CuSO ₄ .5H ₂ O	17
2.	Ag(MBT)	Yellow	AgNO ₃	18
3.	Zn ₂ (OH)(MBT) ₃	Light yellow	ZnCl ₂	19
4.	Cd(NH ₃) ₂ (MBT) ₃	Yellowish white	Cd(C ₂ H ₃ O ₂) ₂ .2H ₂ O	16
5.	Hg(MBT) ₂	Yellow-white microcrystalline	HgCl ₂	18
6.	Co ₂ (MBT) ₃	Green	Co(C ₂ H ₃ O ₂) ₂ .4H ₂ O	17
7.	Ni(MBT) ₂	Brown sparkling microcrystalline	NiSO ₄ .6H ₂ O	17
8.	Tl(MBT)	Yellow	Tl ₂ CO ₃	20
9.	Pb(MBT) ₂	Lemon yellow	Pb(NO ₃) ₂	20
10.	Bi(MBT) ₃	Chrome yellow	Bi(NO ₃) ₂ .5H ₂ O	20
11.	Th(MBT) ₄	Yellowish white	Th(NO ₃) ₄ .6H ₂ O	21
12.	Cu(OH)(MBI)	Grey blue	CuSO ₄ .5H ₂ O	22
13.	Ag(MBI)	Greenish yellow	AgNO ₃	24**
14.	Cd(OH)(MBI).(NH ₃)	Crystalline white	CdCl ₂ .2.5H ₂ O	23
15.	Hg(OH)(MBI)	Greenish white	HgCl ₂	25**
16.	Co(OH)(MBI)	Greenish blue	CoCl ₂ .6H ₂ O	*
17.	Pb(OH)(MBI)	Silky white flakes	Pb(NO ₃) ₂	23
18.	Te(MBI).SO ₄	Reddish-brown	TeO in 9M H ₂ SO ₄	26

(MBT) = C₆H₄NCS₂

(MBI) = C₇H₅N₂S

* Preparation described under experimental ** Prepared via metal-EDTA complex

TG and DTA data. The temperatures referred to are the procedural decomposition temperatures at the heating rate indicated.

Copper mercaptobenzothiazole, Cu(MBT)₂: The TG curve discloses that the complex is stable up to 265°. Then the destruction of the complex though occurring in a single step, follows a complicated course and does not lead to pure cupric oxide and this is in accordance with the information reported by Duval [10] as well. The DTA curve contained two endothermic peaks. A small endothermic peak centered at about the temperature range 150–183° followed by a much larger peak from 300 to 387° for the decomposition reaction.

Silver mercaptobenzothiazole, Ag(MBT): In view of the corrosive nature of this silver complex, it has been investigated by the method of DTA only. A sharp DTA endotherm in the range 296–306° corresponded to the decomposition of this complex. This was preceded and followed by broad exotherms representing oxidation. However, an endotherm, centered at 135°, appeared, revealing the expulsion of the adsorbed water.

Zinc mercaptobenzothiazole, Zn₂(OH)(MBT)₃: This complex decomposes step-wise. As is apparent from the TG curve, the complex is quite unstable. The initial

loss of about 1% up to 200° is accounted for by the escape of adsorbed moisture. Above 245°, a very slow decomposition sets in and becomes rapid near 370° after a loss of about 3.5% of the initial weight. A simultaneous decomposition and oxidation of the product markedly influenced the weight loss curve and arresting to some extent the weight loss. The process is complete at 695° and then the horizontal due to zinc oxide appears. The DTA curve shows a very shallow endothermic band from 90–120° representing the loss of adsorbed moisture. A sharp endothermic band from 324–350° represents decomposition of the complex over this region.

Cadmium mercaptobenzothiazole, $\text{Cd}(\text{NH}_3)_2(\text{MBT})_2$: The initial loss of about 2% in weight of the complex up to 120° was apparently due to the escape of adherent water. A rapid decomposition of the complex sets in around 250°, as revealed by the TG trace. A horizontal, probably due to a mixture of cadmium oxide and sulphide, appears at 580°. The small endothermic peak between 114–195°, resulting from the loss of adherent water is followed by two broad peaks covering a temperature range 250–580°, corresponding to the decomposition of the complex.

Mercury mercaptobenzothiazole, $\text{Hg}(\text{MBT})_2$: Owing to extremely capricious TG curve that is obtained, probably due to high volatility of the mercury complex, only DTA curve could be recorded and discussed. The DTA curve furnishes well defined, and widely separated two endotherms for the decomposition reaction. A sharp endotherm in the region 159–202° was followed by a much broader one from 325 to 409°.

Cobalt mercaptobenzothiazole, $\text{Co}_2(\text{MBT})_3$: The TG curve for the complex has the initial horizontal extending up to 245° and then a slow, immediately followed by a rapid decomposition. The level probably due to mixed oxides, $\text{Co}_2\text{O}_3 + \text{Co}_3\text{O}_4$ (black residue) appears around 610°. The DTA curve exhibited a rather broad shallow endothermic peak from 90–171° caused by the dehydration of the superficially adsorbed moisture. This was followed by another endotherm covering a temperature range 300–361° corresponding to the decomposition of the complex.

Nickel mercaptobenzothiazole, $\text{Ni}(\text{MBT})_2$: The complex was stable up to 270°. A rapid one-step decomposition followed up to 615°, giving a black residue, the molecular weight of which corresponded to NiO. The DTA curve furnishes a single endotherm from 298 to 320°, representing the decomposition of the complex.

Thallium mercaptobenzothiazole, $\text{Tl}(\text{MBT})$: The TG curve of the inner complex of thallium shows a horizontal extending up to 210°. Then the complex decomposes rapidly. The progressive oxidation of thallos sulphide to sulphate and the simultaneous decomposition of the complex affected the normal course of the curve. The product at 515° roughly corresponded to the trioxide, Tl_2O_3 . The lone DTA endotherm between 292–314° reveals the decomposition of the complex. However, a broad exotherm extending as far as 468° indicates oxidation of the sulphide.

Lead mercaptobenzothiazole, $\text{Pb}(\text{MBT})_2$: The explosive nature of the complex prevented us from getting the curves.

Bismuth mercaptobenzothiazole, $\text{Bi}(\text{MBT})_3$: The complex produces a horizontal extending as far as 200° and then decomposes stepwise. Above 210° , a slow decomposition sets in and becomes rapid immediately afterwards. A slight arrest in the decomposition rate occurs around 320° , probably due to some oxidation of the elemental bismuth as is evident by a very small exotherm in that region of the DTA trace. Then the decomposition is rapid and the process is complete at 550° , when a horizontal due to Bi_2O_3 appears, unlike the one at 927° , as reported by Duval [10]. The DTA curve exhibits two endotherms. A sharp peak at 284° (range $263-294^\circ$) and a subsequent broad endotherm covering a temperature range $321-460^\circ$ both due to the decomposition of the complex.

Thorium mercaptobenzothiazole, $\text{Th}(\text{MBT})_4$: The decomposition of the complex sets in right from the beginning. The initial downslope in the TG profile from 40° extends up to 180° , and after a loss of nearly 7% of the initial weight, decomposition becomes rapid and slopes downward continuously. The DTA curve showed two widely separated endothermic peaks over a very broad range from 83 to 363° representing decomposition over this region.

Copper mercaptobenzimidazole, $\text{Cu}(\text{OH})(\text{MBI})$: The TG curve of the greyish-blue copper complex showed an initial loss in weight of about 0.8% up to 200° , apparently due to the loss of adsorbed moisture. Above 200° a slow decomposition sets in which accelerates beyond 410° , resulting in a loss of about 20% of the initial weight. The process is complete at 585° , when a horizontal due to cupric oxide appears. An exothermic peak at 222° (range $150-240^\circ$) on the DTA curve represents decomposition over this region.

Silver mercaptobenzimidazole, $\text{Ag}(\text{MBI})$: The corrosive nature of the silver complex, like the $\text{Ag}(\text{MBT})$ counterpart, led to the omission of the TG studies. However, the complex was investigated by DTA technique. The DTA curve exhibits three peaks. A broad endotherm in the range $82-207^\circ$ is followed by a very small exothermic peak in the range $207-242^\circ$, both representing decomposition of the complex. A third exothermic peak representing oxidation and decomposition of the residue covers a temperature range $323-378^\circ$.

Cadmium mercaptobenzimidazole, $\text{Cd}(\text{OH})(\text{MBI})\cdot\text{NH}_3$: The complex yields a thermolysis curve which steadily slants downward from 180° onwards. A one-step decomposition is followed up to 540° and a horizontal probably due to a mixture of cadmium oxide and sulphide appears. The DTA curve showed two consecutive peaks. A broad endothermic peak in the range $300-390^\circ$ representing endothermic decomposition, which is followed by a sharp exothermic peak in the range $390-438^\circ$, which can be ascribed partly due to the exothermic decomposition and partly to the oxidation over this region.

Mercury mercaptobenzimidazole, $\text{Hg}(\text{OH})(\text{MBI})$: The TG curve produces a horizontal extending up to 295° . A three step decomposition of the complex sets in at 295° and which proceeds over a very broad temperature range $295-710^\circ$. This stops abruptly and the crucible is found to be completely empty at 710° , yielding a white sublimate. The DTA trace reveals three distinct changes. The endothermic peak at 295° corresponding to decomposition is followed by an exo-

therm at 300°, representing some oxidation of the elemental mercury produced. The residue decomposes over the broad endothermic range 348–423° to complete the process.

Cobalt mercaptobenzimidazole, Co(OH)(MBI): The pyrolysis curve initially shows a slow descent up to 140°, apparently due to the loss of adsorbed water. Immediately after the expulsion of water the decomposition of the complex sets in. After a loss of nearly 14% of the initial weight around 400°, decomposition becomes fairly rapid. The horizontal level due to the black-grey oxide, Co₂O₃ begins at 550°. The DTA shows a broad endotherm in the range 79–180° superimposing the effects due to the expulsion of adsorbed moisture, and decomposition of the complex. The endotherm is followed by a broad exotherm, representing further exothermic decomposition, and oxidation.

Lead mercaptobenzimidazole, Pb(OH)(MBI): The TG curve includes a horizontal extending up to 200°. A slow decomposition sets in and becomes rapid after a loss of about 2% of the initial weight. The rapid one-step decomposition followed up to 445° yielding metallic lead. The DTA reveals a lone broad exothermic band from 300–445° corresponding to exothermic decomposition and oxidation of metallic lead.

Tellurium mercaptobenzimidazole, Te(MBI)-SO₄: The decomposition of the complex sets in right from the beginning. The initial loss of about 2% in weight up to 105° was apparently due to the escape of adherent moisture. Then the step-wise destruction of the complex begins, following a very complicated course not yielding any pure product. In view of this, this method had to be abandoned. However, the DTA shows two superimposed endothermic peaks over a broad range 75–183°, superimposing the effects due to the expulsion of adherent moisture and decomposition of the complex. This is followed by a very sharp and a well defined endothermic peak from 204–288°, characterizing the decomposition reaction.

Experimental

Materials

2-Mercaptobenzothiazole (MBT): The commercially available reagent (Fluka AG, Switzerland) was further purified by the method of Walliczek [9] and a freshly prepared 1 per cent solution in alcohol was used.

2-Mercaptobenzimidazole (MBI): Procured from Schuchardt München, Germany. A freshly prepared 1 per cent solution in an EtOH.H₂O mixture was used.

Metal complexes: The preparatory methods for the metal complexes, as adopted are summarized in Table (3).

Cobalt mercaptobenzimidazole Co(OH)(MBI): To an aqueous solution of cobalt chloride (1 mole) added excess of ammonium chloride and ammonium hydroxide. To this a slight excess of hot 1 per cent reagent (MBI) was added, until precipitation was complete. This was then heated to gentle boiling with stirring until the

precipitate coagulated and settled which was digested for about 1/2 hour. After allowing to stand for 4–5 hours, it was filtered through a medium porosity sintered glass crucible and washed several times with 0.1N NH_4OH , followed by hot distilled water and finally with 5% alcohol. The precipitate is dried at room temperature for about 72 hours by keeping in a vacuum desiccator.

Methods

Thermogravimetry (TG) of the complexes was carried out with a Stanton's automatic thermorecording balance model MF-L1 No. 25105. Sample weight: 100–120 mg. Heating rate: $4 \pm 0.2^\circ\text{C}$ per minute in a 'self-produced' atmosphere using silica crucible. The sensitivity of the balance per small chart division was 100 mg. All data used in the preparation of the TG curves were corrected for buoyancy (experimentally determined for the crucible used).

The DTA of the complexes was carried out with a Leeds and Northrup DTA unit (USA), using ceramic sample holders and sample cell of Grimshaw pattern. Reference material: Highly calcined and finely powdered α -alumina. Heating rate: $10^\circ\text{C}/\text{minute}$. Sample weight: 400–600 mg.

Purity of the samples: The infrared spectra of the complexes were recorded on the Perkin-Elmer 137 (Infracord) in KBr phase. The bands in the spectra were assigned, and the identity and purity of the complexes checked by comparing the spectra with the data reported in the literature.

*

We are grateful to Prof. K. C. Joshi, Head of the Chemistry Department and Dr. A. K. Rai of Rajasthan University, Jaipur for permitting the generous use of the thermorecording balance at the University and to Dr. E. R. Saxena, Assistant Director, Mineral Products and Inorganic Chemicals Division and Mr. P. Narayanachar of Regional Research Laboratory, Hyderabad for their valuable assistance in taking DTA trace. Thanks are also due to Prof. V. V. S. Murti, Head of the Chemistry Department, University of Delhi for his interest in the work. The author (K. A. V.) thanks the University Grants Commission, New Delhi for the award of the fellowship under which these investigations have been carried out.

References

1. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Current Sci. India* 36 (1967) 458.
2. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Current Sci. India* 36 (1967) 515.
3. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *J. Thermal Anal.*, 2 (1970) 37.
4. K. KODAMA, *Methods of quantitative Inorganic Analysis*, Interscience, 1963.
5. F. J. WELCHER, *Organic Analytical Reagents*, Vol. IV, Van Nostrand, N. Y. 1948, p. 113, 127.
6. A. K. MAJUMDAR and M. M. CHAKRABARTTY, *Z. Anal. Chem.*, 162 (1958) 96, 101.
7. A. K. MAJUMDAR and M. M. CHAKRABARTTY, *Anal. Chim. Acta*, 20 (1959) 386.
8. D. KRÜGER and E. TSCHIRCH, *Z. Anal. Chem.*, 97 (1934) 61.
9. E. G. WALLICZEK, *Talanta*, 11 (1964) 573.
10. C. DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam 1963.

11. B. C. BERA and M. M. CHAKRABARTTY, *Talanta*, 13 (1966) 1549.
12. A. W. COATS and J. P. REDFERN, *Nature*, 201 (1964) 68.
13. J. ZSAKÓ, *J. Thermal Anal.*, 5 (1973) 239.
14. A. W. COATS and J. P. REDFERN, *J. Polymer Sci.*, Pt. 3 (B) (1965) 917.
15. H. J. BORCHARDT and F. DANIELS, *J. Am. Chem. Soc.*, 79 (1957) 41.
16. G. SPACU and M. KURAŠ, *Z. Anal. Chem.*, 102 (1935) 24; *C. A.*, 29 : 7213 (7, 9).
17. G. SPACU and M. KURAŠ, *J. Prakt. Chem.*, 144 (1935) 106; *C. A.* 30 : 2872 (9).
18. L. ERDEY, *Gravimetric Analysis, Part II*, Pergamon Press, Oxford, 1965, p. 16.
19. S. KACANI and L. STEFANKA, *Czech. J. Chem.* 124, 384 (Cl. Co7d), 15 Sept. 1967, *Appl.* 20 Jul. 1965; 2 pp., *C. A.* 69: 43905r.
20. G. SPACU and M. KURAŠ, *Z. Anal. Chem.*, 104 (1936) 88; *C. A.* 30: 2875 (9).
21. G. SPACU and TH. I. PIRTEA, *Acad. Rep. Populare Române, Bul. Stiint., Ser.: Mat., Fiz., Chim.*, 2 (1950) 669; *C. A.* 45: 7910h.
22. M. KURAŠ, *Chem. Obzor*, 14 (1939) 51; *C. A.* 33: 7233 (4).
23. M. KURAŠ, *Chem. Obzor*, 14 (1939) 49; *C. A.* 33: 7298 (9).
24. T. TAKIGUCHI, M. ABE, K. KUROSUKI, E. ASADA and M. NAKAGOME, *Kogyo Kagaku Zasshi*, 70 (7) 1967, 1182; *C. A.* 68: 22046a.
25. M. KURAŠ, *Chem. Obzor*, 13 (1938) 95; *C. A.* 33: 941 (6).
26. E. RAMANAUSKAS, and S. GRODNIKAS, *Khim. khim. Tekhnol.*, 12 (1970) 33; *Anal. Abstr.*, 22 (1972) Ab. 1557.

RÉSUMÉ — Etude de la décomposition thermique en phase solide de plusieurs complexes thiols hétérocycliques par thermogravimétrie (TG) et par analyse thermique différentielle (ATD). La méthode de Coats et Redfern a été appliquée pour déterminer la cinétique du processus de la décomposition thermique. Les variations d'enthalpie et les énergies d'activation de la décomposition ont été calculées.

ZUSAMMENFASSUNG — Die thermische Zersetzung in fester Phase wurde an einigen heterozyklischen Thiolkomplexen mit den Methoden der dynamischen Thermogravimetrie (TG) und der Differentialthermoanalyse (DTA) untersucht. Die Methode von Coats und Redfern wurde zum Studium der Kinetik des thermischen Zersetzungs Vorganges eingesetzt. Die Enthalpie-Änderungen und Aktivierungsenergien der Zersetzung wurden berechnet.

Резюме — С помощью динамической термогравиметрии (TG) и дифференциального термического анализа (DTA) было изучено термическое разложение ряда гетероциклических тиольных комплексов в твердой фазе. Для изучения кинетики процесса термического разложения был использован метод Коутса и Редферно. Вычислены изменения энтальпии и энергий активации процесса разложения.