# THERMAL DECOMPOSITION OF TRIS(PIPERIDYLDITHIO-CARBAMATES) OF As(III), Sb(III) AND Bi(III)

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Thermal studies by TG, DTG and DTA of tris(piperidyldithiocarbamates) of arsenic(III), antimony(III) and bismuth(III) of the general type $M[S_2CN(CH_2)_5]_3$ ($M$ = As, Sb and Bi) have been carried out in nitrogen and air, as well as under vacuum, to determine their modes of decomposition. The apparent activation energies were determined by graphical methods and the TIN temperatures were calculated from the TG profiles.

A possible mechanism of the decomposition reaction is suggested on the basis of the results of their pyrolysis and their mass spectral data.

The intermediates obtained at the end of various decomposition steps were identified via their elemental analysis, i.r. spectral data and X-ray diffraction studies. A dimeric structure of type $M_2[S_2CN(CH_2)_5]_4$ ($M$ = As, Sb) is proposed.

As part of a research project which started several years ago in our laboratory, a large number of dithiocarbamato complexes with various metals have been synthesized, and their structures and chemistry have been studied extensively. In the knowledge of their applications and importance in industry, it was of interest to carry out thermal studies on these complexes.

Hitherto, several papers have appeared concerning the thermal behaviour of transition metal dithiocarbamato complexes. However, the thermal studies on the dithiocarbamato complexes of As(III), Sb(III) and Bi(III) are limited to only three papers. A brief review of these is given below, highlighting the points connected with our work.

The thermal stability in air of dithiocarbamato complexes of antimony(III) and bismuth(III), $Sb[S(S)CNR_2]_3$ and $Bi[S(S)CNR_2]_3$ ($R$ = ethyl, $n$-butyl, $n$-isobutyl, $n$-amyl, $n$-isoamyl and $n$-octyl) was studied on the basis of their TG, DTG and DTA curves by Afanasova et al. [1]. The apparent activation energies ($E^*$) were determined by Piloyan's methods and a presumed decomposition reaction was given. Kumar et al. [2] investigated the thermal behaviour of the tris-$N$(ethyl-$m$-tolyl) dithiocarbamates of the same metals in nitrogen and air. The $E^*$ values were calculated for the first stage of the decomposition for all the complexes in a nitrogen atmosphere, employing the graphical method of Coats and Redfern. Very recently, thermal studies

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on the 4-aminophenazonedithiocarbamato complex of antimony, $Sb(4-Apdtc)_3$, in oxygen atmosphere were carried out by TG and DTG techniques [3], the $E^*$ values again being calculated by the graphical method of Coats and Redfern.

In the present paper, thermal studies on tris(piperidyldithiocarbamates) of arsenic(III), antimony(III) and bismuth(III) by simultaneous TG, DTG and DTA in dynamic atmospheres of air and nitrogen, and under vacuum ($10^{-2}$ Torr), are reported and discussed. The pyrolysis results, $E^*$ values derived from Piloyan's method, TIN (10% tangential temperature) calculations and a proposed mechanism of the decomposition are also reported and discussed.

### Experimental

All complexes were prepared by known methods [4]. The thermal decomposition was carried out on a Netsch 429 apparatus at a heating rate of 2 degree/min up to 600°, using a sample mass of 25 mg and $\alpha\text{-Al}_2\text{O}_3$ as reference. The measurements were performed in dynamic atmospheres of air and nitrogen and under vacuum ($10^{-2}$ Torr).

X-ray powder diffraction analyses of the final residues were made with a Phillips PW 1130/00 X-ray diffractometer, using Cu-Kα radiation. For the determination of TIN, the areas of the TG curves were measured with a Coradi Cora-Senior planimeter.

Carbon, hydrogen and nitrogen determinations were performed on a Perkin—Elmer 240 microanalyser. Infrared spectra were recorded in the range 4000—250 cm$^{-1}$ on a Perkin—Elmer 467 spectrophotometer, using KBr pelletts. Mass spectra were recorded on a R.M.V.-6L-Hitachi--Perkin—Elmer mass spectrometer. Molecular weight measurements were made on a Perkin—Elmer 115 molecular weight apparatus. $^1$H n.m.r. spectra were recorded on a Varian A 60 A (60 MHz) machine, using TMS a as internal standard.

### Pyrolysis

The pyrolysis of all complexes was carried out in a dynamic nitrogen atmosphere.

A 0.5—0.7 g sample of the compound was introduced into a two-necked round-bottomed flask equipped with a heating mantle, the heating rate being about 5 degree/min. The temperature was raised up to the first step of decomposition of each reaction, 200—250°; the exact value was found from the corresponding thermogravimetric curve.

The compound melted as the temperature was raised up to the first step of decomposition, the heating was continued for 1/3 h, and the material was then left to cool.

The highly volatile products of decomposition, such as $CS_2$, were collected in a liquid air trap.

The less volatile decomposition components remained on the neck and the cool parts of the flask, from where they could be removed with $CHCl_3$ or $C_2H_5OH$, and separated on a silica gel 70—230 mesh column, using $CHCl_3$ as eluent. The higher ratio products of pyrolysis were identified by spectroscopic methods (i.r., n.m.r. and M.S.), elemental analyses and molecular weight determinations.

## Results and discussion

### Thermal analysis

All thermoanalytical curves (TG, DTG and DTA) of the complexes under study are given in Figs 1 to 6.

The TG curves in air and nitrogen exhibit similarities and show that decomposition begins at about 200°, just after the melting point. The first decomposition step is common in both atmospheres and involved sudden and considerable losses of mass (56—74%). The DTA profile shows a sharp exothermic peak in air, whereas in nitrogen the peak is endothermic, in accordance with the decomposition of other dithio-carbamato complexes [5—7]. The temperature ranges and percentage mass losses in
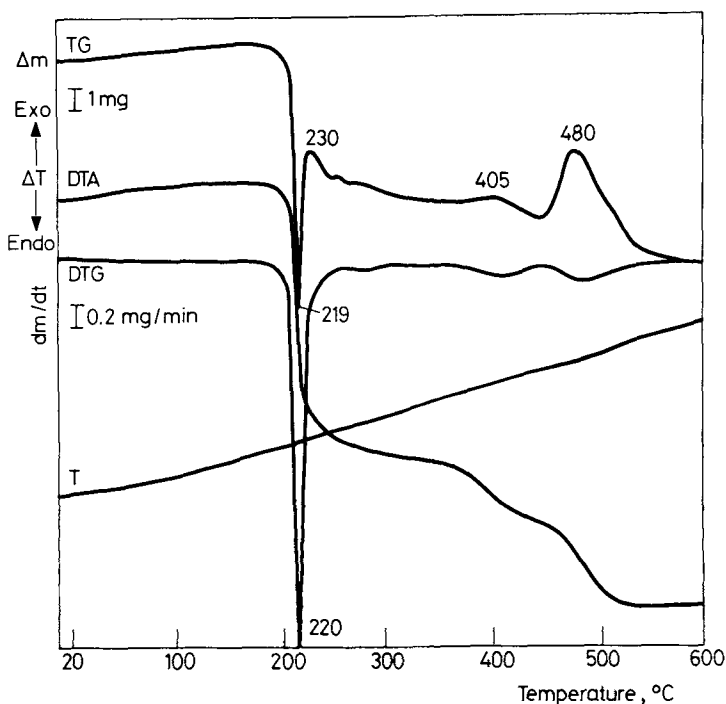


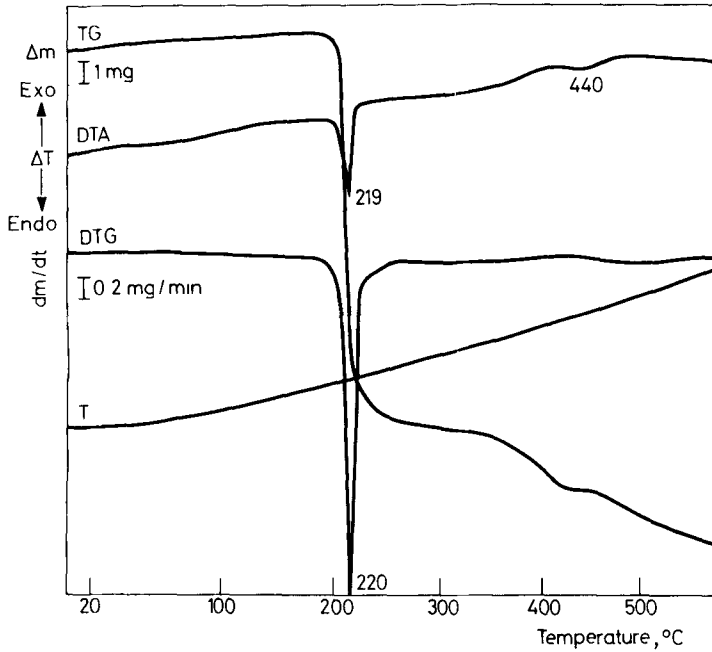Fig. 1 Thermoanalytical curves of $As[S_2CN(CH_2)_5]_3$ in air

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Fig. 2 Thermoanalytical curves of $As[S_2CN(CH_2)_5]_3$ in nitrogen
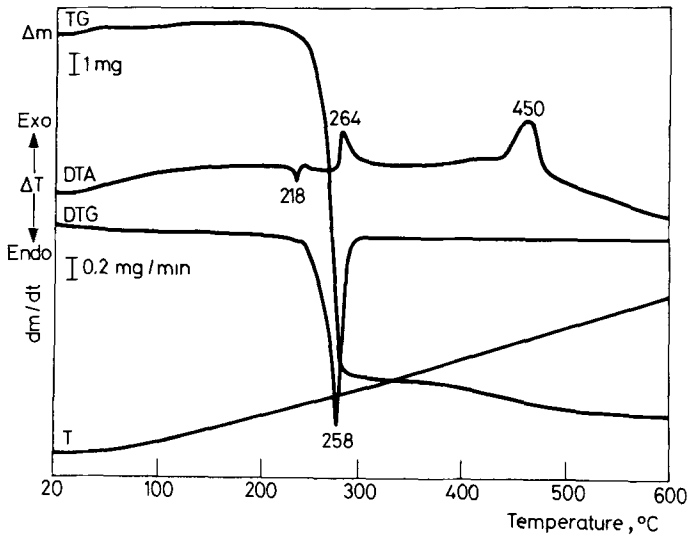


Fig. 3 Thermoanalytical curves of $Sb[S_2CN(CH_2)_5]_3$ in air
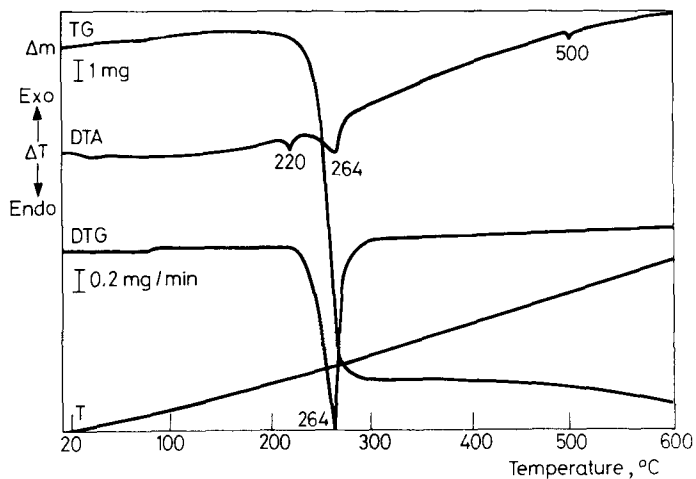
Fig. 4 Thermoanalytical curves of Sb[S$_2$CN(CH$_2$)$_5$]$_3$ in nitrogen
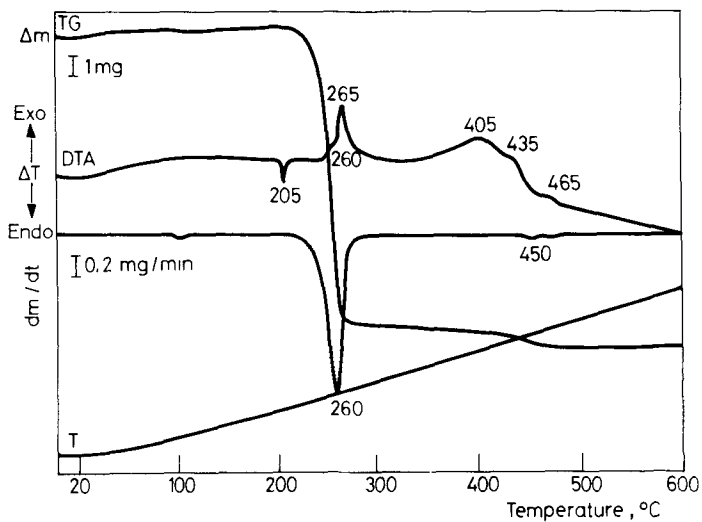


Fig. 5 Thermoanalytical curves of Bi[S$_2$CN(CH$_2$)$_5$]$_3$ in air

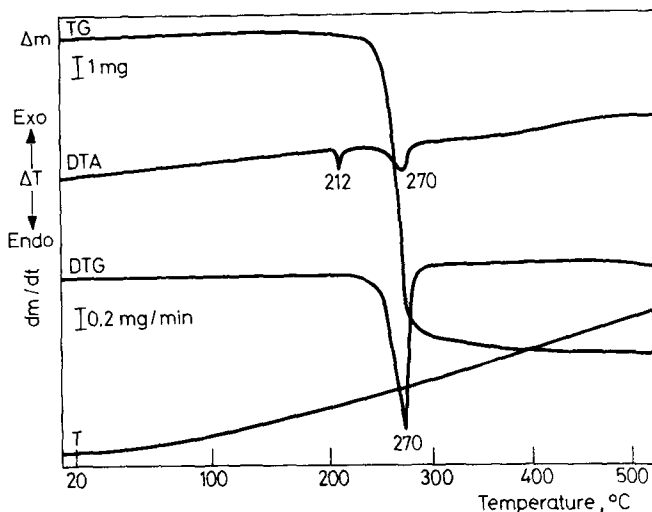**Fig. 6** Thermoanalytical curves of $Bi[S_2CN(CH_2)_5]_3$ in nitrogen

the decomposition are given in Tables 1 and 2. The temperatures of the greatest rate of decomposition ($DTG_{max}$) the theoretical percentage mass losses and the DTA data are also given.

The possible intermediate after the first step in both air and nitrogen is considered to be $M_2S_3$ ($M$ = As, Sb and Bi), which can be found in nitrogen as residual metal sulfides, in accordance with recent results [3].

In air, the second step of decomposition involves the oxidation of the metal sulfides. In the case of the arsenic complex, $As_2S_3$ is apparently formed at 370°, and is further oxidized to $As_4O_6$, as can be seen from the characteristic shape of its thermogravimetric curve [8]. The third step involved the gradual sublimation of the oxide, leading to a plateau at 530°, where the sublimation is complete, leaving the crucible without a residue. Both the second and the third steps are exothermic, at 405 and 480°, also the positions of the $DTG_{max}$.

The DTA curve of the antimony complex shows that after the melting of the intermediate $Sb_2S_3$, with an endothermic peak at 500°, oxidation begins. The final residue, which is stable at 520—600°, corresponds to be mixed antimony oxide $Sb_2O_4$ and was identified by X-ray powder diffraction study. The bismuth analogue ($Bi_2S_3$) yields as final residue $(BiO)_2SO_4$ instead of $(Bi_2O_3)$, as others reported [2], the reason being the greater thermal stability of the former at 480—600°. This residue was identified by X-ray powder diffraction studies and infrared spectroscopy.

The thermoanalytical curves of all complexes (Figs 7—9) run under vacuum indicate that only the behaviour of the arsenic(III) complex is different from that in nitrogen, owing to the volatility of its decomposition products. In particular, there appears to

Table 1 Thermoanalytical results (TG/DTG/DTA) of tris(piperidyldithiocarbamates) of As(III), Sb(III), Bi(III) in air atmosphere

| Complex | DTA results | | TG/DTG results | | | | Evolved moiety | |
|---|---|---|---|---|---|---|---|---|
| | m.p., °C endothermic peak | Temperature peak, °C endothermic (−) exothermic (+) | Stage | Temperature range, °C | DTG$_{max}$ °C | Mass loss % | Formula | Mass calcd. % |
| As[S$_2$CN(CH$_2$)$_5$]$_3$ | 219 | 219 (−), 230 (+) | 1 | 195–240 +* | 220 | 66.5 | S$_2$CN(CH$_2$)$_5$ + SCN(CH$_2$)$_5$ + N(CH$_2$)$_5$ + | 67.01 |
| | | | | 240–370 | | 7.8 | CS | 7.91 |
| | | 405 (+) | 2 | 370–460 | 405 | 7.6 | As$_2$S$_3$ → As$_2$O$_3$ | 8.65 |
| | | 480 (+) | 3 | 460–530 | 480 | 18.0 | As$_2$O$_3$(As$_4$O$_6$) | 17.80 |
| | | | residue | > 530 | | 0 | | |
| Sb[S$_2$CN(CH$_2$)$_5$]$_3$ | 218 | 264 (+) | 1 | 180–260 | 258 | 61.8 | S$_2$CN(CH$_2$)$_5$ + SCN(CH$_2$)$_5$ + N(CH$_2$)$_5$ | 61.73 |
| | | 450 (+) | 2 | 340–520 | — | 11.6 | Sb$_2$S$_3$ → Sb$_2$O$_4$ | 5.31 |
| | | | residue | > 520 | | 26.6 | Sb$_2$O$_4$ | 25.51 |
| Bi[S$_2$CN(CH$_2$)$_5$]$_3$ | 205 | 260 (+), 265 (+) | 1 | 210–280 | 260 | 56.0 | S$_2$CN(CH$_2$)$_5$ + SCN(CH$_2$)$_5$ + CN(CH$_2$)$_5$ | 55.64 |
| | | 405 (+), 435 (+) | 2 | 430–470 | 450 | 5.0 | Bi$_2$S$_3$ → (BiO)$_2$SO$_4$ | |
| | | 465 (+) | residue | > 470 | | 39.0 | (BiO)$_2$SO$_4$ | 39.62 |

* two consecutive steps.

Table 2 Thermoanalytical results (TG/DTG/DTA) of tris(piperidyldithiocarbamates) of As(III), Sb(III), Bi(III) in nitrogen atmosphere

| Complex | DTA results | | TG/DTG results | | | | Evolved moiety | |
|---|---|---|---|---|---|---|---|---|
| | m.p., °C endothermic peak | Temperature peak, °C endothermic | Stage | Temperature range, °C | $DTG_{max}$ °C | Mass loss % | Formula | Mass calcd. % |
| $As[S_2CN(CH_2)_5]_3$ | 219 | 219 | 1 | 200–240 | 220 | 66.5 | $S_2CN(CH_2)_5 + SCN(CH_2)_5 + N(CH_2)_5$ | 67.01 |
| | | 440 | 2 | 370–440 | | 8.0 | CS | 7.91 |
| | | | 3 | 440–580 | | 10.5 | | |
| | | | residue | > 540 | | 11.5 | $As_xS_y$ | |
| $Sb[S_2CN(CH_2)_5]_3$ | 220 | 264 | 1 | 180–270 | 264 | 61.8 | $S_2CN(CH_2)_5 + SCN(CH_2)_5 + N(CH_2)_5$ | 61.73 |
| | 500 | | 2 | 340–600 | — | 9.2 | CS | 7.29 |
| | | | residue | > 600 | | 29.0 | $Sb_2S_3$ | 28.16 |
| $Bi[S_2CN(CH_2)_5]_3$ | 212 | 270 | 1 | 210–280 | 270 | 56.0 | $S_2CN(CH_2)_5 + SCN(CH_2)_5 + CN(CH_2)_5$ | 55.64 |
| | | | 2 | 280–420 | | 6.5 | 1,5 S | 6.94 |
| | | | residue | > 420 | | 37.20 | $Bi_2S_3$ | 37.25 |

be only one step, involving a sudden and total loss of mass. However, the DTG curve indicates that this step is a combination of two immediately consecutive processes at 200–225° ($DTG_{max}$ 220°) and 225–240° ($DTG_{max}$ 235°), involving the losses of mass given in Table 3. In the case of the antimony(III) complex, the experimentally found percentage of the residue (12.00%) is lower than the calculated one (20.23%) if it is considered to be elemental antimony, but the X-ray powder diffraction data are not sufficiently clear to elucidate its chemical nature. The residue of the bismuth(III) complex corresponds to bismuth(III) sulfide of the type $BiS_2$.

Our results showed that the whole procedure of the thermal decomposition of the studied complexes depends on the nature of the metal. This fact was established by determining the TIN of the complexes from their corrected TG curves (Fig. 10), also taking into account the buoyancy effect. TIN was proposed by Reich and Levi [9] as a criterion of the thermal stability of organic compounds.

Thus, the TIN values indicate clearly that the complexes of arsenic(III) and antimony(III) decompose at the same temperature, ca. 190°, while their bismuth analogue decomposes at higher temperature (200°).

*Apparent activation energy (E\*)*

$E^*$ was calculated only for the complexes of Sb(III) and Bi(III) by the modified $n = 1$ method of Freeman–Carroll [10] and Piloyan's two methods [11, 12]. The $E^*$ values are referred to the first and main step of decomposition in air and are given in Table 4.

The $E^*$ values of the two complexes are fairly close, in agreement with the suggestion that complexes of a given ligand with metals of one group have approximately the same $E^*$ values. Moreover, the $E^*$ values of 37 and 46 kcal/mol derived from Piloyan's TG method for the complexes of antimony(III) and bismuth(III), respectively, are close to those reported by others [1, 3]. The same methods applied to the arsenic(III) complex do not give acceptable $E^*$ values.

*Pyrolysis*

The TG and DTA techniques do not often provide adequate information for the necessary conclusions on the mode of decomposition, since neither the amounts of the evolved products nor their nature are known. In order to overcome this difficulty, the pyrolysis technique was used (see experimental). This showed that the thermal degradation of the three complexes can be achieved in one well-separated stage, usually affording a complicated mixture of products. The sample was heated in nitrogen atmosphere up to the temperature of the end of the first and main decomposition step. The most volatile product of the pyrolysis of the complexes is $CS_2$, which was detected in the liquid air trap. A white solid, which seems to be produced first during the decomposition, was identified as the piperidinium salt of piperidinodithiocarbamic acid, $(CH_2)_5NC\bar{S}_2H_2\overset{+}{N}(CH_2)_5$.

**Table 3** Thermoanalytical results (TG/DTG/DTA) of tris(piperidyldithiocarbamates) of As(III), Sb(III), Bi(III) under vacuum $10^{-2}$ Torr

| Complex | DTA results | | TG/DTG results | | | | Evolved moiety | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | m.p., °C endothermic peak | Temperature peak, °C endothermic (−) exothermic (+) | Stage | Temperature range, °C | $DTG_{max}$ °C | Mass loss % | Formula | Mass calcd. % |
| As[S$_2$CN(CH$_2$)$_5$]$_3$ | 215 | 215 (−), 235 (−) | 1 | 20–240 | 235 | 98.0 | S$_2$CN(CH$_2$)$_5$ + 2 SCN(CH$_2$)$_5$ + As$_2$S$_3$ | 57.66 |
| | | | 1 α | 200–225 | 220 | 57.0 | 2 S$_2$CN(CH$_2$)$_5$ | 42.31 |
| | | | 1 β | 225–240 | 235 | 41.0 | SCN(CH$_2$)$_5$ + As$_2$S$_2$ | |
| | | | residue | > 580 | | ~0 | | |
| Sb[S$_2$CN(CH$_2$)$_5$]$_3$ | 207 | 280 (−) 538 (+) | 1 | 220–280 | 275 | 69.5 | S$_2$CN(CH$_2$)$_5$ + 2 SCN(CH$_2$)$_5$ | 69.08 |
| | | | 2 | 480–550 | 538 | 18.5 | Sb | 20.23 |
| | | | residue | > 550 | | 12.0 | unknown | |
| Bi[S$_2$CN(CH$_2$)$_5$]$_3$ | 200 | 270 (−) | 1 | 220–300 | 270 | 60.0 | S$_2$CN(CH$_2$)$_5$ + 2 SCN(CH$_2$)$_5$ | 60.27 |
| | | | residue | > 300 | | 40.0 | possible BiS$_2$ | 39.56 |
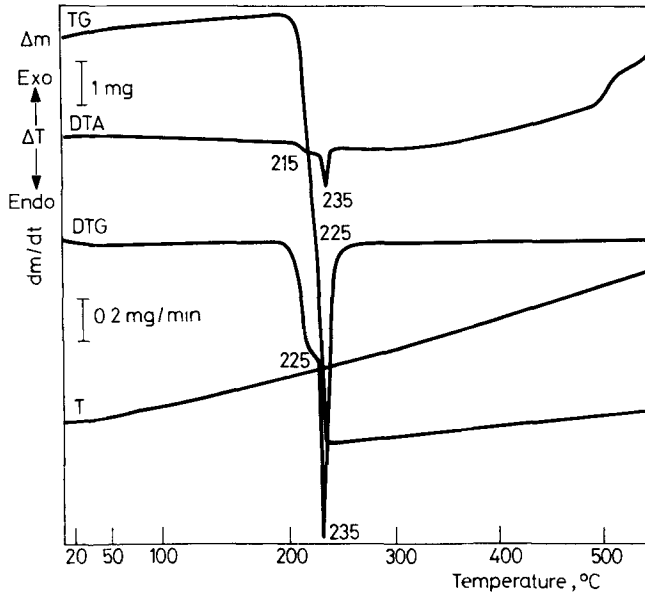
Fig. 7 Thermoanalytical curves of As[S$_2$CN(CH$_2$)$_5$]$_3$ under vacuum
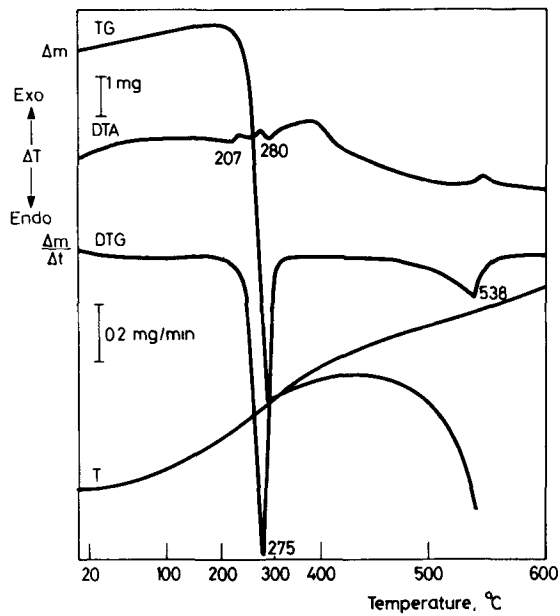


Fig. 8 Thermoanalytical curves of Sb[S$_2$CN(CH$_2$)$_5$]$_3$ under vacuum

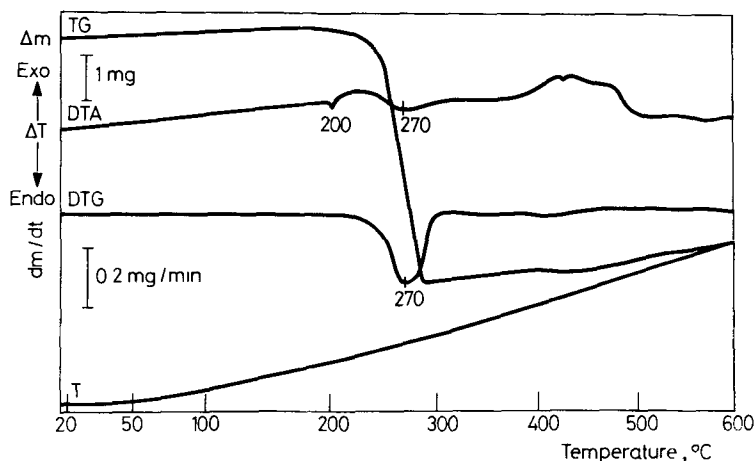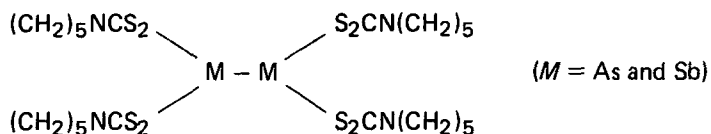**Fig. 9** Thermoanalytical curves of $Bi[S_2CN(CH_2)_5]_3$ under vacuum

As the decomposition proceeds further, the dipiperidinodithiocarbamylsulfenamide, $(CH_2)_5N-C(:S)-SN(CH_2)_5$ is formed as a yellow-red liquid, which can be solidified with difficulty. A white solid which was isolated in small quantities was identified as a derivative of thiourea with piperidine, $(CH_2)_5N-C(:S)-N(CH_2)_5$. Though this compound is a pyrolysis product, it also seems rational to assume its formation from piperidine sulfenamide, which can be transformed to thiourea on standing in air [13]. A faster transformation can be achieved on heating the sample.

Another more important compound was isolated by adding diethyl ether or petroleum ether to the chloroform solution of the volatile pyrolysis products of the studied complexes. A light-brown solid was precipitated, this being formulated as the following dimeric species:

$$(CH_2)_5NCS_2 \diagdown \qquad \diagup S_2CN(CH_2)_5$$
$$M - M \qquad (M = \text{As and Sb})$$
$$(CH_2)_5NCS_2 \diagup \qquad \diagdown S_2CN(CH_2)_5$$

In the case of the arsenic(III) complex, analysis of the corresponding compound fits well the expected results for the above formula (found: C, 37.05; H, 5.37; N, 7.41; calculated: C, 36.45; H, 5.06; N, 7.08); it melts at 215–17°. The mass spectrum of this new diarsenic species consists of peaks corresponding to the dithiocarbamato group of the parent compound and its fragments. Certain ions at higher $m/e$ values can be attributed to condensation products of various fragments. In the case of the antimony(III) complex, the corresponding compound also gives a good analysis (found: C, 31.70; H, 4.12; N, 5.76; calculated: C, 32.52; H, 4.52; N, 6.33), and melts
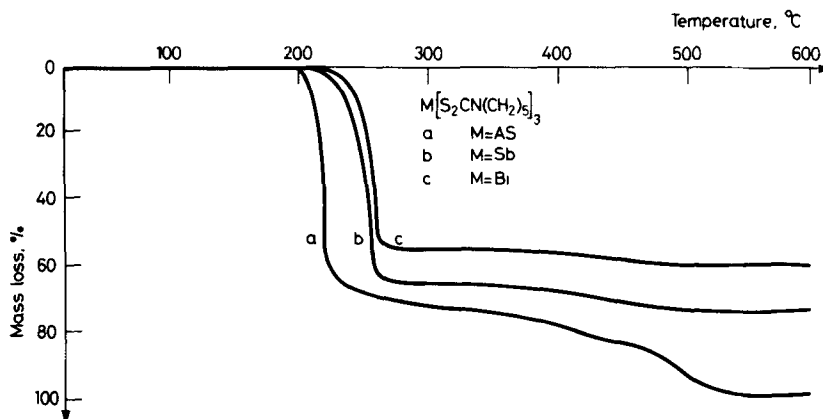
Fig. 10 Corrected TG curves of tris(piperidyldithiocarbamates) in air

Table 4 Activation energy's values, $E^*$, of tris(piperidyldithiocarbamates) of Sb(III) and Bi(III)

| Complex | Activation energy, $E^*$, kcal/mol | | |
|---------|------------------|--------|-----|
| | Freeman–Carroll | Piloyan | |
| | ($n = 1$) | TG | DTG |
| $Sb[S_2CN(CH_2)_5]_3$ | 45 | 37 | 39 |
| $Bi[S_2CN(CH_2)_5]_3$ | 76 | 46 | 52 |

at 230–2°. The ir spectra of all dimeric compounds show the characteristic bands of the dithiocarbamate ligand attached in a bidentate manner [14].

The expected dimeric species from the pyrolysis of the bismuth complex turned out to be an unknow compound. Its elemental analysis does not fit the required one, and the i.r. and mass spectra definitely show the absence of the dithiocarbamate ligand. The lack of $>$ Bi–Bi $<$ bond [15, 16] justifies the absence of any such compound.

After the completion of the pyrolysis, all complexes leave a black residue at the bottom of the flask in which the corresponding sulfides of the trivalent metals were detected. The i.r. spectra of these residues showed no presence of organic compounds; however, they contain 8–18% elemental carbon, explaining the black colour of the residues, as reported in a previous case [17].

From what has been said, it is obvious that the thermal decomposition of the studied complexes in nitrogen is practically achieved in one step.

*Mechanism*

The mechanism of thermal decomposition of the tris(piperidyldithiocarbamate) complexes of arsenic(III), antimony(III) and bismuth(III) proposed below does not follow the rather simple scheme suggested by Magee et al. [18] for the complexes $M[S_2CNEt_2]_X$ ($M$ = Cu and Sn) ($X$ = 2 and 4). Two possible parallel mechanisms are proposed, which can be explained by a combination of radical and ionic reactions, as is shown in Scheme 1. Mechanism I involves the homolytic dissociation of a dithiocarbamato group and the subsequent reaction of two of them to form thiuram disulfide.
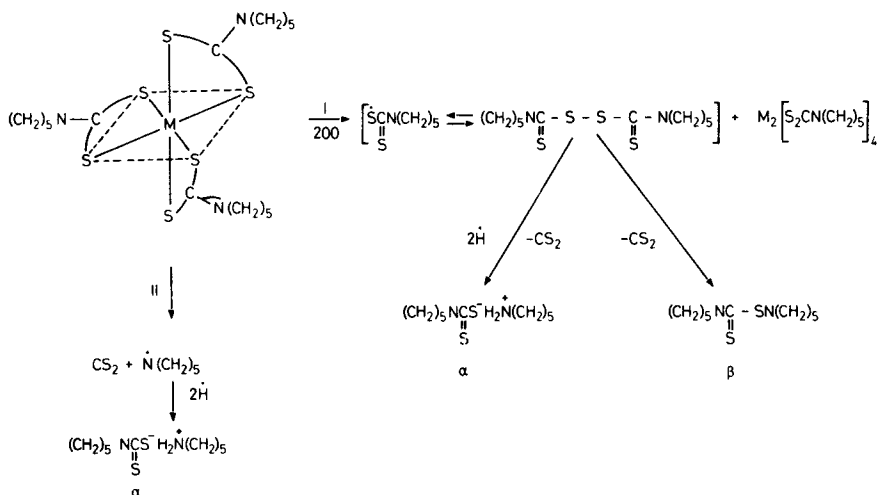


**Scheme 1** Thermal decomposition of the complexes $M[S_2CN(CH_2)_5]_3$ ($M$ = As, Sb, Bi)

The dissociation of one dithiocarbamato group is favoured by the screening effect of the lone pair [19, 20] of electrons in each metal, which makes one of the ligands more labile than the others. The tetrapiperidylthiuram disulfide formed decomposes further to yield $CS_2$ and either dithiocarbamic salt ($\alpha$), $(CH_2)_5NC(:S)\bar{S}H_2\overset{+}{N}(CH_2)_5$, or sulfenamide ($\beta$), $(CH_2)_5NC(:S)SN(CH_2)_5$. This mechanism of primary decomposition is in accord with that proposed previously [21, 22] for the thermal decomposition of $Sn[S_2CNEt_2]_4$ and $UO_2[S_2CNEt_2]_2$.

The pyrolysis of tetrapiperidylthiouram disulfide was carried out in nitrogen, in order to substantiate the proposed mechanism. It decomposed just after melting, evolving a white sublimable solid, which turned out to be dithiocarbamic salt ($\alpha$), and a mixture of sulfenamid ($\beta$), with minor amounts of thiourea ($\gamma$), (Scheme 1), as a yellow liquid. $CS_2$ was also detected in the liquid air trap.

Mechanism II involves the decomposition of a dithiocarbamato group with simultaneous rupture of carbon—nitrogen and carbon—sulfur bonds. $CS_2$ and amine are

proouced, which on heating interact together to give the dithiocarbamic salt as is well known [23].

The important fact in the thermal decomposition of the studied complexes is the formation of the dimeric compounds $M_2[S_2CN(CH_2)_5]_4$ $(M = As$ and Sb), from which the metal sulfides are produced on further heating.

The pyrolysis of this intermediate in nitrogen up to 350° yields only two volatile compounds: the dithiocarbamic salt ($\alpha$) (Scheme 2) and thiourea ($\gamma$). Interestingly, no $CS_2$ was detected among the pyrolysis products of this intermediate. The mass spectrum of the same compound does not give a parent molecular ion.
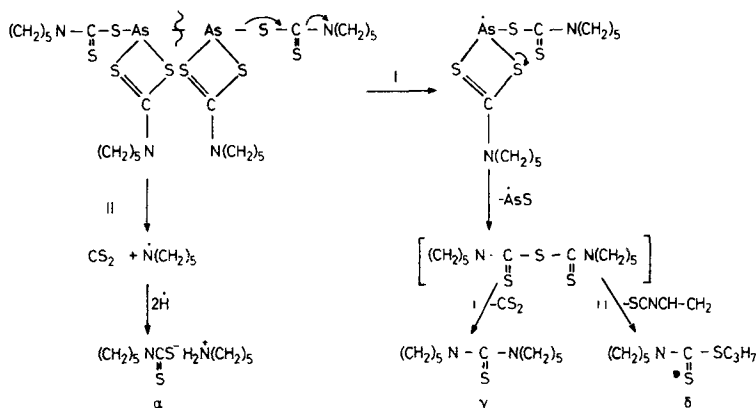


**Scheme 2** Thermal decomposition of the dimeric compound $As_2[S_2CN(CH_2)_5]_4$

The main ions observed were those corresponding to $S_2CN(CH_2)_5^+$ and $AsS^+$. However, polynuclear groups were detected at higher *m/e* values. Their existence is associated with the pyrolytic decomposition of the complexes in the probe, followed by condensation reactions affording polynuclear complexes. Based on what has been said above, we suggest the following decomposition of the dimeric species as the second stage mechanism of the first step of the thermal breakdown.

Scheme 2 likewise includes two parallel mechanism I and II. In the first the rupture of an As—As bond occurs, whereas the second includes the breaking of carbon—nitrogen and carbon—sulfur bonds. Mechanism I may end in two different products if we accept the formation of piperidyl monosulfide, which is in accord with fragmentation pattern of the mass spectra of tris(dithiocarbamato) complexes [24]. This intermediate can decompose further either by breaking of its piperidyl ring to give the ester ($\delta$), $(CH_2)_5NC(:S)C_3H_7$ or by forming thiourea ($\nu$). In the mass spectrum of piperidyl monosulfide a peak at *m/e* (203) $(CH_2)_5NC(:S)SC_3H_7$ was detected in accord with the above proposal. On the other hand, $CS_2$ was not detected as a

pyrolysis product of the dimeric arsenic complex, required to substantiate the formation of thiourea [25].

At this point it is interesting to note an important difference between our results and those reported earlier by Afanasova et al. [1], who studied the thermal behaviour of dithiocarbamato complexes of antimony(III) and bismuth(III) with various amines by employing TG, DTG and DTA techniques. On the basis only of information taken from the curves, they proposed $CS_2$, alkenes ($RCH=CH_2$), amine and isothiocyanate (RNCS) as volatile products of the decomposition. Of the above products, we have isolated only $CS_2$, and thus we cannot accept their proposed decomposition mechanism.

The thermal decomposition of the bismuth(III) complex is more or less similar to that of the arsenic(III) and antimony(III) complexes, the only difference being the non-isolation of the dimeric product in the bismuth(III) case. Its formation is perhaps possible, but it might be highly unstable under the thermal conditions of the experiment, and we were therefore not able to isolate it.

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**Zusammenfassung** — TG-, DTG- und DTA-Untersuchungen von Tris(piperidyldithiocarbamaten) von Arsen(III), Antimon(III) and Wismut(III) des allgemeinen Typs $M[S_2CN(CH_2)_5]_3$ ($M =$ As, Sb und Bi) wurden sowohl in Stickstoffatmosphäre und Luft als auch unter Vakuum ausgeführt,um die Art der Zersetzung zu ermitteln. Die scheinbaren Aktivierungsenergien wurden nach der graphischen Methode bestimmt und die TTN-Temperaturen aus den TG-Profilen berechnet. Es wird ein auf den Ergebnissen der Pyrolyse der Verbindungen und der dabei erhaltenen massenspektrometrischen Daten beruhender Mechanismus für die Zersetzungsreaktion vorgeschlagen. Die am Ende der verschiedenen Zersetzungsschritte erhaltenen Zwischenprodukte wurden durch Elementaranalyse, IR-Spektrophotometrie und Röntgendiffraktometrie identifiziert. Eine dimere Struktur des Typs $M_2[S_2CN(CH_2)_5]_4$ ($M =$ As, Sb) wird vorgeschlagen.

**Резюме** — Трис-пиперидилдитиокарбаматы трехвалентных мышьяка, сурьмы и висмута общей формули $M[S_2CN(CH_2)_5]_3$, где $M =$ As, Sb, Bi, были изучены методом ТГ, ДТГ и ДТА в вакууме, в атмосфере воздуха и азота с целью определения типа их разложения. Кажущиеся энергии активации были вычислены графическими методами, а ТИН температуры были вычислены на основе профиля кривых ТГ. Исходя из результатов анализа продуктов пиролиза и масс-спектроскопических данных, предложен возможный механизм разложения этих соединений. Промежуточные продукты, получаемые на различных стадиях разложения, идентифицированы посредством элементарного анализа. ИК спектроскопии и рентгенографии. Предложена димерная структура типа $M_2[S_2CN(CH_2)_5]_4$, где $M =$ As, Sb.

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