

MODES OF DECOMPOSITION OF SILVER, LEAD AND MERCURIC TOLUENEDITHIOLATES. A SYNTHETIC AND ANALYTICAL STUDY

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The silver, lead and mercuric toluenedithiolates were synthesised and analysed by both conventional chemical methods and thermoanalytical methods. The thermal decomposition was studied by thermogravimetric analysis in air, nitrogen and vacuum. The formulae of the decomposition products were derived using the mole weights and i.r. absorption spectra. The activation energies for the first stage of decomposition were calculated. The volatile products contain mostly carbon and hydrogen while the residues contain the corresponding metals either free or combined with sulfur.

Considerable interest exists in the study of the modes of decomposition, phase changes and products of decomposition of chemical compounds. Thermoanalytical techniques lend themselves well to the study of the above properties in the solid state. Thermogravimetric analysis [1–3] is used to study the stages of decomposition and changes associated with them. Also it is used as a means for synthesizing new compounds [4, 5].

Today because of environmental concern there is much interest in the properties of the compounds of lead and mercury. Toluene-3,4-dithiol has been used to identify these metals and make complexes with many other elements [6–10]. It has been used to reduce the toxic effects of poisonous elements such as lead and mercury in rats and as an antidote against N,N-bis(2-chloroethyl)methylamine [11].

The objectives of this study were to synthesize for the first time and analyze the silver, lead and mercuric toluenedithiolates, explore their stability and modes of decomposition and identify the decomposition products formed. The thermogravimetric technique enabled us to determine the modes of decomposition and calculate the activation energies.

Experimental

Starting materials. Toluene-3,4-dithiol was purchased from Eastman Kodak company. Silver nitrate, methyl iodide and the metal acetates were high purity reagent grade chemicals.

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Preparation. The metal toluenedithiolates were prepared all in a similar way. As a specific example the synthesis of silver toluenedithiolate is given: an acidified with 6 N HNO₃ silver nitrate solution (1.8 mmoles) is mixed with a methanol solution of toluene-3,4-dithiol (1.9 mmoles). The mixture is digested in a steam bath for 10 min. It is allowed to cool, filtered through a sintered glass crucible, dried in air at 115° and weighed.

The metal iodides were also prepared all in a similar way. Small quantities of the metal toluenedithiolates are suspended in methanol and methyl iodide is added in excess with stirring until a precipitate begins to form, having the characteristic color of the metal iodide, f.i. yellow in the case of silver iodide.

Apparatus and procedure. The decompositions were carried out using the Dupont Thermogravimetric Analyzer, models 950 and 951. The TG, model 951, possesses derivative thermogravimetric (DTG) capability. The TG results were plotted as weight lost against temperature. DTG curves were obtained as the rate of weight loss against temperature. Pure nitrogen was used and both nitrogen and air were dried before passing over the sample. The heating rates were 20° min⁻¹. Samples up to 40 mg were used and the sample holder was a small platinum boat 0.5 cm in depth, attached to a quartz rode. The samples were loaded by means of a micro-spatula.

Infrared spectra were recorded on the Perkin – Elmer spectrophotometer, model 621, on samples pressed into CsI pellets over the frequency range 4000 – 200 cm⁻¹. The spectra of several samples were also obtained from Nujol mulls to remove uncertainty of a CsI matrix effect. The spectrophotometer was calibrated against the polystyrene spectrum. To protect the sample from moisture during the run the spectrophotometer was provided with a dry controlled atmosphere compartment. The pellets were prepared in a dry box and were pressed using a mini press.

Results and discussion

Silver toluenedithiolate

The composition of this compound was established (a) by the yield from a silver nitrate solution of known composition, Table 1, (b) by the direct ignition in air at 800°, Table 2 and (c) by the precipitation of silver iodide, Table 3. In most cases the experimental result approximates closely the values required by theory.

Thermogravimetric analysis

Thermogravimetric analysis data obtained for this compound are indicated in Tables 5 and 6. The symbols are defined as follows: T_i is for the temperature of inception, T_g for the temperature at which the reaction is maximum and T_r for the temperature at which the reaction ends. Data in Tables 5 and 6 indicate that the

Table 1
Data for the composition of silver toluenedithiolate

Compounds reacting silver nitrate, moles $\times 10^{-3}$	Toluene-3,4-dithiol, moles $\times 10^{-2}$	Product silver toluenedithiolate	
		Found, g	Calc, g
2.6	1.30	0.4902	0.4850
2.3	1.15	0.4290	0.4250
2.0	1.00	0.3750	0.3700
1.5	0.75	0.2760	0.2720

Table 2
Amount of silver obtained by direct ignition in
air of silver toluenedithiolate, at 800 °C

Amount ignited g	Silver residue	
	Found, %	Calc., %
0.1995	58.5	58.3
0.2350	58.0	58.3
0.2700	59.0	58.5
0.3500	57.8	58.4

Table 3
Metal iodides formed by reacting each compound with methyl iodide

Compound	Methyl iodide,		Metal iodide moles $\times 10^{-4}$	
	moles $\times 10^{-4}$	moles $\times 10^{-4}$	Exp.	Calc.
Silver tol/ate	0.55	1.14	1.12	1.13
Silver tol/ate	2.83	5.67	5.90	5.70
Lead tol/ate	0.57	1.16	0.57	0.58
Lead tol/ate	1.62	3.26	1.63	1.65
Mercuric tol/ate	0.61	1.23	0.64	0.60
Mercuric tol/ate	2.50	5.10	2.40	2.48

Table 4
Carbon hydrogen analysis of lead and mercuric tol/ates

Compound	Carbon, %		Hydrogen, %	
	Found	Calc.	Found	Calc.
Lead tol/ate	23.8	23.2	1.60	1.66
Mercuric tol/ate	24.0	23.8	1.15	1.13

Table 5
Procedural decomposition temperatures (°C) for the metal tol/ates

Compound	First stage			Second stage		
	T_i	T_s	T_f	T_i	T_s	T_f
Silver tol/ate						
Air	260	380	400	450	485	500
Nitrogen	250	390	420	—	—	—
Vacuum	250	380	440	—	—	—
Lead tol/ate						
Air	260	320	350	350	377	425
Nitrogen	250	290	350	380	410	450
Vacuum	—	—	—	—	—	—
Mercuric tol/ate						
Air	240	340	400	—	—	—
Nitrogen	320	370	420	—	—	—
Vacuum	—	—	—	—	—	—

silver toluenedithiolate decomposes below 700°. The decomposition occurs in three stages in air in accordance with the equations:

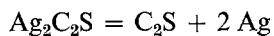
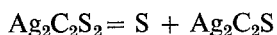
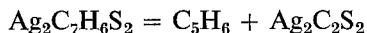


Table 6
TG data of silver toluenedithiolate

Atmosphere	Sample wt, mg	Decomposition stages					
		First		Second		Third	
		loss, %	temp. °C	loss, %	temp. °C	loss, %	temp. °C
Air	40.0	17.0	353	27.5	485	40.5	620
Air	12.4	19.0	381	29.0	583	—	—
Air	36.5	16.0	410	26.0	494	39.0	700
Nitrogen	39.0	21.5	390	—	—	—	—
Nitrogen	13.0	21.0	390	—	—	—	—
Vacuum	38.0	26.7	380	—	—	—	—
Vacuum	40.0	27.0	362	—	—	—	—

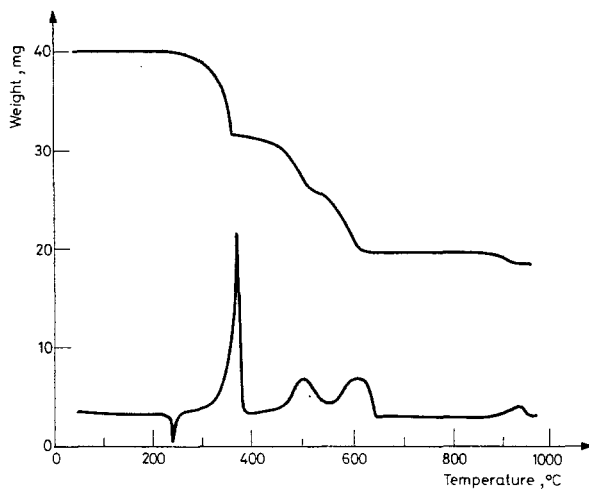
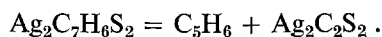


Fig. 1. TG and DTG curves of silver toluenedithiolate in air

In nitrogen only one well defined step is detected:



In vacuum the decomposition appears to follow a third mode of decomposition the first step of which is indicated below:



Further decomposition occurs but cannot be definitely characterized. Typical thermal curves for the decomposition of this compound in air, nitrogen and vacuum are given in Figs 1, 2 and 3. Data supporting the mode of decomposition are recorded in Table 7. One sees that the agreement between the experimental results and

Table 7

Data for the composition, of the decomposition products, of silver toluenedithiolate

Atm/stage	%loss	Temp, °C	Mole wt. of fragment			Mole wt. of residue		
			Exp.	Calc.	Formula	Exp.	Calc.	Formula
Air								
1 st	18.0	381	67.0	66.0	C ₅ H ₆	303.0	304.0	Ag ₂ C ₂ S ₂
2 nd	26.8	485	34.0	32.0	S	270.0	272.0	Ag ₂ C ₂ S
3 rd	41.5	620	52.0	56.0	C ₂ S	216.0	216.0	2Ag
Nitrogen								
1 st	21.5	390	82.0	78.0	C ₆ H ₆	288.0	292.0	Ag ₂ CS ₂
Vacuum								
1 st	26.7	380	99.0	98.0	C ₅ H ₆ S	271.0	272.0	Ag ₂ C ₂ S

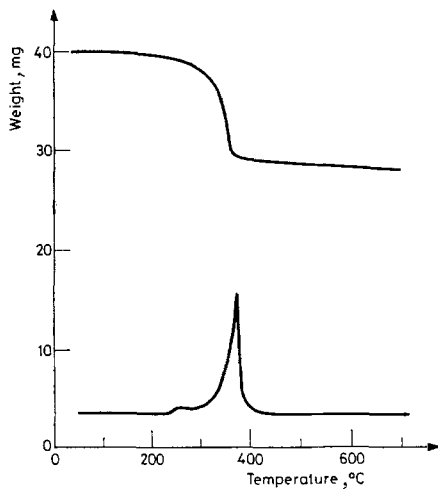


Fig. 2. TG and DTG curves of silver toluenedithiolate in nitrogen

the calculated results is quite good. In addition to the mole weight, infrared spectra were also used to identify the decomposition products of silver toluenedithiolate. Infrared spectral data are listed in Tables 8 and 9. The bands observed in the residues of the three steps of decomposition support the formulae of the fragments and residues. Thus the first residue in air does not exhibit any C-H band, so the fragment formula whose mole weight is estimated 67, is C_5H_6 . In the second residue we see a band for Ag-S and the mole weight found is 34, so one sulfur atom is lost.

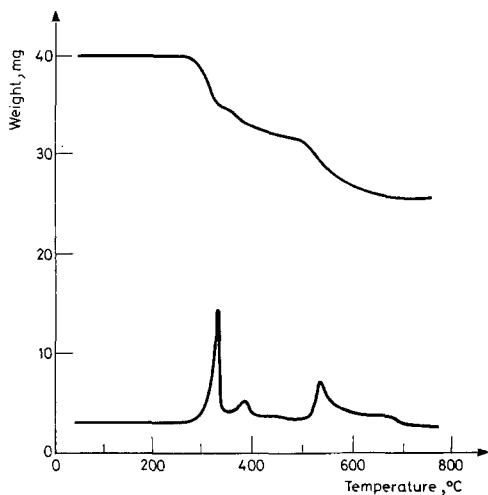


Fig. 3. TG and DTG curves of silver toluenedithiolate in vacuum

Table 8
I.R. spectra of toluene-3,4-dithiol and metal tol/ates (frequency cm^{-1})

Toluene-3, 4-dithiol	Toluenedithiolates			Band assignment**
	silver	lead	mercuric	
3450b*	3500b	3500b	3450b	HOH stretch
3065sh	—	—	—	C—H stretching
3040w	3040w	3040w	3040w	C—H stretching
2930s	2930s	2930m	2930s	C—H stretch(CH_3)
2870sh	2870sh	2875w	2870w	C—H stretch(CH_3)
2740m	2740m	—	—	C—H stretch
2545vs	—	—	—	S—H stretching
2350b	2350b	—	—	C—H stretching
1950w	—	—	—	C—H overtone band
1890m	—	—	—	C—H overtone band
1740mb	1740w	—	1740w	C—H out of plane deformation
1595sp,vs	1595s	1580m	1590m	C—C stretching
1550m	—	—	—	C—S stretching
1465sp,vs	1465sp,vs	1460s	1465sp,vs	C—H stretch(CH_2)
1385s	1375m	1370m	1370m	C—H sym deformation(CH_2)
1315w	—	—	—	C—H in plane deformation
1270sp,vs	1270s	1265s	1270sp,vs	C—C stretching
1215sp,vs	1215w	1210w	1210w	C—C stretching
1125sp,vs	—	—	—	S—H stretching
1110s	1110s	1110s	1110sp,vs	DOD bent
1040sp,vs	1040sp,vs	1035s	1035s	C—C stretch
1000m	—	—	—	C—C stretch
928s	—	—	—	C—H bending
868sp,vs	868sp,vs	870s	865m	C—H out of plane deformation
810sp,vs	810sp,vs	810s	810sp,vs	C—H out of plane deformation
695sh	695sp,s	—	—	C—H stretching
685sp,vs	685sp,vs	685m	685m	C—S stretching
630vs	630s	630m	630w	C—S stretching
540vs	560s	540w	550s	C—S stretching
—	450s	450m	450m	metal-sulfur bond
380w	380w	—	—	Lattice bands
360w	360w	350w	350w	Lattice bands
280w	280w	—	280w	Lattice bands
270w	270w	270w	—	Lattice bands
245w	245w	250w	—	Lattice bands
215w	—	—	—	Lattice bands

* b = broad, m = medium, s = strong, sp = sharp, sh = shoulder, v = very, w = weak

** Band assignments were obtained from Bellamy and Silverstein [15, 16].

The formula C_2S in the third stage of decomposition is supported by a mole weight of 52 and by the absence of any Ag—S band in the spectra.

Lead toluenedithiolate

The composition of this compound was determined (a) by carbon hydrogen analysis, Table 4 and (b) by precipitation of lead iodide with methyl iodide, Table 3.

Table 9

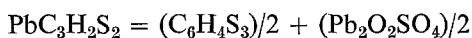
I.R. spectra of the TG residues of silver tol/ate (frequency cm^{-1})
decomposition stages

First 400 °C	Second 550 °C	Third 900 °C	band assignment**
3450b*	3450b	3450b	HOH stretch
350w	450w	—	Ag—S bond
380w	380w	—	Lattice bands
360w	360w	—	Lattice bands
280w	280w	—	Lattice bands

* b = broad, m = medium, s = strong, sh = shoulder, sp = sharp, v = very, w = weak

** Band assignments were obtained from Bellamy and Silverstein [15, 16].

Lead toluenedithiolate decomposes in three definite steps in air. The results are indicated in Tables 5 and 10. The decomposition occurs in accordance with the equations:



In nitrogen the mode of decomposition is:

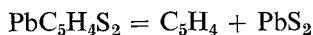


Table 10

TG data of lead toluenedithiolate

Atm	Decomposition stages						
	Sample wt	First		Second		Third	
	mg	loss, %	Temp, °C	loss, %	Temp, °C	loss, %	Temp, °C
Air	40.4	8.0	300	13.5	372	25.0	532
	37.5	9.0	295	14.5	353	24.1	560
	31.5	8.0	295	14.5	383	25.0	495
	35.0	9.0	314	14.8	379	26.0	545
	38.0	8.0	314	14.0	419	25.0	579
Nitrogen	38.5	7.0	325	23.3	420	—	—
	42.0	7.0	330	23.5	410	—	—

Table 11

Data for the composition, of the decomposition products, of lead toluenedithiolate

Atm/stage	Mole wt of fragment					Mole wt of residue			
	loss, %	Temp. °C	Exp.	Calc.	Formula	Exp.	Calc.	Formula	
Air									
1 st	8.0	314	28.9	26.0	C ₂ H ₂	332.1	335.0	PbC ₆ H ₄ S ₂	
2 nd	15.0	377	25.3	26.0	C ₂ H ₂	307.0	309.0	PbC ₃ H ₃ S ₂	
3 rd	25.0	550	86.0	86.0	(C ₆ H ₄ S ₃)/2	270.8	271.0	(Pb ₂ O ₂ SO ₄)/2	
Nitrogen									
1 st	7.0	293	25.0	26.0	C ₂ H ₂	336.0	335.0	PbC ₆ H ₄ S ₂	
2 nd	23.5	410	60.0	64.0	C ₃ H ₄	276.0	271.0	PbS ₂	

Procedural decomposition temperatures support the three step mechanism and the mole weight data in Table 11 support the decomposition products postulated. The mode of decomposition is clearly indicated in Fig. 4. Further support for the identification of the decomposition products is provided by the i.r. spectra recorded in Tables 8 and 12. The presence of the methyl and C-H band in the i.r. spectra of the first residue in air and the mole weight 28.9 support the fragment formula C₂H₂. In the second stage the fragment formula is supported by the mole weight 25.3 and by the presence of a CH₂ band in the spectra. The i.r. spectra of the final residue exhibit a band at 630 cm⁻¹ which indicates the presence of a sulfate group also there is no C-H band. Since the mole weight of the fragment is 86 its formula is (C₆H₄S₃)/2.

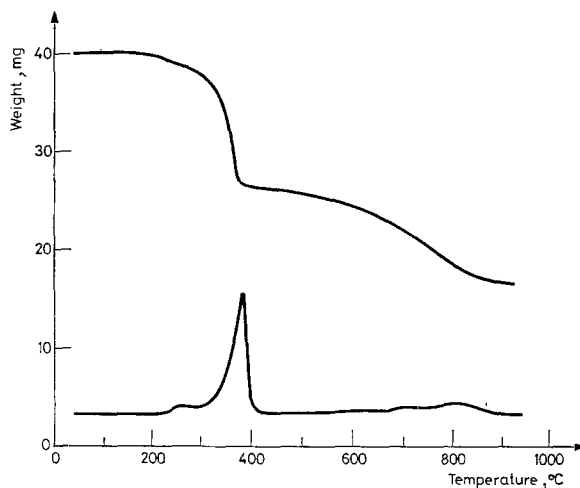


Fig. 4. TG and DTG curves of lead toluenedithiolate in air

Table 12

I.R. Spectra of TG residues of lead toluenedithiolate (frequency cm^{-1}), decomposition stages

First 330 °C	Second 400 °C	Third 900 °C	Band assignment**
3500b	3500b	3500b	HOH stretch
2930m	—	—	C—H stretch(CH_3)
2860w	2865w	—	C—H stretch (CH_2)
2340b	2340b	—	C—H stretch
1580m	—	—	C—C stretching
1460sp,vs	—	—	C—H deformation(CH_3)
1370w	—	—	C—H deformation(CH_3)
1170w	1170w	—	C—H out of plane deformation
1110b	1110b	—	DOD bent
1035sp,vs	—	—	C—S stretch
865sp,vs	—	—	C—H out of plane
810sp,vs	—	—	C—H out of plane
680sp,vs	—	—	C—H out of plane
630s	625m	630sp	Sulphate
450w	450w	450w	Pb—S bond
440s	—	—	Lattice bands
350w	350w	—	Lattice bands
280w	280w	—	Lattice bands
250w	250w	—	Lattice bands

* b = broad, m = medium, s = strong, sp = sharp, sh = shoulder, v = very, w = weak

** Band assignments were obtained from Bellamy and Silverstein [15, 16].

Mercuric toluenedithiolate

The composition of this compound was determined (a) by carbon hydrogen analysis and (b) by the precipitation of mercuric iodide with methyl iodide, Tables 4 and 3.

Table 13

TG data of mercuric toluenedithiolate decomposition

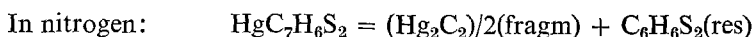
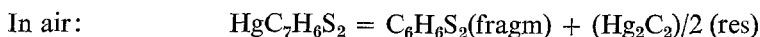
Stage	In air			In nitrogen		
	sample, mg	loss, %	Temp, °C	sample, mg	loss, %	Temp, °C
first	38.0	42.0	391	34.8	67.0	372
(only one)	32.5	41.0	335	25.0	67.0	365
	37.5	41.0	391	38.0	68.0	370
	39.3	41.0	343	—	—	—
	40.0	41.5	350	—	—	—

Table 14

Data for the composition, of the decomposition products, of lead toluenedithiolate

Atm/stage	loss, %	Temp, °C	Mole wt of fragment			Mole wt of residue		
			Exp.	Calc.	Formula	Exp.	Calc.	Formula
Air								
First	41.0	343	145.5	142.0	C ₆ H ₆ S ₂	209.5	213.0	(Hg ₂ C ₂)/2
Nitrogen								
First	67.0	372	212.0	212.5	(Hg ₂ C ₂)/2	143	142.0	C ₆ H ₆ S ₂

Thermogravimetric analysis data are shown in Tables 5 and 13. Mercuric toluenedithiolate decomposes in one step in both air and nitrogen. The proposed mode of decomposition is indicated below:



Support for this mode of decomposition comes from the procedural decomposition temperatures and the mole weights indicated in Table 14. The mode of decomposition is clearly seen in Fig. 5. The i.r bands exhibited by this compound are given in Tables 8 and 15. For the fragment formula C₆H₆S₂ in air we have a mole weight 142

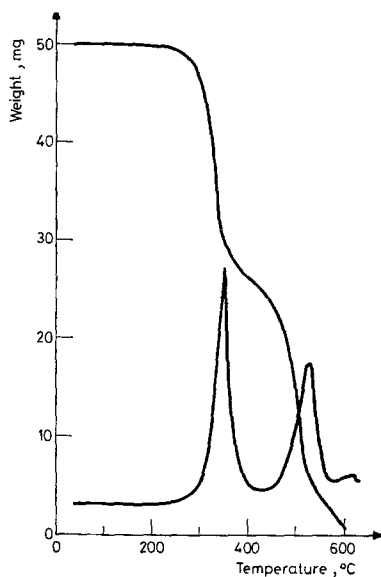


Fig. 5. TG and DTG curves of mercuric toluenedithiolate in air

Table 15

I.R. spectra of the TG residues of mercuric toluenedithiolate (frequency cm^{-1})

Atm	Decomposition at 420 °C	Band assignment**
Air	3500b	HOH stretch
	350w	Lattice bands
	280w	Lattice bands
	250w	Lattice bands
Nitrogen	2930s	C-H stretch(CH_3)
	2870w	C-H stretch(CH_3)
	2740m	C-H stretch(CH_3)
	2340b	C-H stretch (CH_2)
	1740m	C-H stretch(CH_2)
	1530b	C-H deformation(CH_3)
	1370w	C-H deformation(CH_3)
	1115w	DOD bent
	810m	C-H out of plane
	630w	C-S stretching
	350vs	Lattice bands
	280w	Lattice bands
250m	Lattice bands	

* b = broad, m = medium, s = strong, sh = shoulder, sp = sharp, v = very, w = weak

** Band assignments were obtained from Bellamy and Silverstein [15, 16]

and evidence from the i.r. spectra that all the hydrogen and sulfur atoms are lost. The mode of decomposition appears to be inverted when the atmosphere is changed to nitrogen. This is supported by the i.r. spectra which exhibit the bands for C-S, CH_3 and CH_2 groups.

Activation energies

The activation energies for the first step of decomposition of these compounds, were calculated by the method of Horowitz and Metzger [12] with the modification given by Dharwadkar and Karkhanavala [13]. The equation used for calculation is:

$$E_a = \text{Slope} \frac{T_f - T_i}{100} RT_i^2 \quad (T = \text{degrees Kelvin}).$$

The slope is obtained by plotting: $\ln \ln \frac{W_0 - W_f^t}{W - W_f^t}$ vs. Θ . A typical plot is given in Fig. 6. Here $\Theta = T - T_s$, W_0 stands for the initial weight, W for the weight remaining at a given temperature, W_f^t for the final weight of the particular decomposition step. Table 16 gives the activation energies in air, nitrogen and vacuum. The varia-

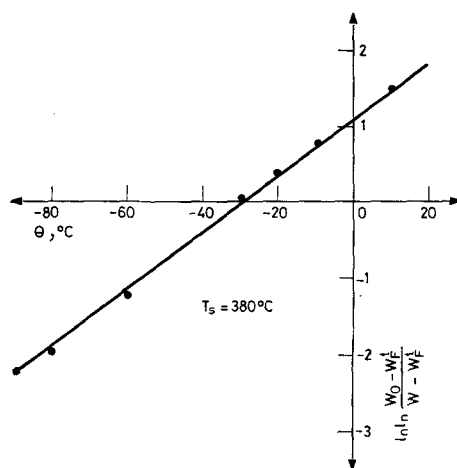


Fig. 6. Plot of $\ln \ln \frac{W_0 - W_F^t}{W - W_F^t}$ vs. Θ for thermogravimetric analysis of silver toluenedithiolate in air

tion of the modes of decomposition in air, nitrogen and vacuum depends on the activation energies. Thus in Table 16 we see that the activation energies decrease as the atmosphere is changed from air to nitrogen. We can see also that in both air and nitrogen the activation energies decrease with increasing atomic number.

The analytical results are verified by thermal analysis. The yield of the reaction of silver nitrate with toluene-3,4-dithiol is supported by the fact that mercaptans are analyzed using aqueous silver nitrate. The result obtained by the direct ignition at 800° , as shown in Table 2, is correct since formation of oxide or sulfide is excluded at this temperature. Further support for this comes from thermal analysis where at 620° we get pure silver as a residue.

The infrared spectra of the toluenedithiolates are quite similar to the infrared spectrum of the toluene-3,4-dithiol and exhibit well defined stretching modes; however the bending and overtone modes are not observed. The band at 2545 cm^{-1}

Table 16

Activation energy data for the first step of decomposition, of silver, lead and mercuric toluenedithiolates

Compound	Activation energies, kJ/mole in		
	Air	Nitrogen	Vacuum
Silver tol/ate	117.8	100.3	103.6
Lead tol/ate	91.2	87.8	—
Mercuric tol/ate	125.8	61.0	—

which is characteristic of the S-H bond is absent in the spectra of the metal toluenedithiolates. Its absence proves that the metals are bonded to both sulfurs. The metal-sulfur bond is expected to form due to the poor overlap of the 1 s orbital of the hydrogen atom to the 3 p orbital of sulfur. On the other hand the low electronegativity of sulfur allows its electrons to be shared with atoms having larger valence shells resulting in stronger bonds than the S-H bond.

The band at 450 cm^{-1} which is present only in the spectra of the metal toluenedithiolates is attributed to the metal-sulfur bond. The i.r. absorption spectra indicate that the organic molecule does not adhere on the surface of the metal.

The bands: 1890, 1550, 1125 and 928 cm^{-1} are not exhibited by the spectra of the metal toluenedithiolates. These bands represent the C-H bending and overtone modes also the C-S and S-H stretching modes. These bands are weak due to the change of the symmetry of the molecule upon coordination.

Toluene-3,4-dithiol bands which are greatly reduced in the spectra of the metal toluenedithiolates are the following: 1595, 1215 and 685 cm^{-1} . These bands may be due to the perturbed C-C and C-S bonds. The weak water bands in the spectra are believed to result from adsorbed water on CsI. Thermoanalytical data indicate no water in these compounds. The band at 1110 cm^{-1} is possibly due to polywater [14].

Examination of Tables 6, 9, 10 and 13, reveals no appreciable variation of decomposition temperatures with the nature of the medium. The decomposition temperatures appear to decrease with increasing atomic number of the metal.

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ZUSAMMENFASSUNG — Die Silber-, Blei- und Quecksilber-Toluoldithionate wurden synthetisiert und sowohl mit konventionellen chemischen Methoden als auch thermoanalytisch analysiert. Die thermische Zersetzung wurde durch thermogravimetrische Analyse in Luft, Stickstoff und Vakuum untersucht. Die Formeln der Zersetzungsprodukte wurden aus den Molekulargewichten und den Infrarot-Absorptionsspektren abgeleitet. Die Aktivierungsenergien für den ersten Zersetzungsschritt wurden berechnet. Die flüchtigen Produkte enthalten hauptsächlich Kohlenstoff und Wasserstoff, während die Rückstände die entsprechenden Metalle in freier Form oder in Form von Schwefelverbindungen enthalten.

Резюме — Синтезированы и исследованы обычными химическими методами и термоаналитическими методами толуолдителилаты серебра, свинца и ртути. Термическое разложение было изучено термогравиметрическим анализом в вакууме и в атмосфере воздуха и азота. Используя молярные веса и ИК спектры, были выведены формулы продуктов разложения. Вычислены энергии активации первой стадии разложения. Летучие продукты содержали главным образом углерод и водород, а твердые остатки содержали соответствующие металлы в свободном состоянии или с серой.