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THERMAL BEHAVIOUR OR THALLIUM(I) FATTY ACID SALTS, I

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We have studied the thermal behaviours of the fatty acid (C_1-C_9, C_{12}, C_{14}, C_{16} and C_{18}) thallium(I) salts.

Investigating the dependence of the thermal decomposition reactions on the experimental conditions, we established that they decompose differently depending on the atmosphere, and on the shape and material of the sample holders.

We also determined the heat-stable temperature ranges of the compounds in which they can be investigated without any thermal decomposition.

The temperatures and enthalpy changes of the polymorphic and phase changes were measured and the corresponding entropy changes were calculated.

We have recently reported on the thermal behaviours of the ammonium and sodium salts of fatty acids, paying special attention to the liquid crystalline properties of the latter [1–3].

In the present paper we deal with the thallium(I) salts of the same homologous series, because these compounds show several similarities with the alkali metal salts, and also have liquid crystalline phases; in addition, the thallium salts can more conveniently be investigated [4] as they have relatively low transition temperatures [5–7] and are easy to produce and purify. Except for the case of the formate [11, 12] we could find no data in the literature, concerning their thermal properties and thermal decompositions.

We have produced the thallium(I) salts of the C_1-C_9, C_{12}, C_{14}, C_{16} and C_{18} fatty acids, determined the temperatures and heats of their polymorphic and phase changes, and investigated the circumstances of their thermal decompositions. Using several experimental techniques, we have also studied their thermoelectrical properties. These data have already been published in part [8] and a more detailed report on this will be given in the second part of this paper.

Experimental

The thallium(I) salts were produced in our laboratory, according to the following reaction-scheme:

$$Tl_2CO_3 + 2R-COOH \rightarrow 2R-COOTl + H_2O + CO_2$$

The heterogeneous reaction was carried out in dry methanol and the resulting salts were recrystallized from an ethanol-ether mixture and washed with dry ether. The melting points were measured, and the thallium contents were checked by chemical analysis. The IR spectra showed no acid-content in the samples.

The measured melting points and the corresponding literature data are listed in Table 1.

Table 1

Transition temperatures of Tl(I) fatty acid salts

Chain-length	Transition temperatures, °C					
	Solid-mesophase			Mesophase-isotropic liquid		
	[4]	[5]	This work	[4]	[5]	This work
C_1			101*			
C_2			131*			
C_3			195*			
C_4			186*			
C_5	181.0	175.0	182	215.5	212.0	214
C_6	149.0	152.0	145	229.5	224.0	227
C_7	142.8	143.0	146	227.5	227.0	228
C_8	135.7	136.0	130	222.5	220.0	221
C_9	138.6	130.0	137	217.0	215.0	217
C_{12}	124.7	123.0	125	197.0	197.0	198
C_{14}	120.0	119.0	120	185.0	181.5	187
C_{16}	118.2	116.0	117	175.5	172.0	177
C_{18}	119.0	118.0	112	167.0	163.0	171

* Solid-isotropic liquid

The complex thermal behaviours of the salts were investigated with a Derivatograph. A detailed description of the apparatus can be found in the literature [9, 10].

It is well known that the thermal degradation of organic compounds is generally much more complicated than that of inorganic compounds, and the measured data depend sensitively on the experimental circumstances. The shapes of the curves depend primarily on the atmosphere applied in the furnace chamber, the heating rate and the weight of samples, and to a lesser extent on the geometry and material of the sample holders. For this reason we systematically changed the atmosphere, the sample weight, and the heating rate in our measurements with the derivatograph. We also found that the reactions are much more affected by the geometry and material of the sample holders than usual, and therefore it seemed necessary to investigate this effect too. The weight-losses of the sample holders (caused by the corrosion effect of the residues) had to be corrected for. The gas-flow in the furnace chamber was designed specially to avoid sedimentation of the products.

Heated Al_2O_3 was used as reference material, with air, oxygen and nitrogen (deoxygenized with a BSA catalyzer) atmospheres and 15–20 l/h flow-rates. The average sample weight was about 100 mg.

In order to investigate the effect of the sample weight, the compounds were also studied with a Cahn RG electrobalance, because the Derivatograph is not suitable for measurements in the milligram range. The sample weights in this case were 2–4 mg, the heating rate was 5 °/min and the atmosphere was purified nitrogen with a flow-rate of 10 l/h.

Calibrations (necessary because of the buoyancy) were carried out for each gas and flow-rate, and were applied in evaluation of the TG curves.

In order to detect the solid–solid polymorphic transitions and phase changes, to determine their characteristic temperatures, to establish whether the transitions are monotropic or enantiotropic, and to measure the transition heats, we carried out investigations with a Mettler TA 2000 apparatus. Samples with weights in the mg range were placed in closed sample holders. The samples were measured in both heating and cooling cycles, and the apparatus was calibrated with indium for the quantitative measurements.

Results and conclusions

Investigations with the derivatograph

Because of the different thermal behaviours of the compounds investigated, our observations will be discussed in the following grouping:

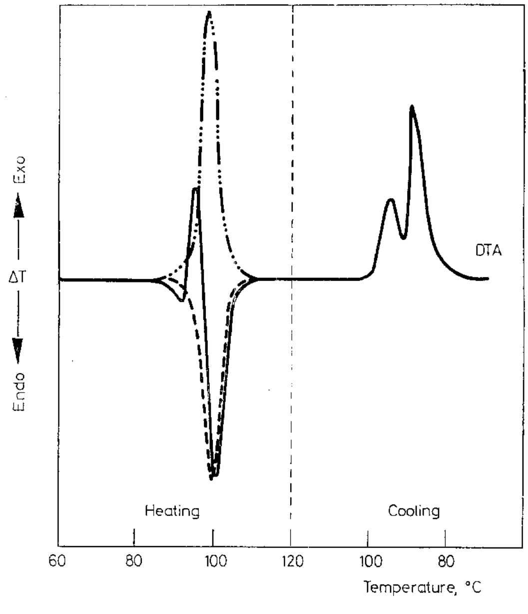

Fig. 1. DTA curves of thallium(I) formate, measured with a derivatograph

a) *Evaluation of the derivatograms of thallium(I) formate*

The shape of the peak corresponding to the melting of the salt in the DTA curve differed from the general type. It was also unusual that the estimated melting heat was outstandingly high, being in the range of the heats of degradation reactions taking place in an oxygen atmosphere. Measured by quantitative DTA it was 2.6 kcal/mole.

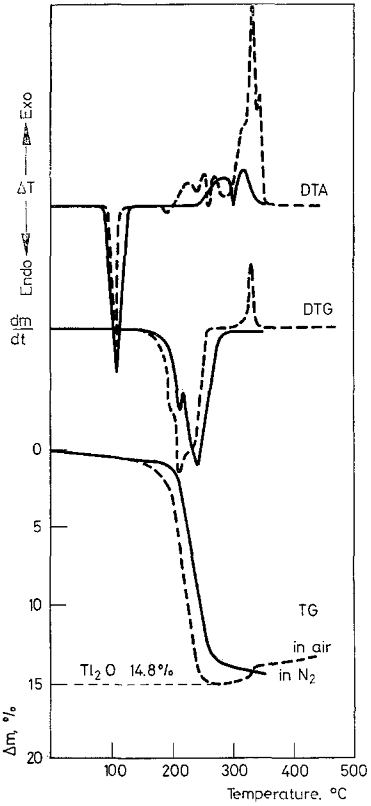

Fig. 2. Thermal curves of thallium(I) formate in air and in nitrogen

Melting was recorded sometimes as an exothermic process, sometimes as the well-recognizable resultant of exothermic and endothermic peaks (Fig. 1). The DTA curve of the derivatograms in cooling cycles revealed two well-separated exothermic DTA peaks. This phenomenon was reproducible with the Mettler instrument too. The reason for this phenomenon is most probably that the isotropic liquid does not pass directly into the crystal solid on cooling, but is transformed first to a glassy state, which crystallizes later.

The exothermic melting always took place only during the first heating after recrystallization. In repeated heating periods the same sample always melted in a regular endothermic process. It is most probable that recrystallization of the sample from a solvent yields an unstable structure, while crystallization from the melt phase is a two-step equilibrium process.

The thermal decomposition of thallium(I) formate depends very sensitively on the atmosphere in the furnace chamber (Fig. 2). In nitrogen metallic thallium is formed in a nearly stoichiometric ratio. This is indicated by the sharp DTA peak around 300° characterizing the melting of the metal (the melting point of thallium is 303.5° [13]). The decomposition in nitrogen (even if this has been thoroughly freed from oxygen) is exothermic, and the measured weight-loss does not reach the calculated 18.6%, but varies in the range 14.0–15.5%. This is probably due to the fact that in addition to the metal a small amount of Tl_2O and relatively more cracked carbon was found in the residue.

The character of the data obtained from experiments carried out in air or oxygen atmospheres differed from those measured in nitrogen. The decomposition temperatures were 20–25° lower and the weight of the residue corresponded to the theoretical value for thallium(I) oxide. The thallium(I) oxide melt underwent a relatively intensive exothermic reaction at 300–350°, forming thallium(III) oxide. This reaction caused a weight-increase of about 1%.

b) *Thermal properties of C_2–C_4 fatty acid thallium(I) salts*

The thermal properties of these compounds differ from those of thallium(I) formate as regards their decompositions, and from those of the higher molecular weight members of the homologous series because they do not exhibit mesomorphic properties.

Table 2

Decomposition temperatures of Tl(I) fatty acid salts

Compounds	In air, °C	In inert atmosphere, °C
Formate	120	140
Acetate	180	200
Propionate	200	210
Butyrate	200	220
Valerate	210	260
Caproate	250	280
Heptanoate	250	290
Caprylate	270	300
Pelargonate	270	300
Laurate	210	260
Myristate	270	320
Palmitate	240	330
Stearate	230	320

The data obtained from the DTA and DTG curves measured with the Derivatograph characterize the dynamic thermal stability of these compounds (Table 2). These salts showed uniform melting and unambiguous endothermic decomposition in oxygen-free atmosphere. As an example we give the thermal curves of thallium(I) acetate in Fig. 3.

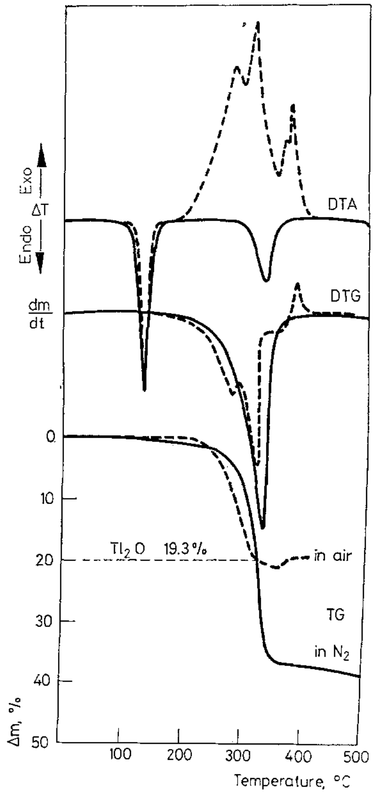

Fig. 3. Thermal curves of thallium(I) acetate in air and in nitrogen

Quantitative evaluation of the TG curves of the salts established that the weight losses are significantly larger than the calculated values for both metal and metal oxide. In a more detailed investigation of this question it turned out that this increased weight-loss is caused by distillation of the salts in the molecular state: after every run solid could be found at different parts of the apparatus and could be identified as the starting material via its melting point and IR spectra. This weight-losing starts only after the melting point of the sample (illustrated in the DTA and DTG curves) and thus the process is distillation and not sublimation. This was also proved by separate atmospheric distillation experiments.

This phenomenon, which is quite rare among salts, can be explained by the appreciable covalency of the carboxylate-metal ion bond, and is also suggested by the low melting points of the compounds. The extent of distillation is strongly affected by the experimental conditions, as follows:

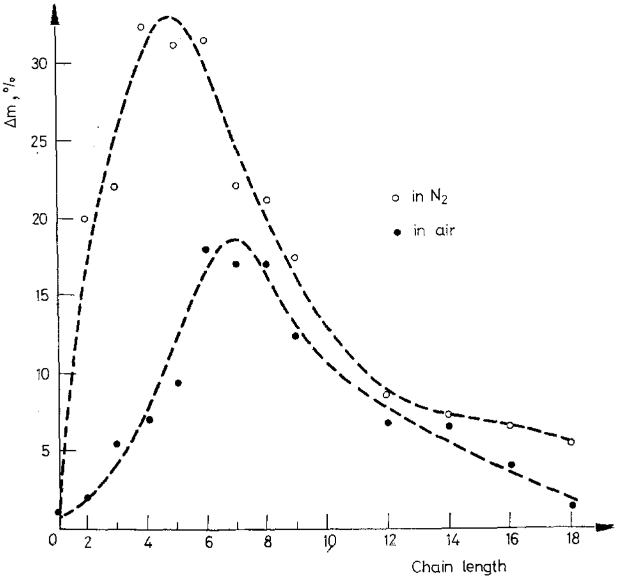

Fig. 4. Percentage difference of the decomposition residue from the calculated theoretical value for Tl(I) oxide as a function of the chain-length

1. The nature of the atmosphere is the basic determining factor. Figure 4 shows the weight-differences from the theoretical values for thallium oxide as a function of the chain-length, in both oxidizing and inert atmospheres. The molecular state distillation is more significant in the latter, which explains the higher differences from the theoretical values.

2. Figure 4 also illustrates that the tendency to distillation depends on the molecular size too, this function exhibiting a maximum. This behaviour is due to the opposite trends of the dependences of the distillation on the covalency of the salt bond and on the molecular weight.

3. The rate of distillation also depends on the specific surface of the sample, as is well illustrated by the curves measured in a crucible-type and in a plate-type sample holder (Fig. 5).

4. Studying the effect of the material of the sample holders, we found that the decomposition products corrode platinum crucibles. Application of the inexpensive aluminium oxide crucible suggested by Porubszki et al. [14] was not successful because the metal oxide formed can diffuse through the wall of the crucible, caus-

ing significant weight-losses. Using a heat-resistant glass crucible, the formation of a small amount of yellow thallium silicate has to be taken into consideration.

The TG curves differ after the ending of the main decomposition reaction. In an inert atmosphere the weight of the residue is practically constant after the decomposition reaction and distillation, and the residue consists of thallium(I) oxide and cracked carbon. The thallium(I) oxide is converted into thallium(III) oxide in an oxidizing atmosphere in a relatively fast exothermic reaction which is followed by its thermal decomposition. The process is quite complex. According to the literature [13], thallium(III) oxide is transformed into $Tl_2O.3Tl_2O_3$ at 360–440°; this compound is stable in the interval 440–565°, and then loses oygen till 815°. In a pure oxygen atmosphere thallium(III) oxide is formed directly, and therefore only the oxygen-losing process can be observed.

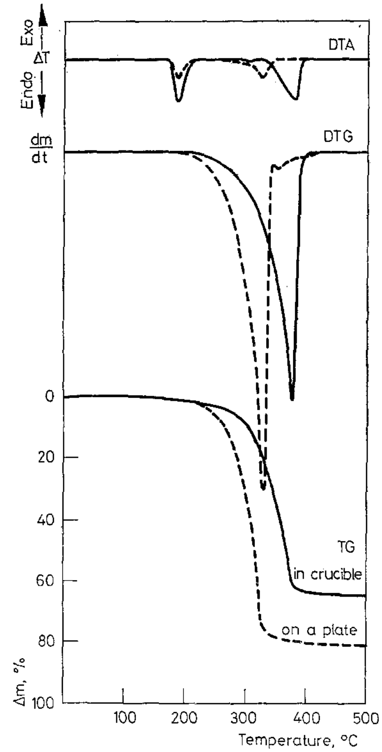

Fig. 5. Thermal curves of thallium(I) butyrate, measured in a crucible and in a plate-type sample holder

c) *Investigation of the* C_5-C_9, C_{12}, C_{14}, C_{16} *and* C_{18} *fatty acid thallium(I) salts*

Compared with the above-mentioned members of the homologous series, these salts exhibit many more DTA peaks, corresponding to polymorphic transitions as well as to the solid-mesophase and mesophase-isotropic liquid transitions (Figs 6 and 7). With the help of the DTA and DTG curves we determined the dynamic thermal stabilities of these compounds too. According to the results listed in Tables 1 and 2, it is not necessary to ensure an absolute oxygen-free atmosphere in investigations of the melt phase.

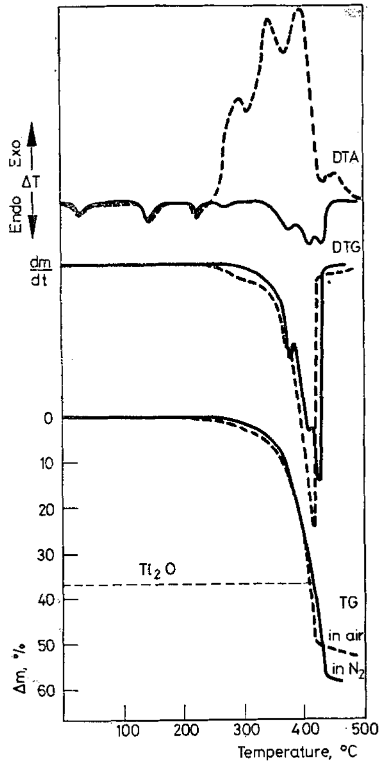

Fig. 6. Thermal curve of thallium(I) heptanoate

The conclusions from the complex thermal investigations are as follows:

1. The results and their evaluation helped the planning of further investigations of the melt phases of these salts.

2. The results also called our attention to the fact that the thermal decomposition is complex (consisting of parallel and consecutive processes), and is strongly affected by the experimental conditions and the molecular weight.

3. No quantitative data can be obtained for chemical analysis of the decomposition in this case.

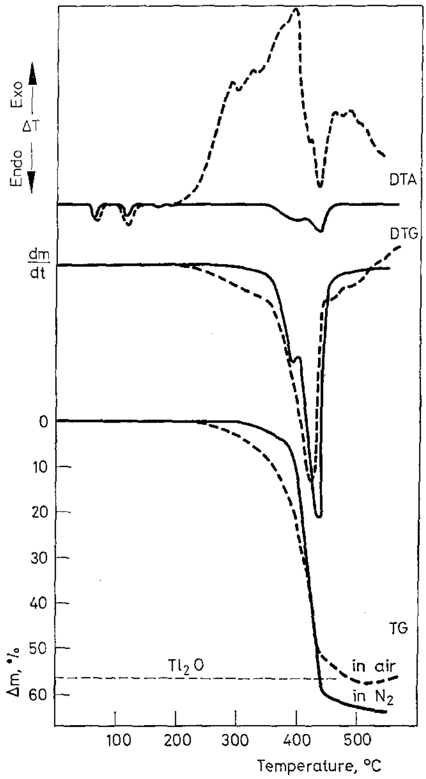

Fig. 7. Thermal curve of thallium(I) stearate

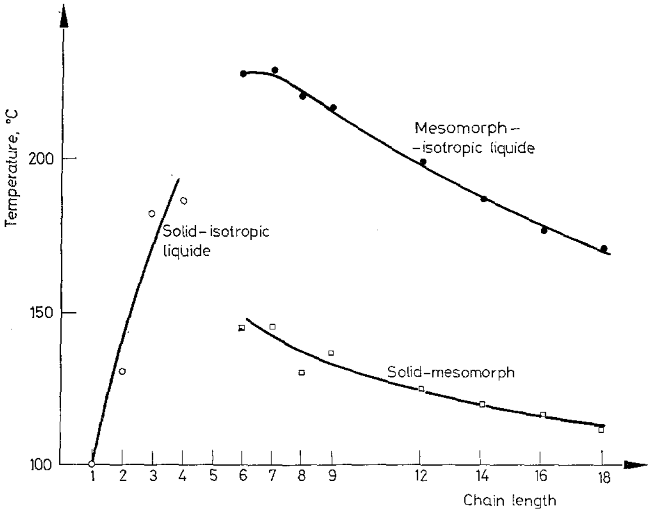

Fig. 8. Transition temperatures as a function of the chain-length

Quantitative DTA measurements

Quantitative DTA investigations were carried out for all the compounds mentioned earlier with a Mettler TA 2000 apparatus.

The transition temperatures, heats and entropies are listed in Table 3. The transition temperatures are plotted in Fig. 8 as a function of the chain-length of the anion. The smooth curves represent the temperatures of the solid-mesophase and mesophase-isotropic liquid transitions. These tendencies are similar to those measured for the sodium salts [1,2]. The enthalpy and entropy changes corresponding to the solid-mesophase and mesophase-isotropic liquid transitions are plotted against the chain-length of the anion in Fig. 9.

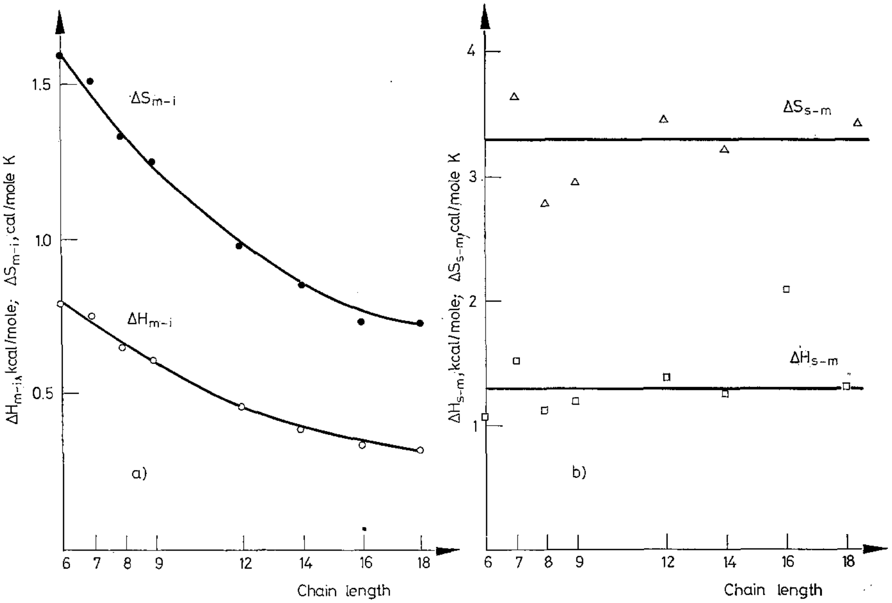

Fig. 9. Transition enthalpies and entropies; a) mesophase-isotropic liquid, b) solid-mesophase

According to the literature [17], more characteristic information can be obtained on the thermal behaviour of compounds if we investigate the sum of the entropy changes for all the transitions taking place from 0 K; however, the available data in the literature [15, 16] are usually transition entropy changes summed only from an arbitrary temperature, for example from 25°, assuming that there are no transitions of the members of the series below this. Though our results computed on the same basis show similar trends to those cited above (Table 3), the assumption is very questionable in our view.

Table 3

Transition temperatures, enthalpies and entropies of Tl(I) fatty acid salts

Compounds	Solid–solid			Solid–mesophase			Mesophase–isotropic liquid			
	T, °C	ΔH, kcal/mole	ΔS, cal/mole K	T, °C	ΔH, kcal/mole	ΔS, cal/mole K	T, °C	ΔH, kcal/mole	ΔS, cal/mole K	$\Sigma\,\Delta S$, cal/mole K
Formate				101*	2.6	6.9				
Acetate				131*	4.2	10.4				
Propionate	92	0.09	0.25	195*	2.2	4.8				
Butyrate				186*	1.6	3.4				
Valerate	81.5	0.54	1.5	182	1.3	2.9	214	0.73	1.5	5.9
Caproate	122	0.043	0.11							
	139	0.18	0.44	145	1.07	2.6	227	0.79	1.6	4.7
Heptanoate	26	0.66	2.2	146	1.5	3.6	228	0.75	1.5	7.3
Caprylate				130	1.12	2.8	221	0.65	1.3	4.1
Pelargonate	27	0.40	1.3							
	42	0.63	2.0							
	57	1.8	5.3	137	1.2	2.9	217	0.61	1.2	12.8
Laurate	39	0.91	2.9							
	81	0.58	1.6	125	1.4	3.4	198	0.46	0.98	9.0
Myristate	40	2.8	8.9							
	98	0.75	2.0	120	1.3	3.2	187	0.39	0.85	14.9
Palmitate	54	2.6	8.0	117	2.1	5.3	177	0.33	0.73	14.1
Stearate	51	2.3	7.0							
	107	1.1	2.9	112	1.3	3.4	171	0.33	0.73	14.0

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Résumé — Etude du comportement thermique des sels de thallium(I) d'acides gras (de C_1 à C_9, C_{12}, C_{14} et C_{18}). L'étude de la décomposition thermique en fonction des conditions expérimentales a permis d'établir que les sels étudiés se décomposent différemment suivant l'atmosphère utilisée, ainsi que suivant la forme et la nature des supports échantillons. Détermination des domaines de température où ces composés restent thermiquement stables. Mesure des températures et des variations d'enthalpie des transitions de phase et des transitions polymorphiques et calcul des variations d'entropie correspondantes.

Zusammenfassung — Das thermische Verhalten der Thallium(I)-Salze der Fettsäuren mit C_1 bis C_9, C_{12}, C_{14} und C_{18} wurden untersucht. Die Temperaturen und Enthalpien der einzelnen polymorphen und Phasenänderungen, sowie die thermische Stabilität der Verbindungen wurden bestimmt. Es wurde festgestellt, daß die zu Ketonen und Gemischt-Ketonen führende thermische Zersetzung in der Schmelzphase von Destillationsprozessen begleitet wird, welche von der Molekülstruktur und von zahlreichen Versuchsbedingungen abhängig sind.

Резюме — Исследовано термическое поведение солей жирных кислот таллия(I) с числом углеродных атомов C_1—C_9, C_{12}, C_{14}, C_{16}, C_{18}. Измерены температуры полиморфных и фазовых превращений, энтальпии и термическая стабильность этих соединений. Было установлено, что при тепловом разложении расплава образуются кетоны и смеси кетонов, причем этот процесс сопровождается дистилляционными процессами, которые зависят от строения молекул и некоторых экспериментальных обстоятельств.