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ON THE THERMAL ANALYSIS OF ALIPHATIC CARBOXYLIC ACIDS AND THEIR SALTS

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The thermal behaviour of oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, and of their mono- and disodium salts and calcium salts has been studied by derivatography. Some of the acids were distilled off without decomposition, while the others were decomposed in accordance with the rule of Blanc.

Up to 600°, the decomposition of the monosodium salts consists of two principal steps. The first process is the liberation or the decomposition of the acid formed from the salt, the second step the decomposition of the normal salt into sodium carbonate and "organic" molecules. This decomposition mechanism was verified also by tracer technique on compounds labelled with the ^{14}C isotope. With most of the compounds unable to form ketones, the decomposition of the normal salt yields a great variety of organic compounds. In the case of adipates and pimelates the formation of cyclanones predominates.

Aliphatic dicarboxylic acids and their salts are decomposed in various ways on an increase in temperature. Several authors have studied this thermal decomposition using different methods and with different aims. The laws governing the changes in acids produced by heat are described by the rules formulated by Blanc [1] and elaborated by Carless and Kalt [2]. Ruzicka and co-workers [3] investigated optimum conditions for the formation of cyclic ketones in the heating of various metal salts of dicarboxylic acids. The kinetics and mechanism of the decarboxylation reaction have been the subject of a number of studies [4—17]. Several authors investigated exhaustively the behaviour of oxalic acid and its salts [18—20] by thermogravimetry and by derivatography. Wendlandt studied dicarboxylic acids by differential thermal analysis and by gas volumetric techniques [21]. Several publications deal with the products formed during the decomposition of these compounds [2, 3, 22, 27].

Experimental part

Acids used in our investigations were of a purity to give the theoretical melting point. The disodium salts were prepared by the reaction of a stoichiometric quantity of the acid and sodium hydroxide. The volume of the solutions was reduced by evaporation in vacuo, and the compounds were crystallized. Monosodium salts of stoichiometric composition were obtained by the complete evaporation of their aqueous solutions. The calcium salts were precipitated from the aqueous solutions of the disodium salts with calcium chloride. The metal content of the single salts was determined by chemical analysis, and the water of crystallization by Karl Fischer's method.

The measurements were carried out by means of a Derivatograph [28]. An instrument featuring a recorder, constructed in our own laboratory, was used in one part of the investigations by differential thermal analysis. For the isolation of volatile products, an apparatus consisting of an oven with programmed heating and a trap system was used. Compounds obtained were analysed with a gas chromatograph, Model Carlo Erba. In our derivatographic investigations a heating rate of 5°C/min was used. Recordings were made in air and in an oxygen-free nitrogen atmosphere, changed 100 times per hour. The difference in the derivatograms obtained under the two kinds of atmospheres was reflected primarily in the course of the DTA curves.

The values of characteristic temperatures measured in the individual processes are somewhat different from those reported in the literature, presumably owing to the dynamic character of the method of investigation.

Derivatographic analysis of the aliphatic dicarboxylic acids

Figs 1, 2 and 3 show the derivatograms of the acids investigated, recorded under a nitrogen atmosphere. It can be seen from the curves of the derivatograms that the acids investigated departed up to 600° completely from the sample

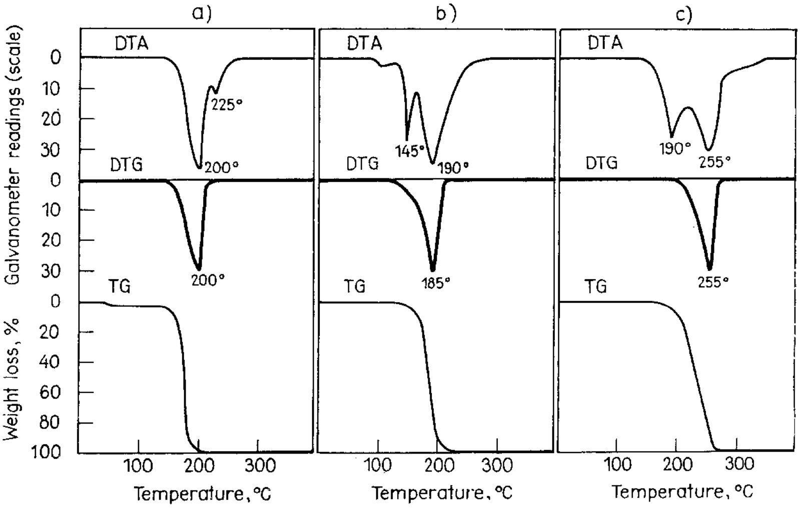


Fig. 1. Derivatograms of *a)* Oxalic acid; *b)* Malonic acid; *c)* Succinic acid

holder crucible, and during the decomposition of azelaic and sebacic acid carbon was formed by cracking, which, in experiments carried out in air, was burned at 410° and 415—440°, respectively. A decomposition of this character was not observed with the other compounds. Oxalic acid and malonic acid were decomposed as described in the literature [18, 19], i.e. the decomposition products of maleic acid consisted only of carbon dioxide and acetic acid in stoichiometric quantities. The decomposition products of oxalic acid dihydrate were carbon dioxide, carbon monoxide and water. 1 to 2 per cent of oxalic acid dihydrate sublimates, while this phenomenon was not met with in the anhydrous compound. In the case of succinic acid and glutaric acid, in accordance with the rule of Blanc, the formation of the acid anhydride is the dominating process. In the case of succinic acid 77 mole per cent, and in that of glutaric acid 57 mole per cent, is converted into the anhydride. A small amount of these two acids was decarboxylated, 4 mole per cent of succinic acid and 8 to 9 mole per cent of glutaric acid was decomposed to the corresponding monocarboxylic acid and to carbon dioxide. A substantial part of these acids was distilled, and this process was furthered also by the constant scavenging of the atmosphere. In the thermal decomposition of adipic acid and pimelic acid, showing the greatest tendency to cyclanone formation, this reaction remains rather in the background, owing to the dynamic character of the method of investigation. After melting, their decomposition yielded a small amount of cyclanone and monocarboxylic acid, but predominantly the distillation of the acids took place. With adipic acid, the formation of the polyanhydride, as reported in the literature, could not be observed. The DTA curves of suberic acid, azelaic acid and sebacic acid exhibit

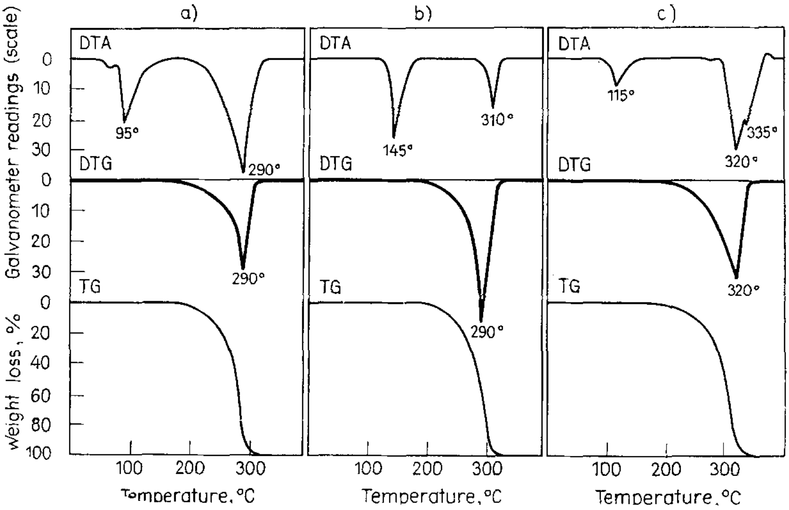


Fig. 2. Derivatograms of *a)* Glutaric acid; *b)* Adipic acid; *c)* Pimelic acid

an exothermic process. These acids were also primarily distilled. During the heating of the acids, transformations into various crystal modifications could be observed with several of the compounds. This transformation is indicated by the DTA peak, occurring in the case of malonic acid at 105°, and in that of glutaric acid at 75°. Melting points could be easily reproduced. Temperatures appertaining to the thermal decomposition of the individual acids cannot be arranged on the basis of the even or uneven number of the carbon atoms into two series, as, for example, in the case of the melting point or of the solubility in water, owing to their cisoidetransoide properties.

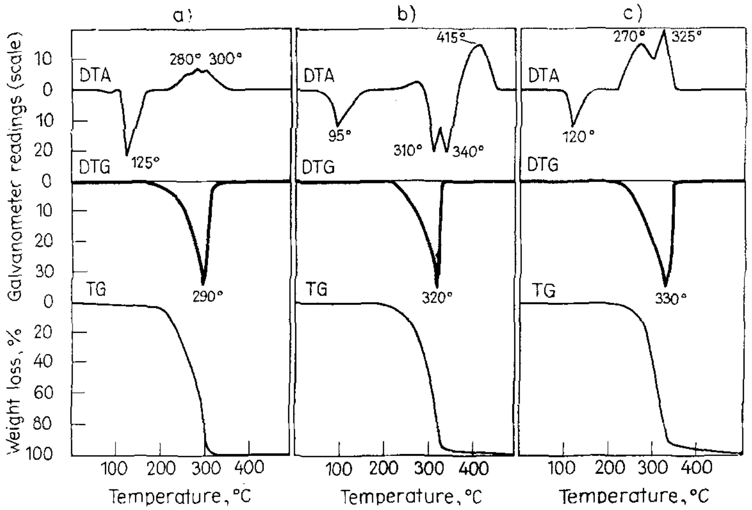


Fig. 3. Derivatograms of *a)* Suberic acid; *b)* Azelaic acid; *c)* Sebacic acid

Thermal behaviour of the monosodium salts of dicarboxylic acids

The derivatograms of the compounds investigated are shown in Figs 4, 5 and 6. It will be seen that the thermal decomposition of the monosodium salts involves two principal steps. Out of these, the first is characterized by a considerable loss in weight, and, with the exception of sodium oxalate, azelainate and sebacate, by a distinct endothermic DTA peak. After the termination of the process, a section of constant weight follows for a relatively long period. The limit of temperature of this section of constant weight decreases with the increasing number of carbon atoms in the salt, but the next step of decomposition is well separated in each case. The second decomposition process is also accompanied by a substantial decrease in weight, though of slighter degree than that in the first step. Evaluated on the basis of the DTG curves, the decrease in weight, particularly with the derivatives of acids with a higher carbon number, proceeds in more than one step up to 600°. Now, another section of constant weight follows, which lasts until the end of the thermal stability of the sodium

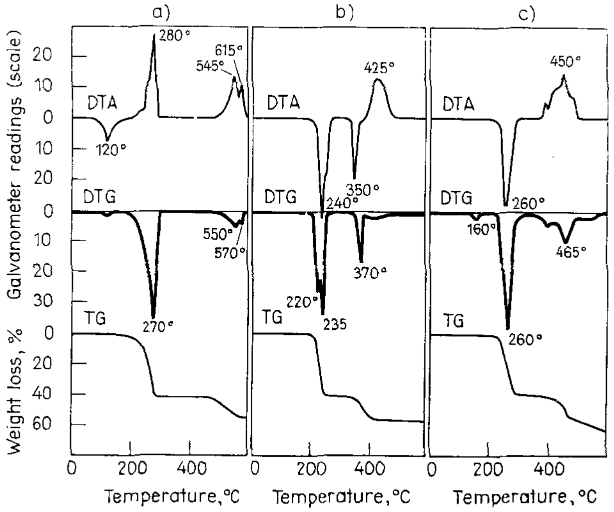


Fig. 4. Derivatograms of *a)* Monosodium salt of oxalic acid; *b)* Monosodium salt of malonic acid; *c)* Monosodium salt of succinic acid

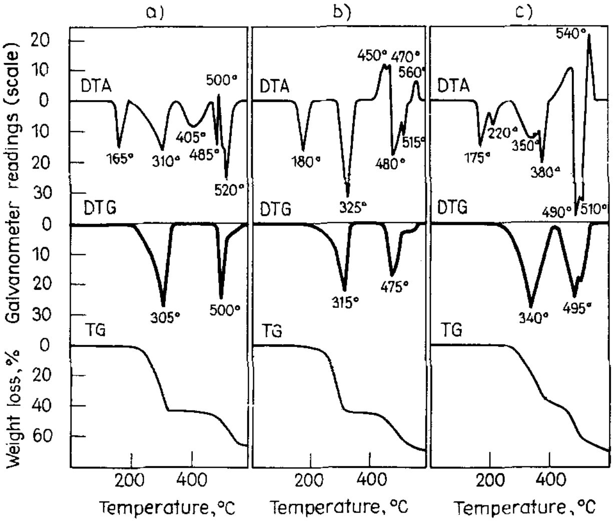


Fig. 5. Derivatograms of *a)* Monosodium salt of glutaric acid; *b)* Monosodium salt of adipic acid; *c)* Monosodium salt of pimelic acid

carbonate formed. DTA peaks belonging to the decomposition processes consist in several cases of distinctly separated endothermic and exothermic parts. The chemical reactions taking place could be established on the basis of the chemical analysis of the products formed in the decomposition processes, and on the basis of the quantitative evaluation of the TG curves.

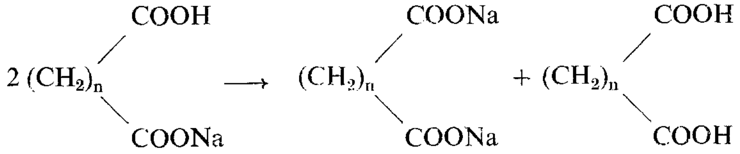
Results of the evaluation made on the basis of the TG curves are summarized in Table 1.

Table 1

Monosodium salt of the acid	Sodium carbonate, %		Acid, % loss from 1 mole of the monosodium salt		Organic part, % loss from 1 mole of the normal salt	
	Calc.	Found	Calc.	Found	Calc.	Found
Oxalic	47.4	47.0	40.2	40.0	12.4	12.5
Malonic	42.1	42.0	41.3	42.0	16.6	16.0
Succinic	37.7	38.0	42.2	42.0	19.6	20.0
Glutaric	34.5	34.0	42.8	42.5	22.4	23.0
Adipic	31.6	31.0	43.5	44.0	24.9	25.0
Pimelic	29.2	31.0	44.0	41.0	26.8	28.0
Suberic	27.0	30.0	44.4	42.0	29.6	28.0
Azelaic	25.2	24.5	44.8	42.0	30.0	33.0
Sebacic	23.2	24.0	45.2	45.0	31.6	31.0

The calculations were carried out on the basis of the assumption that monosodium salts are decomposed according to the following reaction scheme:

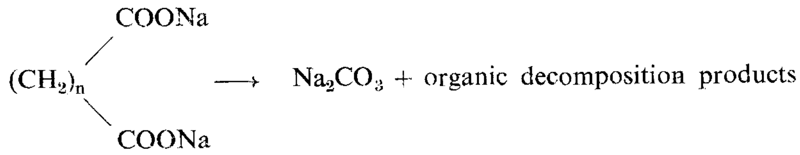
I.



$$2\,(CH_2)_n\begin{matrix}COOH\\COONa\end{matrix} \longrightarrow (CH_2)_n\begin{matrix}COONa\\COONa\end{matrix} + (CH_2)_n\begin{matrix}COOH\\COOH\end{matrix}$$

The first decomposition step is due to the loss of acid formed in process I. The second process, resulting in a decrease in weight, is characteristic of the decomposition of the normal salt.

II.



$$(CH_2)_n\begin{matrix}COONa\\COONa\end{matrix} \longrightarrow Na_2CO_3 + \text{organic decomposition products}$$

The loss in weight, calculated and found, as well as the residual substance show a good agreement for the two decomposition processes. The decomposition of the monosodium salts in the way indicated above is also supported by the following experimental findings.

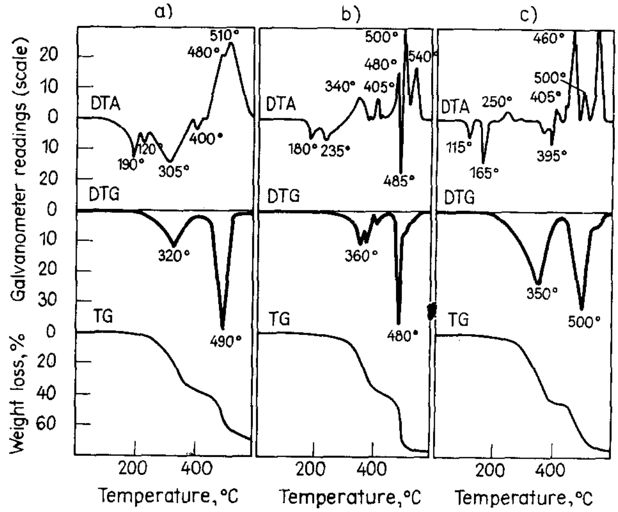


Fig. 6. Derivatograms of *a)* Monosodium salt of suberic acid; *b)* Monosodium salt of azelaic acid; *c)* Monosodium salt of sebacic acid

1. The approximate agreement between the characteristic decomposition temperatures appertaining to the first decomposition step of the dicarboxylic acids and the acid salts, and the good agreement between the characteristic

Table 2

Acid	Decomposition temperature of the pure acid °C	Characteristic decomposition temperature of step I °C	ΔT °C	Decomposition temperature of the pure disodium salt, °C	Characteristic decomposition temperature of step II °C	ΔT °C
Oxalic	200	270	+70	580	560	—20
Malonic	185	220	+35	350	370	+20
Succinic	255	260	+ 5	470	465	— 5
Glutaric	290	305	+15	475	500	—25
Adipic	290	315	+25	475	475	0
Pimelic	320	340	+20	495	500	+ 5
Suberic	290	320	+30	490	490	0
Azelaic	320	360	+40	500	480	—20
Sebacic	330	350	+20	500	500	0

decomposition temperatures appertaining to the second decomposition step of the disodium dicarboxylic acids and the acid salts. Relevant data are summarized in Table 2.

2. The monosodium salts were heated in the oven with programmed heating until the termination of the first decomposition process, and decomposition products were analysed. Also in this case, the same products were obtained as those already mentioned in the discussion of the decomposition of the single acids.

To prove the fact that the monoalkali dicarboxylic salts are not simple mixtures of molar ratio of the corresponding acids and their dialkali salts, as could be formally expected in first approximation on the basis of the TG and DTG curves of the derivatograms, and on the basis of chemical analysis, experiments were carried out with adipic and pimelic acid, labelled with ^{14}C isotope on the carboxyl group. The adipic acid and the pimelic acid containing the tracer atoms were mixed in molar ratios with inactive disodium adipate and pimelate, and heated to 350°. The acids were isolated from the liberated decomposition products. The molar radioactivity of these acids and that of the residual disodium salts were measured. In both cases, the molar activity of the acids and the salts was identical. The same result was obtained when the monosodium salts prepared from the labelled compounds were investigated as described above. It is known [29] that dicarboxylic acids have a tendency to form peracids with their acid salts. It follows from this that acid salts, in accordance with the equilibrium characteristic of the single compounds, are present in anionic, dianionic and free acid forms in their aqueous solutions. This fact can be proved by the extraction of the aqueous solution of the acid salt with ether. In this way, half a mole of the acid salt dissolved can be removed, while half a mole of normal salt remains in the aqueous solution [29, 31]. The distribution ratio between the three forms depends on the difference between the two dissociation coefficients of the acid. The smaller this difference, the less will be the amount of the acid salt, and the more that of the acid and the normal salt [32]. Data in the literature concerning the aqueous solutions and our experimental results reported here support the assumption that, besides in their aqueous solutions, the acid salts of aliphatic dicarboxylic acids are, or may be, present also in the solid phase or in their melts in a distribution of different degrees of neutralization of the acid. If one of the components, e.g. the acid volatilizing or undergoing decomposition is removed from the system by heating, the conversion of the acid salt into acid and normal salt becomes complete. Caley and Brundin [33] and Erdey and co-workers [34] in their examination of the thermal properties of potassium hydrogen phthalate, observed a conversion of similar character. Indeed, the TG and the DTG curves on the derivatograms of the acid salts may be considered as the summation of the corresponding curves of the acids and the normal salts. DTA curves also reflect this compositeness, but in some cases processes accompanied by a change in enthalpy can be observed, which do not occur either with the acids or the dialkali salts.

These changes occurring on the DTA curve are summarized in Table 3.

Table 3

Monosodium salt of the acid	Temperature of the DTA peak, °C	Character
Oxalic, malonic	350	Endothermic
Succinic	390	
Glutaric	165*, 405	
Adipic	180*	
Pimelic	175*, 220*	
Suberic	190*, 220*	
Azelaic	165*, 225*	
Sebacic	115, 165*	

Phenomena marked by * are melting points observed with a hotstage microscope; the others, transformations of crystal modifications, verified by the recording of the cooling curves.

Thermal decomposition of the disodium and calcium salts of dicarboxylic acids

Characteristic decomposition temperatures of the salts investigated by us, and the values calculated and found for processes accompanied by a change in weight are summarized in Table 4. The derivatograms of disodium and calcium salts of pimelic acid are shown in Fig. 7.

Table 4

Disodium and calcium salts of the acids	Decomposition temperature (°C) of the salt		Loss in weight of the disodium salt, %		Loss in weight of the calcium salt, %	
	disodium	calcium	Calc.	Found	Calc.	Found
Oxalic	580	—	64.0	67.0	—	—
Malonic	360	375	42.1	42.0	56.2	58.0
Succinic	470	480	54.6	56.0	57.5	58.5
Glutaric	475	455	55.7	55.0	53.3	54.5
Adipic	475	595	52.0	51.0	49.6	50.0
Pimelic	510	450	48.6	47.0	46.4	48.0
Suberic	490	470	51.4	52.0	56.6	56.0
Azelaic	500	490	43.1	44.0	41.0	43.0
Sebacic	500	495	42.4	44.0	36.3	36.0

It can be seen from the figures and from data in the table that after the splitting off in stoichiometric amounts of the water of crystallization, the salts are stable up to a relatively high temperature, and begin to decompose at a temperature depending on the cation and the number of carbon atoms in the molecule. In most cases, the "organic" part of the molecule was liberated in a stoichiometric quantity, while the residue was alkali or alkali earth metal carbonate. However, in some cases the residue contained, besides the corresponding carbonate, carbon formed by cracking which was oxidized at higher temperatures in the experiments carried out in air. This process is clearly shown by the DTG curves and by the corresponding DTA peaks of exothermic character. The oxidation of the carbon formed was not always complete up to 600°, and this fact is responsible for the differences in values calculated and found. Compounds liberated during the decomposition of the salts were isolated and analysed by gas chromatography. Oxalates are decomposed in the known way to carbon monoxide and carbon dioxide; the nature of the product being dependent on the oxidative properties of the atmosphere. The decomposition products of the malonates could not be isolated, it was established, however, that neither ketene nor diketene were formed during the decomposition. The salts of succinic acid and glutaric acid yield decomposition products of a great variety. According to data in the literature, these may be different aliphatic and aromatic hydrocarbons and phenols. Adipates and pimelates resulted in the corresponding cyclanones, besides a small amount

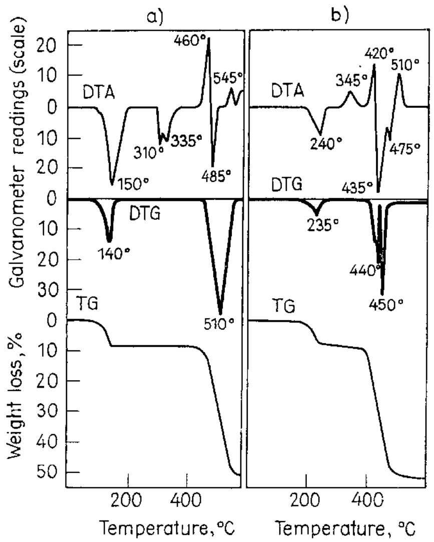


Fig. 7. Derivatograms of *a)* Disodium salt of pimelic acid; *b)* Calcium salt of pimelic acid

of other contaminants. According to our analysis the decomposition products of the salts of suberic acid, azelaic acid and sebacic acid contained only small amounts of oxy-compounds.

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RÉSUMÉ — On a étudié par dérivatographie le comportement thermique des acides oxalique, malonique, succinique, glutarique, adipique, pimélique, subérique, azélaique et sébacique, et de leurs sels mono et disodiques et de calcium. Certains de ces acides distillent sans décomposition, alors que d'autres se décomposent suivant la loi de Blanc.

La décomposition du sel monosodique se déroule en deux étapes jusqu'à 600°. Dans la première, l'acide formant le sel se dégage ou se désompose; dans la deuxième, le sel normal de sodium se décompose en donnant du carbonate de sodium et des molécules "organiques". Le mécanisme de la décomposition a été vérifié à l'aide de combinaisons marquées par le ^{14}C.

La décomposition des sels normaux et des combinaisons impropres à donner des cétones fournit une grand variété de composés organiques. Dans le cas des adipates et des pimélates, la formation de cyclanones prédomine.

ZUSAMMENFASSUNG — Es wurde das thermische Verhalten von Oxalsäure, Malonsäure, Bernsteinsäure, Glutarsäure, Adipinsäure, Suberinsäure, Azelainsäure und Sebacinsäure, sowie ihrer Mono- und Dinatrium- und Calciumsalze derivatographisch untersucht. Einige dieser Säuren destillierten ohne Zersetzung, die übrigen zerlegten sich entsprechend dem Blancs'schen Gesetz.

Die Zersetzung der Mononatriumsalze verlief bis 600° in zwei Stufen. In der ersten wurde die salzbildende Säure freigesetzt oder zersetzt, in der zweiten zersetzte sich das normale Salz in Natriumkarbonat und in "organische" Moleküle. Der Zersetzungsmechanismus wurde mit durch ^{14}C markierten Verbindungen kontrolliert. Bei der Zersetzung der normalen Salze und der Verbindungen, die unfähig sind Ketone zu bilden, entstehen mannigfaltige organische Verbindungen. Im Falle von Adipaten und Pimelinaten überwiegen Cyclanone.

Резюме — Методом дериватографии исследовано термическое поведение щавелевой, янтарной, глутаровой адипиновой, пимелиновой, азелаиновой, себациновой кислот и их одно- и двухзамещенных солей натрия и кальция.

Некоторые из кислот перегонялись без распада, а другие разлагались в соответствии с правилом Бланка. Разложение однозамещенной соли натрия до температуры 600° происходит через две главные ступени. Первым процессом является выделение или разложение кислоти, образованной из соли, а вторым — превращение нормальной соли в карбонат натрия и «органические» молекулы. Этот механизм распада доказан и результатами экспериментов, проведенных с меченными по C^{14} соединениями. При распаде нормальной соли образуется множество органических соединений. В случае адипатов и пимелатов преобладает образование цикланонов.