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THERMAL STUDY OF SOME SULPHOSUCCINATES

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The thermal properties of some sulphosuccinates and their intermediates were studied by using combined dynamic thermal analysis and mass spectrometry. The temperature ranges were similar in the two methods, and a scheme of thermal decomposition of the compounds investigated was suggested. In the first temperature range of thermal decomposition of the sulphosuccinate a β-rupture of the molecular ion occurs. In the second temperature range, the fragmentation proceeds in two directions: either α-rupture of the ethoxylated nonylphenol, or α-rupture of the acid residue of the sulphosuccinates.

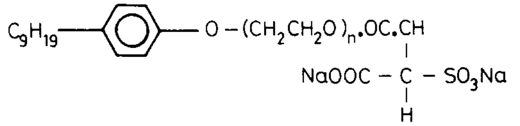
The thermal behaviour of sulphosuccinates is of great interest because of their increasing practical application. Weight losses, thermal effects (endothermic or exothermic), decomposition rates, and corresponding effective activation energies for the thermal decomposition can be obtained. These data are necessary for the sulphosuccinates which are subjected to thermal treatment during use [1–5].

A series of sulphosuccinates and the main intermediates of their production have been investigated, in order to obtain data about the mechanisms of their thermal conversions.

Experimental

Thermal investigations on the following compounds were carried out:

1. Sulphosuccinates from ethoxylated nonylphenol, containing 4 or 6 units of ethylene oxide:



$n = 4, 6$

Disodium nonylphenylethoxysulphosuccinates

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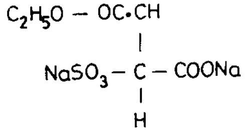
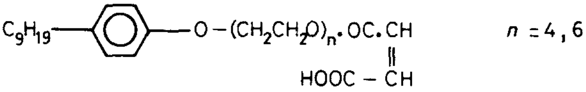
2. Sulphosuccinate of ethanol (standard sample):



$$\begin{array}{c} C_2H_5O - OC \cdot CH \\ | \\ NaSO_3 - C - COONa \\ | \\ H \end{array}$$

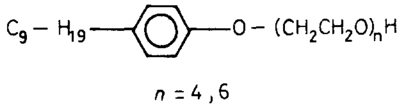
Ethoxysulphosuccinate

3. Monoesters of ethoxylated nonylphenol (Veranol H-4, -6), intermediates of the production of the production of sulphosuccinates (ester H):



Maleic nonylphenylethoxy esters

4. Ethoxylated nonylphenol with 6 units of ethylene oxide (Veranol H-6):



The thermal investigations were carried out with an OD–102 derivatograph under the following conditions: heating rate: 6 deg/min; atmosphere: air (static); ceramic crucible; the sample mass was measured with an accuracy of ±2.5 mg.

The results of the thermal investigations on the sulphosuccinates were supplemented with data from mass spectrometric studies on the same compounds. A KB 2091 mass spectrometer with direct insertion of the sample into the ionization chamber was used, under the following conditions: bombarding electron energy: 70 eV; temperature of ionic source: 270°; temperature of direct heating: from 80 up to 300°.

Results and discussion

The thermal analysis data are presented in Figs 1–5 and Table 1. The activation energy was determined according to the method of Reich [6] from the TG and DTG curves. The curves show some dependences. First of all, Veranol H–6 and the corresponding ester have neighbouring temperature ranges of initial thermal decomposition of 230–320°, with peak at about 255° (Figs 1, 2). The secondary

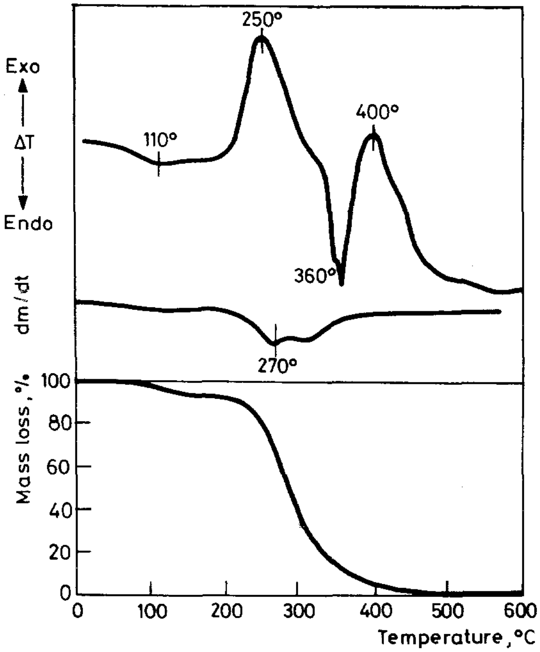


Fig. 1 DTA, TG and DTG curves for Veranol H-6

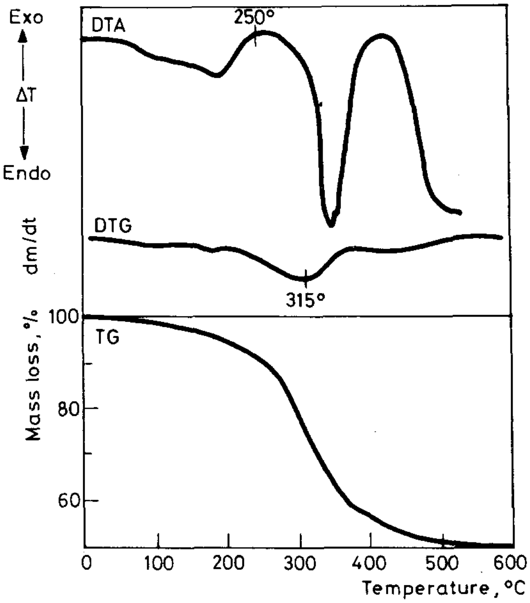


Fig. 2 DTA, TG and DTG curves for the ester of Veranol H-6 (ester H)

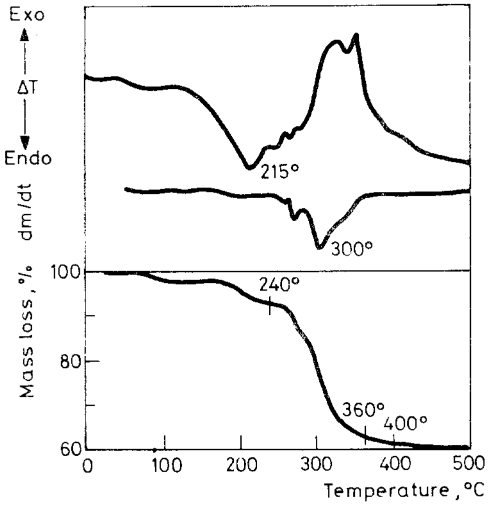


Fig. 3 DTA, TG and DTG curves for the sulphosuccinate from Veranol H–6

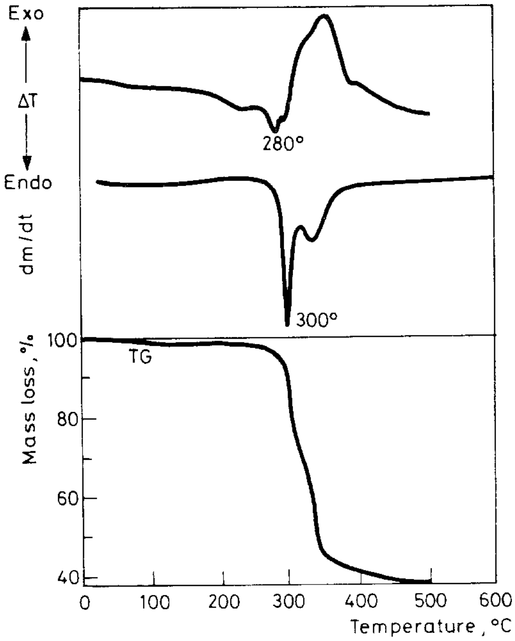


Fig. 4 DTA, TG and DTG curves for sulphosuccinate from Veranol H–4

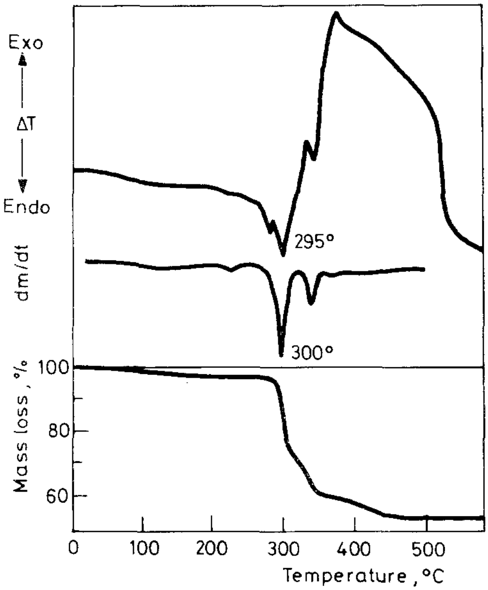


Fig. 5 DTA, TG and DTG curves for the sulphosuccinate from ethanol

Table 1 Effective activation energy values over decomposition temperature ranges

Sample	Temp. range I, °C	Activation energy, kcal/mole	Correlation coefficient	Temp. range II, °C	Activation energy, kcal/mole	Correlation coefficient
Sulpho-succinate H-4	275–320	100	0.99	320–370	24.0	0.99
Sulpho-succinate H-6	160–230	16	0.99	280–320	69.0	0.99
Sulpho-succinate of ethanol	290–330	105.5	0.99	330–370	182.0	0.99
Ester H-6	240–320	21.0	0.99	—	—	—
Veranol H-6	230–275	25.0	0.99	—	—	—

decomposition of both products proceeds with an endothermic effect in the temperature range 300–400°. The sulphosuccinates obtained from them (Figs 3, 4) also have two transition temperature ranges (I and II): the first is endothermic and the second is exothermic. From the curve for the standard sample (Fig. 5), it can be seen that its thermal decomposition also proceeds in two stages in similar temperature ranges and at similar maximum decomposition rate temperatures.

A comparison of the values obtained for the maximum decomposition rate temperatures (from DTG curves) reveals that they are lower for the initial product Veranol H–6 (270°) than for the remaining compounds (300–315°).

The observed differences in the thermal characteristics of sulphosuccinates H–6 and H–4 as regards the TG curve (preliminary stage of slow decomposition in the range 160–230° and the obtained values for the effective activation energy, respectively (Table 1)) are clearly due to the difference in the ethoxyl chain length.

A comparison of the results from the thermal decompositions of sulphosuccinates with different degrees of ethoxylation in the second temperature range (sulphosuccinate H–6 and sulphosuccinate H–4) demonstrates that the activation energy increases with increasing degree of ethoxylation. The standard sample (Fig. 5) decomposes by another mechanism, activation energy obtained (Table 1) is higher. The interpretation of the dependences is based on the mass spectral results.

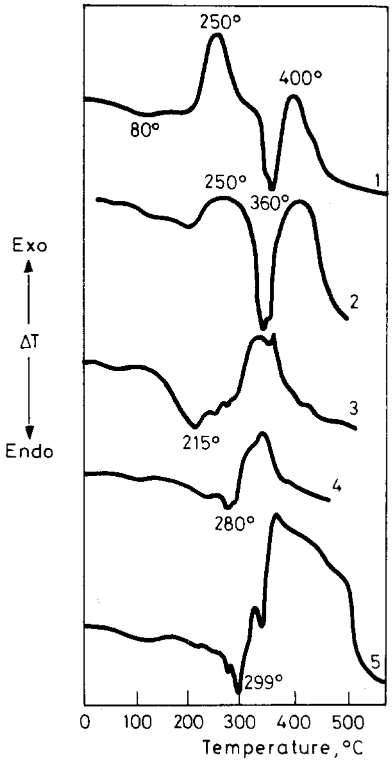
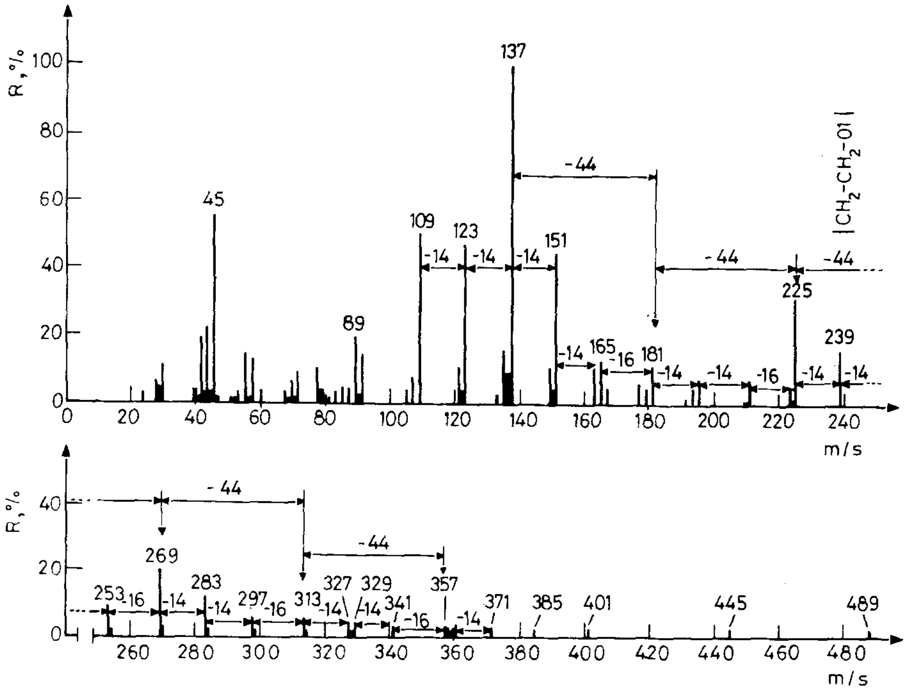
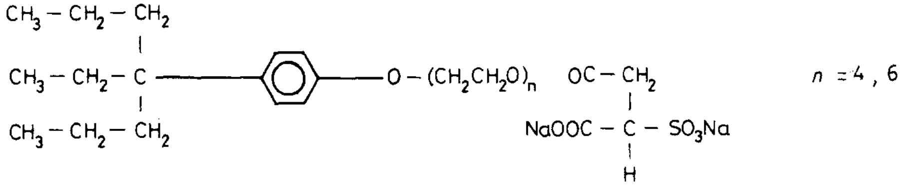


Fig. 6 DTA curves of the investigated compounds: 1. Veranol H–6, 2. Ester from Veranol H–6, 3. Sulphosuccinate from Veranol H–6, 4. Sulphosuccinate from Veranol H–4, 5. Sulphosuccinate from ethanol



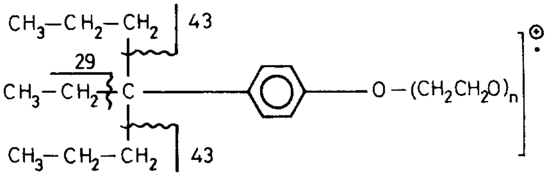
From the mass spectroscopic thermal data and presented in Tables 1 and Fig. 7, the following scheme of thermal decomposition is assumed: in the first temperature range, β-rupture of the molecular ion probably proceeds, with separation of an acid residue from the ethoxylated nonylphenol (Veranol H–6), with an endothermic effect:



Disodium nonylphenylethoxysulphosuccinate

Further, the fragmentation probably proceeds in two directions:

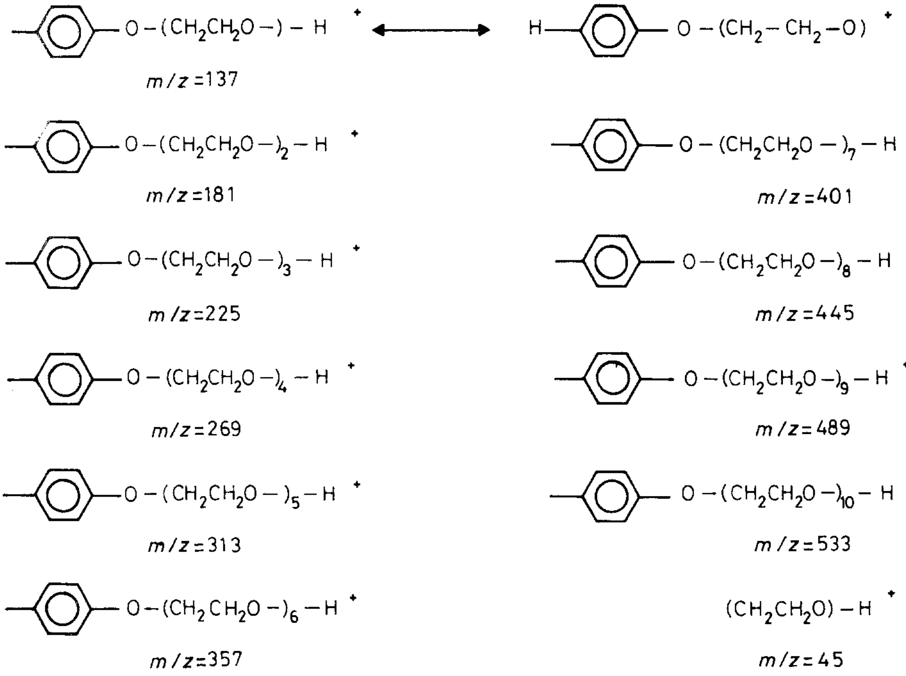
1. α-rupture of the ethoxylated nonylphenol



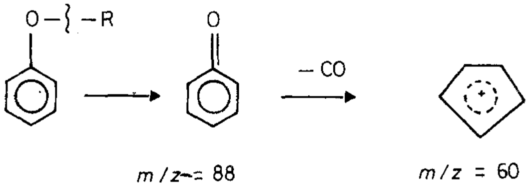
The thermal decomposition of the ethoxylated nonylphenol from the sulphosuccinate in the second temperature range proceeds similarly to the thermal decompositions of Veranol H–6 and H–6, with at exothermic effect.

Since the molecular ion of the branched alkane is weak, the fragmentation probably proceeds at the position of the branching of the fort' quaternary carbon ion. The two radical ions with *m/z* 43 are separated most easily, followed by that with *m/z* 29, free hydrogen ion and free alkyl radicals (Fig. 7).

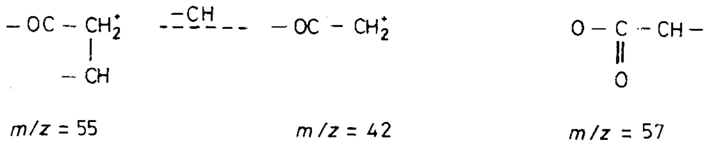
The ethoxyl chains on the phenolic ring are probably separated at the β-bond with respect to the phenolic ring, and decompose to give monomers, dimers and tetramers. Only the molecular ion of the phenyl ether remains with an intense peak:



The alkyl residue (as a free radical) is separated from the phenyl ethers; CO is then separated and the cyclopentadiene ion stabilized by conjugation is formed:



2. α-rupture of the acid residue of the sulphosucinates:



In the mass spectrum the molecular ion of the investigated compound is absent. The $^{-}SO_3Na$ and $^{-}COONa$ groups are not registered in the mass spectra. The same findings result from ^1H NMR spectroscopy [7].

In the mass spectrometric analysis of the compounds studied, the fragmentation proceeds in a temperature range near that of thermal analysis, allowing a certain comparison.

Conclusions

The results of shermal analysis and mass spectrometric analysis yield the temperature limits for the commercial application of the investigated products.

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Zusammenfassung — Mittels einer Kombination von dynamischer Thermoanalyse und Massenspektroskopie wurden die thermischen Eigenschaften einiger Sulfosukzinate und deren Zwischenprodukte untersucht. Im ersten Temperaturbereich der thermischen Zersetzung des Sulfosukzinates findet eine β-Spaltung des Molekülions statt. Im zweiten Temperaturbereich tritt auch ein alternativer Fragmentierungsweg auf: eine α-Spaltung des Säurerestes des Sulfosukzinates.

Резюме — Методом совмещенного динамического термического анализа и масс-спектрометри изучены термические свойства некоторых сульфосукцинатов и их промежуточных продуктов разложения. Предложена схема термического разложения исследованных соединений. В первом температурном интервале термического разложения сульфосукцинатов происходит β-разрыв молекулы-иона. Во втором температурном интервале фрагментация протекает по двум направлениям: наряду с β-разрывом происходит α-разрыв кислотного остатка сульфосукцинатов.