

INVESTIGATION OF COMPLETE OXIDATION OF ORGANIC MATERIALS BY MEANS OF A DERIVATOGRAPH

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(Received April 21, 1978)

Oxidation of three selected organic model materials, saccharose, gelatine and styrene-divinylbenzene with and without combustion catalysts, was studied with a derivatograph.

The catalysts significantly lowered the combustion temperature of the model materials.

The amount of carbon dioxide formed during the oxidation process was simultaneously determined gas-titrimetrically. The catalysts used ensured complete carbon to carbon dioxide conversion in the cases of saccharose and gelatine.

Complete oxidation of organic material, i.e. total conversion of the organic carbon content to carbon dioxide, is a frequent requirement not only in organic elemental analysis but also in the determination of the carbon contents of many materials of natural origin, e.g. bauxite, soil, ceramic raw materials, etc.

The empty tube method is frequently used to carry out complete oxidation: organic material is combusted in an excess oxygen atmosphere at 900–1000° [1–3]. Another method calls for combustion catalysts which, apart from significantly lowering the oxidation temperature, ensure that all organic carbon is converted to carbon dioxide [4–6].

Modern CHN analyzers utilize both methods in due sequence [7].

In this paper the effect of combustion catalysts on the oxidation temperature and organic carbon conversion were followed by complex thermoanalytical methods, with a derivatograph equipped with a gas-titrimetric unit.

This analytical system can be used advantageously, for the thermoanalytical curves provide information on the number and types of the oxidation stages, the existence of other auxiliary thermal processes (e.g. thermal decomposition), and the corresponding weight changes and temperatures.

Organic model compounds of different structures and carbon contents were selected to represent materials both easy and difficult to oxidize.

Commercial and laboratory-prepared catalysts and pure chemicals with known combustion rate-increasing properties were studied as oxidation-enhancing catalysts.

Experimental

Organic model materials:

Saccharose, C content 42.1%.

Styrene-divinylbenzene copolymer, C content 83.6%.

Gelatine, C content 48.0%.

(Actual carbon content data indicated were obtained with a CHN analyzer, Type 1102 Carlo Erba, Italy.)

Catalysts studied

Silver permanganate was prepared according to Körbl [8]. Silver permanganate precipitated from a solution containing equivalent amounts of silver nitrate and potassium permanganate was filtered off, washed, air-dried, heated at 150° in air for half an hour, and at 480° in flowing oxygen atmosphere for ten hours. Copper oxide reagent grade (Merck, GFR).

Copper oxide (silver) catalyst containing some silver was precipitated from a copper salt solution containing silver nitrate, filtered off, washed, air-dried and heated at 500° in flowing oxygen atmosphere.

Catalyst M_4 [11] contained manganese and iron oxide as well as alkali metal and alkaline earth metal promoters.

Combustion catalysts: vanadium(V) oxide, tungstene(VI) oxide, lead(II) chromate, chromium(III) oxide, cobalt (II, III) oxide [1] were obtained from Carlo Erba.

Molybdenum(VI) oxide: analytical-grade chemical (Hungary).

Cobalt(II, III) oxide [2] reagent-grade chemical (Merck, GFR).

Coboxide catalyst: combustion catalyst of Perkin Elmer (Maywood, Ill., USA) containing, according to our experiments, mostly cobalt(II, III) oxide.

γ -Aluminium oxide: aluminium oxide calcined at 1200°.

Apparatus

A derivatograph (MOM, Hungary) was used for the thermoanalytical studies in flowing oxygen atmosphere. The gas-collecting adapter developed by Paulik and Paulik [9], installed in the oven of the derivatograph, allowed continuous introduction of oxygen and collection of the gaseous products. Input oxygen flow rate and suction rate were adjusted to exclude air from the surroundings of the crucible. 25–30 l/hr oxygen input flow rate and 6–10 l/hr suction flow rate were maintained throughout all experiments.

In order to ensure efficient contacting of oxygen and organic material, the crucible was perforated at the bottom and the side (Fig. 1).

Quartz wool was placed at the bottom of the crucible to prevent the loss of material.

The organic material + catalysts mixture was covered with a platinum grid.

Carbon dioxide formed during the oxidation was sucked through the gas-collecting adapter and two absorbers, connected in series, equipped with gas distributor plates. Barium hydroxide solution corresponding to twice the amount of carbon dioxide expected from the reaction was measured into the absorbers. Excess barium hydroxide was determined according to Maros et al. [12] using hydrochloric acid titrant.

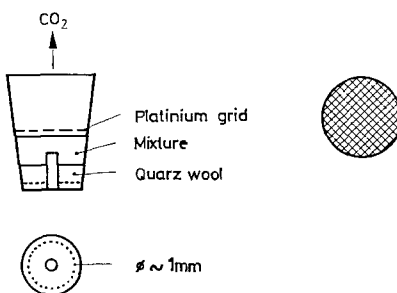


Fig. 1.

The amounts of carbon dioxide liberated in flowing oxygen atmosphere from known amounts of potassium hydrogen carbonate and calcium carbonate were used to calibrate the gas-collecting system and the measurement method.

Thermoanalytical methods

Organic model compounds and all combustion catalysts were separately ground in a ball-mill and passed through a 0.125 mm sieve.

Catalysts and organic model materials in a 5 : 1 ratio were weighed and homogenized in a two-ball vibrating homogenizer for one hour.

20.0 mg and 120.0 mg quantities of the organic material and organic material + catalyst mixture, respectively, were weighed into the crucible of the derivatograph. Oxygen flow and heating were resumed. A heating rate of $6^\circ/\text{min}$ was applied up to 600° .

Occasionally, e.g. in the case of saccharose and copper oxide or copper oxide (silver) catalyst mixtures, violent reactions took place, blowing out the reaction mixtures. To prevent such problems, the 5 : 1 catalyst + organic material mixture was diluted with an equivalent weight of aluminium oxide.

100.0 mg catalysts were weighed into the crucible for study of their thermal behaviours. Identical conditions were used.

Determination of carbon dioxide

A. Method and calibration

20–50 mg CaCO_3 or 50–100 mg KHCO_3 was weighed into the crucible. 10.00–30.00 ml 0.05 M Ba(OH)_2 and 10 ml ethanol were added to the first absorber and brought to 200 ml with freshly-boiled, cooled distilled water. 5.00 or 10.00 ml 0.05 M Ba(OH)_2 and 5 ml ethanol were added to the second absorber and brought to 100 ml with freshly-boiled and cooled distilled water. Some *n*-pentane was carefully layered on top of the solution. Oxygen flow and heating were started. BaCO_3 was formed from carbon dioxide evolved during the thermal decomposition. After the run, the contents of the absorbers were carefully washed into a 500 ml conical flask and excess Ba(OH)_2 was titrated with standardized 0.1 M HCl (indicator: thymol blue). The error of the CO_2 determination was ± 0.05 mg.

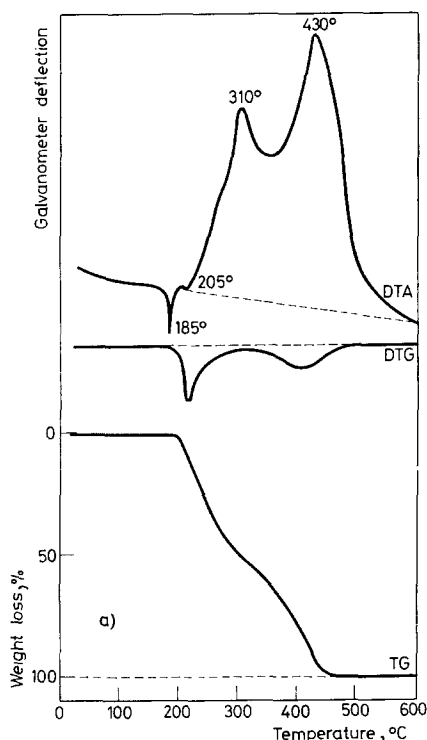


Fig. 2a. Thermal curves of saccharose

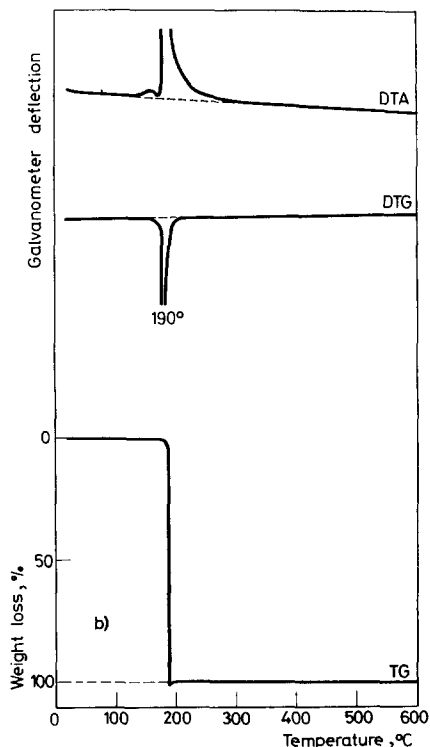


Fig. 2b. Thermal curves of saccharose and copper(II)oxide (silver) mixture

B. Determination of CO_2 formed during oxidation

The amounts of CO_2 released during the thermoanalytical experiments with the organic model materials and their mixtures were determined simultaneously. 20.00 or 30.00 ml and 5.00 or 10.00 ml 0.05 M $\text{Ba}(\text{OH})_2$ solutions were placed into the first and second absorber, respectively. Ethanol and water were added as described above in section A. After the heating program, excess $\text{Ba}(\text{OH})_2$ was determined with 0.1 M HCl titrant.

Results

1. Thermoanalytical curves of the organic model materials without catalysts, recorded in flowing oxygen atmosphere, are presented in Figs 2a, 3a and 4a.

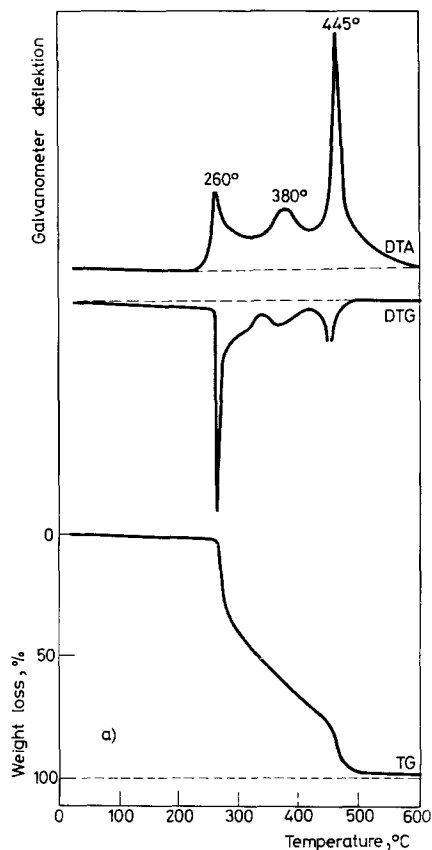


Fig. 3a. Thermal curves of styrene-divinylbenzene copolymer

The first, sharp endotherm at 185° on the DTA curve of saccharose indicates its melting, while the second, less sharp peak probably corresponds to some loss of water. Oxidation occurs at 310° and 400° , as substantiated by the presence of exotherms. Oxidation is over at 440° and it is apparent from the TG curve that saccharose burned without leaving any solid residue (cf. Table 1).

The DTA curve of the styrene-divinylbenzene copolymer reveals three separate exotherms, at 250° , 380° and 450° , reflecting the oxidation process. The TG curve indicates that oxidation leaves practically no solid residue when the run is determined at $490-500^{\circ}$ (cf. Table 2).

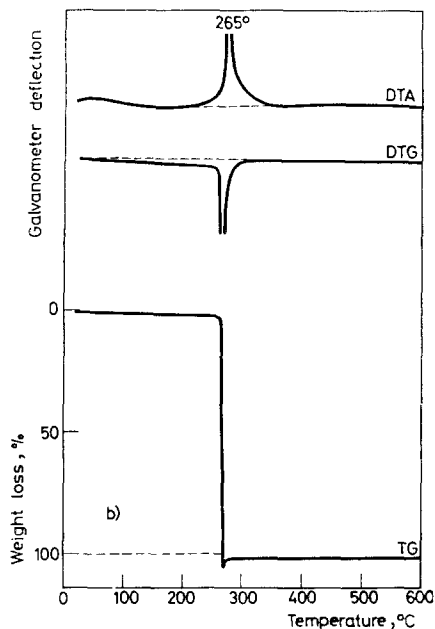


Fig. 3b. Thermal curves of styrene-divinylbenzene copolymer and copper(II)oxide mixture

The thermoanalytical curves of gelatine show that water is released in an endothermic process up to 120° (7% water); oxidation then takes place, as indicated by the three exotherms at $270-300^{\circ}$, 470° and 550° . The oxidation of gelatine ends at 560° .

2. According to the TG and DTA curves, weight losses amounting to 0.5–1.5%, without peaks in the DTA curves, are found when the catalysts or combustion-promoting materials are heated (between 20 and 600°) in flowing oxygen atmosphere.

3. A few characteristic thermal curves of the organic material + catalyst mixture are presented in Figs 2b, 3b and 4b. Results of the other experiments are summarized in Tables 1–3.

The curves of a saccharose + copper oxide (silver) mixture are shown in Fig. 2b. In the presence of this catalyst oxidation takes place in a single "step", immediately after saccharose melts at 185–190°. (Oxidation ends at 440° in the absence of catalyst.) The height of the step in the TG curve corresponds to the total quantity of saccharose added. Once oxidation is finished, the TG curve is practically horizontal up to 600°.

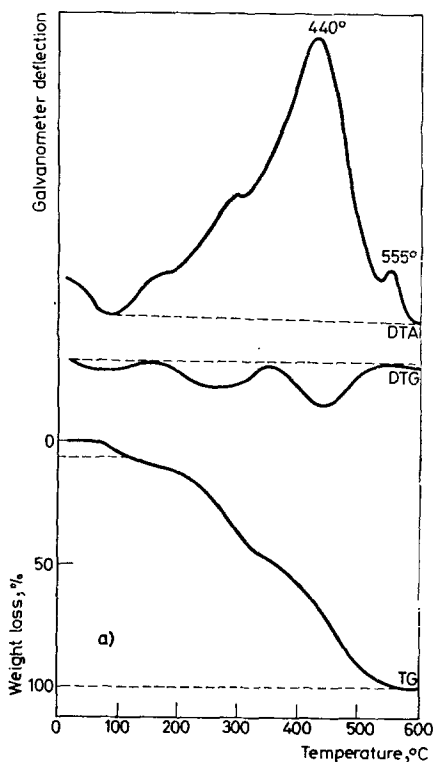


Fig. 4a. Thermal curves of gelatine

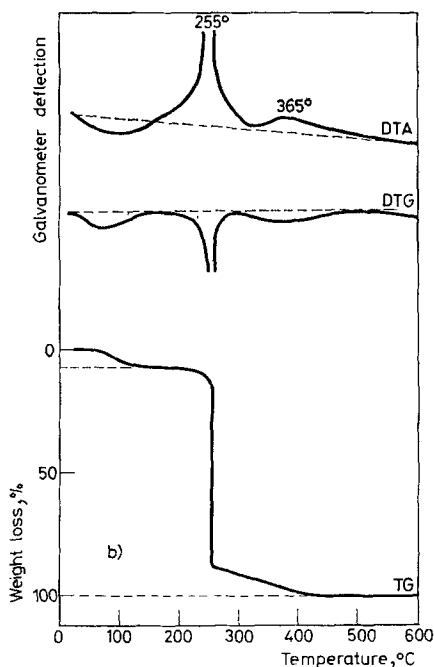


Fig. 4b. Thermal curves of gelatine and Coboxide catalyst mixture

The thermal curves of a styrene-divinylbenzene copolymer + copper(II) oxide catalyst mixture are shown in Fig. 3b. Oxidation again occurs in a single step at a temperature 200° lower than in the absence of catalyst. The amount of copolymer in the mixture can be directly read off the TG curve.

The thermal curves of a gelatine + Coboxide catalyst mixture are shown in Fig. 4b. The bulk of gelatine is oxidized in one step at 255° in the presence of the catalyst. However, at 365° there is yet another, rather flat oxidation peak in the DTA curve. The total weight loss determined from the TG curve corresponds to

Table 1
Oxidation of saccharose in flowing oxygen atmosphere
Temperature limits: 20–600°C

	TG total weight loss, mg	DTA peak temperatures, °C				Oxidation ends at, °C
		endothermic		exothermic		
Saccharose Sample: 20.0 mg	20.5	178	205	305	430	450
	21.0	180	210	310	445	450
	20.0	180	205	310	415	440
5 : 1 Catalyst: saccharose mixtures Sample: 120.0 mg						
Silver permanganate	(24.5) 21.5		180		200	200
Copper(II)oxide	21.0		175		185	200
Copper(II)oxide (silver)	20.5		170		190	190
Catalyst M ₄	20.0 (29.0)		170		195	205
Vanadium(V)oxide	25.0		135		215	220
Tungstene(VI)oxide	22.5		110		225 350	380
Lead(II)chromate	31.0		175		190 255	260
Molybdenum(VI)oxide	23.5		165		205 250	250
Chromium(III)oxide	20.5		160		205 280	280
Cobalt(II, III)oxide (1)	21.0		175		195 275	280
Cobalt(II, III)oxide (2)	25.5		170		205 320	325
Coboxide	20.5 (21.0)		170 (195)		190 (230)	190 (230)
γ -Alumina	23.0		175 205		265 360	390

the overall amount of gelatine in the mixture. The TG curve is horizontal from 400° on.

4. Along with the thermal curves, the amounts of carbon dioxide formed during the oxidation of organic materials with and without catalysts were also determined. Conversions were calculated from carbon dioxide and carbon content figures.

Results obtained under the present experimental conditions are listed in Table 4.

Table 2

Oxidation of the styrene-divinylbenzene copolymer in flowing oxygen atmosphere
Temperature limits: 20–600 °C

	TG total weight loss, mg	DTA peak temperatures, °C exothermic			Oxidation ends at, °C
Styrene-divinylbenzene copolymer	19.0	260	380	455	490
	19.5	255	385	465	500
Sample: 20.0 mg	19.5	260	400	465	510
5 : 1 Catalyst: copolymer mixtures					
Sample: 120.0 mg					
	(23.0)				
Silver permanganate	21.0	255			255
Copper(II)oxide	21.0	265			265
Copper(II)oxide (silver)	19.0	265	325		420
Catalyst M ₄	21.5	235	355		370
	(24.0)				
Vanadium(V)oxide	29.5	245			250
Tungstene(VI)oxide	20.0	275	385		435
Lead(II)chromate	(22.5)				
	20.0	270			270
Molybdenum(VI)oxide	20.5	265			270
Chromium(III)oxide	20.0	250	320		330
Cobalt(II, III)oxide (1)	20.0	270	325		330
Cobalt(II, III)oxide (2)	24.5	270	395		455
Coboxide	(20.0)				
	20.5	250	(260)		250
γ-Alumina	21.0	270	435		450

Discussion

Complete oxidation of saccharose (cf. Table 4) was feasible with copper(II) oxide (silver), Coboxide and silver permanganate catalysts. These combustion catalysts, along with catalyst M₄, decreased the final oxidation temperature of saccharose from 450° to 185–200° (cf. Table 1). In their presence saccharose oxidation took place in a single step and the saccharose content could be obtained

Table 3
Oxidation of gelatine in flowing oxygen atmosphere
Temperature limits: 20–600 °C

	TG total weight loss, mg	DTA peak temperatures, °C			Oxidation ends at, °C
		endothermic		exothermic	
Gelatine, air dry	20.0	70	190	295 440 555	560
Sample: 20.0 mg	20.0	80	190	270 440 550	560
Gelatine, dried at 130 °C					
Sample: 20.0 mg	20.5	190		305 470 550	560
5 : 1 Catalyst: gelatine mixtures					
Sample: 120.0 mg					
Silver permanganate	20.0	70	205	265 475	495
Copper(II)oxide	20.5	70	205	265 455	490
Copper(II)oxide (silver)	21.5	120		275 440	450
Catalyst M ₄	26.5	200		320 485	500
Vanadium(V)oxide	24.5	105		270 440	505
Tungstene(VI)oxide	27.0	125		290	550
Lead(II)chromate	21.0	90		330 460	480
Molybdenum(VI)oxide	23.0	155		325 485	515
Chromium(III)oxide	18.5	150		285 435	440
Cobalt(II, III)oxide (1)	22.5	130		255 325 470	480
Cobalt(II, III)oxide (2)	21.5	130		280 335 460	520
Coboxide	20.5	120		255 365 (400)	400
γ-Alumina	23.0	130		275 470 550	580

directly from the step in the TG curve. An anomalous result was obtained with silver permanganate catalyst, for the amount of saccharose read off the TG curve exceed the amount taken.

It was noted that Coboxide stored in an ambient atmosphere for two years was less effective in decreasing the combustion temperature (cf. DTA figures in parentheses in the Tables).

Copper(II) oxide and Coboxide catalysts brought about a decrease of some 200° in the oxidation temperature of styrene-divinylbenzene (cf. Table 2). These catalysts lead to a single-step oxidation and the step height in the TG curve corresponds

Table 4
Conversion of organic carbon to carbon dioxide, %

Without catalyst	Saccharose	Styrene-divi- nylbenzene	Gelatine
	68-72	35-38	75-78
5 : 1 catalyst: organic material mixtures			
Copper(II) oxide	85	71	86
Copper(II) oxide (silver)	99	85	98
Coboxide	100	76	99
Silver permanganate	99	90	98

to the amount of the copolymer. The combustion temperature is even lower with silver permanganate or vanadium(V) oxide catalysts. However, the steps in the TG curves correspond to excessive amounts of the copolymer (cf. TG figures in parenthesis in Table 2).

However, it can be seen from Table 4 that the carbon to carbon dioxide conversion in the case of styrene divinyl benzene copolymer is less than 100% even when combustion catalysts are used.

By means of the final three catalysts listed in Table 4 the carbon content of gelatine can be converted virtually completely to carbon dioxide. At the same time the combustion temperature reduction achieved with these catalysts amounted only to some 150° (cf. Table 3).

The total weight loss determined from the TG curves, however, corresponded to the total amount of gelatine added.

Thus, it can be concluded that none of the above catalysts simultaneously satisfy all the three requirements for all three materials tested: (1) a significant decrease in combustion temperature; (2) complete carbon to carbon dioxide conversion; and (3) the height of the single oxidation step in the TG curve is directly related to the amount of organic material in the mixture.

However, if the problem at hand does not call for all three requirements simultaneously, then there are appropriate catalysts which ensure either lower combustion temperature, complete carbon to carbon dioxide conversion or a TG curve-step height directly related to the amount of organic material.

It has to be noted that the experimental conditions used may be inadequate to ensure complete carbon to carbon dioxide conversion in the case of the styrene-divinylbenzene copolymer. Quantitative conversion can probably be ensured by post-catalytic oxidation of the exhaust gases.

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The authors are indebted to L. Vajda of the Hungarian Heavy Chemical Research Institute (NEVIKI, Veszprém) for the carbon content analyses and donation of catalysts obtained from Carlo Erba.

Thanks are also due to A. Balogh of the Hungarian Gas and Oil Research Institute (MÁFKI, Veszprém) for the catalyst M_4 .

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RÉSUMÉ — On a étudié à l'aide d'un Derivatograph l'oxydation, avec et sans catalyseurs de combustion, de trois substances types organiques sélectionnées: le saccharose, la gélatine et le styrène-divinylbenzène.

Les catalyseurs abaissent les températures de combustion de ces substances types d'une manière appréciable.

Le taux d'anhydride carbonique formé lors du processus d'oxydation a été déterminé simultanément par dosage de la phase gazeuse. Dans le cas du saccharose et de la gélatine les catalyseurs utilisés ont assuré une conversion complète du carbone en anhydride carbonique.

ZUSAMMENFASSUNG — Die Oxidation dreier ausgewählter organischer Modellsubstanzen, sowie Saccharose, Gelatine und Styrol-Divinylbenzol, mit und ohne Verbrennungskatalysatoren wurde in einem Derivatographen untersucht.

Die Katalysatoren setzten die Verbrennungstemperaturen der Modellsubstanzen bedeutend herab.

Die Menge des im Laufe des Oxidationsprozesses gebildeten Kohlendioxids wurde gleichzeitig gasitrimetrisch bestimmt. Die eingesetzten Katalysatoren bewirkten im Falle der Saccharose und der Gelatine eine vollständige Umwandlung von Kohlenstoff zu Kohlendioxid.

Резюме — С помощью дериватографа было изучено окисление трех модельных органических соединений: сахарозы, желатины и стирол-дивинилбензола в присутствии катализаторов горения и без них. Установлено, что катализаторы значительно понижали температуру горения исследованных модельных соединений. Количество двуокси углерода, образующегося в процессе окисления, одновременно определяли газ-титриметрическим методом. В случае сахарозы и желатины использованные катализаторы способствовали полному превращению углерода до двуокси углерода.