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STEPWISE SUBSTRACTION OF OXYGEN-CONTAINING COMPOUNDS BY BORIC ACID AND LITHIUM ALUMINIUM HYDRIDE

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SUMMARY

The amounts of reagents necessary to carry out the group identification of oxygen-containing compounds and the identification of compounds having iso and normal structures have been examined.

INTRODUCTION

Boric acid, hydroxylamine, zinc oxide, sodium and lithium boron hydrides, lithium aluminium hydride, sodium trimethoxyboron hydride, *o*-dianisidine and benzidine[1–4] have been used as specific reagents for the substraction of oxygen-containing compounds in reaction gas chromatography (GC).

The aim of the present work was to investigate the effect of the amount of the reagent used in the reactor on the selectivity of the extraction of the functional group and to use reaction GC for establishing the compositions of the by-products obtained in the synthesis of butyl alcohols.

EXPERIMENTAL

An LHM-7A gas chromatograph from Mosneftekip with temperature programming was used. The reactor, in the form of a small pre-column, was placed in the thermostat in front of the separation column, which was packed with 25 % of Apiezon L on 60–80-mesh Chromosorb W.

Mixtures of primary, secondary, tertiary and unsaturated alcohols; aldehydes and ketones; esters, alcohols and acetals; and hydrocarbons were used as model substances.

The reagents used were boric acid in amounts of 0.5 and 5 % on Chromosorb W and lithium aluminium hydride powder in amounts of 0.05–0.5 g.

RESULTS AND DISCUSSION

We have found that primary, secondary, isomeric and unsaturated alcohols are substracted by the reactor containing 0.5–5 % of boric acid with the same selectivities. Tertiary alcohols, however, are almost not substracted on to the packing containing a small amount of boric acid (0.5 %). Results for the substraction of alcohols in reactors

containing different amounts of boric acid are given in Table I. The use of a combination of two reactors containing 0.5 and 5 % of boric acid makes it possible to identify tertiary alcohols in a mixture of alcohols of different structures.

Oxygen-containing compounds are completely substracted by a reactor containing lithium aluminium hydride, irrespective of the functional groups present. How-.

TABLE I

SUBSTRACTION OF ALCOHOLS (%) BY REACTORS CONTAINING DIFFERENT AMOUNTS OF BORIC ACID

No.	*Alcohol*	*Amount of boric acid in the reactor (%)*		
		0.5	*5*	*20*
1	*n*-Butanol	100	100	100
2	*n*-Octanol	100	100	100
3	*n*-Decanol	100	100	100
4	*n*-Undecanol	100	100	100
5	*sec.*-Butanol	100	100	100
6	*sec.*-Octanol	100	100	100
7	Trimethylcarbinol	up to 5	95	98
8	*tert.*-Pentanol	up to 3	88	90
9	*tert.*-Octanol	0	*ca.* 60	—
10	2-Ethylhexen-2-ol	100	100	100
11	Isobutanol	100	100	100

TABLE II

SUBSTRACTION OF OXYGEN-CONTAINING COMPOUNDS (%) BY REACTORS CONTAINING DIFFERENT AMOUNTS OF LITHIUM ALUMINIUM HYDRIDE

No.	*Compound*	*Amount of lithium aluminium hydride in the reactor (g)*			
		0.0583	*0.1700*	*0.2127*	*0.5119*
	I. Alcohols				
1	Trimethylcarbinol	54	50	93	100
2	*n*-Butanol	80	100	100	100
3	*n*-Octanol	96	100	100	100
4	2-Ethylhexanol	97	100	100	100
	II. Esters				
1	Isobutyl isobutyrate	17	74	100	100
2	Isobutyl butyrate	41	88	100	100
3	*n*-Butyl *n*-butyrate	50	93	100	100
4	Ester of isobutyric acid with 2-ethylhexanol	60	82	100	100
5	Ester of *n*-butyric acid with 2-ethylhexanol	80	95	100	100
	III. Acetals				
1	Acetal of isobutyric aldehyde and isobutanol	0	13	35	100
2	Acetal of isobutyric aldehyde and *n*-butanol	0	48	65	100
3	Acetal of *n*-butyric aldehyde and *n*-butanol	0	68	100	100
	IV. Aldehydes and ketones				
1	Caprylic aldehyde	94	100	100	100
2	Pelargonic aldehyde	97	100	100	100
3	Heptyl methyl ketone	98	100	100	100

ever, it is possible to distinguish between the selectivities for different oxygen-containing compounds when using lithium aluminium hydride by changing the amount of the reagent present in the reactor. Results for the extraction of alcohols, esters and acetals in reactors containing different amounts of lithium aluminium hydride are given in Table II.

The substraction of the model alcohol mixture is shown in Fig. 1 and the substraction of the model mixture of esters and acetals is shown in Fig. 2.

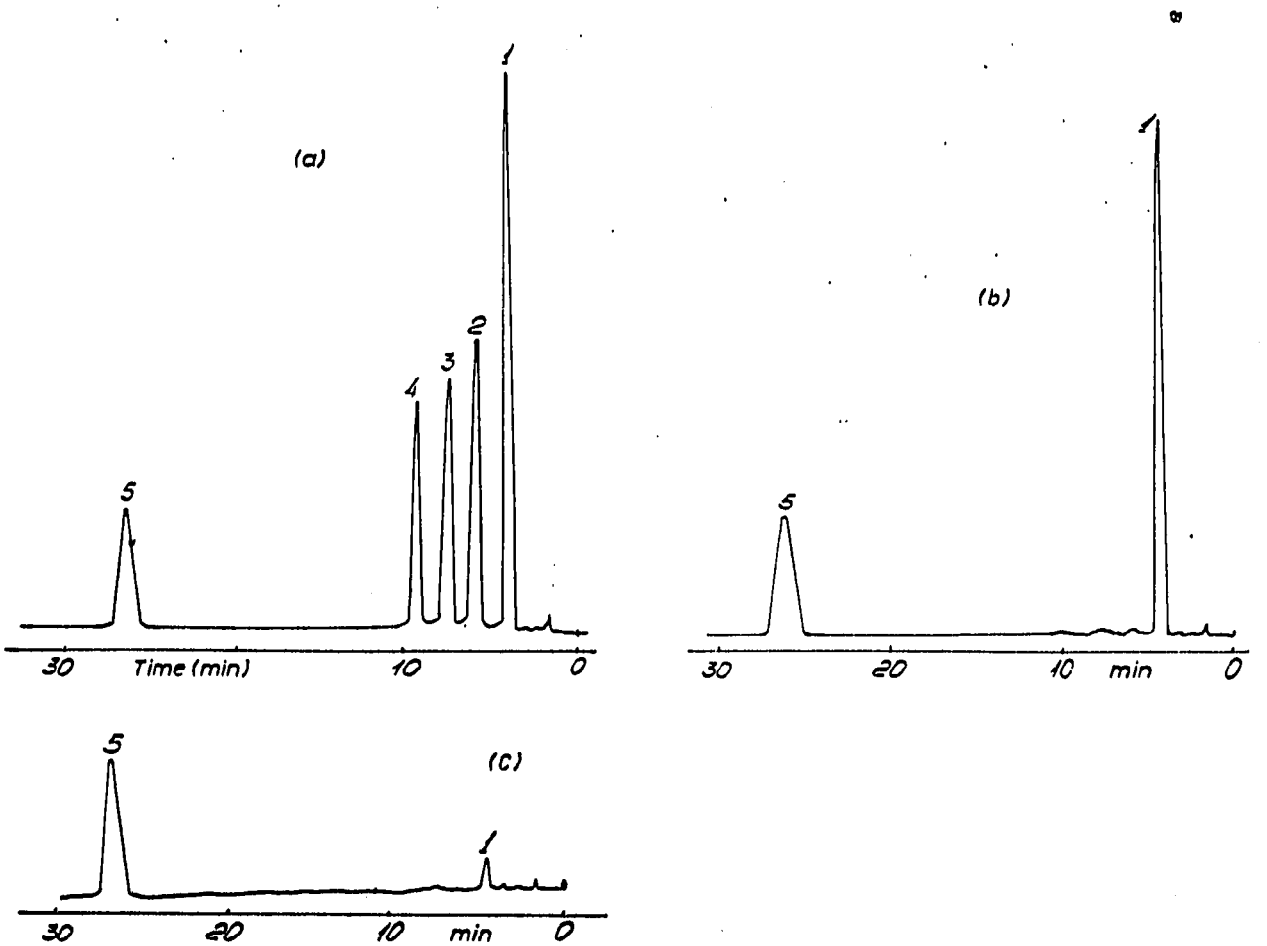

Fig. 1. Substraction of alcohols in reactors containing 0.5 and 5% of boric acid. (a) Without the reactor; (b) with the reactor packed with 0.5% of boric acid; (c) with the reactor packed with 5% of boric acid. 1 = Trimethylcarbinol; 2 = *sec.*-butanol, 3 = isobutanol: 4 = *n*-butanol; 5 = *n*-octane (internal standard).

The results obtained in the reaction chromatography of oxygen-containing compounds were used to solve a particular problem — the identification of the by-products obtained in the synthesis of butyl alcohols and which represent a complex multicomponent system.

Fig. 3 represents chromatograms of the technical-grade product taken from the column without the reactor (a), with reactors packed with 0.5 or 5% of boric acid (b and c, which are identical) and with reactors packed with 0.05 or 0.15 g of lithium aluminium hydride (d and e, respectively).

The use of reactors containing different amounts of boric acid and lithium aluminium hydride enabled it to be seen that the components of the investigated product belonged to a certain class of compounds, and in some instances it was possible to propose the structure of the determined compounds.

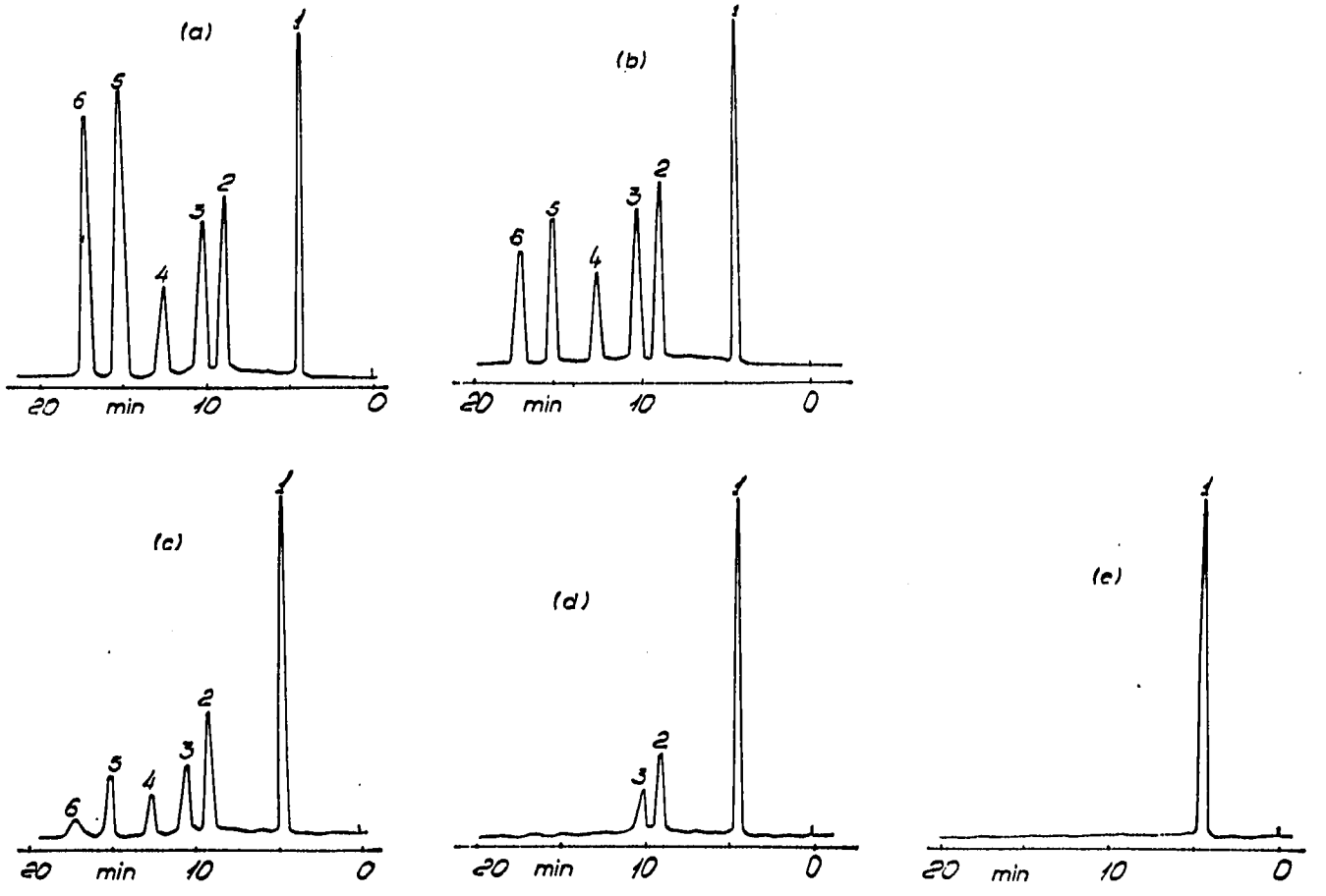

Fig. 2. Substraction of esters and acetals in reactors containing different amounts of lithium aluminium hydride. (a) Without the reactor; (b), (c), (d) and (e) with the reactor packed with 0.05, 0.17, 0.21 and 0.5 g of lithium aluminium hydride, respectively. 1 = *n*-Octane (internal standard); 2 = acetal of isobutanol and isobutyric aldehyde; 3 = acetal of *n*-butanol and isobutyric aldehyde; 4 = acetal of *n*-butanol and *n*-butyric aldehyde; 5 = ester of isobutyric acid with 2-ethylhexanol; 6 = ester of *n*-butyric acid with 2-ethylhexanol.

Fig. 3. Chromatograms for the extraction of components from the technical-grade product. Temperature increase programmed at 4°/min. (a) Without the reactor; (b) and (c) with the reactor packed with 0.5 and 5% of boric acid, respectively; (d) and (e) with the reactor packed with 0.05 and 0.15 g of lithium aluminium hydride, respectively. 1 = Isobutyric aldehyde; 2 = *n*-butyric aldehyde; 3 = isobutanol; 4 = *n*-butanol; 11 = isobutyl isobutyrate; 13 = *n*-butyl isobutyrate; 15 = isobutyl *n*-butyrate; 17 = 2-ethylhexanal; 18 = *n*-butyl *n*-butyrate; 19 = 2-ethyl-4-methylpentanol; 20 = 2-ethylhexanal; 21 = 2-ethylhexanol; 24 = acetal of isobutanol and isobutyric aldehyde; 27 = acetal of isobutanol and *n*-butyric aldehyde; 28 = 2-ethylhexyl isobutyrate; 30 = acetal of *n*-butanol and isobutyric aldehyde; 31 = 2-ethylhexyl butyrate; 34 = acetal of *n*-butanol and *n*-butyric aldehyde; 35 = ester of isobutyric acid and 2-ethylhexanol; 38 = ester of *n*-butyric acid and 2-ethylhexanol. The other peaks have not been identified.

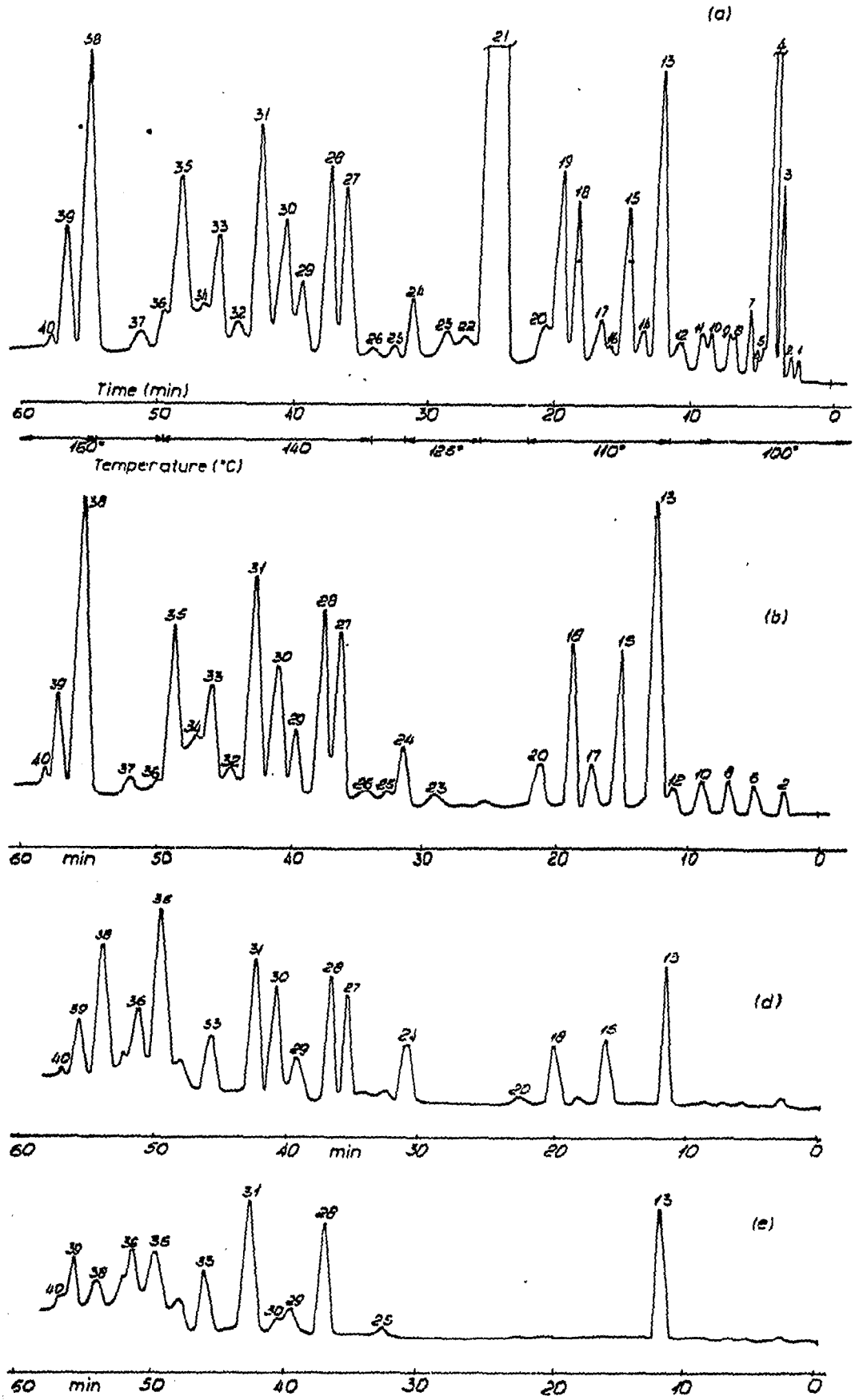
(a)
Time (min)
60 50 40 30 20 10 0
160° 140 125° 110° 100°
Temperature (°C)
(b)
60 min 50 40 30 20 10 0
(d)
60 50 40 min 30 20 10 0
(e)
60 min 50 40 30 20 10 0

Fig. 3

The exact composition of the product shown in Fig. 3 was determined after the results obtained by means of reaction chromatography had been confirmed by chromatography–mass spectrometry.

Borates and complex compounds of lithium aluminium hydride with oxygen-containing compounds were eluted from the chromatographic column much later and did not interfere with the identification of the compounds being studied.

The stability of the reactor operation should be continuously controlled with the help of the model mixture.

We have found that reliable and reproducible results with a single reactor can be obtained when analyzing 8–10 samples, after which the reactor is packed with another batch of reagent.

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