Gas chromatography of methyl esters of aromatic mono-, di-, and tricarboxylic acids formed during oxidation of a mixture of trimethylbenzenes

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Relative elution time of six methyl dimethylbenzoates, five isomeric methylphthalic acids and three isomeric benzenetricarboxylic acids was estimated on packed and capillary columns. Apiezon L, QF-1, Reoplex-400 and ethylene glycol succinate + 2% H_3PO_4 at 140—214°C were the liquid phases in the packed columns, Apiezon K and Reoplex-400 at 209 and 168°C, respectively in the capillary ones. It has been found that no satisfactory separation of all theoretically possible isomeric methyl dimethylbenzoates took place at any of the packed columns; isomeric methyl methylphthalates were well separated on 10% ethylene glycol succinate + 2% H_3PO_4; a good separation of all isomeric methyl dimethylbenzoates and methyl phthalates was achieved on a 45-m Reoplex capillary column at 168°C.

The oxidation of trimethylbenzenes in liquid phase under catalysis of salts of transition metals afforded, in addition to tricarboxylic acids, also a certain amount of isomeric dimethylbenzoic and methylphthalic acids. Their content in oxidation products depends on the depth of oxidation of the respective trimethylbenzenes.

Chromatographic methods and particularly gas chromatography were shown to be most suitable to separate the mixture of benzenecarboxylic acids. Since gas chromatography of free benzenecarboxylic acids is rather complicated considering their low vapour pressure and relatively easy decarboxylation at higher temperatures [1], they have to be separated as methyl [2—5] or trimethylsilyl esters [6—8]. So far, the estimation of all isomeric carboxylic acids formed during oxidation of xylene was reported [9—11]. *Jirák* and *Dvořák* [12] determined trimellitic acid and lower aromatic acids in the oxidation products of pseudocumene. This method cannot be, however, applied to the determination of position isomers of three methylphthalic acids, particularly, it was not succeeded to separate 2,4-dimethyl- from 2,5-dimethylbenzoic acid. Some dimethylbenzoic and methylphthalic acids were also gas chromatographed [14].

When studying oxidation of trimethylbenzenes, all theoretically possible isomeric benzenecarboxylic acids have to be estimated. This was the reason why we investigated the gas chromatographic behaviour of aromatic mono-, di-, and tricarboxylic acids on various stationary phases and column supports.

Experimental

Apparatus

Gas chromatograph CHROM-3 provided with a flame-ionization detector (Laboratorní přístroje, Praha). The thermostat temperature was thyristor controlled within ± 0.3°C. Columns were made of stainless steel, nitrogen at 1 to 3.5 kp cm^{-2} was used as carrier gas. The injection port temperature was 50 $\pm$ 5°C higher than that of the column. Characteristic data of columns employed are listed in Table 1.

Table 1

Characteristic data of columns employed

Column	Packing	Length [m]	Diameter [mm]	Graining [mesh]
I	10% Apiezon L on silanized Gaschrom P	1.8	3	100–120
II	7% Apiezon L on Chromosorb W	3.6	3	60–80
III	10% Apiezon L on Chromosorb P	1.8	3	100–120
IV	7% QF-1 on silanized Chromosorb W	2.0	3	60–80
V	10% Reoplex-400 on silanized Chromosorb W	1.8	3	100–120
VI	10% ethylene glycol succinate + 2% H_3PO_4 on Chromosorb W	3.6	3	100–120
VII	Capillary column with Apiezon K	100	0.25	–
*VIII**	Capillary column with Reoplex-400	45	0.25	–

* Capillary column (Laboratorní přístroje, Praha) was impregnated with 15% Reoplex in chloroform by dynamic method.

Reference substances

2,4-Dimethyl-, 2,5-dimethyl-, and 3,4-dimethylbenzoic acids were prepared from *o*-, *m*-, and *p*-xylenes of high purity grade by chloromethylation [15], Sommellet reaction and oxidation of the respective aldehydes with silver oxide [16]. 3,5-Dimethylbenzoic acid was prepared by oxidation of pure mesitylene with manganese dioxide in acid medium to yield 3,5-dimethylbenzaldehyde [17] the latter being oxidized further with silver oxide [16]. 2,3-Dimethylbenzoic acid was obtained according to *Birch* method [18]. 2,6-Dimethylbenzoic acid was synthesized from 2,6-dimethylbromobenzene [19]. 2-Methylterephthalic acid was prepared according to *Nightingale* [20]. 4-Methylisophthalic acid was obtained from *p*-toluic acid by chloromethylation and oxidation of the chloro derivative with potassium permanganate in sodium hydroxide medium [21]. 3-Methylphthalic acid was prepared according to [22] from methyl 2-cyanometatoluate. 5-Methylisophthalic acid was obtained from mesitylene by oxidation with dilute nitric acid [23]. 2-Methylisophthalic acid was synthesized from 2,6-dicarboxyphenylglyoxalic acid [24]. Trimellitic, trimesinic, and hemimellitic acids were obtained by oxidation of trimethylbenzenes (pseudocumene, mesitylene, and hemimellitene) with potassium permanganate [25]. Melting points of acids thus obtained were after recrystallization in accordance with those reported.

Table 2

Relative retention times of methyl esters of aromatic acids on various columns at various temperatures [°C]

Methyl	*I*	*II*	*III*	*IV*	*V*	*VI*		*VII*	*VIII*	*a*	*b*
	214	214	210	140	170	174	196	209	168	190	200
2,6-Dimethylbenzoate	0.51	0.50	0.52	0.50	0.56	0.57	—	0.53	0.57	—	—
2,5-Dimethylbenzoate	0.78	0.74	0.72	0.62	0.65	0.66	0.67	0.71	0.64	0.82	—
2,4-Dimethylbenzoate	0.78	0.74	0.75	0.65	0.67	0.66	0.67	0.76	0.68	0.77	—
2,3-Dimethylbenzoate	0.82	0.81	0.82	0.82	0.81	0.79	—	0.81	0.82	0.84	—
3,5-Dimethylbenzoate	0.82	0.81	0.82	0.82	0.78	0.76	—	0.81	0.78	0.88	—
3,4-Dimethylbenzoate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	—
2-Methylterephthalate	2.20	2.25	—	3.47	—	4.43	3.78	2.34	4.41	3.07	—
2-Methylisophthalate	1.95	1.98	—	—	—	4.72	—	2.07	4.56	—	—
4-Methylisophthalate	2.20	2.25	—	3.88	—	4.94	4.15	2.46	4.87	3.25	—
3-Methylorthophthalate	1.52	1.70	—	—	—	5.25	—	1.68	4.66	2.67	—
5-Methylisophthalate	2.40	2.59	—	—	—	5.59	4.42	2.70	5.56	3.58	—
Trimellitate	4.50	5.14	—	—	—	—	22.20	—	—	—	0.72
Trimesinate	5.60	6.96	—	—	—	—	20.90	—	—	—	0.60
Hemimellitate	3.90	5.45	—	—	—	—	25.30	—	—	—	1.00

a) 25% Silicone DC-550 on Shimalite 30—60 mesh; column ⌀ 3 mm × 1.5 m [14].
b) 1—6% 1,2,3,4-Tetrakis-(2-cyanoethoxy)butane; column ⌀ 6 mm × 0.83 m [13].
Relative elution times in case *b* are calculated on trimethyl hemimellitate.

Methyl esters

Diazomethane was used to esterify the above-mentioned aromatic acids. The purity of the respective esters was checked by gas chromatography. Single methyl esters and their mixtures were injected into the apparatus as ethyl ether solutions.

Results and discussion

The relative elution times of methyl benzenecarboxylates listed in Table 2 were calculated in regard to the elution time of 3,4-dimethylbenzoic acid. This Table includes, for comparison purposes, also the relative elution times of some methyl benzenecarboxylates for nonpolar phase Silicone DC-550 [14] and polar phase 1,2,3,4-tetrakis-(2-cyanoethoxy)butane [13] (columns *a*, *b*).

To chromatograph methyl benzenecarboxylic acids, we used nonpolar phases Apiezon L, or Apiezon K, slightly polar QF-1 and two medium polar phases Reoplex-400 and ethylene glycol succinate. Besides the polarity of phase also the supports influenced the elution of the respective methyl esters and that is why we investigated Chromosorb P, Chromosorb W, silanized Gaschrom P in connection with the Apiezon phase. The most convenient from the viewpoint of symmetry of peaks appeared to be 10% of Apiezon L over silanized Gaschrom P (column *I*). Chromatographic peaks are symmetrical also for methyl benzenetricarboxylates.

The following pairs of isomeric methyl esters could not be separated on this packing (column *I*): 2,5-dimethyl-, 2,4-dimethylbenzoic acid; 2,3-dimethyl-, 3,5-dimethylbenzoic acid; 2-methylterephthalic-, 4-methylisophthalic acid. Relative elution times of methyl esters di- and tricarboxylic acids increased with Chromosorb W, what is likely due to the adsorption of these substances on the surface of Chromosorb W. The influence of the support "polarity" was seen mainly with Chromosorb P (column *III*). Methyl methylphthalates and benzenetricarboxylates revealed markedly unsymmetrical peaks.

Relative elution times of substances separated on columns *II*, *III*, and *VI* are only outlined, since the elution times on these columns depended partly on the concentration of substances to be separated [26]. The effect of adsorption is evident from the comparison of the relative elution times of methyl benzenetricarboxylates on Apiezon phase (column *I* and *II*). Replacement of silanized Gaschrom P by Chromosorb W resulted in the reverse elution order of methyl trimellitate and hemimellitate. Silicone phase QF-1 (column *IV*) enables, in contrast to the Apiezon phase, to separate methyl 2-methylterephthalate from 4-methylisophthalate and in part also methyl 2,5-dimethylbenzoate from 2,4-dimethylbenzoate. Similarly to Apiezon phase, methyl 2,3-dimethylbenzoate and 3,5-dimethylbenzoate were concurrently eluted from QF-1.

Due to greater interactions of methyl dicarboxylates and tricarboxylates with polyester stationary phases the relative elution times increased. These interactions influenced the elution order of some methyl esters. Thus methyl 3-methylphthalate, which has the smallest relative elution time value on the nonpolar stationary phase, is eluted from the polyester phase as the last but one of methyl methylphthalates. Similarly, methyl hemimellitate eluates as first on the nonpolar and as last on the polyster phase when separated from methyl benzenetricarboxylates.

The interchange of elution order in both cases is due to mutual influence of carboxyl groups in *ortho* position (*ortho* effect).

Even the polarity increase of the phase did not satisfactorily influence the separation of methyl 2,5-dimethylbenzoate from methyl 2,4-dimethylbenzoate and methyl 2,3-di-

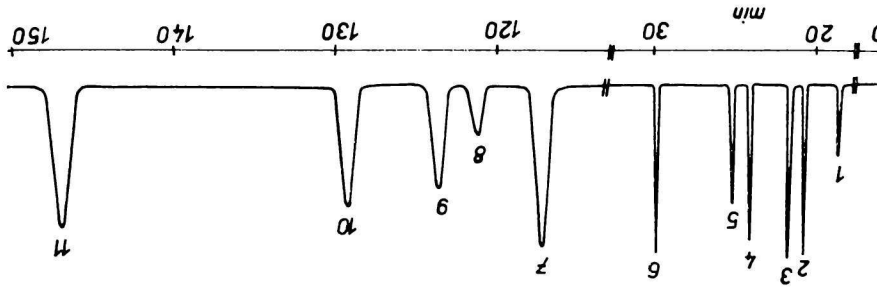

Fig. 1. Chromatogram of methyl benzenecarboxylates on Reoplex capillary column at 168°C.
1. 2,6-dimethylbenzoic acid; *2.* 2,5-dimethylbenzoic acid; *3.* 2,4-dimethylbenzoic acid; *4.* 3,5-dimethylbenzoic acid; *5.* 2,3-dimethylbenzoic acid; *6.* 3,4-dimethylbenzoic acid; *7.* 2-methylterephthalic acid; *8.* 2-methylisophthalic acid; *9.* 3-methylorthophthalic acid; *10.* 4-methylisophthalic acid; *11.* 5-methylisophthalic acid.

methylbenzoate from methyl 3,5-dimethylbenzoate on packed columns. Satisfactory separation of all mentioned esters was achieved using Reoplex capillary column. The chromatogram in seen in Fig. 1.

The elution order and time are in accordance with those hitherto reported with the exception of methyl 2,5-dimethylbenzoate and 2,4-dimethylbenzoate which are eluted either from the nonpolar (Apiezon L, QF-1) or polar phase (Reoplex, ethylene glycol succinate + 2% H_3PO_4) in the reverse order as reported by *Dozen* [14].

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