Separation of the methyl esters of benzenecarboxylic acids by thin-layer chromatography

Benzenecarboxylic acids, resulting from vigorous oxidation of alkylated benzenes and polynuclear compounds have frequently been utilized to provide structural evidence regarding the parent substance.

These acids were formerly isolated by conversion to methyl esters, followed by separation *via* fractional crystallization or distillation. This method is not well suited to a qualitative and quantitative analysis of mixtures of ^{14}C-labelled benzenecarboxylic acids.

The methyl esters of benzene mono-, di-, tri-, tetra-, penta- and hexacarboxylic acids have been well resolved by gas chromatography, but the separation of the methyl esters of isomeric di-, tri- and tetracarboxylic acids has been incomplete[1].

This communication describes the application of thin-layer techniques to the separation of the methyl esters of benzenecarboxylic acids.

Experimental

The acids were obtained commercially with the exception of the 1,2,3,4-benzenetetracarboxylic acid, which was prepared as described by READ AND PURVES[2]. The acids were converted to the corresponding methyl esters by treatment with diazomethane generated from "Diazald". The resulting liquid esters were purified by distillation while the solid esters were recrystallized to constant melting point from methanol.

Preparation of plates. A slurry of "Camag" (30 g) in water (65 ml) was applied to 5 × 20 and 20 × 20 cm glass plates using a Brinkmann spreader. The plates were dried at 110° for 45 min.

Chromatography. Several systems were examined and the following proved to be most satisfactory for the separation of the mixture.

TABLE I

R_T VALUES OF METHYL ESTERS OF BENZENECARBOXYLIC ACIDS

Solvent: 100% chloroform.

$$R_T = \frac{\text{migration distance of methyl ester}}{\text{migration distance of the trimethyl ester of 1,3,5-benzenetricarboxylic acid}}$$

No.	*Methyl ester of*	*R_T value*
1	Benzoic acid	1.78
2	Phthalic acid	1.13
3	Isophthalic acid	1.41
4	Terephthalic acid	1.39
5	1,2,3-Benzenetricarboxylic acid	0.59
6	1,2,4-Benzenetricarboxylic acid	0.87
7	1,3,5-Benzenetricarboxylic acid	1.00
8	1,2,3,4-Benzenetetracarboxylic acid	0.47
9	1,2,3,5-Benzenetetracarboxylic acid	0.63
10	1,2,4,5-Benzenetetracarboxylic acid	0.69
11	Benzenepentacarboxylic acid	0.53
12	Benzenehexacarboxylic acid	0.50

A solution (1 %) of each isomer in methanol–chloroform (20:80) was prepared. The resulting solutions were spotted (10 μl; 100 μg) on a thin layer of silica gel containing a fluorescent indicator as prepared by STAHL. The chromatoplate was developed with chloroform (100 %) and observed under a 254 mμ U.V. light in the dark. Blue spots of varying intensity appeared against a greenish background.

Discussion

Chromatographic data for various methyl esters of benzenecarboxylic acids are summarized in Table I. Migration rates are given as R_T values (where R_T is the migration distance of the ester divided by the migration distance of the trimethyl ester of 1,3,5-benzenetricarboxylic acid) rather than as R_F values.

While gas chromatography has provided an effective method for the qualitative analysis of these esters, it has been of limited value in effecting a quantitative separation. The TLC technique described has provided a means of overcoming this limitation.

Acknowledgements

This work was supported by a grant from The Research Foundation of State University of New York.

State University of New York at Albany,
Albany, N.Y. (U.S.A.)

P. G. OLAFSSON
A. GAMBINO

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Received February 21st, 1966