Journal of Chromatography, 82 (1973) 390–393

CHROM. 6732

Note

Gas chromatographic analysis of monohalobenzoic acid isomers

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(Received March 9th, 1973)

Commercially available halogen-substituted benzoic acids may contain varying amounts of isomers. Gas chromatographic (GC) separations of the methyl esters of several isomeric nitrobenzoic acids[1] and of di-, tri- and tetrachlorobenzoic acids[2] with columns containing liquid phases such as polyesters or silicones have been reported in the literature. Only poor separations were obtained with isomers that have very similar physical characteristics, *e.g.*, the isomers of the monosubstituted halobenzoic acids, unless special conditions are adopted such as the use of capillary columns.

In the present paper, we describe a GC separation and quantitative determination of the *ortho-*, *meta-* and *para-*isomers of monochloro-, monobromo- and monoiodobenzoic acids with a column containing 5% Bentone and 5% trimer acid on acid-washed Chromosorb W.

EXPERIMENTAL

Gas chromatography

A Carlo Erba Fractovrap GV 200 gas chromatograph equipped with a flame ionization detector was used. The areas of the peaks were determined by using a Carlo Erba Model 45 integrator attached to a Leeds and Northrup Speedowax W recorder.

Glass U-shaped columns of length 2 m and I.D. 3 mm were used, packed with 5% Bentone 34 (dimethyldioctadecylammonium-bentonite) and 5% trimer acid on acid-washed Chromosorb W, 80–100 mesh.

The carrier gas was nitrogen at a flow-rate of 50 ml/min.

The operating temperature was fixed, under isothermal conditions, between 140° and 160°, depending on the retention times of the esters.

Reagents

The acids were all of analytical grade and were obtained from E. Merck, Schuchardt, Fluka and B.D.H.

The various methyl esters were prepared with diazomethane at 0° in diethyl ether and were redistilled under vacuum.

Procedure

The free acids are esterified by the method described elsewhere[3] using N,N'-

dicyclohexylcarbodiimide (DIC) as the esterifying agent. 10 mequiv. of the *ortho-*, *meta-* and *para-*isomers of the halobenzoic acids are dissolved in 25 ml of methanol and 0.4 ml of pyridine is added. DIC in excess of the theoretical amount (12 mequiv.), or in even larger amounts if the acids used are not dry and the water reacts with the DIC, is added and the mixture is stirred 30 min at room temperature.

The halobenzoic acids are esterified completely in 15–30 min at 20° using only small amounts of pyridine as catalyst, which improves the subsequent GC analysis as much less tailing of the pyridine peak occurs.

The N,N′-dicyclohexylurea formed is allowed to settle and 0.1–0.5 μl of the clear supernatant solution is injected into the gas chromatograph. The response of the flame ionization detector is modified according to the type of analysis and small amounts of isomers present in a single product are calculated from the areas of the peaks.

RESULTS AND DISCUSSION

In several attempts to separate the halobenzoic acid isomers with columns packed with Carbowax 20M, SE-30 silicone rubber, neopentyl glycol succinate and Reoplex 400, only incomplete separation of the peaks, corresponding to the *meta-* and *para-*isomers, was obtained. With a liquid phase of Bentone 34 and 5% trimer acid supported on acid-washed Chromosorb W, the results were much better and the quantitative determination of a mixture of *ortho-*, *meta-*, *para-*chlorobenzoic acids was possible even with one of the three isomers present at the level of 0.1%. In fact, the methyl *meta-* and *para-*chlorobenzoates, which elute together from most columns, have, in this instance, a coefficient of resolution *R* (Table I) of about 1.0 and therefore the two peaks are completely separated.

TABLE I

SEPARATION OF METHYL HALOBENZOATES

Ester	*Column temp. (°C)*	*Relative retention times*	*Coeff. of resolution, R, between two close peaks*
Methyl *o*-chlorobenzoate	140	1.00	3.1
Methyl *m*-chlorobenzoate	140	0.65	1.0
Methyl *p*-chlorobenzoate	140	0.57	
Methyl 2,4-dichlorobenzoate	140	1.80	
Methyl *o*-bromobenzoate	160	1.00	3.2
Methyl *m*-bromobenzoate	160	0.69	1.05
Methyl *p*-bromobenzoate	160	0.60	
Methyl *o*-iodobenzoate	160	1.00	3.1
Methyl *m*-iodobenzoate	160	0.71	1.1
Methyl *p*-iodobenzoate	160	0.62	

The coefficient of resolution *R* was calculated from the simplified equation

$$R = \frac{2(t_2 - t_1)}{W_1 + W_2}$$

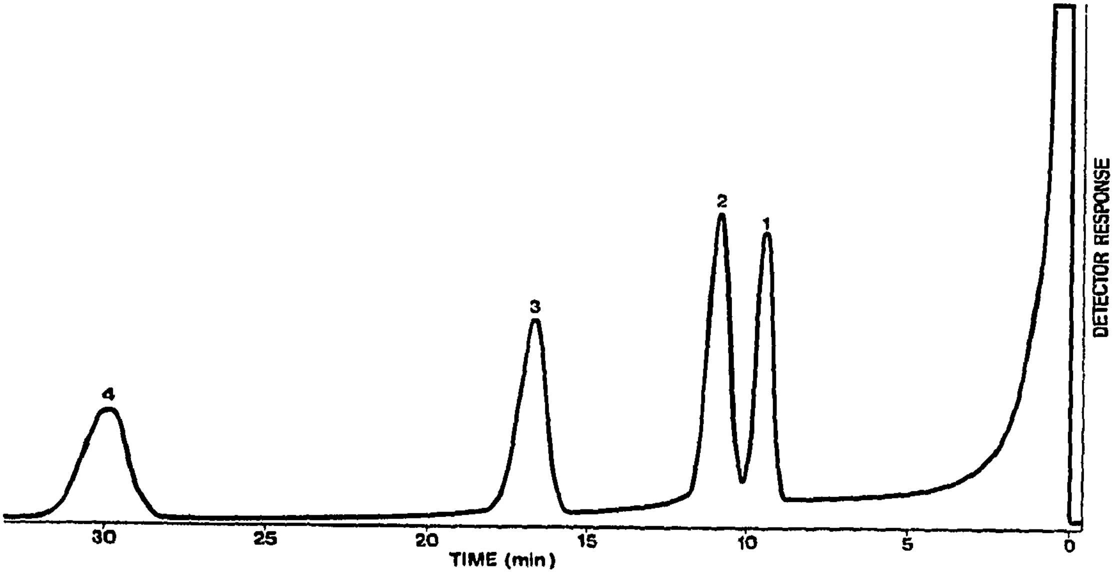

Fig. 1. Chromatogram of chlorobenzoic acid methyl esters at 140°: 1 = methyl 4-chlorobenzoate; 2 = methyl 3-chlorobenzoate; 3 = methyl 2-chlorobenzoate; 4 = methyl 2,4-dichlorobenzoate.

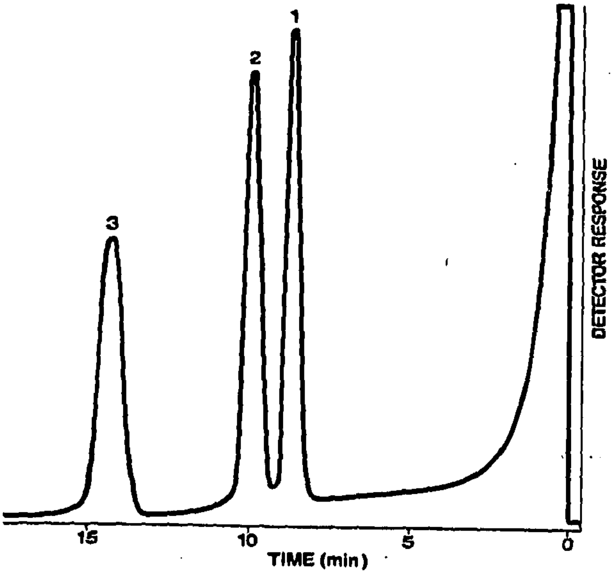

Fig. 2. Chromatogram of bromobenzoic acid methyl esters at 160°: 1 = methyl 4-bromobenzoate; 2 = methyl 3-bromobenzoate; 3 = methyl 2-bromobenzoate.

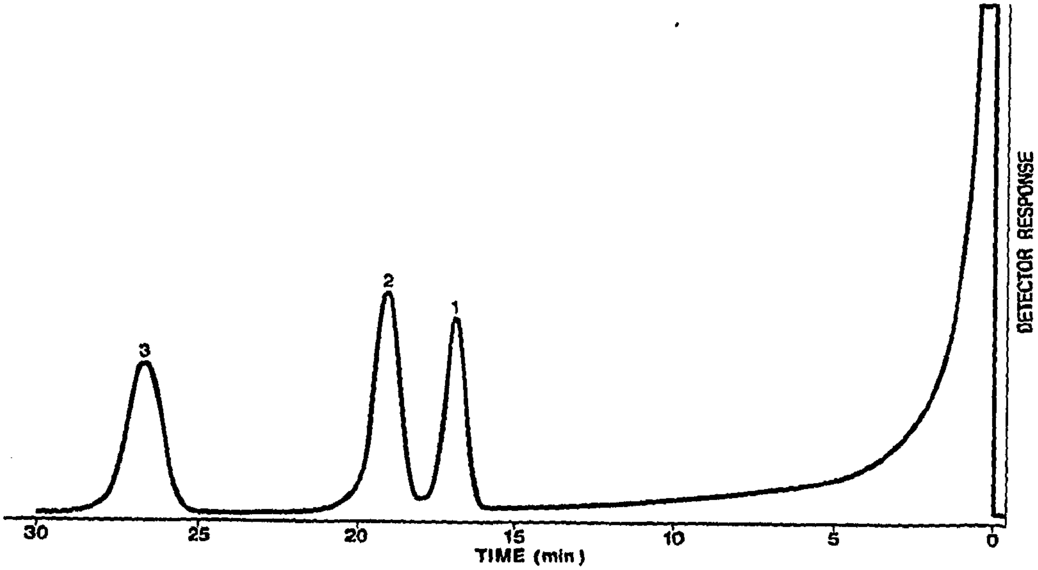

Fig. 3. Chromatogram of iodobenzoic acid methyl esters at 160°: 1 = methyl 4-iodobenzoate; 2 = methyl 3-iodobenzoate; 3 = methyl 2-iodobenzoate.

where t_1 and t_2 are the retention times in minutes and W_1 and W_2 are the peak base lengths in minutes.

There is, however, no problem in separating the methyl ester of *o*-chlorobenzoic acid, which is distant from the peaks of the other two isomers; this is also true for 2,4-dichlorobenzoic acid methyl ester. The bromo- and iodobenzoic acid methyl ester isomers are separated with similar ease (Table I, Figs. 1–3).

REFERENCES

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