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Note

Analysis of *tert.*-butylated cresol mixtures by capillary gas chromatography and capillary gas chromatography–mass spectrometry

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The alkylation of cresol with isobutene is a method often used for the production of *tert.*-butylcresols. Mono- and dialkylated cresols as well as cresylic ether are the reaction products. The xylenols, contained in impure cresol, phenol and guaiacol react in the same way. By alkylation with a technical C_4 fraction, the appearance of disubstituted mixed *sec.*-butyl–*tert.*-butyl derivatives can also be expected.

Table I shows the number of isomers of some types of compounds which theoretically can be formed during the alkylation. Even, if the actual number of isomers produced is less, a multicomponent mixture is expected. The complete analysis of the *tert.*-butylation products of cresol has, to our knowledge, hitherto not been reported. Some workers described only the analysis of selected pairs of isomers on packed columns[2]. We decided to use capillary gas chromatography for the analysis of reaction mixtures.

The only way to identify the constituents was to use gas chromatography–mass spectrometry (GC–MS), since boiling point data are known only for a few constituents (Table II), structure–retention relationships are not available to the extent as, *e.g.*, in the case of alkyl aromatics and generally only a limited number of test substances was available. Thus, whereas the different types of compounds may

TABLE I

THEORETICALLY POSSIBLE ISOMERS OBTAINED UPON *tert.*-BUTYLATION OF TECHNICAL CRESOL MIXTURES

Type of compound	*Number of isomers*
tert.-Butyl-phenols	3
-guaiacols	4
-cresols	10
-xylenols	16
Di-*tert.*-butyl-phenols	6
-guaiacols	6
-cresols	14
-xylenols	16
sec.-Butyl–*tert.*-butyl-cresols	28
	113

TABLE II

BOILING POINTS OF *tert.*-BUTYLATED PHENOLS, CRESOLS AND XYLENOLS[1]

tert.-bu = *tert.*-butyl; *sec.*-bu = *sec.*-butyl; phe = phenol; cre = cresol; xyl = xylenol.

No.	*Compound*	*Boiling point (°C)*
1	6-*tert.*-bu-*o*-cre	231
2	6-*tert.*-bu-*p*-cre	232.7
3	6-*sec.*-bu-*p*-cre	237
4	6-*tert.*-bu-*m*-cre	244
5	6-*sec.*-bu-*m*-cre	246–250
6	4-*tert.*-bu-*o*-cre	246.8
7	4-*tert.*-bu-2,6-xyl	248
8	6-*tert.*-bu-2,4-xyl	249
9	6-*tert.*-bu-2,3-xyl	252
10	2,6-di-*tert.*-bu-phe	253
11	6-*tert.*-bu-3,4-xyl	257
12	4-*tert.*-bu-2,3-xyl	259
13	2,4-di-*tert.*-bu-phe	264
14	4-*tert.*-bu-2,5-xyl	265
15	2,6-di-*tert.*-bu-*p*-cre	265
16	4,6-di-*tert.*-bu-*o*-cre	269
17	2,4,6-tri-*tert.*-bu-phe	278
18	4,6-di-*tert.*-bu-*m*-cre	282
19	4,6-di-*tert.*-bu-2,3-xyl	284

successfully be identified, in most cases their exact isomerism cannot be determined. GC–MS investigations on substituted phenols have been reported by a number of workers, *e.g.*, Hunt *et al.*[3], but *tert.*-butylated cresols were not included in their work.

EXPERIMENTAL

Capillaries of soft glass (60 m × 0.25 mm) were used, which had been pretreated twice with Carbowax 20M according to Aue *et al.*[4] after treatment with hydrochloric acid. The coating with Carbowax 20M was also carried out according to the dynamic method[5]. A Varian 1800 instrument equipped with a glass evaporator and a flame ionization detector was employed. Hydrogen was the carrier gas, and a temperature of 300°C was maintained in the injection system. The temperature of the column was held at 90°C for 8 min, then raised to 200°C at 4°C/min; the analysis was completed isothermally. The constituents were identified with an Hewlett-Packard 5992 B system.

The following compounds were available as authentic samples: 2-*tert.*-butyl-*p*-cresol; 6-*tert.*-butyl-*m*-cresol; 6-*tert.*-butyl guaiacol; 2,6-di-*tert.*-butyl-*p*-cresol; 4,6-di-*tert.*-butyl-*o*-cresol; 4,6-di-*tert.*-butyl-*m*-cresol. Solid samples were dissolved in a small quantity of methanol. The quantitative evaluation was carried out with a computer via an LEDA interface[6].

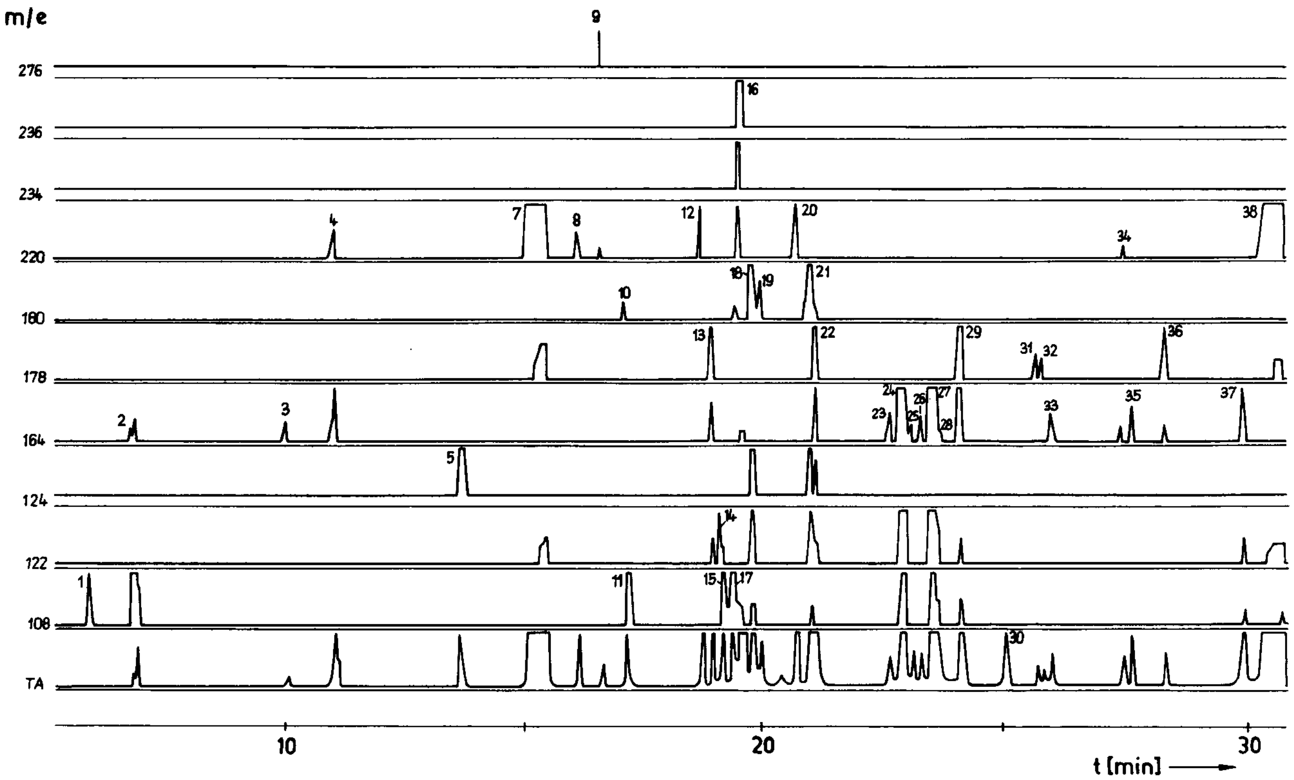

Fig. 1. Mass chromatogram (molecular ions) of a *tert.*-butylated cresol fraction. The peaks are designated according to Table III. The *m/e* values represent the molecular ions of the following compounds (TA = total ionization): 108, cresol; 122, xylenols; 124, methoxyphenols; 164, *tert.*-butylcresols; 178, *tert.*-butylxylenols; 180, methoxy-*tert.*-butylphenols; 220, di-*tert.*-butylcresols; 234, di-*tert.*-butylxylenols; 236, methoxy-di-*tert.*-butylphenols; 276, *tert.*-butoxy-di-*tert.*-butyltoluenes.

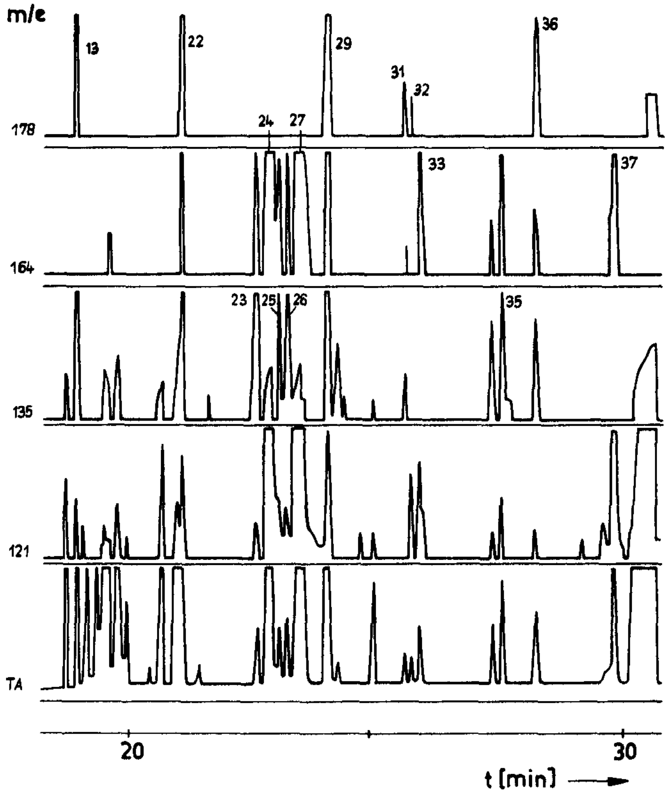

Fig. 2. Mass chromatogram (selected molecular and main fragment ions) of a *tert.*-butylated cresol fraction. The peaks are designated according to Table III (TA = total ionization): 121, main fragment of the *tert.*-butylcresols (M − 43); 135, main fragment of the *sec.*-butylcresols (M − 29); 164, molecular ion of the *tert.*-butylcresols; 178, molecular ion of the *sec.*-butylcresols.

RESULTS AND DISCUSSION

In addition to the molecular peak, the fragment ions M − 15 (basic peak) and M − 43 are significant for the identification of mono- and di-*tert.*-butylated compounds by means of mass spectrometry. In case of *sec.*-butyl–*tert.*-butyl substituted compounds, the fragment M − 29 occurs, whereas *tert.*-butyl–aryl ethers are characterized by the fragment M − 56.

Fig. 1 shows a mass chromatogram in playback representation. The occurrence of some peak overlappings can be seen. For instance, 2,6-di-*tert.*-butyl-*p*-cresol (*m*/*e* = 220) is eluted together with a *tert.*-butylxylenol (*m*/*e* = 178), and a di-*tert.*-butylxylenol (*m*/*e* = 234) and a di-*tert.*-butylmethoxyphenol (*m*/*e* = 236) are coeluted.

Fig. 2 shows the intensities of the key fragments for *tert.*-butylcresols (*m*/*e* = 121) and *sec.*-butylcresols (*m*/*e* = 135) as well as those of the molecular peaks. Both types of derivatives can be clearly differentiated.

Fig. 3. represents a capillary chromatogram of a sample. Table III contains the relative retentions. As expected, compounds with sterically hindered OH groups

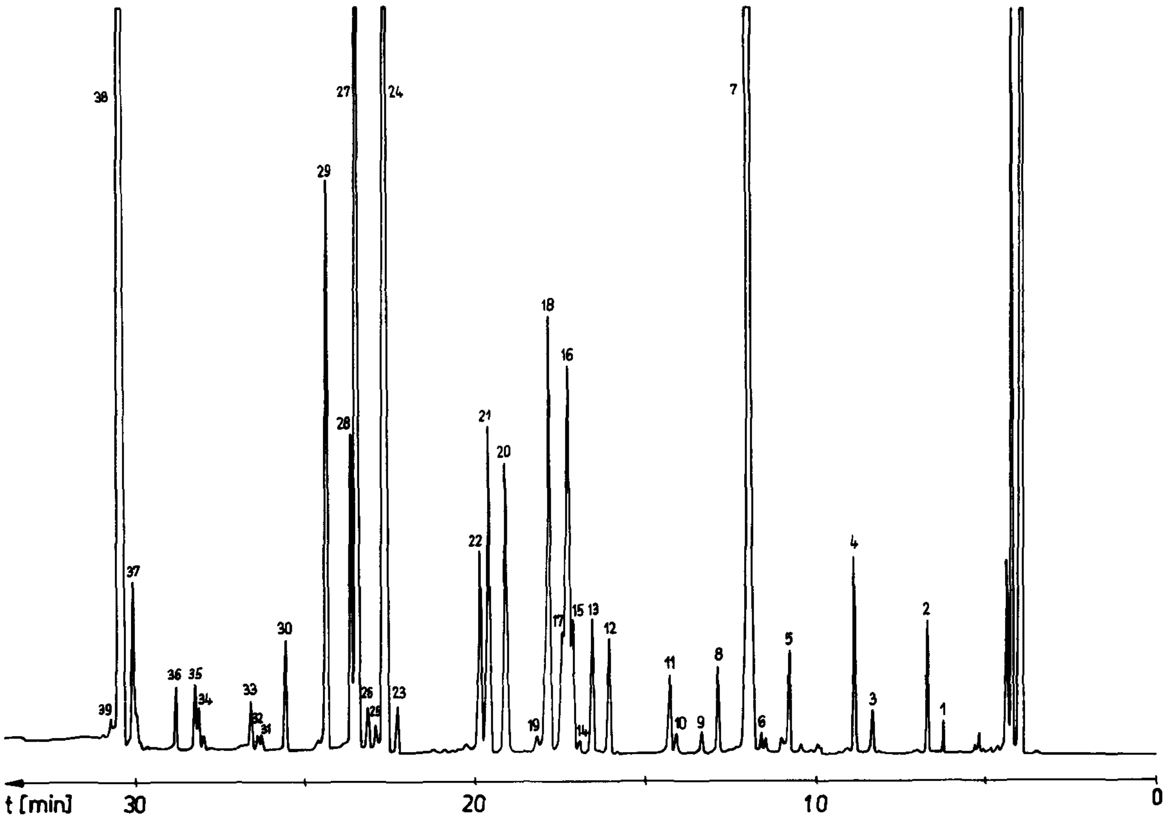

Fig. 3. Capillary chromatogram of a sample of *tert.*-butylated cresols. For conditions see Experimental. The peaks are designated according to Table III.

TABLE III

RELATIVE RETENTIONS

Values are relative to that of 2,6-di-*tert.*-butyl-*p*-cresol, 1.00; for conditions see Experimental. meo = Methoxy; buo = butoxy; bzn = benzene; tol = toluene; gua = guaiacol.

No.	*Substance*	*Relative retention*
1	meo-bzn	0.53
2	*tert.*-buo-tol	0.56
3	*tert.*-bu-cre	0.70
4	*tert.*-buo-*tert.*-bu-tol	0.74
5	Guaiacol	0.90
6	2,4,6-tri-bu-phe	0.92
7	2,6-di-*tert.*-bu-*p*-cre	1.00
8	*sec.*-bu-*tert.*-bu-cre	1.08
9	di-*tert.*-bu-*tert.*-buo-tol	1.13
10	6-*tert.*-bu-gua	1.18
11	*o*-Cresol + 6-*tert.*-bu-*o*-cre	1.19
12	*sec.*-bu-*tert.*-bu-cre	1.33
13	*tert.*-bu-xyl	1.36
14	Xylenol	1.40
15	*p*-Cresol	1.41
16	4,6-di-*tert.*-bu-gua + di-*tert.*-bu-xyl	1.42
17	*m*-Cresol	1.43
18	*tert.*-bu-gua	1.47
19	*tert.*-bu-gua	1.50
20	4,6-di-*tert.*-bu-*o*-cre	1.57
21	*tert.*-bu-gua	1.61
22	*tert.*-bu-xyl	1.63
23	*sec.*-bu-cre	1.83
24	2-*tert.*-bu-*p*-cre	1.85
25	*sec.*-bu-cre	1.87
26	*sec.*-bu-cre	1.89
27	*tert.*-bu-*m*-cre	1.91
28	*tert.*-bu-*o*-cre	1.92
29	*tert.*-bu-xyl	1.98
30	di-*tert.*-bu-phe	2.08
31	*tert.*-bu-cre	2.14
32	*sec.*-bu-xyl	2.15
33	*tert.*-bu-cre	2.17
34	di-*sec.*-bu-cre	2.28
35	*sec.*-bu-cre	2.29
36	*tert.*-bu-xyl	2.34
37	*tert.*-bu-cre	2.43
38	4,6-di-*tert.*-bu-*m*-cre	2.48
39	isooctyl-cre	2.50

(*e.g.*, 2,6-di-*tert.*-butyl-*p*-cresol and 2,4,6-tri-*tert.*-butylphenol) are eluted considerably earlier than would be expected from their boiling points.

For the investigation of such complex mixtures with different qualitative and quantitative compositions the use of the mass-selective detection proved indispensable in many cases in order to identify constituents from their retention data.

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