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Note

Separation of mononitroxylene and xylenol isomers by gas–liquid chromatography

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Although Kreicberga *et al.*[1] and Novrocík *et al.*[2] have reported the separation of 3- and 4-nitro-*o*-xylenes (2,3- and 3,4-dimethylnitrobenzenes) by gas–liquid chromatography (GLC), there have been few systematic separations of dimethylnitrobenzene isomers. These materials are precursors of xylidines and important in industrial chemistry. On the other hand, many papers have been published[3–12] on the separations of alkylphenols, cresol isomers and dimethylphenol isomers by GLC. Brooks[4] separated isomers on 2,4-xylenyl phosphate, Kolšek and Matičič[5] on bis-(3,3,5-trimethylcyclohexyl)phthalate and Janak and Komers[11] on salicylideneaminoguanidine and galactitol, but systematic studies of the separations of the isomers have never been done. Dimethylphenol isomers are also important materials for the chemical industry. For these reasons, the separations of mononitrodimethylbenzene and dimethylphenol isomers were investigated.

EXPERIMENTAL

The gas chromatograph was a Shimadzu GC-5A with a flame ionization detector (FID). The chromatographic column (2.25 m × 3 mm I.D., stainless-steel U-tube) was packed with C_{22} or Celite 545 (60–80 mesh) coated with stationary phase (see Tables I–IV). The temperature of the column was 140° or 150° and that of the injector was 270°. The flow-rate of the carrier gas (nitrogen) was 25 ml/min. The flow-rate of hydrogen was 50 ml/min and that of air was 1 l/min for the FID. The sample size was 0.5–1.0 μl.

The support, Sil-O-Cel C_{22} firebrick (60–80 mesh) (Johns-Manville, Denver, Colo., U.S.A.; purchased from Gaskuro-Kogyo, Tokyo, Japan), was agitated in hot 3 *N* hydrochloric acid for 1 h, then washed with water until neutral and dried prior to use. The C_{22} firebrick was coated with 10, 15 or 20% (w/w) of liquid phase and heated in an electric oven for 16 h in order to remove the solvent at the temperature of the column. The column packed with C_{22} firebrick coated with liquid phase was kept under a stream of nitrogen for 6 h at a temperature *ca.* 20° higher than the column temperature used. The liquid phases, silicone KF-54, FL-100 (Shinetsu, Tokyo, Japan) ethylene glycol phthalate (EGP), ethylene glycol isophthalate (EGIP), ethylene glycol adipate (EGA), polyethylene glycol 20M (PEG-20M), Apiezon L (APL), squalane (SQ), silicone DC-550 (DC-550),dodecylbenzenesulphonate (DBS), Bentone-34 (BT-34), 1,2,3-tris(2-cyanoethoxy)-propane (TCEP) (Gaskuro-Kogyo),

cholesteryl acetate (CHA) (Aldrich, Milwaukee, Wisc., U.S.A.), diphenyl phthalate (DPP), dioctyl phthalate (DOP), Triton X-100 (TRX-100), diisodecyl phthalate (DIIP), liquid paraffin (LP), dioctyl sebacate (DOS), polyethylene glycol 1500, 1540 and 2000 (PEG 1500, 1540 and 2000) and galactitol (GTL) (Nakarai, Kyoto, Japan), were used without any purification.

2,4,7-Trinitrofluorenone[13] (2,4,7-TNF) and 4,4'-methoxyazoxybenzene[14] (4,4'-AZB) were synthesized in the laboratory and were used after purification by recrystallization from ethanol.

Samples

3,5-Dimethylnitrobenzene (3,5-DMNB)[15], 2,5-dimethylnitrobenzene[16] (2,5-DNMB), 2,3-dimethylnitrobenzene (2,3-DNMB)[17] ,3,4-dimethylnitrobenzene (3,4-DMNB)[18], 2,6-dimethylnitrobenzene (2,6-DMNB)[19] and 2,4-dimethylnitrobenzene (2,4-DMNB)[19] were synthesized in the laboratory. 2,3-Dimethylphenol[20] (2,3-DMP), 2,6-dimethylphenol (2,6-DMP)[21], 3,4-dimethylphenol (3,4-DM)P[22], 2,4-dimethylphenol (2,4-DMP)[22,23], 2,5-dimethylphenol (2,5-DMP)[24] and 3,5-dimethylphenol (3,5-DMP)[25] were also synthesized in the laboratory. All these samples were purified by recrystallization or reduced-pressure fractional distillation and their purities were confirmed by GLC and infrared and nuclear magnetic resonance spectroscopy.

RESULTS AND DISCUSSION

Separation of mononitroxylene isomers

The separation in each run (Tables I, II) was performed under the same condi-

TABLE I

RELATIVE RETENTION TIMES OF DIMETHYLNITROBENZENE ISOMERS

Column loadings: 20%, PEG 1540, DOP, LP, SQ, KF-54, FL-100, DIIP, EGA, TRX-100, EGIP, EGIP, APL and PEG-20M; 15%, 2,4,7-TNF; 5%, 4,4'-AZB and (BT-34 + DIIP) (5% + 5%). Column temperature, 150°. Flow-rate of carrier gas (nitrogen), 25 ml/min.

Liquid phase	*2,6-DMNB*	*2,5-DMNB*	*2,3-DMNB*	*2,4-DMNB*	*3,5-DMNB*	*3,4-DMNB*
1 2,4,7-TNF	1.00	1.93	2.13	2.46	2.86	4.06
2 PEG 1540	1.00	1.72	1.88	2.12	2.28	3.72
3 DOP	1.00	1.72	2.05	2.05	2.22	3.27
4 4,4'-AZB	1.00	2.02	2.32	2.49	2.87	4.23
5 LP	1.00	1.80	2.06	2.06	2.33	3.39
6 SQ	1.00	1.92	2.29	2.29	2.63	4.13
7 KF-54	1.00	1.48	1.76	1.63	1.76	2.38
8 FL-100	1.00	1.59	1.90	1.90	2.19	2.92
9 DIIP	1.00	1.51	1.74	1.74	1.96	3.14
10 DPP	1.00	1.85	2.00	2.35	2.63	4.05
11 EGA	1.00	1.76	2.20	2.10	2.33	3.40
12 TRX-100	1.00	1.75	2.08	2.08	2.33	3.25
13 EGIP	1.00	1.94	2.29	2.29	2.47	3.70
14 BT-34 + DIIP	1.00	1.52	1.75	2.43	2.43	2.79
15 APL	1.00	1.86	2.19	2.19	2.50	3.82
16 PEG-20M	1.00	1.92	2.30	2.30	2.30	2.46
*Boiling point**	225°/744 mmHg	237°	246°	239°	273°/739 mmHg	254°/748 mmHg

* *Beilstein Handbuch*, 5 (1922) 368.

TABLE II

SEPARATION FACTORS FOR DIMETHYLNITROBENZENE ISOMERS

Column length and loading as in Table I. Separation factors: S_{16}, between 2,6- and 2,5-DNNB; S_{63}, between 2,3- and 2,5-DNNB; S_{34}, between 2,3- and 2,4-DNNB; S_{42}, between 2,4- and 3,5-DNNB; S_{25}, between 3,5- and 3,4-DNNB.

Liquid phases	S_{16}	S_{63}	S_{34}	S_{42}	S_{25}
1 2,4,7-TNF	0.48	0.09	0.13	0.14	0.29
2 PEG 1540	0.42	0.09	0.11	0.07	0.39
3 DOP	0.42	0.16	0.00	0.08	0.32
4 4,4'-AZB	0.50	0.12	0.07	0.13	0.32
5 LP	0.44	0.26	0.00	0.12	0.31
6 SQ	0.48	0.16	0.00	0.13	0.36
7 KF-54	0.32	0.09	−0.07	0.00	0.26
8 FL-100	0.37	0.16	0.00	0.13	0.25
9 DIIP	0.34	0.13	0.00	0.11	0.38
10 DPP	0.45	0.08	0.15	0.11	0.35
11 EGA	0.43	0.16	−0.05	0.06	0.31
12 TRX-100	0.43	0.16	0.00	0.11	0.28
13 EGIP	0.48	0.15	0.00	0.07	0.33
14 BT-34 + DIIP	0.34	0.13	0.28	0.00	0.13
15 APL	0.46	0.15	0.00	0.12	0.35
16 PEG-20M	0.47	0.16	0.00	0.00	0.07
Mean value	0.43	0.14	0.05	0.09	0.29

tions of column length, column temperature and injector temperature for the purpose of studying the separation behaviour of the six mononitroxylene isomers. It can be seen that the six isomers are separated from each other on PEG 1540, 2,4,7-TNF, 4,4'-AZB, DPP and EGA, and the separation between 2,3- and 2,4-DMNB is the most difficult. These isomers were not separated from the baseline even on these effective stationary liquid phases.

Jones factors [$S_{12} = (t_2-t_1)/t_2$, where t_1 and t_2 are retention times of samples 1 and 2][26] are shown in Table II. Effective separations were obtained: 4,4'-AZB, 2,4,7-TNF, SQ, EGIP, APL and DPP between 2,6- and 2,5-DMNB; LP, DOP, SQ, EGA, FL-100 and TRX-100 between 2,3- and 2,5-DMNB; (BT-34 + DIIP), DPP, 2,4.7-TNF and PEG 1540 between 2,4- and 2,3-DMNB; 2,4,7-TNF, 4,4'-AZB and DPP between 2,4- and 3,5-DMNB; and PEG 1540, DIIP, SQ, DPP and APL between 3,4- and 3,5-DMNB. All the stationary liquid phases used gave better separations between 2,5- and 2,6-DMNB than the other compounds.

The boiling points of the six isomers are shown in Table I. In the GLC separations, they are evaluated from the volatility[27,28] and depend upon the vapour pressure and activity coefficient of the samples. In the separations of 2,5- and 2,3-DMNB and 3,5- and 3,4-DMNB, the elution orders are interesting in relation to the b.p.s.

The important point is that the elution order of 2,3- and 2,4-DMNB on KF-54 and EGA is opposite to that on the other liquid phases, and the separation behaviour on KF-54 and EGA will differ from that on the other phases[27,28].

PEG 1540 separates 2,4- and 2,3-DMNB but PEG-20M does not; this seems to be due to the polarity difference between these phases[29]. Polyesters and esters are effective in this separation, as are also phases which have phenyl groups. 2,4,7-TNF and 4,4'-AZB are special liquid phases, the former separates *m*- and *p*-nitrotoluene[30]

and the latter (liquid crystal)[31] separates *m*- and *p*-aromatic isomers[32–37]. 2,4- and 2,3-DNMB are related to *m*- and *p*-xylene (*o*-nitrotoluene being common to both) and it is believed that this is the reason why they are separated on these two liquid phases.

Ortho steric effects have been proposed by Janák and Komers[38] in the separation of alkylphenols by GLC.

Attempts were made to separate the isomers on other liquid phases (DC-550, (BT-34 + KF-54) and DOS) but were not successful. The following conclusions are: made:

(1) The mononitrodimethylbenzene isomers are effectively separated on PEG 1540, DPP, EGA, 2,4,7-TNF and 4,4'-AZB.

(2) The separation between 2,3- and 2,4-DMNB is the most difficult and the elution order of these isomers on KF-54 and EGA is opposite to that on the other liquid phases.

(3) *Ortho* steric effects are present in these separations.

Separation of xylenol isomers

The separations of dimethylphenol isomers are shown in Tables III and IV. Among the six isomers, the separation of 2,4- and 2,5-DMP was the most difficult, their boiling points being equal[39]. Their separation is thought to be difficult even by GLC.

TABLE III

RELATIVE RETENTION TIMES FOR DIMETHYLPHENOL ISOMERS

Column combination order: T = tail; H = head. Loading of liquid phase: 20% except for 4,4'-AZB (10%). Column length: 25 cm of TCEP. Runs 2, 8, 14, 15 and 18 are mixed phases. Column temperature 140°. Injector temperature, 270°.

Liquid phase	*2,6-DMP*	*2,5-DMP*	*2,4-DMP*	*2,3-DMP*	*3,5-DMP*	*3,4-DMP*
1 PEG 1540	1.00	1.80	2.15	2.15	3.15	4.00
2 KF-54 + FL-100	1.00	2.17	2.17	2.52	2.52	2.94
3 DPP	1.00	1.73	1.73	2.18	2.42	2.93
4 EGP	1.00	1.65	1.65	2.19	2.41	2.94
5 2,4,7-TNF	1.00	1.70	1.85	2.00	2.95	3.60
6 TRX-100	1.00	1.70	1.70	2.23	2.47	3.00
7 DIIP	1.00	1.65	1.65	2.04	2.30	2.73
8 DOP + PEG 1540	1.00	1.16	1.16	2.60	3.20	4.00
9 SQ	1.00	1.64	1.64	2.14	2.50	3.05
10 DC-550	1.00	1.32	1.32	1.58	1.58	1.81
11 LP	1.00	1.62	1.62	2.06	2.23	2.70
12 FL-100	1.00	1.30	1.30	1.56	1.56	1.96
13 DBS	1.00	2.06	2.06	2.37	3.34	4.09
14 PEG 1540 + TCEP (T)	1.00	1.69	1.83	2.04	2.95	3.66
15 PEG 1540 + TCEP (H)	1.00	1.67	1.81	2.09	2.94	3.61
16 APL	1.00	1.85	1.85	2.19	2.61	3.77
17 4,4'-AZB	1.00	1.80	2.00	2.13	3.06	3.60
18 2,4,7-TNF + TCEP (T)	1.00	1.89	2.06	2.37	3.37	4.62
19 GTL	1.00	1.90	1.90	2.42	3.33	4.21
20 PEG 2000	1.00	1.95	2.04	2.04	3.52	3.95
21 CHA	1.00	1.53	1.53	1.91	2.04	2.44
22 TCEP	1.00	1.72	1.72	2.30	2.53	3.19

TABLE IV

SEPARATION FACTORS FOR DIMETHYLPHENOL ISOMERS

Separation factors: S_{65}, between 2,6- and 2,5-DMP; S_{54}, between 2,5- and 2,4-DMP; S_{43}, between 2,4- and 2,3-DMP; S_{35}, between 2,3- and 3,5-DMP; S_{45}, between 3,5- and 3,4-DMP.

Liquid phase	S_{65}	S_{54}	S_{43}	S_{35}	S_{45}
1 PEG 1540	0.44	0.16	0.00	0.63	0.21
2 KF-54 + FL-100	0.53	0.00	0.13	0.00	0.14
3 DPP	0.42	0.00	0.21	0.24	0.17
4 EGP	0.39	0.00	0.25	0.09	0.18
5 2,4,7-TNF	0.41	0.15	0.08	0.32	0.18
6 TRX-100	0.41	0.00	0.24	0.09	0.17
7 DIIP	0.39	0.00	0.19	0.11	0.15
8 DOP + PEG 1540	0.14	0.00	0.55	0.19	0.06
9 SQ	0.39	0.00	0.24	0.14	0.18
10 DC-550	0.24	0.00	0.16	0.00	0.13
11 LP	0.38	0.00	0.21	0.07	0.17
12 FL-100	0.23	0.00	0.17	0.00	0.21
13 DBS	0.51	0.00	0.12	0.29	0.18
14 PEG 1540 + TCEP (T)	0.40	0.07	0.17	0.31	0.19
15 PEG 1540 + TCEP (H)	0.40	0.07	0.13	0.28	0.19
16 APL	0.46	0.00	0.16	0.16	0.31
17 4,4'-AZB	0.44	0.10	0.06	0.30	0.15
18 2,4,7-TNF + TCEP (T)	0.47	0.08	0.13	0.29	0.27
19 GTL	0.47	0.00	0.21	0.27	0.20
20 PEG 2000	0.48	0.04	0.00	0.42	0.11
21 CHA (at 160°)	0.34	0.00	0.19	0.06	0.16
22 TCEP	0.41	0.00	0.25	0.09	0.21

Although Brooks[4] separated these isomers on 2,4-xylenyl phosphate, Kolšek and Matičič[5] on bis(3,3,5-trimethylcyclohexyl)phthalate and Janák and Komers[38] on salicylideneaminoguanidine and galactitol, it has never been reported that PEG 1540, PEG 2000, 4,4'-AZB and 2,4,7-TNF separate them effectively. DPP, EGP, TRX-100, DIIP, SQ, LP, DBS, APL, GTL, CHA and TCEP separated 2,6- (2,4- and 2,5-), 2,3-, 3,5- and 3,4-DMP from each other.

Effective separations were obtained on: (KF-54 + FL-100), DBS, [2,4,7-TNF + TCEP (tail)], GTL and PEG 2000 between 2,6- and 2,5-DMP; PEG 1540, 2,4,7-TNF, 4,4'-AZB, [2,4,7-TNF + TCEP (tail)], [PEG 1540 + TCEP (head)], (PEG 1540 + TCEP (tail)] and PEG 2000, between 2,5- and 2,4-DMP. (DOP + PEG 1540), EGP, TRX-100, SQ, DPP, LP and GTL between 2,4- and 2,3-DMP; PEG 1540, 2000, 2,4,7-TNF [PEG 1540 + TCEP (tail)], 4,4'-AZB, DBS and [2,4,7-TNF + TCEP (tail)] between 2,3- and 3,5-DMP; APL, [2,4,7-TBF + TCEP (tail)], FL-100, TCEP and PEG 1540 between 3,5- and 3,4-DMP.

Separation of the isomers was attempted on galacitol but was not successful. The separation on salicylideneaminoguanidine[38] seems to be dependent on differences in pK_a values (2,4-DMP, 10.60; 2,5 -DMP, 10.41)[40]. Although 2,5-DMP is eluted before 2,4-DMP on PEG 1540, 2,4,7-TNF, 4,4'-AZB and salicylideneaminoguanidine[38], 2,4-DMP is eluted first on 2,4-xylenyl phosphate[4] and bis(3,3,5-trimethylcyclohexyl)phthalate[5,6,7,41]. Mortimer and Gent[10] tried unsuccessfully to separate these isomers on (BT-34 + tritolyl phosphate), but did separate *m*- and *p*-cresol. Separation

of *m*- and *p*-cresol was attempted on PEG 1540, 2,4,7-TNF and 4,4'-AZB but was not successful.

Mixed phases (DOP, PEG 1540 and others) could not separate 2,5- and 2,4-DMP and the additivity of separation ability seems not to occur in this case. Separations on combined columns were therefore performed: [PEG 1540 + TCEP (head)] and [PEG 1540 + TCEP (tail)] were effective, and 2,4,7-TNF gave improved separation when combined with TCEP (25 cm). PEG 1540, 2000 and 20M, could not separate the isomers at less than 20% coatings. A support (C_{22}) coated with PEG 1540 and dried at 170° did not separate the isomers, owing to evaporation from the support caused by overheating. With combined columns, there were differences in the separations according to the order of combination. Thus 2,4,7-TNF shows effective separation below its m.p. (176°) and 4,4'-AZB in the isotropic phase (*i.e.*, not in the nematic phase). *Ortho* steric effects were also found in these separations[38].

The following conclusions can be made:

(1) 2,4,7-TNF and 4,4'-AZB separate the six DMP isomers, and PEG 1540 and 2000 separate 2,5- and 2,4-DMP.

(2) Ester and hydrocarbon phases give better separations than the other phases, except for 2,5- and 2,4-DMP.

(3) Mixed phases give few effective separations, but combined columns yield good separations.

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