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Note

Separation of mononitrotoluidine isomers by gas-liquid chromatography

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Many reports have been published on the separation of mononitrotoluidine isomers by thin-layer chromatography (TLC)^{1,2}, but there have been few on their separation by gas-liquid chromatography (GLC). As it was necessary to prepare pure 4- and 6-nitro-3-aminotoluene, the author investigated their separation by GLC.

EXPERIMENTAL

Apparatus

The gas chromatograph was a Shimadzu GC-5A with a flame-ionization detector.

Chromatography

The chromatographic column was a 100, 150 or 175 cm long, 3 mm I.D. stainless-steel U-tube, packed with C₂₂ or Celite 545 (60-80 mesh) coated with liquid stationary phase (see Table I). The temperature of the column was 220° and that of the injector was 300°. The flow-rate of the carrier gas (nitrogen) was 20 or 50 ml/min (see Table I). The flow-rate of hydrogen was 50 ml/min and that of air was 1 l/min for the flame-ionization detector. The sample size was 0.3-0.5 μ l.

Support. Sil-O-Cel C₂₂ firebrick (Johns-Manville, Denver, Colo., U.S.A.) (60-80 mesh) was agitated in hot 3 N hydrochloric acid for 1 h, then washed repeatedly with water until neutrality and dried prior to use.

Column preparation. C₂₂ firebrick was coated with 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. Then the column, packed with C₂₂ firebrick coated with liquid phase, was kept under a stream of nitrogen for 6 h at a temperature of ca. 20° higher than the column temperature to be applied.

Liquid phase. Silicone KF-54, silicone HV grease, silicone KF-96, silicone KF-965, silicone FL-100, silicone KF-50, ethylene glycol isophthalate, ethylene glycol phthalate, terephthalic acid and PEG 20M were used without any purification.

Silicone KF-50, KF-54, KF-96, KF-965 and FL-100 were obtained from Shinetsu Chemical Co. (Tokyo, Japan), silicone HV grease from Nakarai (Kyoto, Japan), ethylene glycol isophthalate, ethylene glycol phthalate and PEG 20M from Gaskro-Kogyo (Tokyo, Japan) and terephthalic acid from Wako (Osaka, Japan).

The support material (Celite 545, 60–80 mesh) coated with silicone OV-17 (3%, w/w) was purchased from Nishio Kogyo (Tokyo, Japan).

Samples

4- and 6-nitro-3-aminotoluene (4- and 6-N-3-AT) were prepared³⁻⁷, then purified by crystallization from dilute aqueous ethanol. 3- and 5-nitro-2-aminotoluene (3- and 5-N-2-AT)⁸ were prepared, steam distilled and purified by crystallization from water. 5-Nitro-3-aminotoluene (5-N-3-AT)⁹⁻¹², 2-nitro-4-aminotoluene (2-N-4-AT) and 6- and 4-nitro-2-aminotoluene (6- and 4-N-2-AT)¹⁰⁻¹³ and 3-nitro-4-aminotoluene (3-N-4-AT)^{10-12,14,15} were synthesized and purified by crystallization from water or aqueous ethanol. All of the samples were purified and their purities were determined quantitatively by GLC and qualitatively by TLC and GLC.

RESULTS AND DISCUSSION

The results of the separation of nine mononitrotoluidine isomers (3- and 4-N-2-AT, 5- and 6-N-2-AT, 4-, 5- and 6-N-3-AT and 2- and 3-N-4-AT) are shown in Table I and Fig. 1, where it can be seen that 5-N-3-AT, 6-N-3-AT and 5-N-2-AT are separated from the other six isomers and are separated from each other on silicone KF-54, KF-965, FL-100, HV-G, KF-96 and OV-17. 5-N-3-AT and 4-N-2-AT are separated from the other isomers and are separated from each other on silicone KF-54 and OV-17.

TABLE I

RETENTION TIMES OF MONONITROTOLUIDINE ISOMERS ON DIFFERENT LIQUID STATIONARY PHASES

Sample	Retention time (min)					
	OV-17	KF-54	FL-100	KF-965	KF-96	HV-G
3-N-2-AT	3.00	4.10	1.80	1.20	2.40	1.40
4-N-2-AT	4.20	5.30	3.00	1.80	3.20	2.00
5-N-2-AT	6.60	7.50	5.20	2.60	4.80	3.00
6-N-2-AT	3.00	4.10	1.80	1.20	2.40	1.40
4-N-3-AT	3.40	4.50	2.20	1.40	2.80	1.40
5-N-3-AT	3.80	4.90	3.00	1.80	3.20	2.00
6-N-3-AT	5.40	5.90	4.00	2.20	4.00	2.60
2-N-4-AT	3.40	4.50	2.20	1.40	2.80	1.40
3-N-4-AT	3.00	4.10	1.80	1.20	2.40	1.40
Column length (m)	1.50	1.75	1.50	1.00	1.00	1.00
Flow-rate of carrier gas (ml/min)	50	50	50	20	20	20
Loading (%)	3.0	20.0	5.0	20.0	20.0	20.0

On the other hand, 4-N-2-AT, 5-N-3-AT, 6-N-3-AT and 5-N-2-AT are separated from the other five isomers and are separated from each other on silicone KF-54 and OV-17.

Further, the group of 3- and 6-N-2-AT and 3-N-4-AT and that of 2-N-4-AT and 4-N-3-AT are separated from the other isomers and are separated into the two sub-groups on silicone OV-17, KF-54, FL-100, KF-965 and KF-96.

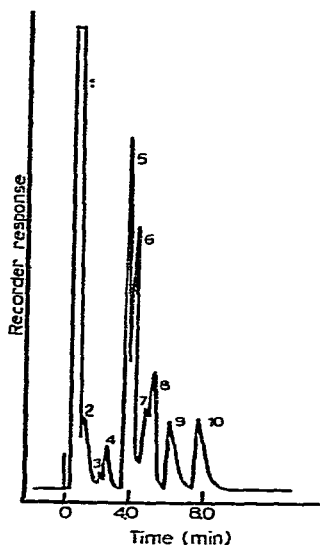


Fig. 1. Separation of mononitrotoluidines on silicone KF-54. Peaks: 1 = tetrahydrofuran (solvent); 2, 3, 4 = impurities in tetrahydrofuran; 5 = 3-N-2-AT, 6-N-2-AT and 3-N-4-AT; 6 = 4-N-3-AT and 2-N-4-AT; 7 = 5-N-3-AT; 8 = 4-N-2-AT; 9 = 6-N-3-AT; 10 = 5-N-2-AT.

From above results, it is found that 5-N-3-AT, 4-N-2-AT, 6-N-3-AT and 5-N-2-AT are separated from each other (four peaks) on silicone KF-54 and OV-17, which are phenylmethylsilicones (containing 25 and 50% of phenyl groups, respectively), but 5-N-3-AT is not separated from 4-N-2-AT on silicone KF-96, KF-965, HV-G and FL-100, which are methylsilicones (FL-100 is 50% trifluoropropylsilicone).

The separations of 3-N-2-AT, 6-N-2-AT, 3-N-4-AT, 4-N-3-AT and 2-N-4-AT are the same on silicone KF-54, OV-17, KF-96, KF-965 and FL-100 (phenylmethyl- or methylsilicone), but silicone HV-G (methylsilicone) cannot separate these isomers above into two groups.

Attempts were made to separate the nine isomers on other liquid phases (ethylene glycol isophthalate, ethylene glycol phthalate, PEG 20 M and terephthalic acid), but effective separations were not achieved.

CONCLUSIONS

- (1) The separation of 4-N-2-AT from 5-N-3-AT is achieved on phenylsilicone.
- (2) The separation of 5-N-3-AT, 6-N-3-AT and 5-N-2-AT from each other is achieved effectively on phenylmethyl- or methylsilicone.
- (3) The separations of 3-N- and 6-N-2-AT, 3-N-4-AT, 4-N-3-AT and 2-N-4-AT are the same on phenylmethyl- and methylsilicone.

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