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Note

Separation of acetamidomononitrotoluene isomers by gas-liquid chromatography

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I have previously reported¹ the separation of monitrotoluidine isomers by gas-liquid chromatography (GLC). Although many reports have been published on the separation of such isomers by paper chromatography²⁻⁴ (PC) and thin-layer chromatography⁵ (TLC), there have been few on the separation of their acetyl isomers by GLC. For this reason, the separation of these isomers by GLC was investigated.

EXPERIMENTAL

Chromatography

The gas chromatograph was a Shimadzu GC-5A with a flame ionization detector (FID). The chromatographic column (75, 100 or 150 cm × 3 mm I.D.) was a stainless-steel U-tube, packed with C₂₂ or Celite 545 (60-80 mesh) coated with a 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 ml/min (see Table I). The flow-rate of hydrogen was 50 ml/min and that of air was 1 l/min for the FID. The sample size was 1.0-1.5 μl. The sample solution contained *ca.* 40 mg of each constituent in 8 ml of tetrahydrofuran. The support was Sil-O-Cel C₂₂ firebrick (Johns-Manville, Denver, Colo., U.S.A.) (60-80 mesh) agitated in hot 3 N hydrochloric acid for 1 h, then washed repeatedly with water until neutrality and dried prior to use. The firebrick was coated with 10 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 the 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. The liquid phases silicone KF-54, KF-96, KF-965 and FL-100 (Shinetsu, Tokyo, Japan), silicone HV grease (Nakarai, Kyoto, Japan), Apiezon L, ethylene glycol isophthalate, ethylene glycol phthalate, and PEG 20M (Gasukuro-Kogyo, Tokyo, Japan) and terephthalic acid (Wako, Osaka, Japan) were used without any purification. 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-acetamidotoluene (4- and 6-N-3-AT) were prepared⁶⁻¹⁰ then

TABLE I

RETENTION TIMES OF ACETAMIDOMONONITROTOLUENE ISOMERS ON DIFFERENT LIQUID STATIONARY PHASES

Compound	Retention time (min)								
	EGP	EGIP	TPA	FL-100	KF-96	KF-965	HF-G	OV-17	KF-54
3-N-2-AT	6.80	4.60	3.40	3.40	1.00	2.40	2.20	3.10	6.60
4-N-2-AT	38.80	24.60	21.80	8.40	4.40	5.20	5.40	10.10	20.40
5-N-2-AT	38.80	24.60	16.60	8.40	4.40	5.20	5.40	10.10	20.40
6-N-2-AT	21.00	13.80	14.60	7.40	3.60	4.20	4.60	4.50	13.20
4-N-3-AT	4.60	2.80	2.60	2.00	0.80	2.40	2.20	2.50	6.60
5-N-3-AT	46.20	28.40	21.80	8.40	4.40	5.20	5.40	10.10	20.40
6-N-3-AT	46.20	28.40	14.60	7.40	4.40	5.20	5.40	8.30	18.40
2-N-4-AT	38.80	24.60	16.60	8.40	3.60	4.20	4.60	8.30	18.40
3-N-4-AT	5.20	2.80	3.40	2.20	0.80	2.40	2.20	2.50	6.60
Column length (m)	0.75	0.75	1.00	1.00	0.75	0.75	1.00	1.50	1.00
Flow-rate of carrier gas (ml/min)	20	20	20	20	20	20	20	20	20
Loading (%)	10	10	10	20	20	20	20	3	20

purified by recrystallization from aqueous ethanol; 6-nitro-3-acetamidotoluene obtained from aqueous solvents contains a molecule water of crystallization¹¹. 3- and 5-nitro-2-acetamidotoluene (3- and 5-N-2-AT)^{9,12,13} were prepared, separated from each other and purified by recrystallization from aqueous ethanol. 5-Nitro-3-acetamidotoluene (5-N-3-AT)¹⁴, 2-nitro-4-acetamidotoluene (2-N-4-AT)¹⁴ and 6- and 4-nitro-2-acetamidotoluene (6- and 4-N-2-AT)^{10,15-17} obtained from nitroamines by acetylation, and 3-nitro-4-acetamidotoluene (3-N-4-AT)¹⁸, obtained from acetamidotoluene by nitration, were purified by the procedure mentioned above. All of the samples were purified and their purities determined by TLC, GLC and IR and NMR spectroscopy.

RESULTS AND DISCUSSION

The results of the separation of nine acetamidomononitrotoluene 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 4-N-3-AT, 3-N-4-AT, 3- and 6-N-2-AT are separated from the other five isomers and separated from each other on ethylene glycol phthalate (EGP). 3-N-2-AT and 6-N-2-AT are separated from the other isomers and separated from each other on ethylene glycol isophthalate (EGIP), silicone OV-17 (OV-17) and EGP. 4-N-3-AT and 3-N-4-AT are separated from each other on terephthalic acid (TPA), EGP and silicone FL-100 (FL-100). Thus, it is found that 3-N-4-AT, 3- and 6-N-2-AT and 4-N-3-AT are separated from each other (four peaks) on EGP but 3-N-4-AT is not separated from 4-N-3-AT on EGIP.

The separation of 3-N-4-AT from 4-N-3-AT (on TPA, EGP and FL-100) and that of 3-N-2-AT from 6-N-2-AT (on EGIP, EGP and OV-17) are achieved on some of the liquid phases in Table I, but the separation of the isomers having high boiling points (the boiling points have not been reported; 4- and 5-N-2-AT, 5- and 6-N-3-AT and 2-N-4-AT) is not effective on these liquid phases. EGP and EGIP (polyester liquid

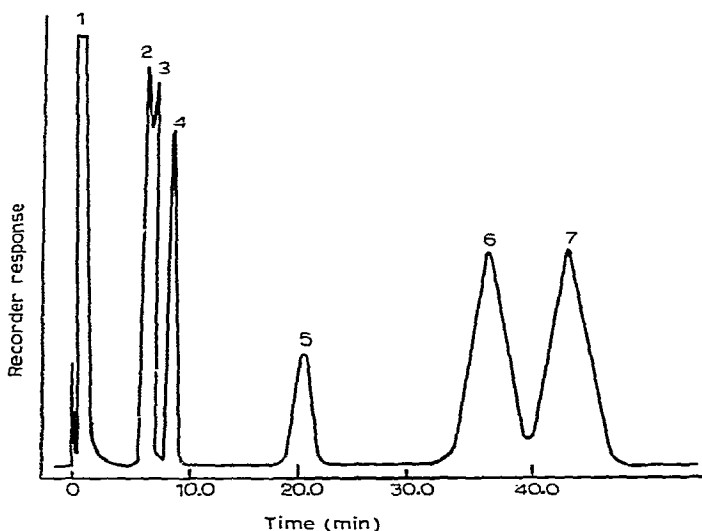


Fig. 1. Separation of acetamidomononitrotoluene isomers on EGP. Peaks: 1 = tetrahydrofuran (solvent); 2 = 4-N-3-AT; 3 = 3-N-4-AT; 4 = 3-N-2-AT; 5 = 6-N-2-AT; 6 = 2-N-4-AT, 4-N-2-AT and 5-N-2-AT; 7 = 5-N-3-AT and 6-N-3-AT.

phase) are the most effective of the liquid phases, and phenyl polysiloxane is the most effective of the polysiloxanes, in the separation of the nine isomers.

Attempts were made to separate the nine isomers on other liquid phases (Apiezon L and PEG 20M), but effective separations were not achieved.

The identification of 6-N-3-AT and its monohydrate was attempted by GLC but the latter compound was dehydrated at 102° (ref. 11) and the compounds showed only one peak; so the monohydrate was used as the sample in this study. In the preparation of the samples, 6- and 3-nitro-2-diacetylaminotoluene were obtained by refluxing the corresponding amines with acetic anhydride; these preparations have not been previously reported. The preparations of the samples were carefully performed by the procedure mentioned in the Experimental section. Details will be reported elsewhere.

CONCLUSION

EGP is the best liquid phase for the separation of acetamidomononitrotoluene isomers and EGIP is the next best of the phases examined, but they cannot be used above 220° and have longer retention times for samples than polysiloxanes at the same temperature.

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