CHROMATOGRAPHIC SEPARATION OF NITROGEN-CONTAINING SUBSTANCES IN THE SYSTEM GAS-LIQUID. III.*

SEPARATION OF SOME 1-ALKYLPIPERIDINES

M.ŠAFÁŘ, V.GALÍK, Z.KAFKA and S.LANDA

Laboratory of Synthetic Fuels,
Institute of Chemical Technology, Prague 6

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Relative elution volumes of 1-alkylpiperidines of b.p. up to 300°C have been determined. The stationary phases, polyethylene glycol 1500, Carbowax 20 M, tetrakis-(β-cyanoethoxy)-neopentane, and silicone oil AK 30 000 cSt, were fixed on porous sintered corundum.

This paper is a continuation of our previous study[1], solving the problem of the analysis of free alkylpiperidines of b.p. up to 300°C. In addition to other heterocyclic bases alkylpiperidines were analysed by Wawzonek and Culbertson[2]. A mixture of pyridine, 2-methylpyridine, piperidine and 2-methylpiperidine was separated by Kametani[3]. Moll[4] investigated a mixture of natural nitrogenous substances, piperidine, 2-propylpiperidine, 2,6-dimethylpiperidine and 1-methyl-2-propylpiperidine by gas-chromatography. 1-Ethylpiperidine and 1-ethyl-3-methylpiperidine were analysed by Ferles and Čaplovič[5]. In addition to these alkylpiperidines 1-methylpiperidine[6] has also been chromatographed. Quantitative and qualitative determination of 2-methylpiperidine and 2-ethylpiperidine is described in[7]. Piperidine, 2-methylpiperidine and 3-methylpiperidine were also separated on a capillary column[8]. Pyridine bases and piperidine were analysed by Jakerson[9] and coworkers. Piperidine was also chromatographically analysed in a mixture of organic bases[10]. Unsaturated piperidine derivatives and 1,3-dimethylpiperidine were studied by Janák and coworkers[11]. Ferles and Holík have discussed the determination of 1-methylpiperidine and 1,3-dimethylpiperidine[12]. Alkylpiperidines and alkylpiperideines were investigated by Grundon and Reynolds[13], isoalkylpiperidines by Nazareva and Freidlin[14]. The effect of the steric arrangement of the 1-alkylcyclohexylpiperidines molecule on chromatographic behaviour is discussed by Cabaret and coworkers[15].

EXPERIMENTAL

Apparatus: A gas chromatograph of our own construction was provided with a thermal conductivity detector[1]. The glass chamber for evaporation, partly filled with glass beads, always had the temperature of 200°C, at column temperatures 175°C it was 240°C.

Columns and fillings: Glass columns were of U-shape, 6 mm I.D., 90 cm long. Carrier gas was nitrogen, with a flow rate of about 50 ml/min. Stationary phase carrier was porous sintered corundum (Jiskra, Tábor, Czechoslovakia) which had negligible adsorption capacity for piperi-

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dine in comparison with Porovina. This carrier enabled the use of the stationary phases given in Table I.

Preparation of 1-alkylpiperidines: The majority of the investigated 1-alkylpiperidines is described in the preceding paper[16]. Other alkylpiperidines were prepared by the procedure described below. Their physical constants were in agreement with the literature data. 1-Isopropylpiperidine was prepared by alkylation of piperidine with isopropyl bromide, b.p. 149—150°C. 1-Cyclopentylpiperidine was prepared by hydrogenation of a mixture of piperidine and cyclopentanone on Raney nickel[17], b.p. 209—210°C. 1,5-Dipiperidinopentane was prepared by hydrogenation of a quaternary salt obtained from 1,5-dibromopentane and pyridine[18], b.p. 106—108°C/0·4 Torr. 1,2-Dipiperidinoethane was prepared from 1,2-dibromoethane and pyridine in an analogous manner, b.p. 126—128°C/10 Torr. Pyridine and piperidine (Lachema) were dried and distilled.

RESULTS AND DISCUSSION

The specific elution volume of piperidine (or 1-amylpiperidine) was calculated and taken as basis. A list of relative elution volumes of 1-alkylpiperidines is given in Table II. On polar stationary phases, *i.e.* polyethylene glycol 1 500, Carbowax 20 M, and tetrakis-(β-cyanoethoxy)neopentane, separation takes place on the basis of intermolecular interactions. Piperidine forms hydrogen bonds between the NH-group hydrogen and the electron pairs of oxygen or nitrogen atoms of the stationary phases.

1-Alkylpiperidines have smaller elution volumes then piperidine due to the loss of hydrogen in consequence of the substitution on the nitrogen atom; for example, 1-propylpiperidine on polyethylene glycol, 1-ethylpiperidine on Carbowax 20M, and 1-butylpiperidine on tetrakis-(β-cyanoethoxy)neopentane have elution volumes

TABLE I
Fillings of Chromatographic Column

Column	Stationary phase	Granulation of the carrier mesh	Concentration of the stationary phase, mass %	Weight of the filling, g
A	polyethylene glycol 1 500[a]	80—100	2·5	39·8
B	Carbowax 20 M[b]	60— 80	2·5	36·0
C	tetrakis-(β-cyanoethoxy)-neopentane[c]	80—100	3·0	36·9
D	silicone oil AK 30 000 cSt[d]	60— 80	2·5	36·3
	Carbowax 20 M[e]		0·4	

[a] Lachema, Brno; [b] Carlo Erba, Milano; [c] see[19]; [d] Wacker, Munich; [e] Carbowax 20 M was applied as the first stationary phase in order to eliminate tailing.

practically identical with piperidine. A larger sterical shielding of the active center of the molecule by the branched alkyl group corresponds to smaller elution volumes of 1-isoalkylpiperidines in contrast to corresponding 1-alkylpiperidines.

Appreciable differences in elution volumes, especially on polar stationary phases (Table II, column B), were found for 1-cyclopentylpiperidine (2·25) and 1-amylpiperidine (1·00). The elution volume of 1-cyclopentylpiperidine is even larger than that of 1-hexylpiperidine (1·62).

TABLE II
Relative Specific Elution Volumes of 1-Alkylpiperidines

Compound	B.p.	Column A			Column B		Column C	Column D	
		80°C	125°C	175°C	80°C	175°C	80°C	125°C	175°C
Piperidine	105	1·00	1·00	—	1·00	—	1·00	1·00	—
1-Methylpiperidine	106	0·40	0·50	—	0·44	—	0·35	1·00	—
1-Ethylpiperidine	127	0·67	0·75	—	0·75	—	0·50	1·80	—
1-Propylpiperidine	151	0·96	1·00	—	1·22	—	0·61	3·00	—
1-Isopropylpiperidine	149	0·96	1·00	—	1·22	—	0·61	3·00	—
1-Butylpiperidine	175	1·77	1·62	—	2·33	—	1·04	5·40	—
1-Isobutylpiperidine	160	0·83	1·00	—	1·22	—	0·42	3·80	—
1-Amylpiperidine	198	3·26	2·75	1·00	4·33	1·00	1·81	9·40	1·00
1-Isoamylpiperidine	187	2·30	2·12	—	3·05	—	1·31	7·60	—
1-Cyclopentylpiperidine	210	—	6·38	2·18	—	2·25	5·11	14·80	1·60
1-Hexylpiperidine	218	6·10	4·62	1·64	8·32	1·62	3·15	16·80	1·60
1,2-Dipiperidinoethane	126—8/10	—	31·90	8·18	—	8·50	—	—	5·50
1,5-Dipiperidinopentane	106—8/0·4	—	—	26·70	—	28·50	—	—	19·60
Pyridine	115	2·27	2·0	—	2·72	—	2·85	1·20	—
V_g^0 of piperidine, ml		224	54	38[a]	156	31[a]	152	35	72[a]

[a] Determined for 1-amylpiperidine.

A difficult separation problem is 1-isopropylpiperidine which both on polar and unpolar stationary phases has identical elution volumes as 1-propylpiperidine. Only on a column 2·25 m long, containing 3·5% of polyethylene glycol 6000, at 90°C, a differentiation of these isomers took place. Their relative elution volumes are: piperidine 1·00, 1-propylpiperidine 1·20, 1-isopropylpiperidine 1·25.

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