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Note

Gas chromatography of alkyl halides on a silicone oil capillary column

D. R. HEPBURN and H. R. HUDSON

Department of Chemistry, The Polytechnic of North London, Holloway Road, London, N7 8DB (Great Britain)

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The complete and accurate analysis of alkyl halide isomers is of importance in the study of alkyl rearrangements which occur during the replacement of hydroxyl by halogen and in the development of improved procedures for alkyl halide preparation[1]. It is also important that commercially available alkyl halides should be checked for purity before use. Thus, of twenty-seven samples of secondary alkyl halides which we have recently obtained from six different suppliers, only two were found to contain more than 99% of the named isomer; twenty-one contained less than 90% and eight contained less than 70%. (See Results and discussion.) The present work demonstrates the high efficiency of a silicone oil-coated capillary column for the separation and identification of alkyl halide isomers and provides the first reported method for the separation of all eight pentyl isomers on a single column.

EXPERIMENTAL

Materials

Propyl, butyl, pentyl, and octyl halides were obtained or prepared as described[2–5]. Commercially available secondary pentyl, hexyl, heptyl, and octyl halides were obtained from six suppliers.

Apparatus

Analyses were carried out on a Perkin-Elmer Model F11 chromatograph fitted with a flame-ionization detector, a 50-m × 0.25-mm-I.D. stainless-steel wall-coated capillary column containing silicone fluid MS 550, and a No. 18 stream splitter. Column conditions are given in the tables.

RESULTS AND DISCUSSION

Complete analysis of the propyl, butyl, and pentyl isomers was possible on the silicone oil capillary column at 20°. Retention data are given in Table I and a typical chromatogram of the pentyl bromides is shown in Fig. 1. Halides were eluted in order of increasing boiling point, except that *tert.*-butyl chloride and *tert.*-butyl bromide had slightly lower retention times than did the lower-boiling *n*-propyl analogues. Previously, the propyl and butyl halides have been analyzed on squalane[6], dinonyl

TABLE I

RELATIVE RETENTION TIMES FOR THE ISOMERIC PROPYL, BUTYL, AND PENTYL HALIDES ON A SILICONE OIL CAPILLARY COLUMN*

Alkyl halide (RX)	*X = Cl*	*X = Br*	*X = I*
2-Halogenopropane	1.00	1.00	1.00
2-Halogeno-2-methylpropane	1.10	1.17	1.24
1-Halogenopropane	1.15	1.22	1.36
2-Halogenobutane	1.40	1.65	2.09
1-Halogeno-2-methylpropane	1.45	1.74	2.14
1-Halogenobutane	1.72	2.22	2.86
1-Halogeno-2,2-dimethylpropane	1.77	2.34	3.00
2-Halogeno-2-methylbutane	1.80	2.39	3.09
2-Halogeno-3-methylbutane	2.20	3.13	4.18
2-Halogenopentane	2.38	3.35	4.41
3-Halogenopentane	2.50	3.56	4.82
1-Halogeno-3-methylbutane	2.60	3.69	4.86
1-Halogeno-2-methylbutane	2.72	3.82	5.18
1-Halogenopentane	3.48	5.21	6.09

* All at 20°. Nitrogen inlet pressure (p.s.i.)/t_R (min) for first to elute: 4/20 (Cl); 10/11.5 (Br); 15/11 (I).

phthalate[7], or bis-(2-cyanoethyl) ether[4], but complete separation of the *sec.*-butyl and isobutyl halides was only possible on a 1/16-in.-O.D. packed squalane column[2]. Almost identical retention indices have been reported for *sec.*- and isobutyl iodides on tricresyl phosphate (TCP)[8]. Analysis of the eight pentyl isomers previously required two columns, one containing squalane and the other containing silicone oil modified by the addition of Bentone 34 (ref. 3). Retention data for up to seven of the pentyl isomers (chlorides, bromides, and iodides) on TCP, Apiezon L, and Carbowax 20M

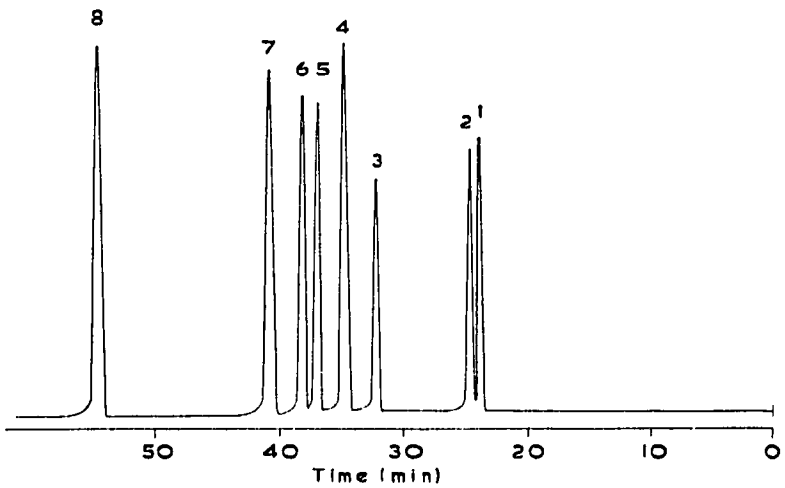

Fig. 1. Separation of isomeric pentyl bromides on a silicone oil capillary column (conditions as in Table I). 1 = 1-Bromo-2,2-dimethylpropane; 2 = 2-bromo-2-methylbutane; 3 = 2-bromo-3-methylbutane; 4 = 2-bromopentane; 5 = 3-bromopentane; 6 = 1-bromo-3-methylbutane; 7 = 1-bromo-2-methylbutane; 8 = 1-bromopentane.

TABLE II

RELATIVE RETENTION TIMES FOR THE STRAIGHT-CHAIN SECONDARY HEXYL, HEPTYL, AND OCTYL HALIDES ON A SILICONE OIL CAPILLARY COLUMN*

Alkyl halide (RX)	*X = Cl*	*X = Br*	*X = I*
3-Halogenohexane	1.00	1.00	—
2-Halogenohexane	1.02	1.03	—
4-Halogenoheptane	1.00	1.00	—
3-Halogenoheptane	1.08	1.09	—
2-Halogenoheptane	1.09	1.13	—
4-Halogeno-octane	1.00	1.00	1.00
3-Halogeno-octane	1.08	1.09	1.11
2-Halogeno-octane	1.11	1.15	1.16

* Column temperature (°C)/nitrogen inlet pressure (p.s.i.)/t_R (min) for first to elute: 20/20/20.2 (C_6 chlorides); 50/20/16.0 (C_6 bromides); 50/10/38.2 (C_7 chlorides); 55/15/31.6 (C_7 bromides); 60/15/32.7 (C_8 chlorides); 70/25/27.7 (C_8 bromides); 80/25/50.0 (C_8 iodides).

(refs. 8 and 9) indicate that some separations would be difficult, if not impossible, on these columns.

Other halides which are conveniently resolved on the silicone oil capillary column are the straight-chain secondary hexyl, heptyl, and octyl isomers. Results are given in Table II and the separation of the chloro-octanes is shown in Fig. 2.

In each series the first to elute was the halide having the halogen nearest to the centre of the chain, the retention times increasing in the order 4- < 3- < 2-halogenoalkane. This is the reverse of the order for the 2- and 3-halogenopentanes, of which the 2-isomer elutes first. Considerably better separations of the octyl isomers were achieved than had previously been possible on diethyl or di-*n*-butyl D-tartrate as stationary phases[4–6]. Analytical data for twenty-seven commercially available secondary alkyl halides are given in Table III.

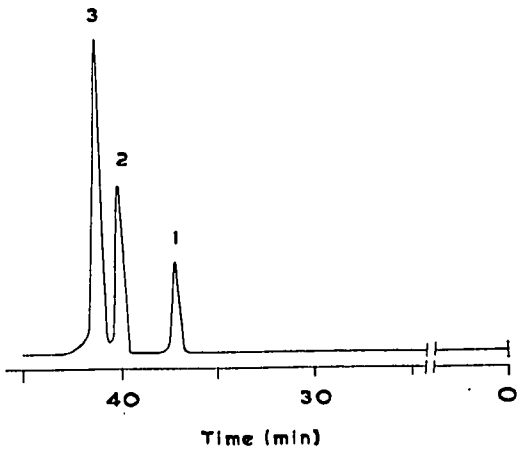

Fig. 2. Separation of straight-chain secondary octyl chlorides on a silicone oil capillary column (conditions as in Table II). 1 = 4-Chloro-octane; 2 = 3-chloro-octane; 3 = 2-chloro-octane.

TABLE III

ANALYTICAL DATA FOR COMMERCIALLY AVAILABLE SECONDARY ALKYL HALIDES

Alkyl halide	*Supplier*	*Isomeric composition (%)**			*Alkyl halide*	*Supplier*	*Isomeric composition (%)**		
		2-	*3-*	*4-*			*2-*	*3-*	*4-*
2-Chloropentane	A	92.0	5.5	—	3-bromoheptane	D	7.8	87.1	5.1
3-Chloropentane	A	5.2	91.1	—	4-bromoheptane	D	6.0	16.8	75.2
2-Bromopentane	B	77.7	22.3	—	2-chloro-octane	F	99.1	0.3	—
2-Bromopentane	C	74.9	25.1	—	2-chloro-octane	D	55.4	29.0	15.6
2-Bromopentane	D	69.9	30.1	—	3-chloro-octane	A	0.2	99.8	—
3-Bromopentane	D	23.8	71.9	—	2-bromo-octane	D	94.5	5.4	trace**
3-Bromopentane	E	29.5	70.5	—	2-bromo-octane	E	83.5	13.6	2.9
2-Iodopentane	D	68.0	32.0	—	2-bromo-octane	F	77.8	15.2	7.0
3-Iodopentane	A	21.9	78.1	—	3-bromo-octane	E	9.4	78.6	11.8
2-Chlorohexane	E	71.9	27.7	—	3-bromo-octane	A	19.7	66.0	19.7
3-Bromohexane	E	21.9	78.1	—	4-bromo-octane	E	trace**	6.6	92.7
3-Chloroheptane	E	19.4	68.1	12.5	4-bromo-octane	A	8.8	23.9	65.7
4-Chloroheptane	E	13.2	31.0	55.8	2-iodo-octane	F	62.4	24.3	13.3
2-Bromoheptane	D	85.5	13.7	0.8					

* Some olefin also present if total $<100\%$.
** $<0.1\%$.

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