

where T is the absolute temperature of the column. Values for constants A and B are shown in Table II.

A mixture of these hydrocarbons (a C_4 cut of pyrolysis product of a Romashkino naphtha) was analysed, and -40°C appeared to be the optimum temperature

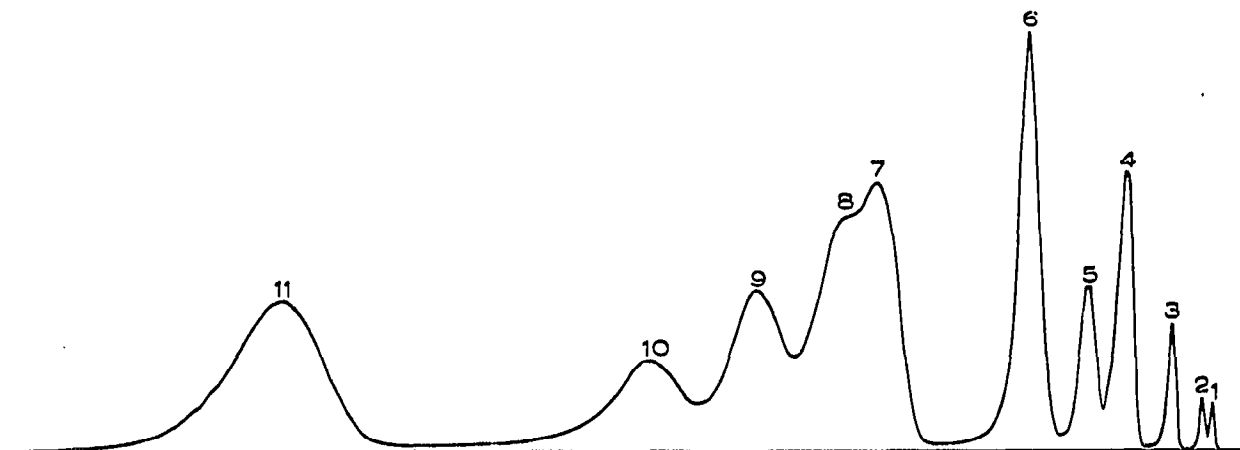


Fig. 1. Chromatogram of a mixture of hydrocarbons at -40°C . 1 = Air; 2 = ethane; 3 = propane; 4 = propylene; 5 = isobutane; 6 = *n*-butane; 7 = *n*-butene-1; 8 = isobutene; 9 = *trans*-butene-2; 10 = *cis*-butene-2; 11 = butadiene-1,3.

for gas chromatographic separation. Below this temperature further improvement in the resolution was hindered by broadening of the peaks. A typical chromatogram at -40°C is shown in Fig. 1. Even butene-1 and isobutene could be detected separately.

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Gas chromatography of isomeric butyl halides

Studies of alkyl rearrangements occurring during the preparation of alkyl halides have necessitated the development of methods for the analysis of mixtures of isomers¹. Alkyl halides are important starting materials in many organic syntheses, *e.g.* in the Wurtz and Grignard reactions, and methods for assessing their isomeric purity are therefore important. Whilst the *n*- and *tert.*-butyl halides were readily separated on a number of stationary phases, including squalane, dinonyl phthalate, and bis (2-cyanoethyl) ether, the *sec.*- and isobutyl halides had identical retention

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times under the conditions used and were distinguishable only by infrared analysis^{2,3}.

Resolution of all four isomers is now reported and their retention times relative to benzene are given.

Experimental

n-Butyl, *sec.*-butyl, and isobutyl halides were obtained commercially and distilled before use. *tert.*-Butyl halides were prepared from *tert.*-butyl alcohol and the concentrated hydrohalic acids at 20°, followed by washing, drying, and distillation. Structures of all compounds were confirmed by n.m.r. examination.

Gas chromatography was carried out on a Perkin-Elmer F.11 chromatograph with flame ionization detector.

The 4 m × 1/16 in. O.D. stainless steel column was packed with squalane (10%) on Chromosorb W. Analyses were performed with nitrogen carrier gas, an inlet pressure of 25 p.s.i. affording a flow rate of *ca.* 15 ml/min. Chlorides and bromides were analyzed at 20°, and iodides at 40°.

Results and discussion

Almost complete resolution of the *sec.*- and isobutyl halides was achieved with the above-mentioned conditions. Retention data are given in Table I.

TABLE I

RELATIVE RETENTION TIMES FOR BUTYL HALIDES (BENZENE = 1.00)

Alkyl group	Chlorides	Bromides	Iodides
<i>n</i> -Butyl (1-Butyl)	0.87	1.98	4.54
Isobutyl (2-Methylpropyl)	0.62	1.41	3.33
<i>sec.</i> -Butyl (1-Methylpropyl)	0.58	1.32	3.12
<i>tert.</i> -Butyl (1,1-Dimethylethyl)	0.30	0.68	1.64

The success of the method is attributed to the use of a narrow-bore column, as no resolution of the *sec.*- and isobutyl halides was obtainable with the same packing in a 1 m × 1/4 in. O.D. glass column.

Present work confirms earlier findings that *sec.*-butyl chloride (but no isobutyl chloride) is present in a number of commercial samples of *n*-butyl chloride, and in the reaction product from *n*-butyl alcohol and hydrogen chloride in the presence of zinc chloride. Commercial samples of all other butyl halides examined were free of isomeric impurities.

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