Relative Retention Times of C_2 to C_7 Saturated and Unsaturated Hydrocarbons and Their Use for the Determination of Boiling Point and Hydrocarbon Type

BENGT SMITH, RAGNAR OHLSON and GUNNAR LARSON

Institutionen för Organisk Kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

Relative retention times are given for 112 hydrocarbons in the C_2 to C_7 range on the following stationary phases: Squalane (Sq), tetraamylsilane (TAS), dioctyl phthalate (DOP), dimethylsulpholane (DMS), β,β'-oxydipropionitrile (ODP) and butylsulphidacetic acid (BSA). Relations between relative retention times on nonpolar columns and boiling points are also given and the determination of the hydrocarbon type on the basis of retention data on polar and nonpolar stationary phases is discussed.

In analytical investigations utilizing gas chromatography, the identification of components in mixtures is largely based on a comparison of relative retention data. With a knowledge of the relative retention values of actual compounds on a number of stationary phases, an unambiguous identification of a compound, responsible for a certain peak in a chromatogram, can often be made. It is therefore of great general interest to get relative retention times established and the present work is an attempt to improve the situation in this respect in the hydrocarbon field.

Although identification merely on the basis of relative retention values is a powerful tool in hydrocarbon research work increased support may be obtained if the relative retention values can be related to the boiling point and the type of compound. It is also the object of this investigation to develop methods for this purpose.

The immediate cause of the present investigation is a research project proceeding in this laboratory aimed at the separation of the benzene pre-run into its components. This fraction contains a large number of hydrocarbons, the analysis of which could only be accomplished by the application of gas chromatographic methods. For the identification of the separated hydrocarbons we needed the relative retention times of hydrocarbons in the C_2 to C_7 range. Although literature values are available for rather many hydro-

carbons in this field, it was felt that the existing material required confirmation and completion.

During the past years a number of stationary phases, among many proposed, has been given a dominating position as standard phases for the separation of hydrocarbons. Thus, among the nonpolar substrates squalane is now predominant. Phthalates are in common use as weakly polar stationary phases and, among the more polar substrates, dimethylsulpholane and β,β'-oxydipropionitrile are frequently employed. In addition, relative retention times were determined on some new substrates developed in this laboratory which were found useful for hydrocarbon separations. The results of the investigations are presented in Tables 1—6.

EXPERIMENTAL

Preparation of the hydrocarbons

Most of the hydrocarbons investigated were prepared in this laboratory. In the following, a brief account of the methods used in their synthesis will be given. The final distillation of the hydrocarbons prepared was, when necessary, made in an efficient still (Todd Scientific Co., Springfield, Pa. USA) having about 50 theoretical plates, and the fractions obtained were characterized by boiling point, density, refractive index, and, for unsaturated compounds, by bromine number.

Alkanes. Three methods were utilized for the synthesis of the alkanes. (1) Grignardation of an alkyl halide and hydrolysis of the Grignard compound to form a hydrocarbon. (2) Catalytic hydrogenation of alkenes, obtained as described below. (3) Reaction between a Grignard compound and a tertiary alkyl chloride in the presence of mercury chloride according to Edgar *et al.*[1] This method afforded alkanes having a quaternary carbon atom. The crude products were purified by shaking them with conc. sulphuric acid and refluxing them over metallic sodium.

Cycloalkanes were prepared (1) By Clemmensen reduction of cycloalkanones or (2) By treatment of dibromoalkanes with zinc powder in ethyl alcoholic solution.

Alkenes. (1) Lower alkenes were obtained from alcohols by dehydration using conc. sulphuric acid or alumina. (2) To get the C_5, C_6 and C_7 alkenes the appropriate alcohols were prepared. *Tert.*alcohols were dehydrated by distillation with iodine; *prim.* and *sec.* alcohols were first converted to the acetates which were then pyrolyzed according to Geldof and Wibaut[2]. (3) 1-Alkenes were also prepared from allylbromide and Grignard compounds. The crude products were refluxed over metallic sodium until no further change in the refractive index occurred.

Alkadienes. (1) Appropriate alkenols were prepared from Grignard compounds and unsaturated aldehydes or by addition of the sodium salt of an alkyne to a carbonyl compound. In the resulting alkynol, the carbon-carbon triple bond was reduced to a carbon-carbon double bond using palladium on calcium carbonate as a catalyst[3]. The alkenols were dehydrated either as such over alumina or they were converted to the acetates and pyrolyzed[2]. (2) The yields of 1,2-alkadienes from alkenols were low. A better method consisted of preparing the 1,2,3-tribromides from the alkenols. Dehydrobromination followed by debromination of the tribromides afforded the 1,2-alkadienes[4]. (3) Another route to the alkadienes started with an aldehyde which was first converted to a chloroacetal. On bromination an α-bromobromoacetal was obtained which was reacted with an alkenylmagnesiumbromide to a vicinal bromoethoxyalkene. Treatment of the latter with zinc afforded the alkadiene[5]. (4) In some instances alkadienes were prepared from glycols via their diacetates. The crude products were treated just like the alkenes.

Unsaturated cyclic hydrocarbons. Cycloalkenes were obtained from appropriate cycloalkanols by dehydration using phosphorus pentoxide, iodine or toluene sulphonic acid. Methylenecyclobutane was prepared by treatment of pentaerythritylbromide with zinc[6].

Of the cycloalkadienes, 1,3-cyclopentadiene was of commercial origin. 1,3-Cyclohexadiene was prepared by adding bromine to cyclohexene and dehydrobrominating the 1,2-

dibromocyclohexane using quinoline [7]. 1,4-Cyclohexadiene was obtained by partial reduction of benzene using sodium and ethyl alcohol in liquid ammonia and further purification of the resulting crude 1,4-cyclohexadiene via its tetrabromide [8]. The crude products were treated just like the alkenes.
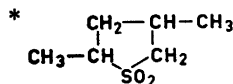
Stationary phases

Tetraamylsilane, $(n\text{-}C_5H_{11})_4Si$ (TAS). The preparation of tetraamylsilane was previously described [9].

Squalane, $C_{30}H_{62}$ (Sq), *dioctyl phthalate*, $C_6H_4(COOC_8H_{17}\text{-}n)_2$ (DOP) and *dimethylsulpholane* * (DMS) were of commercial origin.

β,β′-Oxydipropionitrile, $CNCH_2CH_2OCH_2CN_2CN$ (ODP) was prepared from acrylonitrile according to Bruson and Riener [10].

Butylsulphidacetic acid, $C_4H_9SCH_2COOH$ (BSA) was obtained from thioglycolic acid and isobutene. Thioglycolic acid (0.5 mole) was dissolved in an equal volume of benzene in a wash-bottle and isobutene bubbled through the solution until no further absorption of the latter compound took place. The benzene was distilled from the mixture and the residue fractionated in vacuum yielding about 60 % of butylsulphidacetic acid, b.p. $128-130°$ (10 mm), $n_D^{20} = 1.477$. The acid is believed to be an isobutylsulphidacetic acid since it has been shown that the addition of thioglycolic acid to alkenes in the presence of oxygen takes place against Markownikoff's rule [11].

$$* \quad \begin{array}{c} CH_2\!-\!CH\!-\!CH_3 \\ | \quad\quad | \\ CH_3\!-\!CH\quad\;\; CH_2 \\ \diagdown_{\displaystyle SO_2}\diagup \end{array}$$

Columns

The columns were made from aluminium tubing of 4 mm internal diameter. The stationary phase was applied in solution on to the solid support, using a suitable low-boiling solvent. The solvent was evaporated and the dry powder then evenly packed in the column.

Johns-Manville Chromosorb (30—60 mesh) was utilized as a solid support except in the case of butylsulphidacetic acid where Johns-Manville Chromosorb W (42—60 mesh) was used. The percentages of stationary phase, expressed as a percentage of the total weight of packing, were for squalane and tetraamylsilane 3 %, for dioctylphthalate 10 % and for dimethylsulpholane, β,β′-oxydipropionitrile and butylsulphidacetic acid 20 %.

Procedure

Relative retention times (R_T), using pentane as internal standard, were determined throughout. An appropriate number of hydrocarbons were mixed with pentane and the mixture run on 6 m columns (two 3 m columns in series) at 25°C. Helium was used as carrier gas and the flow rate adjusted to give suitable elution times on the various columns. The following flow rates were used: for the Sq, TAS, BSA and DMS columns 80 ml/min, for the DOP column 120 ml/min and for the ODP column 25 ml/min. For each compound the retention time counted from the air top was measured and the retention time relative to pentane calculated. The absolute retention times for pentane counted from the air top were: on TAS 6.2 min, on Sq 5.7 min, on DOP 8.5 min, on BSA 4.9 min, on DMS 4.2 min and on ODP 2.5 min.

Perkin-Elmer Vapour Fractometers, Models 154 and 116 E, were used. The results of the measurements have been collected in Tables 1—6.

RESULTS AND DISCUSSION

Comparison of the relative retention values with literature values. In addition to the values of the relative retention times measured in this laboratory, some values (within parantheses) obtained at other laboratories, using the same or similar stationary phases and conditions, are given in Tables 1—3 (Refs.[12-15]). It is of interest to compare the two sets of values since it gives an idea of the

Table 1. Relative retention times of alkanes at 25°C (pentane = 1.00).

Hydrocarbon	B.p. °C	TAS 3 %	Sq * 3 %	DOP ** 10 %	BSA 20 %	DMS 20 %	ODP * 20 %
C$_2$ Ethane	−88.6	0.036	0.030	0.027	0.010	0.051	0.065
C$_3$ Propane	−42.1	0.079	0.088	0.091	0.10	0.13	0.16
C$_4$ Butane	− 0.5	0.28	0.30	0.31	0.32	0.36	0.45
2-Methylpropane	−11.7	0.19	0.19	0.20	0.21	0.24	0.31
C$_5$ Pentane	36.1	1.00	1.00 (1.00)	1.00	1.00	1.00	1.00 (1.00)
2-Methylbutane	27.9	0.74	0.73	0.76	0.74	0.77	0.83 (0.81)
2,2-Dimethylpropane	9.5	0.36	0.36	0.34	0.36	0.36	0.39
C$_6$ Hexane	68.7	3.19	3.20 (3.20)	3.05 (3.10)	2.99	2.67	2.15 (2.12)
2-Methylpentane	60.3	2.27	2.26 (2.26)	2.14 (2.15)	2.14	1.93	1.68 (1.6)
3-Methylpentane	63.3	2.62	2.63 (2.62)	2.54 (2.60)	2.55	2.28	2.00 (1.98)
2,2-Dimethylbutane	49.7	1.55	1.53 (1.55)	1.46 (1.45)	1.46	1.36	1.33 (1.31)
2,3-Dimethylbutane	58.0	2.16	2.16 (2.11)	2.14 (2.10)	2.08	1.93	1.74 (1.76)
C$_7$ Heptane	98.4	10.2	10.0 (9.83)	9.28	7.68	7.07	5.08 (4.57)
2-Methylhexane	90.1	7.15	7.03 (6.84)	6.36	5.02	5.50	3.85 (3.40)
3-Methylhexane	91.9	7.74	7.65 (7.88)	7.15	5.71	5.50	4.25 (3.67)
2,2-Dimethylpentane	79.2	4.47	4.32 (4.27)	3.97	2.83	3.34	2.61 (2.48)
2,3-Dimethylpentane	89.8	7.15	7.03 (6.84)	6.64	5.49	5.50	4.25 (4.10)
2,4-Dimethylpentane	80.5	4.61	4.57 (4.51)	4.19	3.00	3.34	2.61 (2.48)
3,3-Dimethylpentane	86.1	6.08	6.07 (6.02)	5.71	4.51	4.89	3.81 (3.69)
2,2,3-Trimethylbutane	80.9	4.92	4.89	4.50	3.53	3.92	3.27
3-Ethylpentane	93.5	8.47	8.43 (8.55)	7.96	6.73	6.57	4.79 (4.47)

* Values within parentheses from Refs.[12],[13] Sq (3 %), ODP (40 %).
** Values within parentheses from Ref.[14] Stationary phase didecylphthalate (40 %), temperature 20°C.

Table 2. Relative retention times of cycloalkanes at 25°C (pentane = 1.00).

Hydrocarbon	B.p. °C	TAS 3 %	Sq * 3 %	DOP 10 %	BSA 20 %	DMS 20 %	ODP * 20 %
C$_4$ Cyclobutane	12.5	0.57	0.58	0.45	—	1.01	1.57
Methylcyclopropane	0.7	0.31	0.33	0.44	—	0.76	1.14
C$_5$ Cyclopentane	49.3	1.93	1.97 (1.96)	2.40	1.44	2.82	3.23 (3.34)
1,1-Dimethycylclopropane	20.6	0.61	0.62	0.73	—	1.02	1.38
1-*cis*-2-Dimethylcyclo-propane	37.0	1.17	1.24	1.42	1.60	2.10	2.43
1-*trans*-2-Dimethyl cyclopropane	28.2	0.80	0.83	0.93	1.01	1.23	1.32
Spiropentane	40.6	1.24	1.24	1.73	—	2.91	4.18
C$_6$ Cyclohexane	80.7	5.84	5.91 (5.80)	6.48	7.00	6.57	6.45 (6.69)
Methylcyclopentane	71.8	4.04	4.06 (4.07)	4.59	4.69	4.74	4.23 (4.48)
C$_7$ Cycloheptane	118.8	27.0		28.5	31.0	26.8	22.6
Methylcyclohexane	100.9	12.2	12.0 (11.8)	12.5	—	10.7	8.70 (9.01)

* Values within parentheses from Ref.[12]. Sq (3 %), ODP (40 %).

reproducibility of relative retention measurements from one laboratory to another.

As seen, the agreement is generally satisfactory. An exception is provided, however, by higher boiling alkanes and cycloalkanes on ODP (*cf.* Tables 1 and 2). The reason is believed to be the bad peak symmetry ("leading") often obtained for these compounds. "Leading" is a phenomenon which is fairly often encountered in gas chromatography, especially when the sample and stationary phase are of different types. It may be caused by a variation in the activity coefficient with the concentration of the sample, by slow evapora-tion of the sample or by a too low column temperature. It is difficult to decide about the reason in our case, but the temperature of the injection chamber was found to influence the retention values and the peak symmetry to a cer-tain extent. The fact that the literature values were obtained on a column containing 40 % of ODP (20 % in our case) might also be of some significance for the deviations obtained *.

The phthalate column used in this work contained dioctyl phthalate (10 %) as the stationary phase while the literature values were measured on a column containing didecyl phthalate (40 %) (*cf.* Tables 1 and 3). Further-more, the hexanes in Table 1 were studied at 20°C while our values were obtained

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* Concerning the influence of the amount of stationary phase on retention data *cf.* Ref.[16]

Table 3. Relative retention times of alkenes at 25°C (pentane = 1.00).

Hydrocarbon	B.p.°C	TAS 3 %	Sq 3 %	DOP* 10 %	BSA 20 %	DMS ** 20 %	ODP ** 20 %
C_2 Ethene	−103.7	0.03	0.03	—	0.03	0.13	0.44
C_3 Propene	−47.7	0.08	0.09	—	0.13	0.21	0.48
C_4 1-Butene	−6.3	0.24	0.28	0.31	0.40	0.58	1.05
cis-2-Butene	3.7	0.36	0.41	0.48	0.62	0.89	1.64
trans-2-Butene	0.9	0.31	0.36	0.43	0.52	0.75	1.33
Isobutene	−6.9	0.24	0.28	0.34	0.40	0.60	1.13
C_5 1-Pentene	30.0	0.81	0.87	1.00	1.16	1.51 (1.51)	1.91 (1.84)
cis-2-Pentene	36.9	1.06	1.20	1.33	1.59	2.04 (2.04)	2.64 (2.64)
trans-2-Pentene	36.4	1.00	1.13	1.26	1.46	1.88 (1.89)	2.25 (2.40)
2-Methyl-1-butene	31.2	0.87	1.00	1.11	1.33	1.88 (1.81)	2.25 (2.24)
3-Methyl-1-butene	20.1	0.56	0.60	0.68	0.78	1.00	1.38
2-Methyl-2-butene	38.6	1.15	1.34	1.48	1.80	2.38 (2.38)	2.98 (3.12)
C_6 1-Hexene	63.5	2.60	2.83	3.12 (3.10)	3.49	4.30 (4.11)	4.15 (4.09)
cis-2-Hexene	68.8	3.24	3.72	3.99 (3.95)	4.51	5.11 (4.60)	5.32 (4.47)
trans-2-Hexene	67.9	3.09	3.51	3.76 (3.60)	4.05	4.63 (5.20)	4.50 (5.41)
cis-3-Hexene	66.4	2.97	3.38	3.56 (3.50)	4.01	4.63 (4.60)	4.50 (4.70)
trans-3-Hexene	67.1	2.97	3.38	3.56 (3.45)	3.81	4.34 (4.34)	4.15 (4.09)
2-Methyl-1-pentene	60.7	2.51	2.83	3.12 (3.05)	3.50	4.06 (4.34)	4.50 (4.47)
3-Methyl-1-pentene	54.1	1.81	1.95	2.11 (2.05)	2.32	2.74 (2.83)	2.90 (2.88)
4-Methyl-1-pentene	53.9	1.81	1.95	2.11 (2.05)	2.33	2.74 (2.82)	2.90 (2.88)
2-Methyl-2-pentene	67.3	3.15	3.64	**3.76** (3.70)	4.37	5.11 (5.20)	5.08 (5.08)
3-Methyl-*cis*-2-pentene	67.6	3.24	3.75	3.90 (4.30)	4.51	5.50 (6.07)	5.71 (6.06)
3-Methyl-*trans*-2-pentene	70.5	3.61	4.23	4.30 (3.90)	5.02	5.96 (5.58)	6.04 (5.68)
4-Methyl-*cis*-2-pentene	56.3	1.98	2.27	2.37 (2.25)	2.61	3.08 (3.14)	2.98 (3.18)
4-Methyl-*trans*-2-pentene	58.6	2.09	2.27	2.37 (2.30)	2.68	2.97 (3.02)	2.98 (3.03)
2,3-Dimethyl-1-butene	55.7	1.98	2.27	2.37 (2.30)	2.67	3.30 (3.36)	3.62 (3.64)
3,3-Dimethyl-1-butene	41.2	1.15	1.20	1.26 (1.20)	—	1.70 (1.74)	1.91 (1.97)

Table 3. Continued

2,3-Dimethyl-2-butene	73.2	4.04	4.89	5.07 (5.05)	—	7.26 (7.32)	7.35 (7.35)
2-Ethyl-1-butene	64.7	2.97	3.34	3.56 (3.45)	4.03	4.80 (4.90)	5.08 (5.08)
C₇ 1-Heptene	93.6	8.18	9.08	9.49	10.1	10.6	9.20
cis-2-Heptene	98.5	10.8	11.2	12.0	12.6	13.4	11.1
trans-2-Heptene	98.0	10.4	10.7	11.2	11.6	12.4	9.73
cis-3-Heptene	95.8	9.45	9.51	9.85	10.7	11.3	9.73
trans-3-Heptene	95.7	9.45	9.51	9.85	10.0	10.4	8.24
2-Methyl-1-Hexene	92.0	7.74	8.70	8.52	9.90	10.7	9.70
2-Methyl-2-hexene	95.4	9.11	10.5	9.84	11.5	11.8	10.4
3-Methyl-cis-2-hexene	94.0	9.05	9.34	10.3	10.1	11.8	10.3
3-Methyl-trans-2-hexene	94.0	9.05	9.34	10.3	9.73	11.8	10.3
3-Methyl-cis-3-hexene	95.3	9.81	10.9	11.2	11.7	13.2	11.8
3-Methyl-trans-3-hexene	93.5	8.23	8.83	9.39	10.8	10.7	10.3
2,3-Dimethyl-1-pentene	84.3	5.67	6.18	6.42	—	7.43	6.97
2,4-Dimethyl-1-pentene	81.6	5.20	5.35	5.85	—	6.55	5.92
2,3-Dimethyl-2-pentene	97.4	9.95	11.9	11.9	—	14.3	12.4
2,4-Dimethyl-2-pentene	83.3	5.54	5.83	6.02	—	6.55	5.92
2,3,3-Trimethyl-1-butene	77.9	4.46	5.00	5.05	5.62	6.48	5.90
2-Ethyl-1-pentene	94.0	9.31	10.1	10.3	11.0	12.7	11.8
3-Ethyl-2-pentene	96.0	9.50	11.1	11.2	11.8	12.9	12.0

    * Values within parentheses from Ref.[14] Stationary phase didecyl phthalate (40 %).
   ** Values within parentheses from Ref.[15] DMS (20 %), ODP (40 %).

at 25°C. In view of these circumstances the agreement is surprisingly good. It may be concluded that the change of the alkyl group of the phthalate from octyl to decyl and the difference in the percentage stationary phase do not appreciably influence the relative retention data in this case, nor does a small change in temperature.

    In Table 3 there are two pairs of *cis-trans* isomers the members of which we believe have been confused by those who have studied them previously. The first pair is *cis-* and *trans*-2-hexene. Our values agree with those of Sullivan *et al.*[14] (DOP) but not with those of Knight [15] (DMS and ODP). It is evident that Knight has confused the two isomers. This is borne out by their retention

Table 4. Relative retention times of alkadienes at 25°C (pentane = 1.00).

Hydrocarbon	B.p. °C	TAS 3 %	Sq 3 %	DOP 10 %	BSA 20 %	DMS 20 %	ODP 20 %
C₄ 1,3-Butadiene	—4.4	0.26	0.30	0.45	0.62	1.32	2.58
C₅ 1,2-Pentadiene	44.9	1.38	1.51	2.19	—	5.00	6.20
1,cis-3-Pentadiene	44.1	1.31	1.56	2.33	3.07	5.90	8.95
1,trans-3-Pentadiene	42.0	1.20	1.41	2.12	2.67	5.30	7.48
1,4-Pentadiene	26.0	0.67	0.75	1.05	—	2.32	3.32
2-Methyl-1,3-butadiene	34.1	0.95	1.06	1.60	2.07	3.80	5.85
C₆ 1,2-Hexadiene	76	4.24	—	—	7.87	12.4	13.1
1,cis-3-Hexadiene	72.5	3.63	4.27	—	—	12.9	15.3
1,trans-3-Hexadiene	72.5	3.63	4.27	—	—	12.9	14.7
1,5-Hexadiene	59.5	2.18	2.52	—	3.93	6.28	7.80
cis-2-cis-4-Hexadiene	83	6.13	7.84	—	—	23.8	30.3
cis-2-trans-4-Hexadiene	81	5.70	7.00	—	—	22.0	27.0
rans-2-trans-4-Hexadiene	79	5.16	6.37	—	—	18.8	21.8
4-Methyl-1,3-pentadiene	76.3	4.27	—	—	—	16.7	20.1
C₇ 1,2-Heptadiene	105	14.1	14.7	20.1	23.2	31.9	28.0

Table 5. Relative retention times of cycloalkenes, cycloalkadienes and benzene at 25° (pentane = 1.00).

Hydrocarbon	B.p.°C	TAS 3 %	Sq 3 %	DOP 10 %	BSA 20 %	DMS 20 %	ODP 20 %
C₅ Cyclopentene	44.2	1.60	1.79	2.37	—	4.06	5.71
Methylenecyclobutane	42	1.48	1.63	2.11	—	3.88	5.42
C₆ Cyclohexene	83.0	6.33	7.30	8.77	11.0	13.5	16.5
1-Methylcyclopentene	75.8	4.80	5.57	6.49	—	9.85	11.0
C₅ Cyclo-1,3-pentadiene	42.5	1.21	1.47	2.46	3.59	7.79	14.2
C₆ Cyclo-1,3-hexadiene	81.5	5.60	6.50	9.80	—	23.4	35.3
Cyclo-1,4-hexadiene	88.5	8.20	9.90	14.6	21.0	35.7	52
Benzene	80.1	4.70	5.85	11.3	17.5	52	83

Table 6. Relative retention times of alkynes at 25°C (pentane = 1.00).

Hydrocarbon	B.p. °C	TAS 3 %	Sq 3 %	DOP 10 %	BSA 20 %	DMS 20 %	ODP 20 %
C_2 Ethyne	− 84 *	0.037	0.035	0.040	0.070	0.42	0.80
C_3 Propyne	− 23.2	0.11	0.18	0.22	−	1.47	3.65
C_4 1-Butyne	8.1	0.28	0.43	0.64	−	3.15	5.95
2-Butyne	27.0	0.71	1.09	1.45	−	5.65	12.0
C_5 1-Pentyne	40.2	0.96	1.35	2.02	2.98	8.05	11.5
2-Pentyne	56.1	1.86	3.05	3.67	2.94	11.2	18.3
C_6 1-Hexyne	71.3	3.31	4.39	6.62	8.52	22.0	26.1
2-Hexyne	84.5	6.50	7.98	−	−	25.7	34.4
3-Hexyne	81.4	4.90	6.15	8.51	12.6	18.6	24.9

* Sublimation point.

times on a silver nitrate/ethylene glycol column on which the compound, assigned as the *cis* isomer in this work, had a retention time nearly four times longer than the other isomer (*cf.* Ref.[17]). By freezing out the compounds in question from a boiling point column (*e.g.* TAS) which separates according to boiling point and re-running them on the DMS and ODP columns, it was also possible to prove that our values are the correct ones.

The other *cis-trans* pair, the retention values of which are confused in the literature, consists of *cis-* and *trans-*3-methyl-2-pentene. The reason for this is the fact that it has been believed until recently that the *cis* isomer was the higher boiling one. It has, however, been shown by Cornforth *et al.*[18] that the reverse is true. In this case the silver nitrate/ethylene glycol column is of no use since the two isomers do not separate on this stationary phase [17].

Relation between boiling point and relative retention times on TAS and Sq. In the separation of mixtures of hydrocarbons by gas chromatography and subsequent identification of the individual members, a knowledge of their boiling points is of great importance. In certain instances these can be obtained using a micro boiling point apparatus. This method necessitates, however, isolation of the compound, the boiling point of which is to be determined. It would be a distinct advantage if the boiling point could be derived directly from the retention data of the compound. Kováts[19] has given a relation between the so-called retention index on a nonpolar stationary phase and the boiling point of certain organic compounds, among them hydrocarbons, which is stated to permit the calculation of an approximate boiling point. No data showing the attainable accuracy have, however, been published. Another method has been developed here which, as will be shown below, in most in-

stances permits a rather accurate calculation of the boiling points of hydro-carbons from their relative retention times on nonpolar stationary phases.

When the logarithms of the relative retention times on TAS of the hydro-carbons studied here were plotted against their boiling points, points were obtained for the straight chain hydrocarbons which lay on a slightly curved line while, for the cyclic hydrocarbons, they fell on a straight line. The curved line could be approximated by two straight lines intersecting at a boiling point of about 50°C, corresponding to a relative retention time of about 1.5 (cf. Fig. 1). By calculating the equation of the three straight lines in Fig. 1, relations were obtained between the logarithms of the relative retention times and the boiling points of the hydrocarbons in Tables 1—6. For the data ob-tained on the Sq column, similar relations existed but in this case the spread of the points was greater and, accordingly, the accuracy of the calculated boiling points inferior (cf. Table 7). This is because TAS is a more nonselective stationary phase than Sq. Apart from a slight retardation of cyclic hydro-carbons in comparison with straight chain hydrocarbons in the same boiling range, it separates rather accurately according to boiling point *.

The three equations relating the boiling point ($B.p.$) to the logarithm of the relative retention time (R_T) are of the form

$$B.p. = k_1 \log R_T + k_2 \qquad (1)$$

In Table 7, the values of k_1 and k_2 calculated according to the method of least squares, using the data tabulated in Tables 1—6, are summarized. The

* An exception was constituted by low-boiling 1-alkynes which moved more rapidly than other hydrocarbons in the same boiling range.
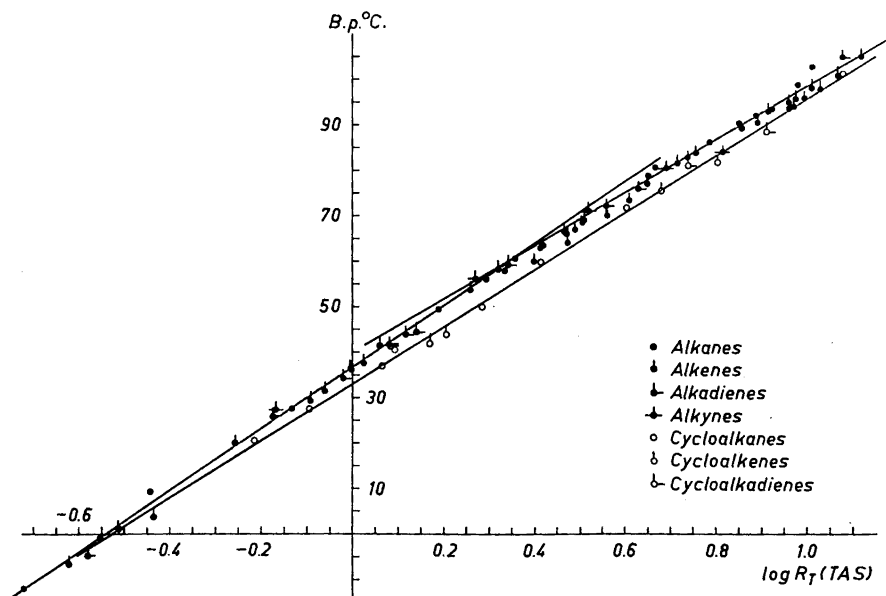

Fig. 1. Plot of boiling point against log relative retention time on TAS.

Table 7. Values of the constants in eqn. 1.

Co-lumn	Hydrocarbon group	Boiling range °C	Relative retention time range	k_1	k_2	Mean deviation °C of the calcul-ated b.p. from the observed
TAS	Low boiling straight chain hydrocarbons *	−10 to +50	0.2 − 1.55	67.7	36.2	± 0.6
	High-boiling straight chain hydrocarbons **	50 to 105	1.55 − 14.1	58.8	39.0	± 0.8
	Cyclic hydrocarbons	0 to 100	0.3 − 12.2	62.5	32.9	± 1.1
Sq	Low-boiling straight chain hydrocarbons *	−10 to +50	0.2 − 1.53	67.9	32.7	± 2.1
	High-boiling straight chain hydrocarbons **	50 to 105	1.53 − 14.7	61.1	34.8	± 2.0
	Cyclic hydrocarbons	0 to 100	0.3 − 12.0	60.9	31.9	± 2.1

* The data of 1-butyne and 1-pentyne were omitted in the calculation.
** The data of some C_8 hydrocarbons, not included in Tables 1 − 6, were also used in the calculation.

mean deviation of the calculated boiling points from the observed values for the three groups of hydrocarbons are also given.

For the calculation of boiling points from relative retention times, using eqn. 1, some knowledge of the hydrocarbon type is also necessary since different constants are used for straight chain and cyclic hydrocarbons. If the hydrocarbon, however, has a relative retention time below about 1.2, corresponding to a boiling point of about 35°C for a cyclic hydrocarbon, the equation for low-boiling straight chain hydrocarbons may be used also for the cyclic compounds with little sacrifice in accuracy. Thus, if the relative retention time is less than 1.2, the equation for low-boiling straight chain hydrocarbons may be applied in all cases. No knowledge of the hydrocarbon type is therefore necessary to calculate the boiling point from the relative retention time. If the relative retention time is more than 1.2, however, a decision has to be made as to the type of hydrocarbon. For this purpose a polar stationary phase must be employed (cf. p. 452). The boundary between the low-boiling and high-boiling straight chain hydrocarbons does not need to be drawn as sharply as in Table 7. It is of minor significance whether the equation for high-boiling straight chain hydrocarbons is applied for a hydrocarbon with a relative

retention time of 1.50 or whether the equation for low-boiling straight chain hydrocarbons is used when the relative retention time is 1.60.

Calculation of relative retention times. Eqn. 1 provides a means for obtaining the approximate relative retention times on TAS or Sq from the boiling points. For the 9 C_7 alkanes in Table 1, for example, the mean deviation between the calculated and observed values (TAS) was 4.0 % and for the 18 C_7 alkenes in Table 3 (TAS) 7.0 %. A better agreement between observed and calculated values for alkanes on TAS could be arrived at by assuming a linear relationship between boiling point and log relative retention time for alkanes of the same carbon number. By this method the relative retention times of the C_7 alkanes in Table 1 could be calculated with an average accuracy of 1.1 %. On squalane an approximate linear relationship of the same form existed for all the C_5 to C_7 alkanes making it possible to calculate the relative retention times of the 17 C_5 to C_7 alkanes in Table 1 with an average accuracy of 2.9 %. A linear relationship often exists between log relative retention time and boiling point within a homologous series. It might also be used for the calculation of retention data. The significance of these relationships between boiling point and relative retention time is that they open the possibility of calculating retention data for other alkanes than those studied in this work.

The linear relationship between log retention value and carbon number for homologous series of organic compounds, first pointed out by James and Martin [20] in their classical work from 1952, might also be used to get the retention data of hydrocarbons for various stationary phases outside the present range. However, since the C_5 hydrocarbons were often the first ones to obey the linear relationship *, the calculations would be based on the data of three, and very often only two, compounds. On this account we consider the available material too scanty to warrant a calculation of the equations of various homologous series at present. When relative retention times for the C_8 hydrocarbons become available, however, it will be possible to derive equations by which the retention data of higher boiling hydrocarbons can be calculated.

Determination of the hydrocarbon type. While the previously discussed columns, TAS and Sq, separate mainly according to boiling point, some of the polar columns used in this investigation sort out hydrocarbons in the same boiling range according to type. The separation factor (α) between two compounds chromatographed on a certain stationary phase is defined as the quotient of their relative retention times (R_{T_1} and R_{T_2}) (*cf.* Ref.[21])

$$\alpha = \frac{R_{T_1}}{R_{T_2}} = \frac{p_1{}^{\circ} \gamma_1{}^{\circ}}{p_2{}^{\circ} \gamma_2{}^{\circ}} \qquad (2)$$

where $p_1{}^{\circ}$ and $p_2{}^{\circ}$ = the vapour pressures of the pure compounds and $\gamma_1{}^{\circ}$ and $\gamma_2{}^{\circ}$ = the activity coefficients of the pure compounds in the stationary phase at infinite dilution.

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* A number of the first members in each series as a rule do not obey the linear relationship.

This equation shows that the separation of two compounds on a certain stationary phase is determined by the quotient of the products of the vapour pressures and the activity coefficients of the compounds in question. If the two compounds boil in the same narrow range ($p_1 \approx p_2$) it is evident that no separation or a poor one will be obtained if the activity coefficients of the two solutes in the stationary phase are of similar magnitude. This is generally the case with hydrocarbons (also for different types) in a nonpolar solvent like TAS and Sq. On this account, these stationary phases are not suitable for separating close-boiling hydrocarbons, as was pointed out previously.

For polar stationary phases, the situation is different. In this case, different types of hydrocarbons generally have different activity coefficients which means that a separation may be achieved of dissimilar compounds in the same boiling range. These facts are illustrated by the figures given in Table 8. In this table, the separation factors on the stationary phases used in this work for various close-boiling pairs of hydrocarbons are given. One of the members in each pair is an alkane, the other a cycloalkane or an unsaturated hydrocarbon. It is seen that: (a) In nonpolar stationary phases (TAS and Sq), the activity coefficients of different types of hydrocarbons are of the same

Table 8. Separation factors for various pairs of hydrocarbons on nonpolar and polar stationary phases.

| Pair of hydrocarbons *	Quotient between the relative retention times of the members in the pairs on various columns					
	TAS	Sq	DOP	BSA	DMS	ODP
Cyclohexane (80.7°) 2,4-Dimethylpentane (80.5°)	1.3	1.3	1.6	2.3	2.0	2.4
2,4-Dimethyl-1-pentene (81.6°) 2,4-Dimethylpentane (80.5°)	1.1	1.2	1.4	—	2.0	2.3
1-Methylcyclopentene (75.8°) 2,2-Dimethylpentane (79.2°)	1.1	1.3	1.6	—	2.9	4.2
1,5-Hexadiene (59.5°) 2,3-Dimethylpentane (58.0°)	1.0	1.2	—	1.9	3.3	4.5
3-Hexyne (81.4°) 2,4-Dimethylpentane (80.5°)	1.1	1.4	2.0	—	5.6	9.5
1,3-Cyclohexadiene (81.5°) 2,4-Dimethylpentane (80.5°)	1.2	1.4	2.3	—	7.0	13.5
1-Hexyne (71.5°) Hexane (68.7°)	1.0	1.4	2.2	2.9	8.2	12.1

* Boiling points within parentheses.
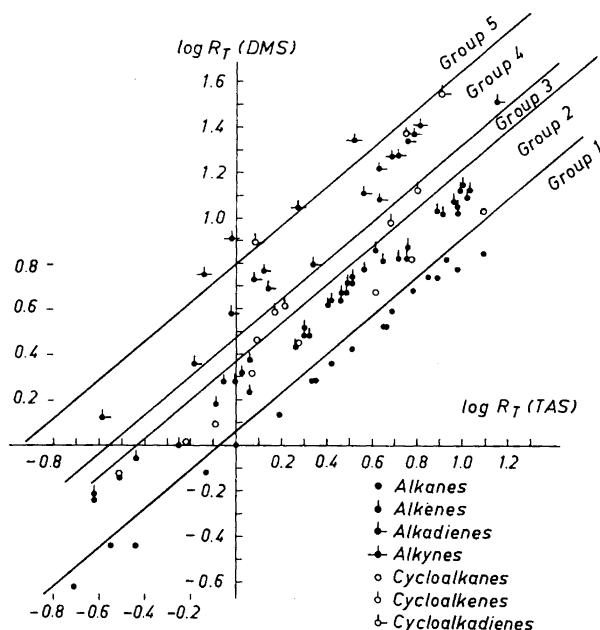
Fig. 2. Two column plot TAS—DMS.

magnitude. However, they are more alike in TAS, thus making this substrate, as was pointed out previously in this work, a more nonselective stationary phase than Sq. (*b*) For the four polar stationary phases, DOP, BSA, DMS, and ODP, the separation factors for an alkane and a hydrocarbon of another type in the same boiling range increase in the order mentioned, reflecting a corresponding increase in the difference between the activity coefficients of the alkanes and the other hydrocarbon types. (*c*) For the classes of hydrocarbons included in Table 8, the separation factors for an alkane and a hydrocarbon of another type in the same boiling range on the more polar stationary phases (DMS and ODP) increase in the order: cycloalkane and alkene— cycloalkene— alkadiene—3-alkyne—cycloalkadiene and 1-alkyne, due to a decrease in the activity coefficients of the cycloalkanes and unsaturated hydrocarbons in the same order.

Fig. 2 gives a clearer view of the separation achieved using the DMS column. The logarithms of the relative retention times on TAS of the C_4 to C_7 hydrocarbons investigated have been plotted against the logarithms of the relative retentions times of the same compounds on DMS. It is seen that the hydrocarbons are gathered together in the following groups: Alkanes (group 1) — alkenes and cycloalkanes (group 2) — cycloalkenes (group 3) — alkadienes,
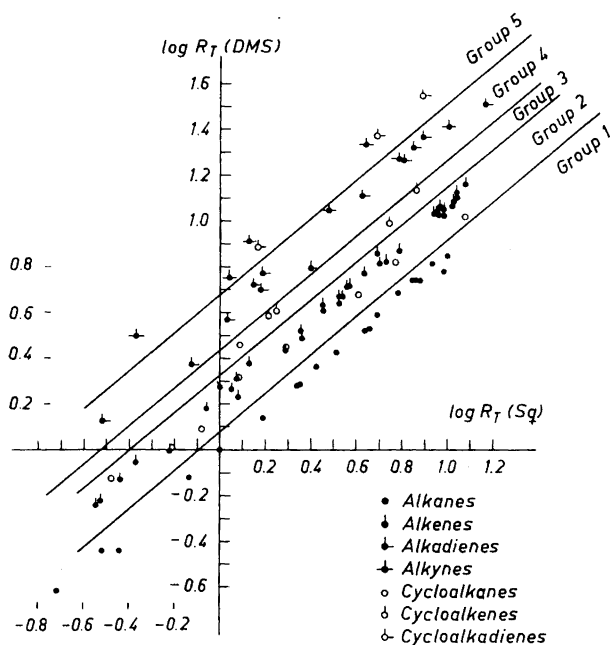
Fig. 3. Two column plot Sq—DMS.

cycloalkadienes and alkynes (group 4) — cycloalkadienes and alkynes *
(group 5). This fact offers a convenient method for determining the type of
hydrocarbon on the basis of Fig. 2 (*cf.* also Fig. 3).

From the retention values on Sq and DMS, a retention diagram similar
to that in Fig. 2 may be obtained (*cf.* Fig. 3). The main difference between the
two diagrams is that 1,3- and 1,4-cyclohexadiene are now found to belong to
group 5 instead of group 4 and 2-pentyne to group 4 instead of group 5. Thus,
group 4 in the Sq—DMS retention diagram is composed of alkynes and alka-
dienes and group 5 of alkynes and cycloalkadienes.

Since most of the groups in the retention diagrams contain more than one
class of hydrocarbons, an unambiguous determination of the hydrocarbon type
cannot generally be arrived at merely on the basis of the diagrams in Figs. 2
and 3. For this purpose, additional investigations must be made and hydrogena-
tion procedures adapted to this problem have been developed at this labora-
tory [22]. In the following, the steps involved in the determination of the hydro-
carbon type will be discussed in some detail.

(*a*) The hydrocarbon is run on the TAS or Sq column. (*b*) The hydrocarbon
is run on the DMS column. (*c*) The logarithms of the relative retention times

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* All 1-alkynes as well as benzene belong to group 5.

obtained are put into the TAS—DMS or Sq—DMS retention diagrams. (d) If the compound is found to belong to group 1, it is an alkane and no further investigation is necessary but, if it belongs to one of the groups 2 to 5, the type determination has to be continued. (e) A hydrocarbon belonging to group 2 may be an alkene or a cycloalkane. A decision between the two possibilities can be made on the basis of a chemical test for unsaturation. Alternatively, an application of the hydrogenation method previously referred to followed by a run of the hydrogenation product on the DMS column will give the required answer. It is not necessary to run the hydrogenation product on TAS or Sq since the only information wanted is whether a change in the relative retention time on DMS has taken place after the hydrogenation *. The possibility of utilizing a silver nitrate/ethylene glycol stationary phase for distinguishing between saturated and unsaturated hydrocarbons should also be borne in mind (cf. Ref.[17]). (f) Since an interference between cycloalkenes and bicyclic alkanes, e.g. spiropentane, might occur in group 3, it is recommended to treat the members of this group in the same way as the group 2 compounds. (g) For the group 4 compounds, the hydrogenation methods have to be used to decide about the type of hydrocarbon. In the TAS—DMS diagram the choice is between alkadienes, cycloalkadienes and alkynes and in the Sq—DMS diagram, between alkadienes and alkynes. By applying a hydrogenation method that will only transform alkynes, e.g. the sodium amide method (cf. Ref.[22]) and then running the hydrogenation product on DMS, information will be obtained about whether an alkyne is present or not. (h) If the compound is found not to be an alkyne, it is fully hydrogenated over platinum dioxide ** (cf. Ref.[22]) and the hydrogenation product run on the DMS column and then on the TAS or Sq columns. The logarithms of the relative retention times are put into the appropriate retention diagram. If the hydrogenation product belongs to group 1, it is an alkane and the original compound must have been an alkadiene — if it belongs to group 2, it is a cycloalkane and the original compound must have been a cycloalkadiene. (i) Group 5 is composed of cycloalkadienes and alkynes. Since all 1-alkynes have been found to belong to this group, a chemical test for this type of hydrocarbon might suffice to solve the identification problem. (j) If not, a full hydrogenation over platinum dioxide has to be performed and the position of the hydrogenation product in the retention diagrams determined in the usual manner ***.

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* However, for the identification of the actual compound and not only a determination of its type, the retention values of the hydrogenation product on TAS and Sq might be essential.

** In the Sq—DMS retention diagram, group 4 is composed of only alkadienes and alkynes. However, since the number of cycloalkadienes tested is rather small, it is possible that cycloalkadienes of other types than those investigated here might fall into this group. Because of this, a full hydrogenation is recommended also for group 4 compounds in the Sq—DMS retention diagram.

*** To assist in the identification of the actual compound in the case of alkadienes, cycloalkadienes and alkynes, methods for their partial hydrogenation have been developed (cf. Ref.[22]).

A method for the calculation of boiling points of hydrocarbons from their relative retention times on TAS and Sq has been described above (*cf.* p. 445). It was pointed out that, when the relative retention time was above 1.2, it was necessary to know whether the hydrocarbon was straight chain or cyclic since different equations were used for these two classes of hydrocarbons. This structural problem may be solved using gas chromatography and hydrogenation as outlined above. However, if only the boiling point is wanted the identification procedure may be simplified since the question is only whether the hydrocarbon is straight chain or cyclic.

Group 1 compounds are straight chain and group 3 compounds cyclic, and no further investigation is necessary. For group 2 compounds, a chemical test for unsaturation might be sufficient to determine whether the hydrocarbon is straight chain or cyclic or, otherwise, the compound is run on a silver nitrate/ethylene glycol column or hydrogenated. If a change in the relative retention time on DMS occurs after the hydrogenation, the hydrocarbon is straight chain — if not, it is cyclic. Group 4 compounds are fully hydrogenated over platinum dioxide and the position of the hydrogenation product in the retention diagrams is determined. A hydrocarbon in group 5 is treated in the same way if a chemical test for 1-alkynes is negative.

Sometimes, it might be difficult to determine, from the two-column plots in Figs. 2 and 3, the group to which a certain hydrocarbon belongs. In such a case, another method may be used. The equation for the straight border lines has the form

$$y = kx + l \tag{3}$$

Since the lines are parallel, all must have the same values for k but differ in the values for l. To determine the group for a hydrocarbon, y in the equation above is put equal to the logarithm of the relative retention time of the hydrocarbon on DMS and x put equal to the logarithm of the relative retention time on TAS or Sq; k is put equal to 0.850 (TAS) or 0.840 (Sq) and then the value of l is calculated. The value obtained for l is compared with the values in Table 9 and the group to which the hydrocarbon belongs is thus determined.

Table 9. Limit values of l in eqn. 3.

Group no.	TAS−DMS	Sq−DMS
1	$l < 0.060$	$l < 0.080$
2	$0.060 < l < 0.365$	$0.080 < l < 0.330$
3	$0.365 < l < 0.475$	$0.330 < l < 0.440$
4	$0.475 < l < 0.800$	$0.440 < l < 0.670$
5	$l > 0.800$	$l > 0.670$

In the foregoing, the use of the DMS column for the determination of the hydrocarbon type has been discussed in some detail. The more polar ODP column might be used for the same purpose. The boundaries between the vari-

ous groups in the retention diagrams are, however, more distinct in the case of DMS which fact has caused us to choose this stationary phase for the determination of hydrocarbon type.

Separation of mixtures of hydrocarbons. The separation of mixtures of hydrocarbons using the stationary phases investigated in this work may be accomplished in several ways. Eggertsen and Groennings [13] have discussed the separation and quantitative analysis of mixtures of C_5 to C_7 saturated hydrocarbons and Knight [15] the determination of C_5 and C_6 olefins using some of the present stationary phases. In both cases the analysis was based on a preliminary carbon number separation by which the mixtures were divided into groups of hydrocarbons having the same carbon number, *e.g.* C_5, C_6, and C_7. These groups were then subjected to regular gas chromatography. Another approach to the problem of separating mixtures of hydrocarbons in the C_2 to C_7 range will be described in a forthcoming paper.

Of the two new stationary phases (TAS and BSA) introduced in this work, TAS and its use for boiling point and type identification has been discussed previously. This stationary phase is also useful for regular gas chromatography of hydrocarbon mixtures, separating mainly according to boiling point. In this respect is it similar to Sq. The BSA stationary phase was developed to get a substrate intermediate in polarity between DOP and DMS. BSA has been found useful in certain instances where other stationary phases did not effect a separation. This was, for example, the case with the troublesome pair *cis*- and *trans*-3-methyl-2-hexene which was not resolved on any of the other columns used in this work and neither was it separated on a silver nitrate/ethylene glycol column (*cf.* Ref.[17]).

The present investigation has furnished retention data for hydrocarbons in the C_2 to C_7 field and demonstrated their utilization for identification purposes. We believe that the methods developed for this range of hydrocarbons could be applied also to higher boiling compounds when sufficient retention data become available.

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