

CHROM. 7166

## GAS CHROMATOGRAPHIC PROPERTIES OF TETRAFLUOROETHYLENE TELOMERS

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(Received October 8th, 1973)

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### SUMMARY

The paper describes an investigation of the gas chromatographic properties of tetrafluoroethylene telomers of general formula  $F(CF_2)_nI$ ,  $Br(CF_2)_nBr$ ,  $Br(CF_2)_nI$ ,  $I(CF_2)_nI$  and  $(CF_3)_2CF(CF_2)_nI$ . The telomers are well resolved on columns with squalene, silicone oil or tritolyl phosphate stationary phases, and relative retention volumes are given for these three columns. The temperature dependence of the relative retention volumes of  $F(CF_2)_nI$  and  $Br(CF_2)_nBr$  telomers has been investigated. The relative retention volumes are correlated with the telomer boiling points, and with structural features of the telomers.

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### INTRODUCTION

When an alkene is treated with a free radical initiator in the presence of sufficient polyhalomethane, a series of telomers is produced incorporating the polyhalomethane and various numbers of alkene units<sup>1,2</sup>. Some telomer mixtures have been separated by gas chromatography (GC)<sup>3,4</sup>, but generally other methods of separation such as gel permeation chromatography<sup>5,6</sup> have been preferred. Tetrafluoroethylene telomers are used commercially as surface-active agents, and are also useful in the synthesis of polymers with perfluoroalkyl side chains which show water and oil repellencies<sup>7</sup>. In this paper it is shown that tetrafluoroethylene telomers with polyhaloalkanes can be easily separated and identified under a variety of GC conditions. The relative retention volumes of the telomers are compared with other physical and structural properties of the molecules.

### EXPERIMENTAL

#### *Materials*

A mixture of telomers of general formula  $CF_3(CF_2CF_2)_nI$  was prepared by ultraviolet photolysis of  $CF_3I$  ( $1.03 \cdot 10^{-3} M$ ) (obtained from Bristol Organics, Bristol, Great Britain) with tetrafluoroethylene ( $1.05 \cdot 10^{-3} M$ ) (kindly donated by I.C.I., polymer division, Macclesfield, Great Britain) in a quartz cell for 45 min at 100°. A mixture of telomers of general formula  $CF_3CF_2(CF_2CF_2)_nI$  was prepared by ultraviolet photolysis of  $C_2F_5I$  ( $1.03 \cdot 10^{-3} M$ ) with tetrafluoroethylene

( $1.05 \cdot 10^{-3} M$ ) under similar reaction conditions. Together these two mixtures gave all the telomers of structure  $F(CF_2)_nI$  from  $n=1$  to  $n=15$ . A mixture of telomers of general formula  $Br(CF_2)_nBr$  was obtained by ultraviolet photolysis of  $CF_2Br_2$  ( $2 \cdot 10^{-3} M$ ) (Peninsular, Gainesville, Fla., U.S.A.) with tetrafluoroethylene ( $3.5 \cdot 10^{-3} M$ ) for 60 min at  $100^\circ$ . All the telomers from  $n=1$  to  $n=13$  were obtained in this way.  $CF_2BrI$  was synthesised by ultraviolet photolysis of  $CF_2Br_2$  (0.03 mol) with iodine (0.03 mol) for 10 h. The resulting mixture was filtered, distilled, and  $CF_2BrI$  separated by preparative GC on a Pye 105 instrument fitted with a 15 ft.  $\times$  3/8 in. glass column packed with 10% silicone oil (May & Baker, Dagenham, Great Britain) on 80–100 mesh Chromosorb G.  $CF_2BrI$  ( $3.2 \cdot 10^{-4} M$ ) was then photolysed with tetrafluoroethylene ( $2.6 \cdot 10^{-4} M$ ) for 45 min at  $100^\circ$ . This produced a mixture of telomers of formula  $Br(CF_2)_nI$  for  $n=1$  to  $n=8$  together with telomers of formula  $I(CF_2)_nI$  for  $n=2$  to 5. Telomers of structure  $(CF_3)_2CF(CF_2CF_2)_nI$  for  $n=0$  to 5 were obtained by ultraviolet photolysis of  $CF_3CFICF_3$  ( $1.03 \cdot 10^{-3} M$ ) (obtained from Bristol Organics) with tetrafluoroethylene ( $1.05 \cdot 10^{-3} M$ ) for 45 min at  $100^\circ$ .

Each telomer mixture was examined by coupled GC–MS using a 15 ft.  $\times$  3/8 in. column packed with 10% silicone oil on 80–100 mesh Chromosorb G in a Pye 104 chromatograph coupled via a single-stage Biemann separator to an AEI MS902C mass spectrometer. A mass spectrum was run on each compound as it emerged into the spectrometer source. Each telomer could thus be unambiguously identified and a definite structure could be assigned to each peak on the chromatogram.

### Method

Analytical data were obtained with a Griffin and George D6 chromatograph with the Martin G.D.B. detector. The D6 inlet system was replaced by a Pye injection head with inlet heater so that direct on-column injection was then possible with a micro-syringe. The oven was also replaced with one suitable for operating with coiled glass columns. Relative retention volumes ( $V_r'$ ) of the telomers were obtained on three different columns using *n*-hexane as internal standard and nitrogen as carrier gas. The first column consisted of a 7 ft.  $\times$  3/8 in. glass spiral packed with 5% w/w squalene on 80–100 mesh Chromosorb G having a resolution of about 350 theoretical plates based on the *n*-hexane standard. The second column was a 15 ft.  $\times$  3/8 in. glass spiral packed with 10% w/w Embaphase silicone oil on 80–100 mesh Chromosorb G having a resolution of about 1400 theoretical plates based on *n*-hexane. The third column was a 15 ft.  $\times$  3/8 in. glass spiral containing 15% w/w tritoyl phosphate on Chromosorb G, having a resolution of about 600 theoretical plates based on *n*-hexane.

## RESULTS AND DISCUSSION

Good separation of the  $F(CF_2)_nI$  telomers was achieved on all three columns, although lower temperatures were required for the analysis on squalene. The separation achieved on silicone oil is illustrated in Fig. 1 for the telomers from the  $CF_3I$ –tetrafluoroethylene mixture.

Relative retention volumes for the complete series of telomers on the three columns at  $120^\circ$  are given in Table I. The temperature dependence of the retention volumes was investigated for the

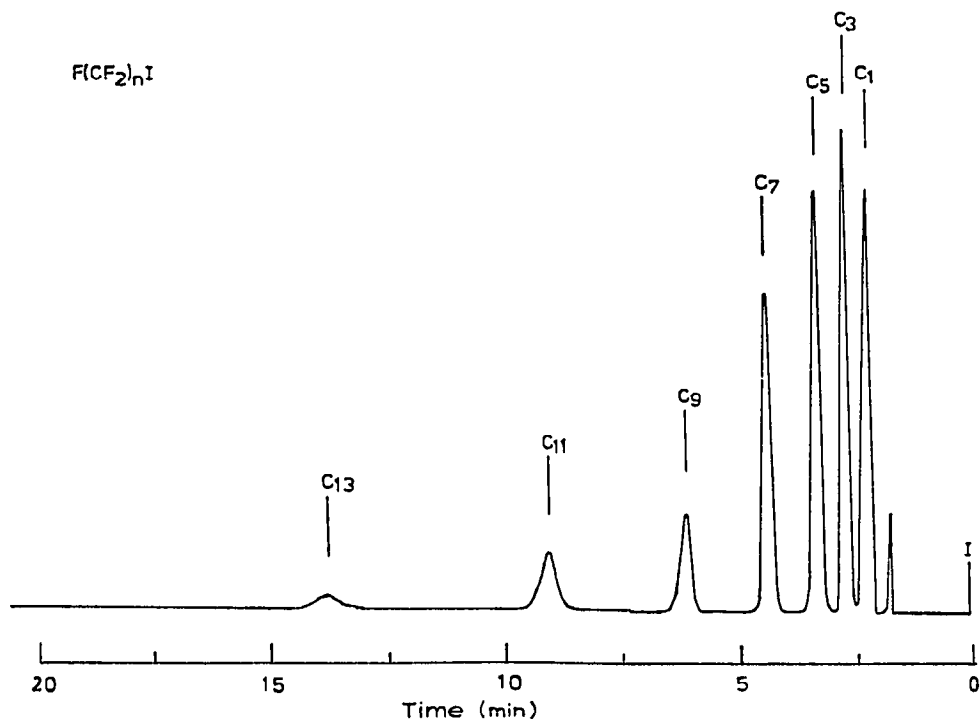


Fig. 1. Separation of telomers from the  $\text{CF}_3\text{I}$ -tetrafluoroethylene mixture on Embaphase silicone oil columns operated at  $140^\circ$  with a nitrogen flow-rate of 50 ml/min.

TABLE I

RELATIVE RETENTION VOLUMES FOR  $\text{F}(\text{CF}_2)_n\text{I}$  TELOMERS.

Columns operated at  $120^\circ$  with a nitrogen flow-rate of 50 ml/min. TTP=tritolyl phosphate.

Compound	B.p. ( $^\circ\text{C}$ ) at 760 torr*	$V_r'$			$\Delta H_s(\text{rel})^{**}$ (kJ/mol)
		Squalene 5%	Silicone oil 10%	TTP 15%	
$\text{FCF}_2\text{I}$	-22.5	0.11	0.15	0.32	-9.6
$\text{F}(\text{CF}_2)_2\text{I}$	13	0.18	0.22	0.39	-6.3
$\text{F}(\text{CF}_2)_3\text{I}$	49	0.28	0.38	0.55	-6.3
$\text{F}(\text{CF}_2)_4\text{I}$	68	0.36	0.52	0.69	-4.2
$\text{F}(\text{CF}_2)_5\text{I}$	95	0.54	0.76	0.80	-1.2
$\text{F}(\text{CF}_2)_6\text{I}$	117	0.75	1.02	0.97	0.0
$\text{F}(\text{CF}_2)_7\text{I}$	136	1.07	1.43	1.11	3.5
$\text{F}(\text{CF}_2)_8\text{I}$	160	1.43	1.94	1.39	5.6
$\text{F}(\text{CF}_2)_9\text{I}$	180	2.02	2.68	1.61	9.8
$\text{F}(\text{CF}_2)_{10}\text{I}$	197	2.77	3.65	2.00	12.8
$\text{F}(\text{CF}_2)_{11}\text{I}$	218	3.79	4.98	2.37	16.1
$\text{F}(\text{CF}_2)_{12}\text{I}$	228	5.30	6.88	3.01	18.4
$\text{F}(\text{CF}_2)_{13}\text{I}$	238	7.26	9.24	3.67	23.6
$\text{F}(\text{CF}_2)_{14}\text{I}$	253	10.09	12.80	4.57	27.8
$\text{F}(\text{CF}_2)_{15}\text{I}$	262	14.30	15.50	-	30.1

\* Values from ref. 8.

\*\* Values from temperature dependence experiments on silicone oil.

analysis on the silicone oil column. In the temperature range 100–140° a linear relationship of the form:  $\log V_r' = \Delta H_s(\text{rel})/2.3RT$ , where  $\Delta H_s(\text{rel})$  represents the difference in the enthalpies of solvation of the telomer and *n*-hexane, was found to be obeyed by each of the telomers. The results are plotted in Fig. 2 and the  $\Delta H_s(\text{rel})$  values are given in Table I. As expected the  $\Delta H_s(\text{rel})$  values show a steady increase as the telomer chain length increases.

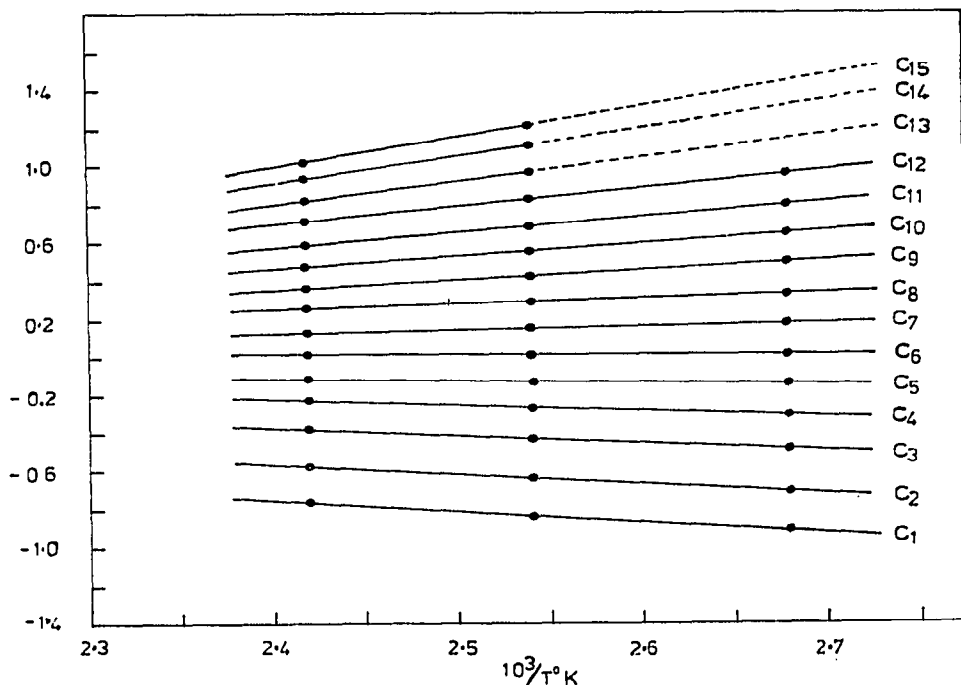


Fig. 2. Temperature dependence of retention volumes of the  $F(CF_2)_nI$  telomers on the 10% silicone oil column at a carrier flow-rate of 50 ml/min.

The telomers  $Br(CF_2)_nBr$  were also well separated on all three columns except for the  $C_1$  and  $C_2$  members, although these could also be resolved at lower temperatures. The relative retention volumes at 120° are given in Table II and the separation on silicone oil is illustrated in Fig. 3.

The temperature dependence of the relative retention volumes was investigated on the tritolyl phosphate column. Plots of the logarithm of the relative retention volumes of the telomers vs. reciprocal temperature (shown in Fig. 4) were found to be linear for the range 100–140° and the  $\Delta H_s$  values, which showed a steady increase with telomer chain length, are given in Table II.

The best separation of the  $Br(CF_2)_nI$  and  $I(CF_2)_nI$  telomers was achieved on the silicone oil column. The relative retention volumes at 120° on the three columns are given in Table III.

The telomers from perfluoroisopropyl iodide were analysed on the silicone oil column and the relative retention volumes are given in Table IV.

TABLE II  
RELATIVE RETENTION VOLUMES FOR  $\text{Br}(\text{CF}_2)_n\text{Br}$  TELOMERS  
Columns operated at  $120^\circ$  with a nitrogen flow-rate of 50 ml/min.

Compound	B.p. ( $^\circ\text{C}$ ) at 760 torr	$V_r'$			$\Delta H_s(\text{rel})^*$ (kJ/mol)
		Squalene 5%	Silicone oil 10%	TTP 15%	
$\text{BrCF}_2\text{Br}$	24.5	0.31	0.44	0.87	-0.90
$\text{Br}(\text{CF}_2)_2\text{Br}$	47.6	0.54	0.65	—	—
$\text{Br}(\text{CF}_2)_3\text{Br}$	74.2**	0.76	0.95	1.31	3.1
$\text{Br}(\text{CF}_2)_4\text{Br}$	97***	1.07	1.33	1.64	5.9
$\text{Br}(\text{CF}_2)_5\text{Br}$		1.44	1.84	1.99	9.1
$\text{Br}(\text{CF}_2)_6\text{Br}$	147***	2.00	2.56	2.36	10.1
$\text{Br}(\text{CF}_2)_7\text{Br}$		2.73	3.48	2.79	12.0
$\text{Br}(\text{CF}_2)_8\text{Br}$	182***	3.78	4.74	3.28	14.2
$\text{Br}(\text{CF}_2)_9\text{Br}$		5.16	6.48	3.88	16.9
$\text{Br}(\text{CF}_2)_{10}\text{Br}$	219***	7.09	8.86	4.58	19.0
$\text{Br}(\text{CF}_2)_{11}\text{Br}$		9.76	12.08	5.46	21.7
$\text{Br}(\text{CF}_2)_{12}\text{Br}$	267***	13.37	16.5	6.56	24.2
$\text{Br}(\text{CF}_2)_{13}\text{Br}$		18.2	22.3	7.95	27.6
$\text{Br}(\text{CF}_2)_{14}\text{Br}$	318***	25.5	—	—	—

\* Relative enthalpies of solution on the TTP column.

\*\* Value from ref. 9.

\*\*\* Values from ref. 10.

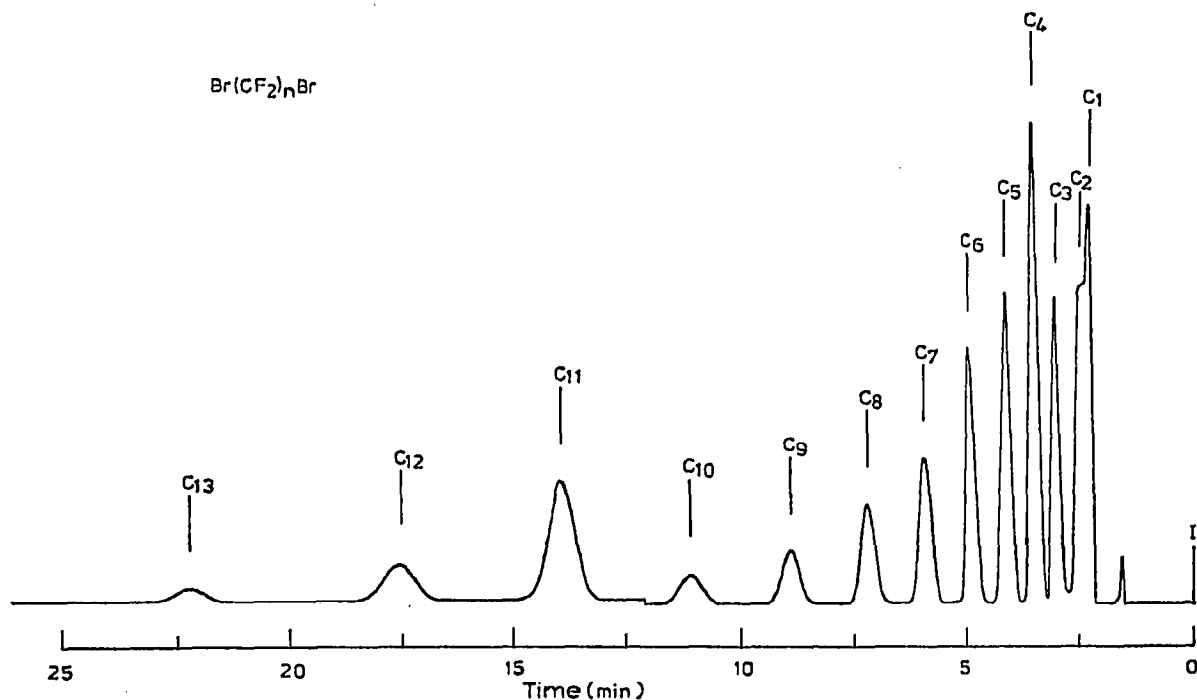


Fig. 3. Chromatogram of the telomers from the  $\text{CF}_2\text{Br}_2$ -tetrafluoroethylene mixture on the silicone oil column operated at  $140^\circ$  with a carrier gas flow-rate of 50 ml/min.

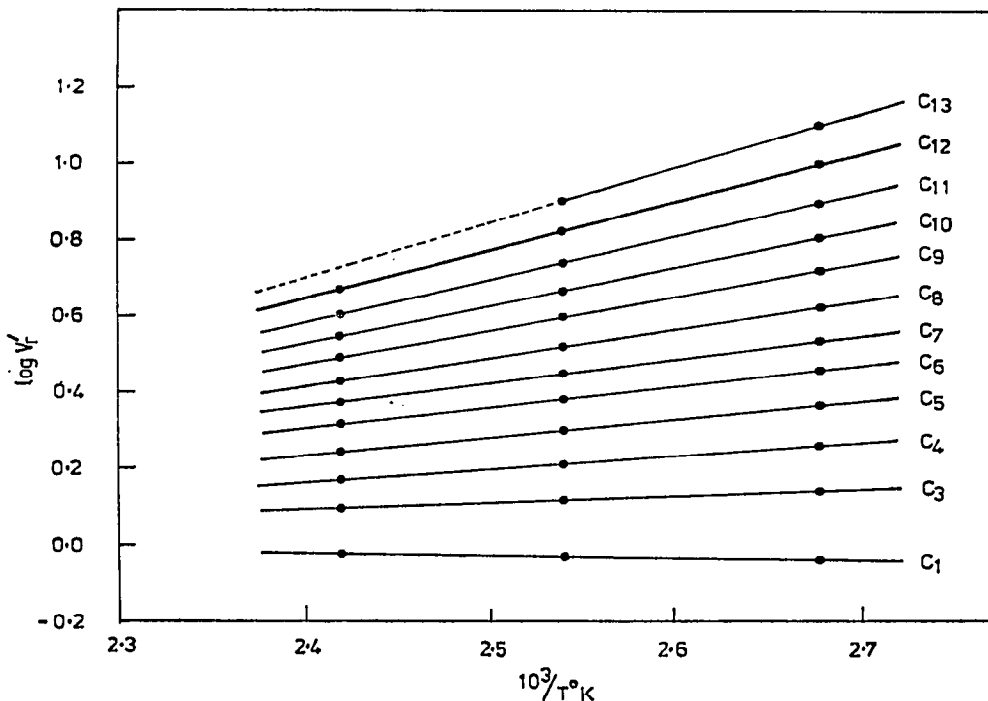


Fig. 4. Temperature dependence of the relative retention volumes of the  $\text{Br}(\text{CF}_2)_n\text{Br}$  telomers on the 15% tritolyol phosphate column at a carrier gas flow-rate of 50 ml/min.

TABLE III

RELATIVE RETENTION VOLUMES FOR  $\text{Br}(\text{CF}_2)_n\text{I}$  AND  $\text{I}(\text{CF}_2)_n\text{I}$  TELOMERS

Columns operated at 120°, nitrogen flow-rate 80 ml/min.

Compound	B.p. (°C) at 760 torr	$V_r'$		
		Squalene 5%	Silicone oil 10%	TTP 15%
$\text{BrCF}_2\text{I}$	(63)	1.00	1.43	4.43
$\text{Br}(\text{CF}_2)_2\text{I}$	81	1.20	1.79	4.83
$\text{Br}(\text{CF}_2)_3\text{I}$	(105)	1.73	2.48	6.27
$\text{Br}(\text{CF}_2)_4\text{I}$	(127)	2.52	3.45	7.77
$\text{Br}(\text{CF}_2)_5\text{I}$	(148)	3.50	4.75	9.52
$\text{Br}(\text{CF}_2)_6\text{I}$	(169)	4.77	6.47	11.45
$\text{Br}(\text{CF}_2)_7\text{I}$	(189)	6.59	8.81	13.65
$\text{Br}(\text{CF}_2)_8\text{I}$	(208)	9.02	11.79	—
$\text{I}(\text{CF}_2)_2\text{I}$	113	2.50	4.17	15.2
$\text{I}(\text{CF}_2)_3\text{I}$	131	4.20	5.93	24.9
$\text{I}(\text{CF}_2)_4\text{I}$	152	5.86	8.08	41.7
$\text{I}(\text{CF}_2)_5\text{I}$	171	8.09	11.10	—

\* Values in parentheses estimated as described in the text.

\*\* Nitrogen flow-rate 50 ml/min.

TABLE IV

RELATIVE RETENTION VOLUMES FOR  $(CF_3)_2CF(CF_2)_nI$  TELOMERSColumn operated at  $120^\circ$  with a carrier gas flow-rate of 50 ml/min.

Compound	B.p. ( $^\circ C$ ) at 760 torr*	$V_r'$
		Silicone oil 10%
$(CF_3)_2CFI$	40	0.36
$(CF_3)_2CF(CF_2)_2I$	90	0.84
$(CF_3)_2CF(CF_2)_4I$	139	1.51
$(CF_3)_2CF(CF_2)_6I$	190	2.84
$(CF_3)_2CF(CF_2)_8I$		5.36
$(CF_3)_2CF(CF_2)_{10}I$		10.40

\* Values from ref. 11.

A plot of  $\log V_r'$  against boiling point at atmospheric pressure is shown in Fig. 5 for the data on silicone oil. The boiling points of the  $I(CF_2)_nBr$  telomers are unknown, as are those of most of the telomers  $Br(CF_2)_nBr$  with  $n$  odd, and these are therefore not included in the plot. Examination of Fig. 5 shows that a series of roughly parallel straight lines is generated. The exception to this is the line for  $F(CF_2)_nI$  which shows curvature for the telomers having  $n \geq 11$ . Two explanations might be offered to account for this curvature: (i) the curvature indicates that some specific interaction between the longer telomers and the

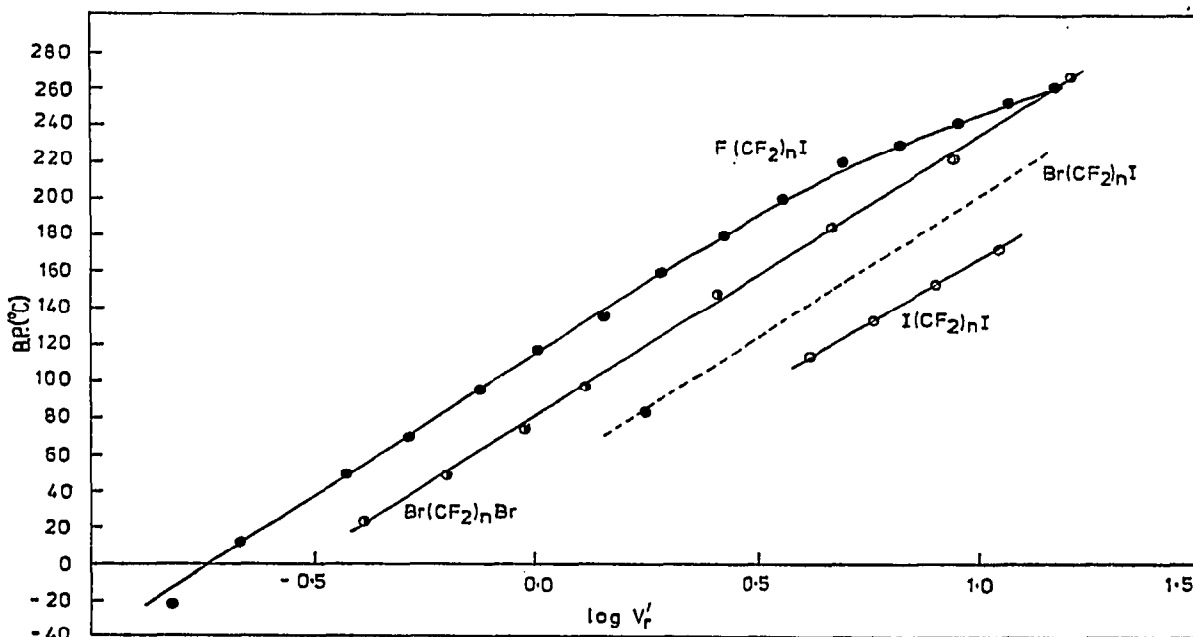


Fig. 5. Correlation of the relative retention volumes  $V_r'$  on silicone oil with boiling points at atmospheric pressure. Dashed line estimated correlation for  $Br(CF_2)_nI$  telomers.

stationary phase comes into play, (ii) the boiling points of the longer telomers are in error. Explanation (i) seems unlikely because the longer telomers in the  $\text{Br}(\text{CF}_2)_n\text{Br}$  group do not show any similar effect. An equivalent plot of the retention volume data from the tritolyol phosphate column showed essentially the same pattern: straight lines for the  $\text{Br}(\text{CF}_2)_n\text{Br}$  and  $\text{I}(\text{CF}_2)_n\text{I}$  data and a similar amount of curvature in the  $\text{F}(\text{CF}_2)_n\text{I}$  plot. Had specific interactions been important, much more extensive curvature of the plots would have been expected on the more polar tritolyol phosphate column. The higher  $\text{F}(\text{CF}_2)_n\text{I}$  telomers are solids at room temperature and atmospheric pressure, and the boiling points were reported at very low pressures as boiling ranges of fractions containing mainly the stated telomers<sup>8</sup>. A long extrapolation was required to obtain the boiling points given in Table I, for which the middle of the reported boiling range was used. In view of this it is probably correct to assign the curvature to inaccurate boiling point data. Better boiling points can be obtained for the  $\text{F}(\text{CF}_2)_n\text{I}$  telomers with  $n \geq 11$  by extrapolation of the straight-line portion of the plot. Boiling points can also be obtained with reasonable accuracy for the  $\text{Br}(\text{CF}_2)_n\text{Br}$  telomers having  $n$  odd by use of the straight line generated from the telomers with known boiling points. The boiling point of  $\text{BrCF}_2\text{CF}_2\text{I}$  is known, so that a rough estimate of the boiling points of the other  $\text{Br}(\text{CF}_2)_n\text{I}$  telomers may be obtained from the straight line drawn through this point parallel to the other telomer lines (shown dotted in Fig. 5). Boiling points estimated in this way are given in parentheses in Table III.

The correlation of the logarithm of the relative retention volumes with the number of carbon atoms in each telomer is shown for the silicone oil data in Fig. 6. It is interesting to note that these fully halogenated compounds give a straight-line correlation, similar to those which have been observed for homologous series of compounds with alkyl chains. The telomers  $\text{I}(\text{CF}_2)_n\text{I}$ ,  $\text{I}(\text{CF}_2)_n\text{Br}$ ,  $\text{Br}(\text{CF}_2)_n\text{Br}$  and  $\text{F}(\text{CF}_2)_n\text{I}$  form a family of parallel lines having intercepts at  $n=0$  which differ by an almost constant increment. The telomers  $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_n\text{I}$ , which have a branched end group, also give a straight line correlation with  $n$ , but the gradient of the line is different from that of the other telomers. Similar effects due to branching have been observed with other haloalkanes<sup>12</sup>. The departure from linearity exhibited by the lowest members of the  $\text{F}(\text{CF}_2)_n\text{I}$  and  $\text{Br}(\text{CF}_2)_n\text{Br}$  groups (lines C and D in Fig. 6) is probably due to the finite size of the injection which could cause distortion for compounds with such small retention times.

The correlation of the  $\log V_r'$  values from the squalene column with  $n$  also generates a family of straight lines having the same gradient and with intercepts differing by a constant increment. For the  $\log V_r'$  values on the more polar tritolyol phosphate column the correlation with carbon number is linear, but each set of telomers lies on an individual straight line and there is no simple relationship between their gradients or intercepts.

A simple empirical relationship can be constructed for the results on silicone oil for predicting the relative retention volume of any 1, $n$ -dihaloperfluoro- $n$ -alkane. If the number of carbon atoms is  $n$ , and the terminal halogen atoms are assigned a number  $m$  corresponding to their period in the periodic table (*i.e.*  $\text{F}=1$ ,  $\text{Br}=3$ ,  $\text{I}=4$ ), then the relative retention volume is given by

$$\log V_r' (n, m_1, m_2) = 0.136n + 0.360 - [8 - (m_1 + m_2)] 0.390$$



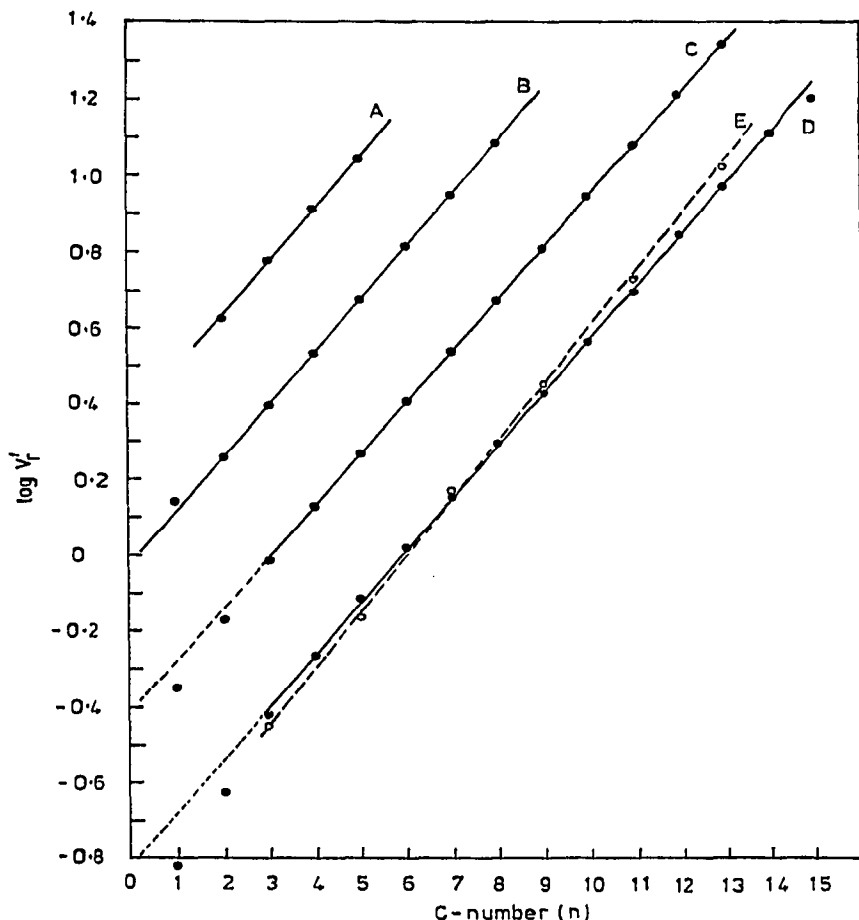


Fig. 6. Correlation of the logarithm of the relative retention volumes on silicone oil ( $V_r'$ ) with the number of carbon atoms in the telomer chain ( $n$ ). A =  $I(CF_2)_nI$  telomers; B =  $I(CF_2)_nBr$  telomers; C =  $Br(CF_2)_nBr$  telomers; D =  $F(CF_2)_nI$  telomers; E =  $(CF_3)_2CF(CF_2)_xI$  telomers ( $n = 3 + x$ ).

where  $m_1$  and  $m_2$  are the periodic numbers corresponding to the two terminal halogen atoms. This expression is capable of reproducing the experimental values of the silicone oil retention volume data for all the 1, $n$ -dihalo-perfluoro- $n$ -alkanes to within  $\pm 3\%$ . It might be expected that this expression would also apply to chlorine-containing telomers. The calculated relative retention volume at  $120^\circ$  on silicone oil for  $Br(CF_2)_2Cl$  ( $n = 2$ ,  $m_1 = 3$ ,  $m_2 = 2$ ) is 0.29 which is in poor agreement with the experimental value of 0.34. Similarly the calculated value for  $Cl(CF_2)_2Cl$ , *i.e.* 0.12, does not agree very well with the experimental value of 0.16. These results suggest that the expression cannot be generalised to include chlorine-containing telomers.

## REFERENCES

- 1 F. R. Mayo, *J. Amer. Chem. Soc.*, 70 (1948) 3689.
- 2 F. M. Lewis and F. R. Mayo, *J. Amer. Chem. Soc.*, 76 (1954) 457.
- 3 C. David and P. A. Gosselain, *Tetrahedron*, 18 (1962) 639.
- 4 Y. Ono and Hiroshi Ubihashi, *Rep. Res. Lab., Asahi Glass Co., Ltd.*, 20 (1970) 55.
- 5 C. A. Barson, R. R. Mather and J. C. Robb, *Trans. Faraday Soc.*, 66 (1970) 2585.
- 6 C. A. Barson, A. R. Luxton and J. C. Robb, *J. Chem. Soc. Faraday I*, 68 (1972) 1666.
- 7 J. H. Simons, in J. H. Simons (Editor), *Fluorine Chemistry*, Vol. 5, Academic Press, New York, 1964.
- 8 R. N. Haszeldine, *J. Chem. Soc. (London)*, (1953) 3559, 3761.
- 9 M. Hauptschein, C. S. Stokes and A. V. Grosse, *J. Amer. Chem. Soc.*, 74 (1952) 848.
- 10 K. C. Smeltz, *U.S. Pat.*, 3,055,953, Sept. 25, 1962.
- 11 R. D. Chambers, J. Hutchinson, R. H. Mobbs and W. K. R. Musgrave, *Tetrahedron*, 20 (1964) 497.
- 12 G. Castello and G. D'Amato, *J. Chromatogr.*, 76 (1973) 293.