Journal of Fluorine Chemistry, 8 (1976) 93–94

Received: November 29, 1975

SHORT COMMUNICATION

THE BOILING POINTS OF PERFLUOROPARAFFINS

A.H.W. ATEN, Jr.*

Subfaculty for Chemistry University of Amsterdam, The Netherlands

Many years ago the author published a discussion [1,2] of a rule for the boiling points of normal paraffin-chain compounds, which had originally been stated by Boggia-Lera [2]. The calculated boiling-point in degrees Kelvin is given by the expression:

$$T_c = (n.D + B)^{\frac{1}{2}} \qquad (1)$$

For all paraffin chains D has the same value D = 20500. For paraffin molecules which carry a substituent at one or both ends, or in the centre, of the chain a suitable value of B will give the correct boiling-points. For mono- and distributed chains the values of B are approximately additive.

It was also shown that in many cases agreement was not as good for the first few members of a series as for the heavier molecules.

There was not in the discussion any argument why a rule of this type should only be valid for hydrocarbon chains, but at that time suitable data were available only for chain molecules consisting of CH_2-groups. However, the fact that at present a number of boiling points are available for perfluoroparaffins, suggests the possibility of applying eq. (1) to this class of compounds. Table I shows that with D = 17000 the boiling points are represented with very reasonable accuracy.

In our earlier publication it was pointed out that eq. (1) is also valid for cycloparaffins, but with a value of

*correspondence: Instituut voor Kernphysisch Onderzoek Oosterringdijk 18a, Amsterdam/The Netherlands

D = 24300. It is seen from Table II that for perfluoro-cycloparaffins the same value of D holds as for straight chains. This is not surprising if one considers that the boiling point of a straight perfluoro-paraffin and that of the corresponding cyclo-compound are almost equal. If one wishes to speculate on the reason for this difference it may be pointed out that in the perfluorocompounds the carbon atoms are covered by fluorine atoms, whereas in an ordinary paraffin chain the hydrogen atoms are more or less imbedded in the carbon atoms. Thus the properties of the latter type of compounds would be likely to be much more affected by the difference in configuration of the carbon chain between straight and cyclo-compounds, than would be the case for fluorinated chains.

Calculated and observed boiling-points

TABLE I: for perfluoro-paraffins and mono-derivatives

$F(CF_2)_n F$ $\quad T^2 = n \times 17{,}000 + 5{,}500$

n	T_c	T_{ex}	n	T_c	T_{ex}
1	150	145	6	328	330
2	199	195	7	353	355
3	238	235	8	376	377
4	271	272	9	398	398
5	301	302	10	419	417

$F(CF_2)_n CF = CF_2$ $\quad T^2 = n \times 17{,}000 + 41{,}000$

$F(CF_2)_n C_6F_{11}$ $\quad T^2 = n \times 17{,}000 + 106{,}500$

n	T_c	T_{ex}	n	T_c	T_{ex}
1	241	244	1	351	349
2	274	274	2	375	374,5
3	303	303	3	397	397
4			4	418	418

TABLE II: for perfluoro-cyclo-paraffins

Cyclo - $(CF_2)_n$ $\quad T^2 = n \times 17{,}000 + 3{,}500$

n	T_c	T_{ex}
4	267	268
5	297.5	295
6	325	326

1 A.H.W. Aten Jr., J. Chem. Physics 5 (1937) 260, 264

2 E. Boggia-Lera, Gazz. Chim. Ital. 29 (1899) 1, 411