RADIOLYSIS PRODUCTS AS REFERENCE SUBSTANCES
IN GAS CHROMATOGRAPHY

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SUMMARY

The possibility of using the many branched hydrocarbons, which are formed by radiolysis of an alkane, as reference substances in qualitative gas chromatographic analyses is suggested. The radiolysis spectra of n-alkanes are discussed in general with the aim of showing the rules for rapid and easy identification of the various products. The heavy parts of the radiolysis spectra of n-heptane and n-octane are described in detail as examples. Simple formulas for an easy and rapid calculation of the boiling point of any heavy radiolysis product are given in an Appendix.

INTRODUCTION

The wide development of gas chromatographic techniques at present allows the separation of very complex mixtures of compounds, even in the field of high-boiling point substances. These techniques find wide application in many fields and certainly have been used to a great extent in the study of the composition of crude oils. The difficulties met today in this kind of research often depend more on the lack of a sufficiently wide collection of reference substances than on the technical problems of separation. For example, in the case of the hydrocarbons, in which we are more directly interested, only a very small fraction of the many possible branched alkanes is available over C_7; the availability of alkenes is even scarcer.

We therefore propose the use of mixtures of hydrocarbons, which are formed by radiolysis of an alkane, as a source of reference substances and wish to demonstrate that this technique of standardisation may be applied very easily and offers wide possibilities.

Radiolysis of any alkane with n C atoms produces many saturated and unsaturated hydrocarbons with a number of C atoms v ranging from $v = 1$ to $v = 2n$. The formation of these compounds follows definite rules which we have deduced by means of much experimental work in the field of radiolysis[1] and which allows the prediction of the full spectrum of the radiolysis products of any alkane. In principle, therefore, an enormous number of heavy branched alkanes could be obtained, on demand, by radiolysis of a lighter hydrocarbon, properly chosen among the available products. However, the usefulness of a particular radiolysis product as a reference substance is conditioned by the ease with which the product can be immediately identified in

the radiolysis spectrum to which it belongs. This condition is fulfilled by practically all the radiolysis products of a normal alkane, but the radiolysis spectrum of a branched alkane is too complex to be of easy and immediate interpretation. For this reason we will restrict our description and discussion to the radiolysis spectra of n-alkanes in which linear and branched products are easily identifiable by their belonging to very characteristic groups and by their relative abundance inside the group.

The radiolysis spectra described here were obtained by irradiating the sample, contained in evacuated capillary ampoules, with ^{60}Co γ-rays at room temperature. It must be noted, however, that one may change some of the conditions, such as the shape of the ampoule, the nature of the ionising radiation (if α-rays or other very high "linear energy transfer" particles are ruled out) or the temperature, without substantially altering the shape of the spectra, at any rate, not to an extent which need be taken into account for the present purpose.

We believe that a sample of an n-alkane irradiated with a dose of 5–50 Mrad under conditions which may be varied considerably may be easily prepared today in any laboratory.

EXPERIMENTAL

The experimental conditions under which the chromatograms of Figs. 1 and 2 were obtained are given in Table I. It must be noted that these conditions were chosen so as to obtain sufficiently compact chromatograms which would give a comprehensive illustration of at least the heavy part of the radiolysis spectra. Obviously, much better resolution may be obtained under other conditions: especially for the products immediately following the parent alkane ("dehydrogenation products" and the first group of "synthesis products"; see further on), which are hidden under the tail of the giant parent-peak in the chromatograms of Figs. 1 and 2, but can easily be resolved in chromatograms obtained under different conditions.

Some further details about the preparation of the columns may be of interest. A soft glass tube (O.D. = 7.6 mm; I.D. = 3.5 mm) was drawn to the required length and thickness by means of an apparatus very similar to that described by DESTY et al.[2]. The capillary column was then: (a) filled with a 10 % solution of NaOH; (b) kept at 110° for 60 min; (c) washed with hot, progressively less basic solutions down

TABLE I

EXPERIMENTAL CONDITIONS

Instrument	"Fractovap Model D" GLC unit (Carlo Erba)
Detector	Hydrogen flame ionisation
Vaporiser temperature	300°
Detector temperature	250°
Detector voltage	150 V
Sample size	∼ 4 μl
Head split ratio	100/1
Column	100 m "attacked" glass capillary × 0.3 mm I.D.; 5% wt. squalane in n-hexane
Column flow	1.25 ml/min
Carrier gas	N_2
Temperature program	Isothermal at ∼ 50° until after elution of n-hexane; then heated to 130° at 1°/min

to neutral reaction; (d) impregnated with a solution of suitable concentration of the chosen stationary phase. Resolving powers of up to 1000 theoretical plates/m were obtained on 100–150 m columns.

Similar results (or perhaps a little less satisfactory) were obtained by coating the internal surface of hard-glass capillary columns with carbon black before impregnation. The carbon deposition was obtained by thermal decomposition of CH_2Cl_2 vapours. The column was filled with a mixture of dry N_2–CH_2Cl_2 vapours, obtained by bubbling dry N_2 through liquid CH_2Cl_2 kept at $0°$. The column was then sealed, heated to $450°$ and kept at this temperature for 1 h.

Very good results were also obtained with micro-packed columns prepared by drawing a glass tube to capillary dimensions ($\sim$ 0.50 mm diameter) previously filled up with Al_2O_3 powder (150–170 mesh, activated at $700°$ for 5 h). These columns, however, require rather high pressures of carrier gas and therefore were used by us for hydrocarbons with up to about six C atoms only. Many different stationary phases were tested and the best results were obtained with Ucon 50 LB 550 X (15 % solution in ether for impregnation). A column prepared with this stationary phase on attacked glass can resolve all the radiolysis products of n-decane, namely, hydrocarbons from methane up to a group of fifteen C_{20} isomers (except for the ethane–ethylene pair).

In general, all the columns described here show a behaviour — from the standpoint of retention times — which is intermediate between that of a packed gas–solid column and that of a normal capillary column for GLC. The behaviour of each column may be largely predetermined (on the basis of particular requirements) by means of a suitable choice of the degree of moisture of the solid support and of the quantity of liquid phase.

Our samples were prepared for irradiation by degassing them (by means of repeated freezing–evacuation–melting cycles) inside small glass capillaries (diameter = 1.5 mm; l = 45 mm), which were then sealed under vacuum and irradiated in a ^{60}Co γ-cell with a dose of up to 22 Mrad. The irradiated capillary was then introduced into a very small bulb-crusher which we had substituted for the customary inlet system of the gas chromatograph and broken in the stream of carrier gas*.

DISCUSSION

The radiolysis spectrum of an n-alkane with n C atoms may be subdivided into four parts: (1) the zone of "fragmentation products", which contains saturated and unsaturated hydrocarbons with the number of C atoms ranging from 1 to $n - 1$; (2) the zone of "dehydrogenation products" which contains unsaturated hydrocarbons with n C atoms; (3) the zone of "synthesis products", which contains saturated hydrocarbons with the number of C atoms ranging from $n + 1$ to $2n - 1$; (4) the zone of "dimerisation products" which contains saturated hydrocarbons with $2n$ C atoms. Each one of these parts is easily recognisable by the methods described below, each of them separately.

We will start our description with the group with the heaviest products because of its greater interest as a source of reference substances.

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* This technique is very useful as it avoids the fractionation of the mixtures when precise quantitative analysis throughout all the spectrum is required. It is obviously unnecessary if only qualitative use of the radiolysis mixtures is made.
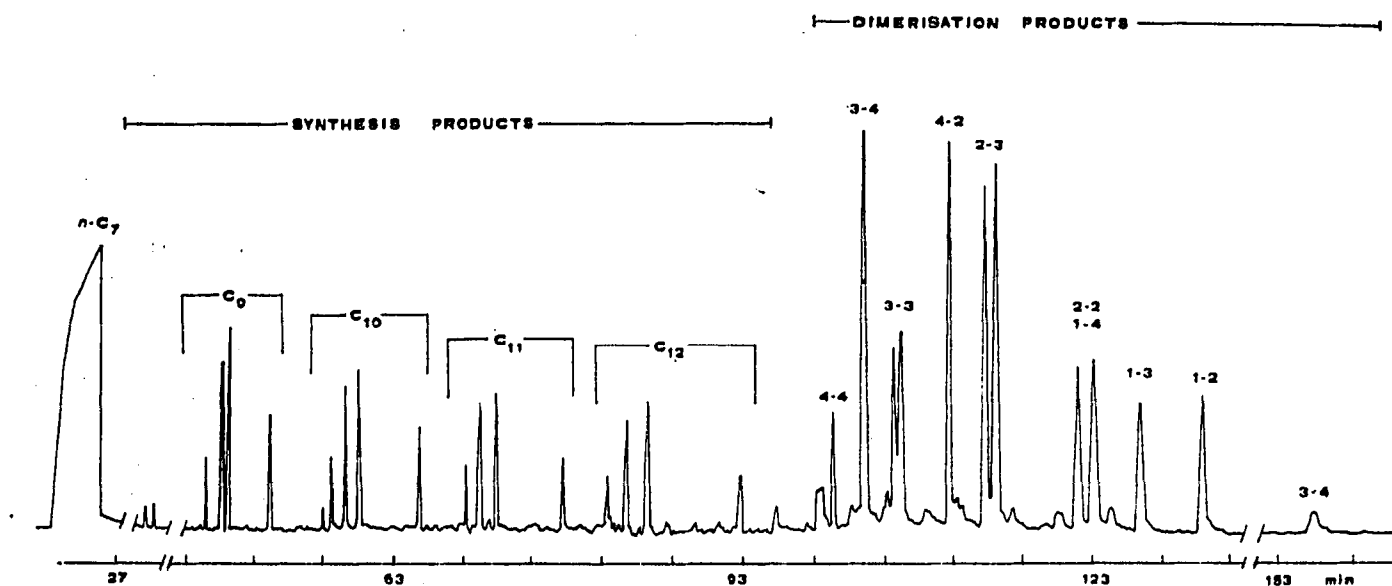
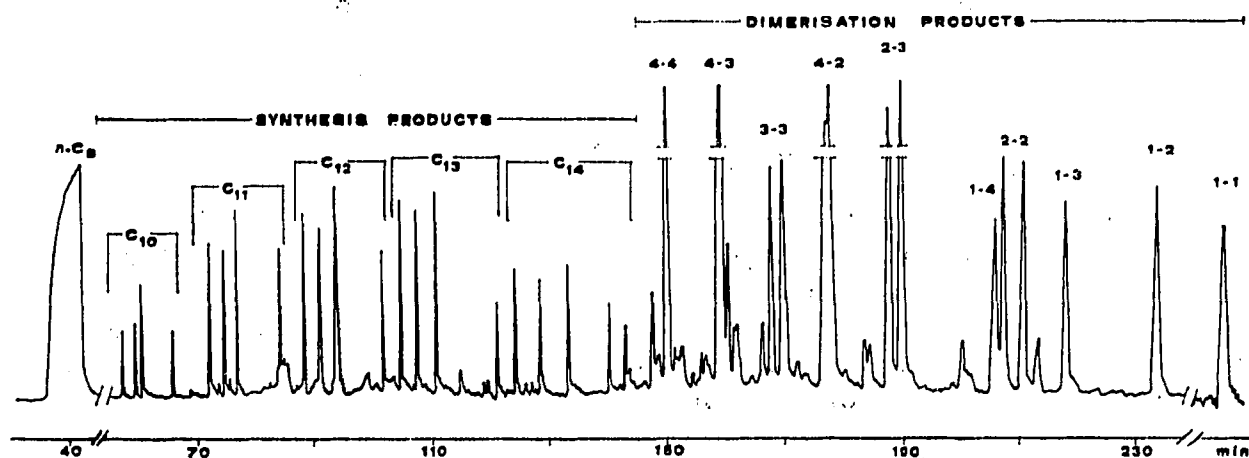Fig. 1. γ-radiolysis spectrum of n-heptane. Zones of products heavier than the parent compound.

Fig. 2. γ-radiolysis spectrum of n-octane. Zones of products heavier than the parent compound.

Dimerisation products

As shown in Figs. 1 and 2, two distinctly separated zones appear in the chromatograms after the giant peak of the parent hydrocarbon; the first one is constituted by rather small peaks, given by "synthesis products", which are formed with low yields; the second one is constituted by much larger peaks (interrupted in Fig. 2), corresponding to the "dimerisation products". The separation of the two zones is clear cut.

The group of "dimerisation products" contains all the C_{2n} alkanes which may be formed by linkage of two individual parent molecules or — in other words — by addition of two parent radicals. In hexane, for instance, the following six C_{12} isomers are to be found: 4,5-diethyloctane, formed by linkage of two 3 positions (3–3); 3-ethyl,4-methylnonane, formed by linkage of the 2 and 3 positions (2–3); 4,5-dimethyldecane, formed by linkage of two 2 positions (2–2); 4-ethyldecane, formed by

linkage of the 1 and 3 positions (1–3); 5-methylundecane, formed by linkage of the 1 and 2 positions (1–2); and *n*-dodecane, formed by linkage of two 1 positions (1–1).

In general, in an *n*-alkane with *n* C atoms one finds $n(n + 2)/8$ different dimers if *n* is even and $(n + 1)(n + 3)/8$ isomers for odd *n*. With nonpolar stationary phases (or of intermediate polarity), the dimers will be eluted according to the order of their boiling points, which may be easily calculated using the rules given in the Appendix. In general, the most branched isomer, which is formed by linkage of the two most central positions, will appear first and the linear one last. The peak of the linear dimer, which appears markedly later than the group of peaks of the branched isomers, is noticeably smaller, clearly marks the end of the chromatogram. It must be noted that a number of branched isomers contain two asymmetric C atoms and are made up of two equally abundant diastereoisomers. High resolution capillary columns, required in this kind of work, usually resolve the two diastereoisomers in a pair of nearby, almost equal (depending on the background) peaks. Three such pairs are shown in Fig. 2, corresponding to the 3–3, 3–2 and 2–2 dimers of *n*-octane. This fact, which causes an increase in the number of peaks, does not introduce any real complication in the identification of the products because of the ease with which a pair may be recognised as such. On the contrary, it sometimes represents a good check of the identification as, for instance, in the case of the dimers 1–4 and 2–2 of Fig. 2.

Another useful tool for checking the identification is the relative abundance of each isomer inside its group.

As a general rule, the dimers given by an *n*-alkane with an even number of C atoms may be subdivided into four groups of increasing abundance*:

  (1) the 1–1 dimer;
  (2) the dimers formed by linkage of the 1 position to any other position;
  (3) the dimers formed by linkage of two C atoms in the same position (other than the 1–1);
  (4) the dimers formed by linkage of two different non-terminal carbons.

For an *n*-alkane with an odd number of C atoms the most central position is represented by one atom only instead of two. Consequently, the yields of the products formed by linkage of this position are lower and the corresponding chromatographic peaks markedly smaller (about half the size of those of the other isomers pertaining to the same group of abundance). The first peak, which is given by the isomer formed by linkage of two central carbons, is about four times smaller than the other ones of the same group (namely, group 3). A "corrected" internal distribution of the dimers given by an odd *n*-alkane may be obtained by multiplying by 4 the area of the first peak and by 2 those of the other peaks supposed to correspond to dimers given by the central carbon; the internal distribution obtained with these new data must coincide with that of the *n* + 1 even *n*-alkane and therefore must follow the general rules just given above for even hydrocarbons.

*Synthesis** products*

Synthesis products are all the saturated hydrocarbons which may be formed by the substitution of a H atom of a parent molecule by an alkyl radical formed by

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  * Detailed quantitative information is given in ref. 1.
  ** Sometimes also called "intermediate" products.

fission of a C–C bond of the parent. In hexane, for instance, five groups of synthesis products are obtained, with 7 to 11 C atoms, and each group will be made up of 3 isomers, namely, the linear and two branched ones, corresponding to the substitution position of the hydrogen, 1, 2 or 3, respectively. In the group of products with 8 C atoms, for instance, we would find: 2-ethylhexane; 3-methylheptane; and n-octane. With nonpolar stationary phases (or of intermediate polarity), where the order of elution follows the order of boiling points of the products, the most branched isomer will appear first and the normal one last, somewhat apart from the others.

Only in the first group (the C_{n+1} products) is the order of elution somewhat different because the 2-derivative, which is characterised by the higher symmetry group $R-CH(CH_3)_2$, is the most volatile compound and is eluted first. The other ones are eluted successively following the order just mentioned for all the other groups.

Furthermore, the height ratios of the various peaks in each group are practically the same in all the groups except for the first (see ref. 1). As a results of this, the zone of synthesis products is consequently made up by the repetition of an "a priori" known number of very typically shaped groups of rather small peaks, which are positioned between the giant peak of the parent hydrocarbon and a group of much larger peaks, the dimers (see Figs. 1 and 2). Owing to these characteristics they cannot be confused by any means with other products and each one of the isomers is very easily identified in an unquestionable manner.

Unsaturated hydrocarbons are practically absent in this part of the spectrum except for the heaviest group of synthesis products (C_{2n-1} isomers) where they are present in amounts comparable to those of saturated isomers and may give rise to some uncertainty in the identification. The alkanes of this last group cannot, however, be used as reference substances in the spectra of hydrocarbons with $n > 6$ because of some overlapping of the most branched dimers (see Fig. 2).

Dehydrogeneration products

All the possible alkenes with one double bond and the same skeleton of C atoms as the parent alkane are contained in this group. The peaks corresponding to them do not appear in Figs. 1 and 2 but they are easily resolved with a liquid phase of intermediate polarity. In chromatograms obtained in this manner they are clearly distinguishable from the nearby synthesis products because of the very high yields with which they are formed. Nevertheless we think that these compounds cannot be of any use as reference substances because their identification is not as simple as it is for the dimerisation and synthesis products just discussed. Indeed, each alkene, except for the first, gives two chromatographic peaks, corresponding to the cis and trans forms, and the relative position of any peak is strongly determined by the operating conditions. Also, the relative abundances are not so markedly different as to provide a useful tool for identification.

Fragmentation products

All the n-alkanes with a number of C atoms smaller than that of the parent and the corresponding 1-alkenes are contained in this part of the spectrum. The alkanes are present at about the same molar concentration, except for methane and the C_{n-1} alkane, whose yields are markedly lower (3–4 times lower). The molar abundance of the 1-alkenes is about 30 % of that of the corresponding alkane. 2-Alkenes and some

acetylene are produced at such low yields that they do not interfere in the identification. Branched hydrocarbons are totally absent. It may be noted that all the "fragmentation products" are hydrocarbons easily available on the market; they may represent, however, a series of reference substances which one can easily and quickly prepare.

APPENDIX

The boiling temperature (b.p.) of any paraffin may be calculated starting from that of the normal isomer* by means of the empirical formula of GREENSHIELDS AND ROSSINI[3]:

$$b.p. \text{ (isomer)} = b.p. \text{ (normal)} - 4.50 \; C_3/n^{1/2} - 5.72 \; C_4/n^{1/2} +$$

$$15.87 \; \Delta P_3/n^{1/2} + 72.93 \; \Delta W/(n^2 - n) + 10.6 \; P_4' \tag{1}$$

where n is the total number of C atoms; C_3 is the number of tertiary C atoms; C_4 is the number of quaternary C atoms; P_3 is the number of pairs of C atoms which lie three bonds apart from each other and $\Delta P_3 = P_3$ (isomer) $- P_3$ (normal); W (Wiener number) is the total number of bonds between all the possible pairs of carbons and ΔW is W (isomer) $- W$ (normal); P_4' is the number of quaternary carbon pairs separated by one carbon atom in the isomer.

It is well known that this empirical formula gives progressively less accurate approximations as the number of C atoms increases and sensible discrepancies between calculated and experimental boiling point may be already found for $n = 12$ when quaternary carbons are present. Radiolysis products of n-alkanes, however, never contain quaternary C atoms and their boiling point may be calculated with satisfactory approximation up to much larger molecular weights.

The computation of the parameters ΔP_3 and ΔW is a rather long and tedious exercise, especially when the boiling point of a number of compounds are to be calculated, as it is for a group of radiolysis products. Therefore we will give below some simple formulas whereby these parameters may be quickly calculated for the isomers we are interested in, namely, branched alkanes with only one or two tertiary carbons. These formulas have been obtained by expanding the double summations contained in ΔP_3 and ΔW and applying the expressions thus obtained in the cases that interest us. The results are collected in Table II.

Let us consider, first, a normal alkane with $n \geqslant 3$. We will have

$$P_3 = n - 3 \tag{2}$$

and

$$W = \sum_{h}^{n} \sum_{t}^{h} (h - t) = (n^3 - n)/6 \tag{3}$$

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* The boiling points of normal alkanes are given in the Am. Petrol. Inst. Project 44 (College Station, Texas) up to C_{100}; the boiling point of branched alkanes are up to C_{12} only.

TABLE II

VALUES OF ΔP_3 AND ΔW FOR SYNTHESIS AND DIMERISATION PRODUCTS

Products with 1 tertiary carbon			Products with 2 tertiary carbons		
ΔP_3			ΔP_3		
$h = \begin{cases} 2 \\ n-l-1 \end{cases}$ $2 < h < (n-l-1)$				$l_1 = 1$	$l_1 > 1$
$l = 1$	0	1	$l_2 = 1$	3	4
$l > 1$	1	2	$l_2 > 1$	4	5
ΔW			ΔW		
$-l(h-l)(N-h)$			$-N[(N+1)(n_1+n_2)-(n_1^2+n_2^2)-2N]$		

Let us consider next:

(a) Branched alkanes with $n - l$ carbons in the main chain and one side chain of l carbons at the kth position. We will have

$$P_3 = n - 1 \text{ if } 2 < k < n - l - 1 \quad \text{and } l > 1 \tag{4}$$

$$P_3 = n - 2 \text{ if } 2 < k < n - l - 1 \quad \text{and } l = 1 \tag{5}$$

$$P_3 = n - 2 \text{ if } k = 2 \text{ or } k = n - l - 1 \text{ and } l > 1 \tag{6}$$

$$P_3 = n - 3 \text{ if } k = 2 \text{ or } k = n - l - 1 \text{ and } l = 1 \tag{7}$$

The Wiener number will be

$$W = \sum_{h}^{n-l} \sum_{t}^{h} (h-t) + \sum_{h}^{l} \sum_{t}^{h} (h-t) + \sum_{h}^{k-1} \sum_{t}^{l} (k-h+t) + \sum_{h}^{n-l} \sum_{t}^{l} (h-k+t) \tag{8}$$

where the first double summation refers to the main chain, the second one to the side chain and the third and fourth to the pairs, one atom of which is in the side chain and the second one on either one side or the other of the main chain. By calculating the summations and rearranging the results one obtains

$$W = (n^3 - n)/6 - l(k-1)(n-k-l) \tag{9}$$

(b) Branched alkane with $n - l_1 - l_2$ carbons in the main chain, l_1 carbons in a side chain at the k_1th position and l_2 carbons in another side chain at the k_2th position. In all the cases we are interested in, we also have $k_2 = k_1 + 1$; $3 \leqslant k_1 \leqslant (n - l_1 - l_2 - 3)$. In these cases we will obtain

$$P_3 = n + 2 \text{ if } l_1, l_2 > 1 \tag{10}$$

$$P_3 = n + 1 \text{ if } l_1 = 1; l_2 > l_1 \tag{11}$$

$$P_3 = n \qquad \text{if } l_1 = l_2 = 1 \tag{12}$$

and

$$W = W_1 + W_2 - \sum_{h}^{n-l_1-l_2} \sum_{}^{h} (h-t) + \sum_{h}^{l_2} \sum_{t}^{l_1} (h+t+k_2-k_1) \tag{13}$$

where W_1 and W_2 are the Wiener numbers calculated by eqn. 9 for the two single branched alkanes with $n_1 = n - l_2$; $l = l_1$; $k = k_1$ and with $n_2 = n - l_1$; $l = l_2$; $k = k_2$ respectively; the third term subtracts the contribution of the pairs in the main chain, which has been considered twice in summing W_1 and W_2; the fourth term represents the contribution of the pairs with one atom in the first side chain and the second in the other one. By calculating the summations and rearranging the results, one gets

$$W = (n^3 - n)/6 - l_1(k_1 - 1)(n - l_1 - l_2 - k_1) - l_2k_1(n - l_1 - l_2 - k_1 - 1) -$$

$$l_1l_2(n - l_1 - l_2 - 2) \tag{14}$$

Subtracting eqn. 3 from eqns. 9 and 14 we immediately obtain the required values of ΔW for cases (a) and (b) respectively.

The expressions of ΔW may be further simplified. Disregarding the official nomenclature, one may consider any product with only one tertiary carbon as the result of the addition of a C_l alkyl radical at the kth atom of the parent chain of N carbons. This gives $n - l = N$ and

$$\Delta W = - l(k - 1)(N - k) \tag{15}$$

Similarly, any product with two tertiary carbons may be considered as the result of the linkage of two C_N parent radicals by means of the n_1th carbon of the first and the n_2th atom of the second one (dimer n_1-n_2, using the nomenclature of the text and figures). This gives

$$n = 2N; \; k_1 = N - n_1 + 1; \; k_2 = N - n_1 + 2; \; l_1 = n_1 - 1; \; l_2 = n_2 - 1$$

and

$$\Delta W = - N[(N + 1)(n_1 + n_2) - (n_1^2 + n_2^2) - 2N] \tag{16}$$

As an example of the easy and immediate applicability of Table II let us consider the 3–4 dimer of n-decane: $C_7H_{15}-CH(C_2H_5)-CH(C_3H_7)-C_6H_{13}$. We have: $l_1 = 3$; $l_2 = 2$; $n_1 = 3$; $n_2 = 4$; $N = 10$ and therefore from the table $\Delta P_3 = 5$ and $\Delta W = -10[(11 \times 7) - (9 + 16) - 20] = -320$ which, inserted in eqn. 1, immediately gives the required boiling point.

REFERENCES

1 E. PANCINI, V. SANTORO AND G. SPADACCINI, Int. J. Radiat. Phys. Chem., 2 (1970) in press.
2 D. H. DESTY, J. N. HARESNAPE AND B. H. F. WHYMAN, Anal. Chem., 32 (1960) 302.
3 J. B. GREENSHIELDS AND F. D. ROSSINI, J. Phys. Chem.,62 (1958) 271.