[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Number of Structurally Isomeric Hydrocarbons of the Acetylene Series[1]

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It has previously been possible, by means of a separation into types, arbitrarily chosen upon the basis of their structural formulas, to establish a relationship between the number of structurally isomeric hydrocarbons[2] and the alkyl groups of which the former may be considered to be composed. It can now be shown that an analogous method of separation into structural types may be utilized successfully in calculating the number of structurally isomeric hydrocarbons of the acetylene series.

The homologs of acetylene are divided into two groups: A, consisting of those hydrocarbons which may be formed, theoretically, by replacing one hydrogen atom of acetylene by an alkyl radical, and B, consisting of those which may be formed by replacing both hydrogen atoms of acetylene by alkyl radicals.

The structural formula of each of the homologs of acetylene of N carbon atoms of group A, R—C≡C—H, may be formed by replacing one hydrogen atom of acetylene by an alkyl radical of $N - 2$ carbon atom content. The total number of structural formulas that may be thus formed will equal the total number of alkyl radicals of $N - 2$ carbon atoms or $T_{(N-2)}$.

$$A_N = T_{(N-2)} \qquad \text{(A)}$$

The number of paraffin alkyl radicals of each carbon content through C_{20} has been previously reported.[3]

The structural formulas of the hydrocarbons of group B, R—C≡C—R′, of N total carbon atom content may be formed by attaching to the —C≡C— group the alkyl radicals R— and R′— (the carbon content of R— plus R′— always equaling $N - 2$). The number of isomers that may be thus formed will equal the total number of possibilities, without exception or repetition, of combining simultaneously with the —C≡C— group every value of R—, taken one at a time, and every complementary value of R′—, also taken one at a time. These possibilities are theoretically of two types: (a), those in which the two alkyl radicals R— and R′— are of unequal carbon content; and (b), those in which the two alkyl groups are of

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(2) Henze and Blair, THIS JOURNAL, **53**, 3077 (1931). It should be noted that the number of structurally isomeric nondecanes given erroneously as 147,248 in Table II, page 3084, should be corrected to read 148,248, as indicated by Perry, *ibid.*, **54**, 2918 (1932).

(3) Henze and Blair, *ibid.*, **53**, 3042 (1931).

equal carbon content. In type (b) there may be further recognized two sub-types; (b_1), in which the two alkyl groups although of the same carbon content are not structurally identical; and (b_2), in which the two alkyl groups are structurally identical. Type (b) is actually impossible with a hydrocarbon of uneven carbon content, for in that type $N - 2$ should be divisible by two. The total number of isomeric homologs of acetylene of all types included in group B may be calculated by the following (finite) recursion formulas according to whether the carbon content is odd or even.

Odd:

$$B_N = T_1 \cdot T_{(N-3)} + T_2 \cdot T_{(N-4)} + \dots \dots + T_{(N-3)/2} \cdot T_{(N-1)/2} \qquad (B_o)$$

Even:

$$B_N = T_1 \cdot T_{(N-3)} + T_2 \cdot T_{(N-4)} + \dots + T_{(N-4)/2} \cdot T_{N/2} + \frac{T_{(N-2)/2} \cdot [1 + T_{(N-2)/2}]}{2} \qquad (B_e)$$

Note that the subscripts in each term add up to $N - 2$, and that the number of terms is $(N - 3)/2$ for odd carbon atom content and $(N - 2)/2$ for even.

Table I indicates the number of structurally isomeric hydrocarbons of the acetylene series as calculated by the use of the recursion formulas.

TABLE I

NUMBER OF ISOMERIC HYDROCARBONS OF THE ACETYLENE SERIES

Carbon content	Number of isomers	Carbon content	Number of isomers
2	1	16	38,422
3	1	17	97,925
4	2	18	251,275
5	3	19	648,061
6	7	20	1,679,869
7	14	21	4,372,872
8	32	22	11,428,365
9	72	23	29,972,078
10	171	24	78,859,809
11	405	25	208,094,977
12	989	26	550,603,722
13	2,426	27	1,460,457,242
14	6,045	28	3,882,682,803
15	15,167	29	10,344,102,122
		30	27,612,603,765

Summary

1. Formulas of the (finite) recursion type are advanced which permit the calculation from their carbon content of the number of structurally isomeric hydrocarbons of the acetylene series. In using these recursion formulas to calculate the total number of such hydrocarbons of any given carbon content, the total number of alkyl radicals of $N - 2$ and all lesser carbon contents must be known.

WILMINGTON, DELAWARE
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