THE ELECTRONIC CONSTITUTION OF NORMAL CARBON CHAIN COMPOUNDS, SATURATED AND UNSATURATED.

BY EUSTACE J. CUY (COUYUMDJOPOULOS).

In a recent paper on "The Electronic Constitution of Acetoacetic and Citric Acids and Some of Their Derivatives," Hanke and Koessler,[1] making the implicit assumption that organic compounds are polar in nature, give the following formulas based on the reactions of these compounds:

Acetic acid:

```
              H        O
              +       ‗‗
              ‗       ++
 H + — C — + C + — O — + H
              ‗
              +
              H
```

Acetone:

```
              H              H
              +              +
              ‗              ‗
 H + — C — + C + — C — + H
              ‗      ++      ‗
              +      ‗‗      +
              H       O      H
```

Acetoacetic acid:

```
            H              H
            +              +
            ‗              ‗
 H + — C — + C + — C — + C + — O — + H
            ‗      ++     ‗      ++
            +      ‗‗     +      ‗‗
            H       O     H       O
```

Acetone dicarbonic acid:

```
          O        H        O        H        O
         ‗‗        +       ‗‗        +       ‗‗
         ++        ‗       ++        ‗       ++
 H + — O — + C + — C — + C + — C — + C + — O — + H
                   +                 +
                   H                 H
```

Citric acid:

```
          O        H       O‾⁺H H        O
         ‗‗        +        ‗        +       ‗‗
         ++        ‗        +        ‗       ++
 H + — O — + C + — C — + C + — C — + C + — O — + H
                   ‗        +        ‗
                   +        ‗        +
                   H        C‡‗O H
                            +
                            ‗
                            O — + H
```

A striking fact is to be observed, namely, that in all 5 of the above

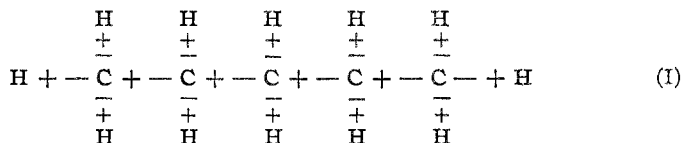[1] Hanke and Koessler, THIS JOURNAL, 40, 1726 (1918).

given carbon chains the carbon atoms are alternately positive and nega-
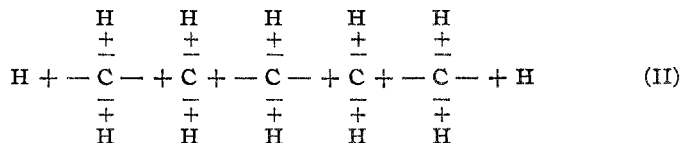tive.

The present paper will adduce evidence tending to establish the fact
that in a chain of carbon atoms the tendency is for these atoms to appear
alternately positive and negative whenever possible, and that the alter-
nating sign of the charge in the above cited 5 examples is not accidental.

We shall exclude from consideration in the present paper carbon chains
including aryl groups, since there is no generally accepted notion of the
structure of the benzene ring.

If it be conceded that organic compounds are polar in nature, as are
inorganic compounds,[1] although possibly to a less degree, then the struc-
ture of a member of the methane series will be either

$$
\begin{array}{ccccc}
H & H & H & H & H \\
\overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} \\
H+-\underset{-}{C}+-\underset{-}{C}+-\underset{-}{C}+-\underset{-}{C}+-\underset{-}{C}-+H \\
\overset{+}{} & \overset{+}{} & \overset{+}{} & \overset{+}{} & \overset{+}{} \\
H & H & H & H & H
\end{array}
\qquad (I)
$$

or

$$
\begin{array}{ccccc}
H & H & H & H & H \\
\overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} \\
H+-C-+C+-C-+C+-C-+H \\
\overset{+}{} & \overset{+}{} & \overset{+}{} & \overset{+}{} & \overset{+}{} \\
H & H & H & H & H
\end{array}
\qquad (II)
$$

or, omitting the hydrogen atoms for the sake of simplicity

$$
-\overset{-}{\underset{-}{C}}+-\overset{-}{\underset{-}{C}}+-\overset{-}{\underset{-}{C}}+-\overset{-}{\underset{-}{C}}+-\overset{-}{\underset{-}{C}}-
\qquad (I)
$$

or

$$
-\overset{-}{\underset{-}{C}}-+\overset{-}{\underset{-}{C}}+-\overset{-}{\underset{-}{C}}-+\overset{-}{\underset{-}{C}}+-\overset{-}{\underset{-}{C}}-.
\qquad (II)
$$
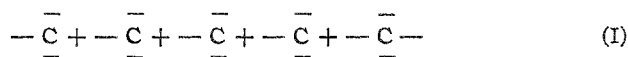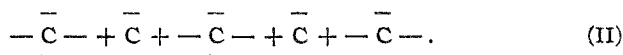
That is, either the positive and the negative charges will in so far as possi-
ble be evenly distributed among the carbon atoms, or the positive charges
will tend to accumulate on alternate carbon atoms and the negative
charges on the remaining carbon atoms.

These two possibilities are not limited to the homologues of methane,
but extend to the homologues of any series as, for example, that of the
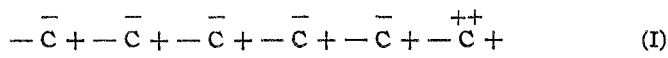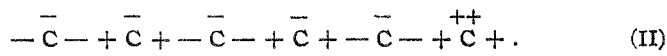monocarboxylic acids.   Capronic acid will be either

$$
\begin{array}{cccccc}
H & H & H & H & H & O \\
\overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{+}{\underset{-}{}} & \overset{--}{\underset{++}{}} \\
H+-\underset{+}{C}+-\underset{+}{C}+-\underset{+}{C}+-\underset{+}{C}+-\underset{+}{C}+-C+-O-+H \\
H & H & H & H & H
\end{array}
\qquad (I)
$$
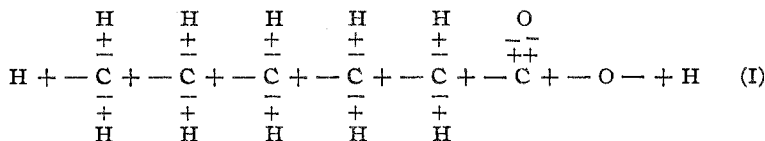
or

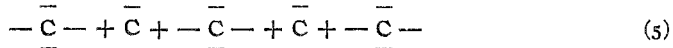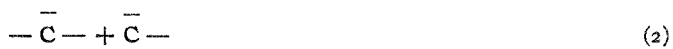   [1] Harkins and King, THIS JOURNAL, 41, 976 (1919), footnote.

$$H + - \overset{\overset{\text{H}}{\underset{\underset{\text{H}}{+}}{+}}}{\underset{+}{C}} - + \overset{\overset{\text{H}}{\underset{\underset{\text{H}}{+}}{+}}}{\underset{+}{C}} + - \overset{\overset{\text{H}}{\underset{\underset{\text{H}}{+}}{+}}}{\underset{+}{C}} - + \overset{\overset{\text{H}}{\underset{\underset{\text{H}}{+}}{+}}}{\underset{+}{C}} + - \overset{\overset{\text{H}}{\underset{\underset{\text{H}}{+}}{+}}}{\underset{+}{C}} - + \overset{\overset{\text{O}}{++}}{C} + - O - + H \quad (II)$$

that is,

$$- \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} + - \overset{++}{C} + \qquad (I)$$

or

$$- \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - + \overset{++}{C} + . \qquad (II)$$
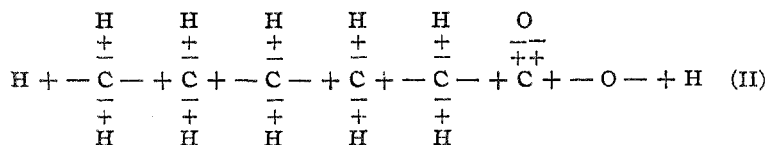
If the Formulas I are correct, it should be found that the addition of successive CH₂ groups causes a change in the physical constants of the compound by a constant amount or by a constantly and continuously changing amount. If X represents the value of a given physical constant of a compound of n carbon atoms in a given series, then we should expect X to vary continuously with the number of carbon atoms in the compound. If X is represented graphically as a function of n, the number of carbon atoms, we should expect all points to lie on a simple, continuous curve. The value of $\Delta X / \Delta n$, the change in the property X for the addition of one carbon atom, would then always have the same sign and would either increase or decrease continuously with n, the number of carbon atoms present in the compound. The latter case is obviously to be expected. A similar continuous curve is to be expected if the differences $\Delta X / \Delta n$ for successive carbon atoms be plotted against values of n. If, on the other hand, Formulas II are correct, then in a homologous series, such as the paraffines, as can be easily seen from the following formulas:

$$- \overset{-}{\underset{-}{C}} - \qquad (1)$$

$$- \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} - \qquad (2)$$

$$- \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - \qquad (3)$$

$$- \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} - \qquad (4)$$

$$- \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - \qquad (5)$$

$$- \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} + - \overset{-}{\underset{-}{C}} - + \overset{-}{\underset{-}{C}} - \qquad (6)$$
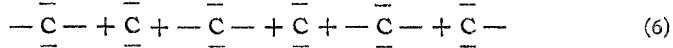
the compounds containing an even number of carbon atoms form a homologous series and those containing an odd number of carbon atoms form another homologous series, since (1) differs from (3) by $+ \overset{-}{C} + - \overset{-}{\underset{-}{C}} -$ and

(3) differs from (5) by the same $+\overline{C}+-\overline{C}-$ group. Similarly, (2)

differs from (4), and (4) from (6) by $-\overline{C}-+\overline{C}+$. But (1) differs from

(2) by a $+\overline{C}-$ group, and (2) from (3) by $\left[+\overline{C}+-\overline{C}-\right]-\left[+\overline{C}-\right]$.

Similar formulas may readily be written and compared in the case of other homologous series with the same result, *i. e.*, that the members containing an even number of carbon atoms and those containing an odd number give 2 distinct series.

If Formulas II are correct, then a given property X should vary continuously for each of the 2 series, the even and the odd, but should not be the same for the 2. Thus, when represented graphically, the compounds with an even number of carbon atoms should give points lying on a simple continuous curve, while compounds containing an odd number of carbon atoms should give points lying on another simple, and perhaps similar curve, not identical with the first. The addition of a single carbon atom would then cause a displacement from one curve to the other, while the addition of 2 carbon atoms should cause a displacement along the same curve. In certain instances the differences between the 2 curves may be small. In that case it is sometimes possible to show the distinctive nature of the odd and the even series by means of plots of the differences $\Delta X/\Delta n$, or even differences of higher order.

It has long been known that the melting points of monocarboxylic
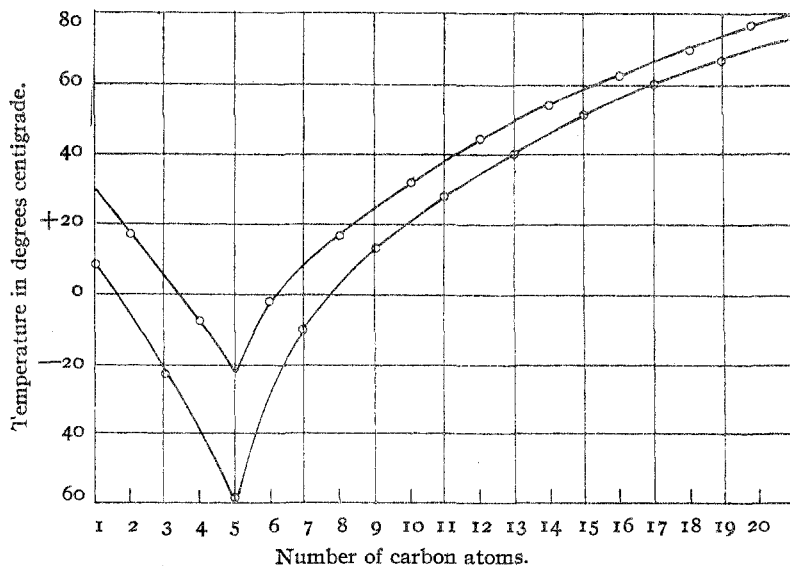
Fig. 1.—Melting points of normal monocarboxylic acids.

acids[1] are alternately high and low and tend toward a common value as the number of carbon atoms increases. In Fig. 1, the melting points of the monocarboxylic acids in degrees centigrade are plotted against the number of carbon atoms in the compounds. As is to be expected on the basis of the present theory, 2 distinct simple curves are obtained which are very similar and which exhibit a break at the fifth carbon atom. This break might perhaps be accounted for on the basis of Baeyer's Strain theory (*Spannunge-theorie*).[2]

Similar alternately high and low values of the melting points giving 2 separate and distinct curves have also been observed in the case of dicarboxylic acids.[3] In Fig. 2, the melting points of the dicarboxylic acids
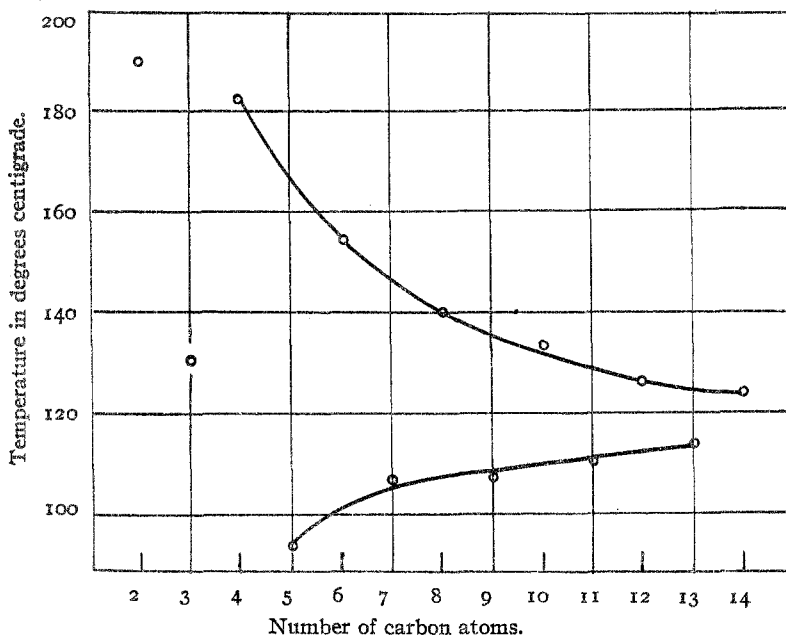
Fig. 2.—Melting points of dicarboxylic acids.

in degrees centigrade are plotted against the number of carbon atoms in the compounds.[4] Again we obtain 2 separate curves as we should expect,[5] and again a break occurs in each curve at about the same point

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[1] Baeyer, *Ber.*, **10**, 1286 (1877).

[2] Baeyer, *ibid.*, **18**, 2277 (1885).

[3] Henry, *Compt. rend.*, **60**, 943 (1885); Baeyer, *Ber.*, **10**, 1286 (1877); Nordlinger, *ibid.*, **23**, 2359 (1890).

[4] The data for Figs. 1 and 2 were taken from "Lehrbuch der Organischen Chemie," by V. Meyer and P. Jacobson.

[5] Falk and Nelson (THIS JOURNAL, **32**, 1640 (1910)) offered a somewhat similar explanation for the alternately high and low values of the melting points of the dicarboxylic acids. They were, however, unable to account for the similar phenomenon in the case of the monocarboxylic acid series, or to establish that *all* series of normal carbon chain compounds should show such an alternating character in their curves.

as in the monocarboxylic acid series, which break might be similarly accounted for.

In Fig. 3, the melting points[1] of the normal paraffines in degrees centigrade are plotted against the number of carbon atoms. Again we obtain 2 separate curves. To make the characteristics of the curves more evi-
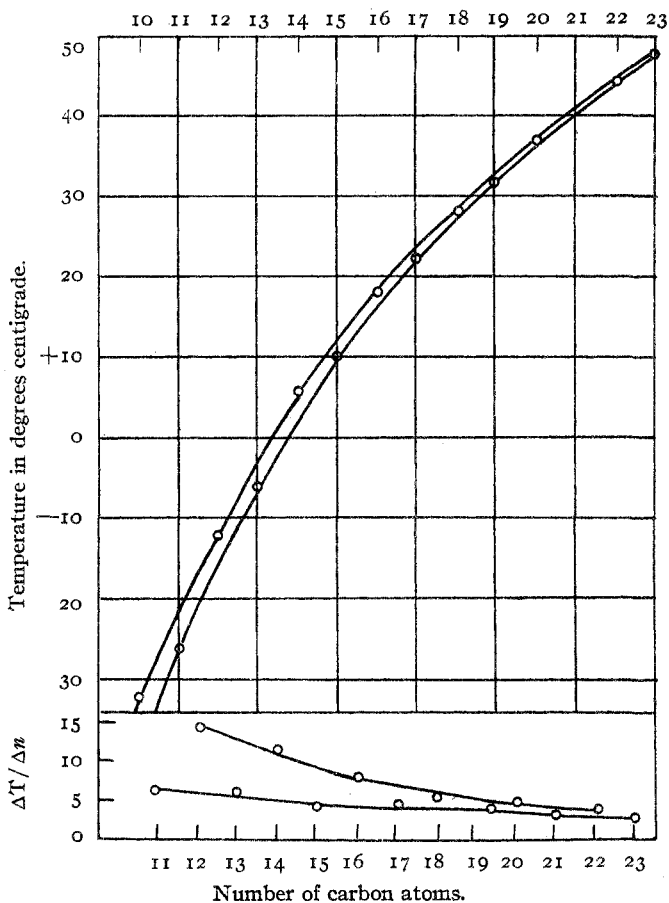
Fig. 3.—Melting points of normal paraffines.

dent the differences $\Delta X/\Delta n$ are also plotted against the number of carbon atoms. Similar curves result in the case of several other series. The necessary data appear in the literature. It is to be noted that the even series give a higher melting-point curve than the odd series.

Biach[2] in his article in *"Über Regelmässigkeiten in homologen Riehen,"* several years ago, gave a very large number of examples of such homologous

[1] The data for Fig. 3 were taken from "The Relation between Chemical Constitution and Some Physical Properties," by S. Smiles.

[2] Biach, *Z. physik. Chem.*, **50**, 43 (1905).

series whose melting point (or whose melting-point differences $\Delta X / \Delta n$) are alternately high and low; including paraffines, alkyl iodides and cyanides, alkylmethyl ketones, fatty acids, dicarboxylic acids, acetamides, acid anhydrides, α-oxy-fatty acids, ketonic acids, normal diamines, lactams, δ-valerolactams, dicarbonic acid anhydrides, alkyl malonic acids, and alkyl succinic acids. Also boiling points of 22 series, densities and molecular volumes of more than 20 series, viscosities of 8 series, solubilities of 3 series and several other series of constants.

Particularly in the case of the melting points, the tendency for the even and the odd carbon atoms to lie upon 2 distinct curves is very noticeable, and, while in the case of the other properties the series do not appear to be so distinct, they, nevertheless, show a like character. Although the 2 curves are not as distinct in some cases as in others, the cases where the 2 curves distinctly appear are altogether too numerous to be attributed to chance. Moreover, it is not improbable that inaccurate data may tend to mask the characteristics of the curves. The physical properties of homologous series seem therefore to support the hypothesis that alternate carbon atoms in a carbon chain tend to become positive and the rest negative.

Further evidence in support of the present hypothesis, namely, that carbon atoms in a normal carbon chain compound are alternately electropositive and electronegative, is found in the addition of hydrogen halides to unsaturated carbon compounds. Markownikoff's rule states: "When unsymmetrically constructed hydrocarbons of the series C_nH_{2n} combine with hydrogen iodide, the iodine is added to the least hydrogenated carbon atom."[1] The rule also holds for other halogen acids. This rule follows from the present hypothesis, since the most hydrogenated carbon atom will be electronegative, the adjacent carbon atom will be electropositive and will unite with the negative radical (Cl^-, Br^-, I^-); that is, each carbon atom tends to assume either an entirely electropositive or electronegative character whenever possible. According to our hypothesis the electronic formula of propylene is

$$
\begin{array}{ccccc}
 & \text{H} & & & \\
 & + & & & \\
 & - & & & \\
\text{H} + - & \text{C} & - + \text{C} \overset{+}{\underset{-}{\text{\textbf{:}}}} \text{C} & - + \text{H} \\
 & - & - & - & \\
 & + & + & + & \\
 & \text{H} & \text{H} & \text{H} &
\end{array}
$$
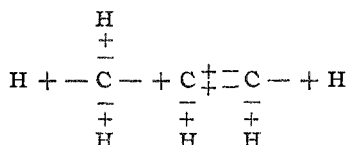
for in accordance with this hypothesis we find the reaction

$$CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBrCH_3.$$

Similarly,

$$CH_3CBr = CH_2 + HBr \longrightarrow CH_3CBr_2CH_3;$$
$$(CH_3)_2C = CH_2 + HBr \longrightarrow (CH_3)_2CBrCH_3.$$
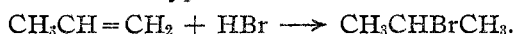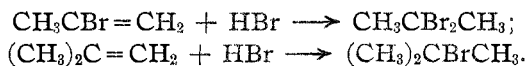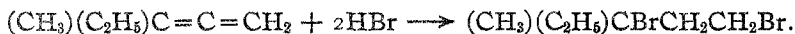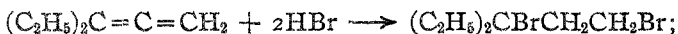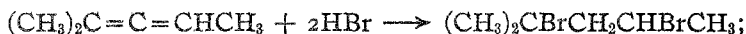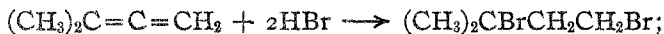
[1] Saytzeff, *Ann.*, **179**, 296 (1875).

It has been shown, however, that Markownikoff's rule fails in several cases. For example, when hydrogen iodide is added to α-ethylidene-propionic acid, $[CH_3CH=C(CH_3)COOH]$, the compound $CH_3CH_2CI-(CH_3)COOH$ should be obtained according to Markownikoff's rule, while, instead, the compound $CH_3CHICH(CH_3)COOH$ is obtained.[1] This case, which proves the insufficiency of Markownikoff's rule, is very readily accounted for by the present hypothesis. The electronic formula for α-ethylidene-propionic acid is

$$
\begin{array}{ccccc}
\overset{+}{\underset{-}{H}} & & & \overset{--}{\underset{++}{O}} & \\
H+-\overset{-}{\underset{+}{C}}-+C\ddagger & \ \overline{\ }C-+C+-O-+H \\
\underset{H}{} & \underset{H}{} & \overset{+}{\underset{-}{}}H+-\overset{-}{\underset{+}{C}}-+H. \\
& & \overset{}{\underset{+}{H}}
\end{array}
$$
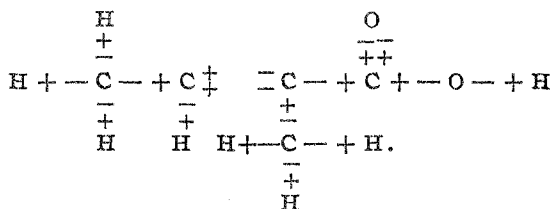
The first and fourth carbon atoms are, respectively, entirely electronegative and electropositive, and the third and second almost entirely so; and the atoms are arranged in the order C negative, C positive, C negative, C positive. When hydrogen iodide is added to this compound, it is to be expected that the electronegative radical I^- will go to the second carbon atom which is electropositive, and the electropositive H^+ atom to the third carbon atom which is electronegative. This has been found to be the case.

The present hypothesis, therefore, embraces Markownikoff's rule since it accounts for all the cases where this rule holds. That it is more general follows from the fact that it also accounts for those cases in which Markownikoff's rule fails.

The addition of hydrogen bromide to unsaturated hydrocarbons having 2 adjacent double bonds offers further evidence corroborating the present theory. According to Ipatieff's rule: "Dihydrobromides are produced by the addition of hydrogen bromide to hydrocarbons of the allene series, *in which both bromine atoms are not attached to neighboring carbon atoms*."[2] For example,[3]

$(CH_3)_2C=C=CH_2 + 2HBr \longrightarrow (CH_3)_2CBrCH_2CH_2Br;$

$(CH_3)_2C=C=CHCH_3 + 2HBr \longrightarrow (CH_3)_2CBrCH_2CHBrCH_3;$

$(C_2H_5)_2C=C=CH_2 + 2HBr \longrightarrow (C_2H_5)_2CBrCH_2CH_2Br;$

$(CH_3)(C_2H_5)C=C=CH_2 + 2HBr \longrightarrow (CH_3)(C_2H_5)CBrCH_2CH_2Br.$

If the electronic formula for $(CH_3)_2C=C=CH_2$ were, for example, $(CH_3)_2C\overset{+}{\underset{-}{\ }}\overline{\ }C\overset{+}{\underset{-}{\ }}\overline{\ }C\overline{\ }\ddagger\overset{H}{\underset{H}{}}$, or some other similar one, where the positive

[1] Cohen, "Organic Chemistry for Advanced Students," 2nd Edition, II, p. 256.

[2] Ipatieff, *Chem. Centr.*, **70**, II, 17 (1899).

[3] Ipatieff, *ibid.*, **67**, I, 835 (1896); **70**, II, 17 (1899).

and negative charges were evenly distributed among the carbon atoms, the addition product ought to be $(CH_3)_2CBrCHBrCH_3$ or $(CH_3)_2CHCH-BrCH_2Br$. According to the present hypothesis the carbon atoms will tend to become alternately entirely positive and negative, as far as possible. Omitting the hydrogen atoms, the electronic formula of $(CH_3)_2C = C = CH_2$ is therefore:

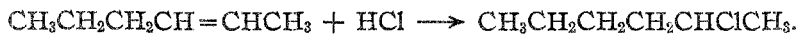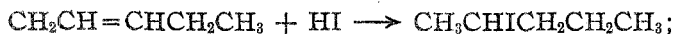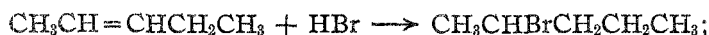$$-\bar{\bar{C}}- + C \ddagger \; \bar{\bar{=}} \; C \bar{\bar{=}} C \ddagger \; C \; \bar{\bar{=}}$$
$$\underset{-\underset{=}{C}-}{\overset{+}{}}$$
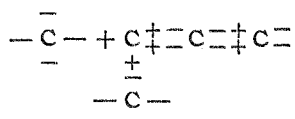
This accounts for the fact that bromine does not add on adjacent carbon atoms, since adjacent carbon atoms are not of the same electronic character. The present hypothesis, therefore, accounts for Ipatieff's rule also.

A very interesting question which Markownikoff's rule does not answer is: How will HX (when X is Cl, Br or I) add when both atoms of an unsaturated hydrocarbon at the double bond are equally hydrogenated, as for example, in $CH_3CH = CHCH_2CH_3$. Saytzeff, who first asked this question, answered it only for the particular case of $CH_3CH_2CH = CHCH_3$, showing experimentally that[1]

$$CH_3CH_2CH = CHCH_3 + HI \longrightarrow CH_3CH_2CH_2CHICH_3.$$

In a straight chain unsaturated hydrocarbon containing an odd number of carbon atoms, it would be expected that the negative radical should add on the second, fourth or an even carbon atom. Since carbon atoms tend to become alternately positive and negative and since the first and last carbon atoms have 3 hydrogen atoms adjoined, they and all the odd carbon atoms will consequently be electronegative and the even ones will be electropositive. Very few cases have been investigated, but they all agree with the present theory. We have[2]

$$CH_3CH = CHCH_2CH_3 + HBr \longrightarrow CH_3CHBrCH_2CH_2CH_3;$$

$$CH_2CH = CHCH_2CH_3 + HI \longrightarrow CH_3CHICH_2CH_2CH_3;$$

$$CH_3CH_2CH_2CH = CHCH_3 + HCl \longrightarrow CH_3CH_2CH_2CH_2CHClCH_3.$$

On the other hand, an unsaturated carbon chain with an even number of carbon atoms may give one or both of the possible addition compounds depending on the nature of the reaction products.
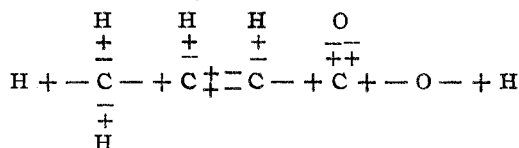
Another example of a similar type is[3]

$$CH_3CH = CHCOOH + HI \longrightarrow CH_3CHICH_2COOH.$$
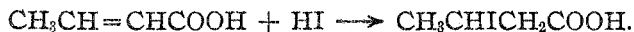
[1] Saytzeff, *Ann.*, **179,** 297 (1875).

[2] Beilstein, "Handbuch der Organischen Chemie," 3rd Edition, I, pp. 176, 193, 154.

[3] Meyer and Jacobson, *loc. cit.*, p. 955.
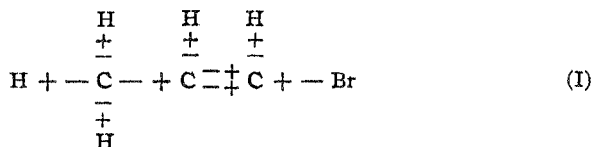
This reaction also is in harmony with our view since in

$$\text{H} + \overset{\overset{+}{-}}{-}\text{C} - + \text{C} \ddagger \overset{+}{-} \text{C} - + \overset{\overset{--}{++}}{\text{C}} + - \text{O} - + \text{H}$$
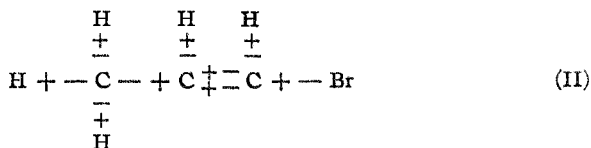
the second carbon atom is electropositive and should add on the electro-negative iodine.

Another case[1] for which there is no rule giving any information as to the course of addition of a hydrogen halide is that of $CH_3CH = CHBr$. It has been found that both possible products are formed, namely, CH_3-CH_2CHBr_2 and $CH_3CHBrCH_2Br$. The electronic formula for $CH_3CH =$ CHBr may be either

$$\text{H} + \overset{\overset{+}{-}}{-}\text{C} - + \text{C} \overset{-}{-} \ddagger \text{C} + - \text{Br} \qquad \text{(I)}$$

or

$$\text{H} + \overset{\overset{+}{-}}{-}\text{C} - + \text{C} \ddagger \overset{-}{-} \text{C} + - \text{Br} \qquad \text{(II)}$$

Since both formulas come equally near to fulfilling the condition for alternately positive and negative carbon atoms, both electronic isomers will coexist and consequently both reaction products should be obtained. This has been found to be the case.

Finally, the isomeric rearrangement of alkyl halides can be readily accounted for, on the basis of the present hypothesis. It is a well-known fact that primary propyl bromide in the presence of catalyzers such as aluminum bromide, goes over to the secondary propyl bromide,[2] thus:

$$CH_3CH_2CH_2Br \longrightarrow CH_3CHBrCH_3,$$

and similarly,[3]
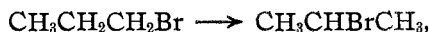
$$(CH_3)_2CHCH_2Br \longrightarrow (CH_3)_2CBrCH_3.$$
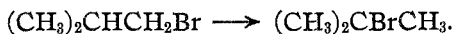
The reverse reactions, however, do not take place. On the other hand, primary butyl bromide does *not* rearrange to give the secondary bromide.[4] An explanation of the striking differences in the behavior of these compounds appears not to have been suggested heretofore. The present hypothesis accounts for the fact that the first 2 reactions take place only
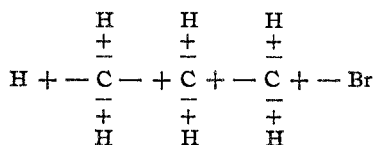
[1] Cohen, *loc. cit.,* p. 115.
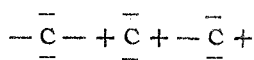[2] Aronstein, *Ber.,* 14, I, 607 (1881); *ibid.,* 16, 391 (1873).
[3] Eltekoff, *ibid.,* 8, 1244 (1873).
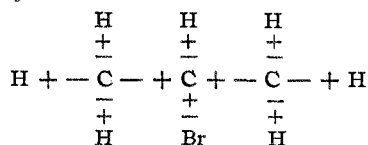[4] V. Meyer and Müller, *J. prakt. Chem.,* 46, 182 (1892).

as written above as well as for the non-occurrence of a similar reaction in the third case. The electronic formula for $CH_3CH_2CH_2Br$ is

$$
\begin{array}{ccc}
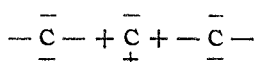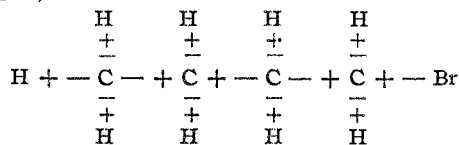H & H & H \\
+ & + & + \\
- & - & - \\
H + - C - & + C + & - C + - Br \\
+ & + & + \\
H & H & H
\end{array}
$$

i. e.,

$$
- C - + C + - C +
$$

and for $CH_3CHBrCH_3$ is

$$
\begin{array}{ccc}
H & H & H \\
+ & + & + \\
- & + & - \\
H + - C - & + C + & - C - + H \\
+ & - & + \\
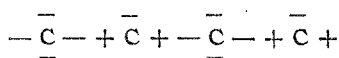H & Br & H
\end{array}
$$

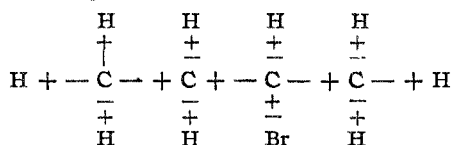*i. e.,*

$$
- C - + C + - C -
$$

It is evident that of the 2, the second formula comes the nearer to fulfilling the condition for alternately positive and negative carbon atoms. Consequently the primary bromide under proper conditions will rearrange to give the secondary bromide, while the reverse reaction will not take place. The reactions of $(CH_3)_2CHCH_2Br$ can be readily accounted for on the same basis. The electronic formula of primary butyl bromide $(CH_3CH_2CH_2CH_2Br)$ is

$$
\begin{array}{cccc}
H & H & H & H \\
+ & + & + & + \\
- & - & - & - \\
H + - C - & + C + & - C - & + C + - Br \\
+ & + & + & + \\
H & H & H & H
\end{array}
$$

i. e.,

$$
- C - + C + - C - + C +
$$

and that of the secondary is

$$
\begin{array}{cccc}
H & H & H & H \\
+ & + & + & + \\
\uparrow & - & - & - \\
H + - C - & + C + & - C - & + C - + H \\
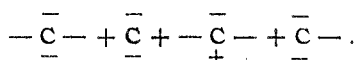- & + & - & + \\
H & H & Br & H
\end{array}
$$

i. e.,

$$
- C - + C + - C - + C - .
$$

It is evident that the carbon atoms in the first formula are approximately alternately positive and negative, while in the second formula the charges are more evenly distributed. According to our hypothesis, of 2 possible isomers that one is more stable which has its carbon atoms alternately

positive and negative, as far as possible. Consequently the transformation of the primary to the secondary bromide should not occur, which is in accordance with the facts. There are no observations available relating to the reverse reaction in this case.

It is to be kept in mind that the present theory is founded on 2 assumptions. First, that carbon compounds are of the same nature as inorganic compounds; that is, they are polar. For example, as NaCl is assumed to be Na^+ ^-Cl, so CH_4 is assumed to be $\substack{H \\ H} \pm \mp C \mp \pm \substack{H \\ H}$. Second, that the carbon atoms in a chain compound tend to become alternately positive and negative, and the more nearly this condition is fulfilled, the more stable is the compound. The first assumption may in a certain sense be considered self-evident, since the division of chemical compounds into organic and inorganic is universally admitted to be arbitrary and since the difference between the two classes seems to be one of degree and not of kind.[1] Many writers on organic chemistry in recent years have employed electronic formulas for organic compounds.[2]

With the aid of these two assumptions it thus becomes possible to account for a great many facts which otherwise appear unrelated on the basis of the common theory of the structure of carbon chain compounds. The fact that the various phenomena discussed above may be accounted for on the basis of the assumptions made, serves as a support for the correctness of these assumptions.

Summary.

Assuming that carbon compounds are polar in nature and that carbon atoms in a chain tend to assume alternately positive and negative charges, it has been shown that the fluctuation in the various physical properties of these compounds such as melting points, boiling points, and so forth, between the even and the odd members of a given series, may be accounted for. Various reactions, in which these compounds take part, such as the addition of halogen acids and the isomeric rearrangement of the halides may likewise be accounted for, on the basis of these assumptions.

WORCESTER, MASS.

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[1] Harkins and King (THIS JOURNAL, 41, 976 (1919)) state: "Thus even carbon compounds seem to be distinctly polar, because they have greater affinity for electrons than hydrogen, etc., and a smaller affinity than chlorine, etc. The polarity is, of course, very much less than that of salts."

[2] Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914); Fry, ibid., 30, 34 (1908); 36, 248 (1914); 34, 664 (1912); Fry, Z. physik. Chem., 76, 385, 398 (1911); 80, 29 (1912); 82, 665 (1913); Nelson, Beans and Falk, THIS JOURNAL, 35, 1810 (1913); Falk and Nelson, ibid., 32, 1637 (1910); 33, 1140 (1911); L. W. Jones, ibid., 36, 1268 (1914); L. W. Jones and Werner, ibid., 40, 1257 (1918); Hanke and Koessler, ibid., 40, 1726 (1918).