[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 47]

ELECTRON DISPLACEMENT IN CARBON COMPOUNDS

I. ELECTRON DISPLACEMENT VERSUS ALTERNATE POLARITY IN ALIPHATIC COMPOUNDS

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RECEIVED MAY 15, 1924 PUBLISHED NOVEMBER 5, 1924

Introduction

Lewis[1,2] was the first one to show that the effect of substituents upon the strength of organic acids can be accounted for satisfactorily on the basis of electron displacement,[3] and to point out that the electron displacement due to any substituent at one end of a chain of atoms extends throughout the entire chain. Latimer and Rodebush[4] have made use of this idea in accounting for the ionization strengths of some of the acids of phosphorus. Also, the properties of many classes of organic compounds can be accounted for satisfactorily on the basis of electron displacement. Another concept has been developed within recent years, which is the opposite of this viewpoint, at least when applied to open-chain compounds. According to it the carbon atoms in a chain are polarized alternately positive and negative. Cuy[5] has brought forward more evidence than any one else[6] in substantiation of the alternate polarity viewpoint in open-chain compounds. It is the purpose of this paper to show that the arguments in favor of alternate polarity are not conclusive, and to apply the displacement principle to some of the phenomena that have been cited in favor of it.

The evidence which Cuy presents may be summarized as follows: (*a*) the alternating character of the melting-point curves of homologous series; (*b*) addition of hydrogen halides to ethylene homologs; (*c*) addition of hydrogen halides to allene homologs; (*d*) rearrangement of alkyl bromides.

a. **Alternating Character of Melting-Point Curves.**—If the alternation of melting points is a function of the molecular structure, a similar alter-

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[1] Lewis, THIS JOURNAL, **38**, 762 (1916).

[2] See Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, for a more extended discussion of electron displacement.

[3] The hypothesis of electron displacement is most easily handled on the assumption that the shared electrons in molecules are stationary. Even though the electrons are moving in orbits about the nuclei which they join, it is still possible to regard the stationary position between the nuclei as a statistical average, and to represent shifting of the orbit by a shifting of the average position.

[4] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

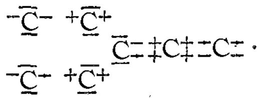
[5] Cuy, *ibid.*, **42**, 503 (1920).

[6] See also Lapworth, *J. Chem. Soc.*, 121, 416 (1920). Kermack and Robinson, *ibid.*, 121, 427 (1920). Stieglitz, THIS JOURNAL, **44**, 1301 (1922). Hanke and Koessler, *ibid.*, **40**, 1726 (1918).

nation of the boiling points should be manifest. The alternation of the boiling points is of small magnitude, and shows little regularity outside of the fatty acid series. Moreover, as Beutler[7] has pointed out, compounds containing even numbers of carbon atoms possess a higher symmetry and therefore higher melting points, than compounds containing odd numbers of carbon atoms. The alternation in melting points is therefore presumably a function of the crystal lattice, and not of the polar conditions within the molecule.

b. **Addition of Hydrogen Halides to Ethylene Homologs.**—The facts regarding the addition of hydrogen halides to olefins cited by Cuy are the action of hydrogen bromide and of hydrogen iodide on 2-pentene to produce 2-bromo- and 2-iodopentane, respectively, and the addition of hydrogen chloride to 2-hexene to produce 2-chlorohexane. Yet the data of Wagner and Saytzeff[8] on the action of hydrogen iodide on 2-pentene show that their product was a mixture of isomeric iodides, and not 2-iodopentane alone as Cuy assumes. Moreover, the data of Morgan[9] on the action of hydrogen chloride with hexene indicate that his hexene, which he prepared by the action of alcoholic potassium hydroxide on isomeric hexyl chlorides, consisted largely of 1-hexene, and not of 2-hexene, as Cuy assumes. The evidence from the addition of hydrogen halides to ethylene homologs therefore is still inconclusive and more accurate data are needed.[10]

c. **Addition of Hydrogen Halides to Allene Homologs.**—Although Cuy interpreted successfully the addition of hydrogen bromide to dimethyl and trimethyl allene, the extension of the principle to diethyl allene fails completely. According to him, the electronic formula of diethyl allene (omitting the hydrogen atoms) should be



$$\begin{matrix} -\overline{\underline{C}}-\ \ +\overline{\underline{C}}+ & \\ & \overline{\underline{C}}\begin{smallmatrix}-\\-\end{smallmatrix}\begin{smallmatrix}+\\+\end{smallmatrix}C\begin{smallmatrix}+\\+\end{smallmatrix}\begin{smallmatrix}-\\-\end{smallmatrix}C\begin{smallmatrix}-\\-\end{smallmatrix}\ \cdot \\ -\overline{\underline{C}}-\ \ +\overline{\underline{C}}+ & \end{matrix}$$

and the addition of hydrogen bromide should give $(C_2H_5)_2CHCBr_2CH_3$ exclusively whereas, as Cuy himself mentions $(C_2H_5)_2CBrCH_2CH_2Br$ is formed.[11]

d. **Rearrangement of Alkyl Bromides.**—Finally, Cuy finds additional support in the behavior of alkyl bromides when heated, in that 1-bromopropane rearranges to 2-bromopropane, 1-bromo-2-methylpropane rearranges to 2-bromo-2-methylpropane, and 1-bromobutane does not rearrange. Now the rearrangement of the latter substance at 248° has been

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[7] Beutler, *Z. anorg. allgem. Chem.*, **120**, 24 (1922). See also Pauly, *ibid.*, **119**, 271 (1921).

[8] Wagner and Saytzeff, *Ann.*, **179**, 321 (1875).

[9] Morgan, *Ann.*, **177**, 304 (1874).

[10] This problem is being investigated in this Laboratory.

[11] Ipatieff, *Chem. Centr.*, **1899**, II, 18.

studied in this Laboratory, and it has been found to proceed smoothly and completely to 2-bromobutane. Moreover, when 2-bromobutane is heated for 29 hours at 248° there is no indication of 1-bromobutane being formed. This is contrary to the alternate polarity idea, which requires that the secondary bromide should be transformed into the primary.

Summarizing, it can be said that experimental evidence which is at all conclusive is opposed to the concept of alternate polarity of carbon atoms in open chains.

Polarity Due to Electron Displacement.—When an electron pair is shifted away from a carbon atom towards a negative substituent, the carbon becomes polarized in the sense that the polarity is reversed on opposite sides of the atom. This is shown in Fig. 1,

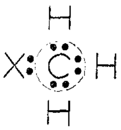
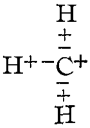


Fig. 1.

where X represents a negative substituent towards which the electron pair is shifted, and the dotted circle represents the surface of the sphere in which electrons lie when they are in their more stable positions,[12] that is, positions characteristic of the typically non-polar unions of methane. Taking the electrostatic conditions on this surface as a measure of the polarity of the carbon atom, there is a positive field in the region adjacent to X, and weaker negative fields in regions adjacent to the hydrogen atoms. The polarity formula of CH_3I may be written  $\mathrm{H}^{+-}\underset{\underset{\mathrm{H}}{+}}{\underset{-}{\overset{\overset{\mathrm{H}}{+}}{\overset{-}{\mathrm{C}}}}}{}^{+-}\mathrm{I}$, which is identical with the usual electronic formula. In ethyl iodide all of the electrons in the molecule are displaced towards the iodine atom, giving rise to conditions best represented by the polarity formula ${}^{-}\underline{\overline{\mathrm{C}}}{}^{+-}\underline{\overline{\mathrm{C}}}{}^{+-}\mathrm{I}$, which is different from the usual so-called electronic formula ${}^{-}\underline{\overline{\mathrm{C}}}{}^{-+}\underline{\overline{\mathrm{C}}}{}^{+-}\mathrm{I}$. By a similar mechanism, an opposite displacement is induced by a positive substituent such as methyl. This concept of polar conditions in the carbon chain is decidedly different from that assumed by Cuy, Lapworth, Kermack and Robinson, and others.

There is a certain disadvantage in the use of such a polarity formula because it does not indicate a difference in the degree of polarity among the various atomic unions. In the formula of ethyl iodide given above, the polarity of a terminal carbon-hydrogen union is small compared to the polarity of the other carbon-hydrogen unions, which in turn is less

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[12] Lewis, Ref. 2, p. 150.

than that of the carbon-iodine bond. In fact, a union some distance from the polar substituent differs but little from the typically non-polar carbon-hydrogen union.

Interpretation of Reactions in Terms of Electron Displacement

It now remains to show that the principle of electron displacement can account for the reactions mentioned above. Inasmuch as the rearrangement of alkyl bromides at elevated temperatures can be regarded as dissociation into hydrogen bromide and alkylene, followed by addition, this reaction can be classified along with the addition of hydrogen halides to olefin and allene homologs, as an example of addition to the double bond. It is only necessary, therefore, to discuss the mechanism of this phenomenon in terms of electrons and electron displacement.

To account for the preponderance of one isomer over another when hydrogen iodide adds to ethylene derivatives, the polar character of substituent groups in the latter must be considered. It is generally recognized that alkyl groups are more positive than hydrogen, while halogens, carboxyl, etc., are more negative. Propylene therefore may be represented as in Fig. 2, in which the four electrons of the double bond lie closer to Carbon 3 than to Carbon 2. The polarity formula of propylene therefore may be written as ${}^{-}\overline{\underline{C}}{}^{+}\,{}^{-}\overline{C}{}^{\pm}\,{}^{\mp}C_{\mp}$, and the reaction with hydrogen iodide as: $H_3C^{+}\,{}^{-}CH^{\pm}\,{}^{\mp}CH_2 + H^{+}I^{-} \longrightarrow H_3C^{+}\,{}^{-}\underset{\substack{+\\-\\I}}{CH}{}^{-}\,{}^{+}CH_3$. Here the positive hydrogen goes to the more negative carbon atom, and the negative iodine to the more positive carbon atom.

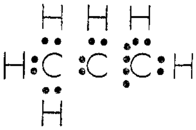

Fig. 2.

In acrylic acid, however, the electron displacement, because of the strong pull of carboxyl on the electron pair, is towards the carboxyl group, as shown in Fig. 3.

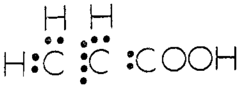

Fig. 3.

which may be written $CH_2{}^{\pm}\,{}^{\mp}CH^{+}\,{}^{-}COOH$. When hydrogen iodide adds, the iodine goes to the beta position: $CH_2{}^{\pm}\,{}^{\mp}CH^{+}\,{}^{-}COOH + H^{+}\,I^{-} \longrightarrow$

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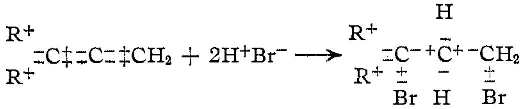
[13] The displacement formulas in this article, like those on this page, are merely qualitative. No attempt is made to indicate displacements other than the ones under discussion, nor the tendency of electrons in the double bond to pair,

$I^{-}\,{}^{+}CH_2^{+}\,{}^{-}CH^{+}\,{}^{-}COOH$. The assumption of alternate polarity of carbon atoms is unnecessary.

When hydrogen bromide adds to members of the allene series, the formation of compounds in which the two bromine atoms are in the 1,3 position may be accounted for on the basis of electron displacement as follows:



$$\begin{matrix} R^+ \\ R^+ \end{matrix}\!\!\overset{-}{\underset{+}{=}}C\ddagger\overset{-}{\underset{+}{=}}C\overset{-}{\underset{-}{=}}\ddagger CH_2 + 2H^+Br^- \longrightarrow \begin{matrix} R^+ \\ R^+ \end{matrix}\!\!\overset{-}{\underset{+}{=}}\underset{\underset{Br}{\pm}}{C^-}\;{}^{+}\overset{\overset{H}{-}}{\underset{\underset{H}{-}}{C}}{}^{+}\;{}^{-}\underset{\underset{Br}{\pm}}{CH_2}$$

The rearrangement of an alkyl bromide when heated may be considered as taking place in two steps; first, the bromide dissociates into hydrogen bromide and alkylene, and second, the products recombine to form the isomeric alkyl bromide. The bromine goes to the more positive carbon atom, which in accordance with the idea of electron displacement is the one to which the most alkyl groups are attached. It should be a general rule that primary bromides will rearrange to give isomers in which the bromine is joined to the second carbon atom, and that these isomers will in turn rearrange to give tertiary derivatives, when the third carbon atom is tertiary. On the basis of alternate polarity, however, the normal primary bromides containing odd numbers of carbon atoms should rearrange to the corresponding secondary derivatives, while those containing even numbers of carbon atoms should not rearrange.

The addition of hydrogen halides to propylene, to acrylic acid, and to dimethyl allene can be explained just as satisfactorily from the standpoint of electron displacement as from that of alternately polarized carbon atoms, while the addition of hydrogen bromide to diethyl allene, and the rearrangement of 1-bromobutane to 2-bromobutane are better explained on the basis of electron displacement.

Experimental Part

The 1-bromobutane was prepared from 1-butanol, Eastman, b. p., 116–117° by treatment with sodium bromide and sulfuric acid;[14] it was washed with concd. sulfuric acid to remove any butanol, then with water until neutral, dried over anhydrous copper sulfate and distilled, the portion boiling at 99.0° (uncorr.) being used in these experiments. The 2-bromobutane, Eastman, was washed with concd. sulfuric acid and with water, dried over calcium chloride, distilled and the portion distilling at 90–91° (uncorr.) was used.

The analysis of mixtures of 1-bromo- and 2-bromobutane was made by delivering known amounts of 1-bromo- and 2-bromobutane into large test-tubes by means of a Lunge acid pipet, stirring at uniform rate for three hours with standard silver nitrate solution,[15] and back titrating the excess of silver nitrate with standard thiosulfate solution. Preliminary experiments[16] showed that 2-bromobutane, when stirred con-

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[14] *Univ. Illinois Bull.*, **6**, 18 (1920).

[15] Michael and Leupold, *Ann.*, **379**, 263 (1911).

[16] By W. P. Baxter in this Laboratory.

tinuously with 0.05 *N* silver nitrate for three hours, reacted to the extent of 67% only. When an excess of approximately 0.2 *N* silver nitrate is used, 82% of the 2-bromobutane reacts in three hours at 22°, whereas only 3.8% of 1-bromobutane reacts.

Fig. 4 is the curve obtained by plotting percentage composition of known mixtures of the two bromides against percentage of bromide as found by analysis, using 0.2 *N* silver nitrate. From this curve one can read off the percentage composition of any unknown mixture of the two bromides, having previously determined the percentage of bromide reacting.

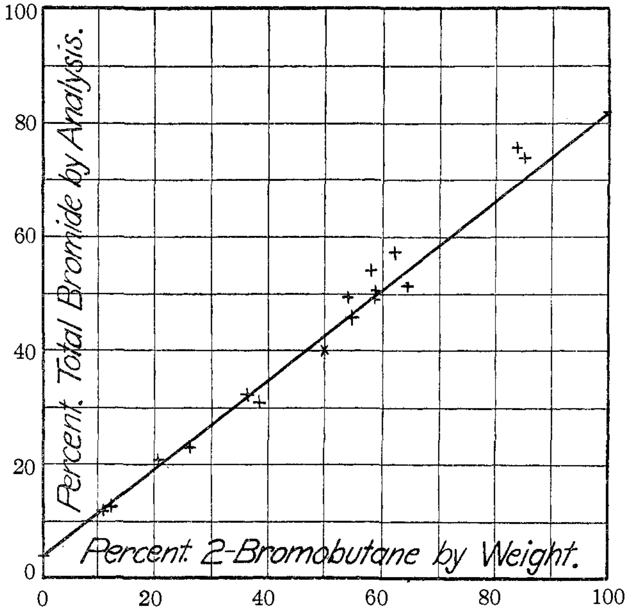

Fig. 4.—Analysis of known mixtures of 1-bromobutane and 2-bromobutane.

Rearrangement of 1-Bromobutane.—This was accomplished by heating 2 to 7 g. of the bromide in sealed glass tubes 12 mm. in diameter and 80 to 150 mm. in length, suspended in the vapors of a boiling liquid. Since a preliminary experiment[16] had shown that only 0.9% of 2-bromobutane was formed during 20 hours' heating at 180°, it was realized that a temperature above 200° would be necessary in order to secure a reasonable rate of reaction. At 248°, the temperature of boiling benzoic acid, rearrangement took place at a satisfactory rate, and all of the work was done at this temperature. Table I gives the results of these experiments over different lengths of time, and Fig. 5 is the curve obtained when the percentage of 2-bromobutane is plotted against time.

The rearrangement of 1-bromobutane to 2-bromobutane at 248° is a monomolecular reaction, as indicated by the velocity constants in Table I.

Table I

Rearrangement of 1-Bromobutane at 248°

Hours heated	3	3.67	7	19	20	27	29	50	80[e]
2-Bromobutane found,[a] %	23.0	20.83[b]	45.5	63.0	64.0	62.5[c]	87.5	96.5[d]	98.0
K, monomol. reaction	0.038	0.028	0.036	0.023	0.022	0.015	0.031	0.029	0.021
									Av. 0.029

[a] Duplicate analysis made.

[b] Experiment in triplicate.

[c] Badly charred.

[d] Dissociation into butylene and hydrogen bromide shown to be 3.1%, by titration of wash water.

[e] Time of heating not definitely known.

The agreement among the individual constants is not very good, a fact which can be attributed in part at least to the errors inherent in the method of analysis. Probably the best individual value is 0.028 which comes from the mean of six results obtained in the 3.67-hour runs, all checking one another quite well. Since the product from Expt. 6 was badly charred, and since the time in Expt. 9 is not known accurately, the value of the constant obtained in these two experiments is disregarded in calculating the mean value, which is 0.029. The curve of Fig. 5 is obtained by using this value, the greatest deviation from which is 0.009, or 31%.

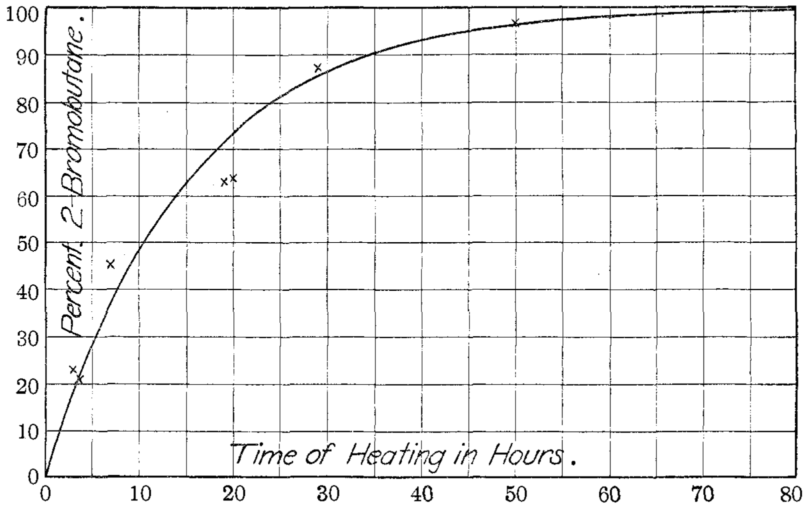

Fig. 5.—Rearrangement of 1-bromobutane at 248°.

Parallel experiments were made in order to determine whether or not the rearrangement is dependent upon the dimensions of the liquid surface[17] or upon the volume of the gaseous phase,[18] but no difference was observed.

[17] The speed with which isobutyl bromide rearranges to tertiary butyl bromide is a function of the surface area. Ref. 15.

[18] Eltekoff, *Ber.*, 8, 1244 (1875).

Evidence of dissociation of the bromide into alkylene and hydrogen bromide was obtained in the last two experiments, in which 3.1% and 4.2% of hydrogen bromide was found by breaking the tubes under water and titrating the resulting aqueous solution with standard base.

Apparently the reaction runs to completion at the temperature of 248°, a behavior in marked contrast with that of *iso-* and *tertiary*-butyl bromides.[15]

That 2-bromobutane is actually formed during the rearrangement, and constitutes almost all the reaction product is shown by the results of the fractional distillation of the product from the 50-hour run. The reaction product was first washed with water to remove hydrogen bromide, dried over anhydrous copper sulfate, and then slowly fractionated by means of a small, efficient, fractionating column.

Fraction	Temperature range (uncorrected) °C.	Approximate percentage of total	Percentage of 2-bromobutane by analysis
1	below 89.6	25	97
2	89.6–90.1	40	96
3	90.1–91.2	17	..
4	91.2–93.5	8	..
5	brown residue	10	..

When 2-bromobutane was heated at 248° for 29 hours in a sealed Pyrex tube, it was concluded that there had been no change into the normal form, because the product was 100% 2-bromobutane by analysis, and when fractionally distilled came over almost entirely below 95°.

Fraction	1	2	3	4	5
Temp. range, °C.	below 89.5	89.5–90.2	90.2–92.0	92.0–95.0	brown residue
Approx. %	20	24	40	8	8

Summary

1. The addition of hydrogen halides to propylene, to acrylic acid and to dimethyl allene can be explained just as satisfactorily from the standpoint of electron displacement as from that of alternate polarized carbon atoms.

2. The addition of hydrogen bromide to diethyl allene, and the rearrangement of 1-bromobutane to 2-bromobutane are better explained on the basis of electron displacement.

3. When heated at 248°, 1-bromobutane rearranges to 2-bromobutane.

4. The reaction is monomolecular. and apparently non-reversible or reversible to a slight extent only.

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