ERRATA.

HEATS OF COMBUSTION OF OCTANES.

T. W. RICHARDS AND R. H. JESSE.

Vol. 32 (1910):

P. 289, line 13, for 4.179 read 1/4.179.

P. 292, line 24, for 110.11 read 114.14.

P. 292, table, last two columns should contain the following figures in order (instead of those given): 5448, 5442, 5454, 5444, 5439 (Kilojoules); 1304, 1302, 1305, 1303, 1301 (Calories).

P. 292, second line below table, for "5247 to 5261" read "5439 to 5454."

P. 293, line 5, for "5253" read "5445."

P. 296, table, the last five numbers in the second column of figures should read "5448, 5442, 5454, 5444, 5439."

P. 296, table, the last five numbers in the last column of figures should read "5482, 5474, 5487, 5477, 5472."

P. 297, line 2, for "688" read "880;" lines 4, and 9, for "172" read "110;" line 4, for "hydrogens" read "hydrogen molecules;" line 11, for "344" read "220" and for "300" read "424."

P. 298, line 13, for "5256" read "5448;" line 14, for "5250," "5261," and "5252" read "5442," "5454," and "5444," respectively; line 15, for "5247" read "5439."

The authors are indebted to Professor W. A. Noyes of Illinois and Professor W. A. Roth, of Greifswald for the discovery of some of these errors, which are in part mere misprints and in part due to an unfathomable mistake in the assumed molecular weight of octane. Fortunately, none of the conclusions of the paper is at all affected by the mistakes, because all of the octanes were equally affected by them.

CORRECTION.

The last half of the sentence at the foot of page 89 (January number of THIS JOURNAL) instead of reading, "and the molal concentration of the H^+ ion $^2 \times 10^4$ being plotted as ordinates," should read, "and the molal concentration of the H^+ ion $\times 10^4$ being plotted as ordinates.[2]" The number (2) refers to a foot-note and does not mean the square of the H^+, as the reading would indicate.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

INTERPRETATIONS OF SOME STEREOCHEMICAL PROBLEMS IN TERMS OF THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

I. ANOMALOUS BEHAVIOR OF CERTAIN DERIVATIVES OF BENZENE.

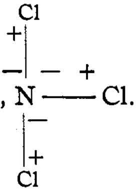
BY HARRY SHIPLEY FRY.

Received December 15, 1913.

The fundamental principles employed in various applications of the electronic conception of positive and negative valences have been presented and discussed in previous papers.[1]

The present series of papers is a further extension of the former principles in an endeavor to interpret only a few of the many stereochemical problems now confronting us and concerning which Cohen[2] tersely remarks: "It must be confessed that we are still profoundly ignorant of the change which substituents effect in the character of the molecule as a whole, the causes which determine the rules of orientation—and a host of other phenomena of a similar nature."

The particular problems to be considered in this paper relate to the anomalous behavior of certain derivatives of benzene, and the interpretations herewith offered should be regarded as an extension of those principles which are related to the electronic formula of benzene. Therefore, it will be necessary to recall briefly a few of those principles in order to present more clearly the present topics, both theoretical and experimental.

As a guiding principle, in the application of the electronic conception of positive and negative valences to the atoms of any molecule, let it be recalled that if the valence of an element is (n) the element may function in ($n + 1$) different ways. A simple illustration is found in the case of univalent chlorine ($n = 1$), which may function in ($n + 1$), *i. e.*, two different ways: positively univalent chlorine, $\overset{+}{\mathrm{Cl}}$, and negatively univalent chlorine, $\overset{-}{\mathrm{Cl}}$. Experimental evidence for the existence of positive chlorine was presented first by W. A. Noyes[3] relative to the constitution of nitrogen trichloride,  $\begin{array}{l} \mathrm{Cl} \\ +| \\ -|\;\;-\;\;+ \\ \mathrm{N}\text{——}\mathrm{Cl} \\ |- \\ |+ \\ \mathrm{Cl} \end{array}$.[4] Stieglitz[5] also postulated the existence of positively and negatively functioning chlorine from the standpoint of the interaction of chlorine and water according to the equation $\mathrm{Cl_2} + \mathrm{HOH} \rightleftarrows \mathrm{HCl} + \mathrm{HOCl}$. Employing electronic formulas, this reaction is represented as follows:

$$\mathrm{Cl}\overset{-\;+}{\text{——}}\mathrm{Cl} + \mathrm{H}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{H} \rightleftarrows \mathrm{H}\overset{+\;-}{\text{——}}\mathrm{Cl} + \mathrm{H}\overset{+\;-}{\text{——}}\mathrm{O}\overset{-\;+}{\text{——}}\mathrm{Cl}.$$

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[1] Fry, THIS JOURNAL, 30, 34 (1908); *Z. physik. Chem.*, 76, 385, 398, 591 (1911); 80, 29 (1912); 82, 665 (1913); THIS JOURNAL, 34, 664 (1912).

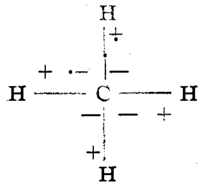
[2] "Organic Chemistry for Advanced Students," p. 293.

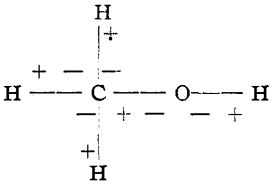
[3] THIS JOURNAL, 23, 460 (1901).

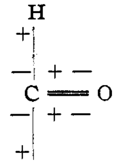
[4] *Ibid.*, 35, 767 (1913).

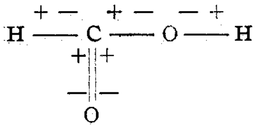
[5] *Ibid.*, 23, 796 (1901).

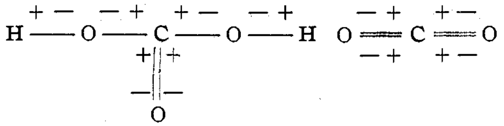
Consider now the valences of the carbon atom in the electronic formulas[1] of the typical compounds, methane, methylalcohol, formaldehyde, formic acid, carbonic acid and its anhydride, carbon dioxide. If, in these compounds, the hydrogen valences are positive and the oxygen valences negative, then the following electronic formulas result:


I.

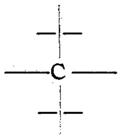

II.

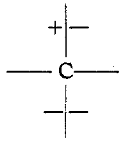

III.

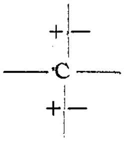

IV.


V.

The valence (n) of the carbon atom is 4; the number of ways in which the carbon atom may function ($n + 1$) is 5. The five types (I to V) as derived from the above electronic formulas may be indicated as follows:


I.


II.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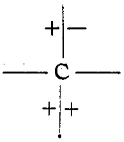
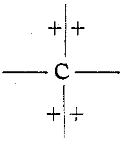

IV.


V.

In terms of the electron theory the acquirement of electrons or negative valences corresponds to reduction; the loss of electrons, *i. e.*, the development of positive valences corresponds to oxidation. The above types represent the successive stages of oxidation in the transitions from methane to carbonic acid or its anhydride.

If benzene nuclei (centric formulas) are composed of the several types of carbon atoms noted above, every possible symmetrically constituted formula for benzene requires that the hydrogen atoms in positions 1, 3, and 5 are negative while the hydrogen atoms in positions 2, 4, and 6 (relatively speaking) are positive.[2] Omitting centric and double bonds, the abbreviated electronic formula of benzene is represented as follows:

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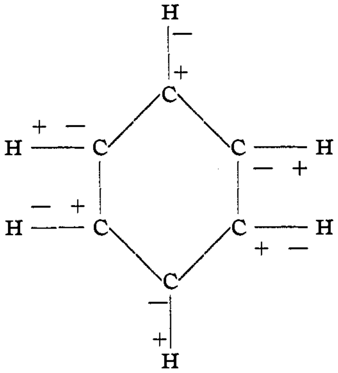
[1] Fry, *Z. physik. Chem.*, **76**, 405 (1911).

[2] *Ibid.*, **76**, 388 (1911).



Some of the reasons for the proposed electronic formula for benzene may be summarized briefly as follows:

(1) The Kekulé and centric formulas of benzene fail to show any structural basis for the relationships existing between ortho and para positions in contradistinction to the meta positions. The electronic formula shows that if a given hydrogen atom or substituent is negative, then those hydrogen atoms or substituents ortho and para to it are each positive while those meta to it are each negative.

(2) Collie's space formulas for benzene[1] constructed with tetrahedron models of carbon atoms shows the existence of two distinct sets of hydrogen atoms, namely, the 1,3,5-set and the 2,4,6-set. Concordantly the electronic formula for benzene presents two distinct sets of hydrogen atoms, namely, the 1,3,5-set which functions negatively in contradistinction to the 2,4,6-set which functions positively. This feature is maintained when the electronic formulas or "electromers" of benzene are in the states of dynamic equilibria presented by Collie's space formulas.[2]

(3) The existence of two sets of hydrogen atoms enabled Collie to propose a stereochemical explanation of the Crum Brown and Gibson Rule.[3] The electronic formula of benzene likewise lends itself to an interpretation of the same rule, showing how meta disubstitution derivatives are formed in some cases while ortho and para diderivatives result in others.[4]

One of the many anomalies encountered in the formation of disubstitution derivatives of benzene is the behavior of chlorobenzene and nitrobenzene when nitrated and chlorinated, respectively. Chlorobenzene when nitrated gives ortho and para chloronitrobenzenes while nitrobenzene when chlorinated yields only metachloronitrobenzene. According to principles previously developed from the Crum Brown and

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[1] *J. Chem. Soc.*, 71, 1013 (1897).

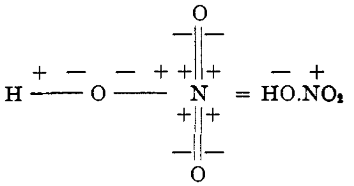
[2] Fry, *Z. physik. Chem.*, 76, 400 (1911).

[3] *J. Chem. Soc.*, 61, 366 (1892).

[4] Fry, *Z. physik. Chem.*, 76, 391 (1911).

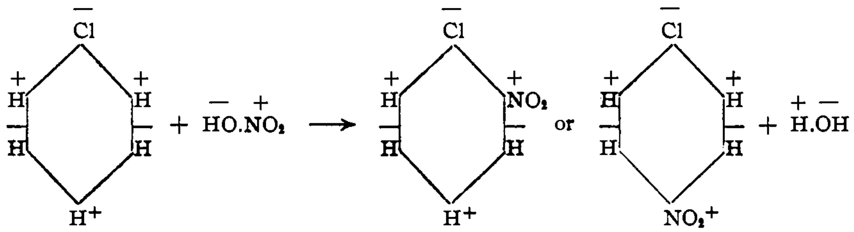
Gibson Rule, the electronic formula of chlorobenzene is $\overset{+}{C_6H_5}.\overset{-}{Cl}$ while that of nitrobenzene is $\overset{-}{C_6H_5}.\overset{+}{NO_2}$. Hypochlorous and nitric acids are represented thus:

$$\overset{+\ \ -}{H\text{——}O}\overset{-\ \ +}{\text{——}Cl} = \overset{-}{HO}.\overset{+}{Cl};$$

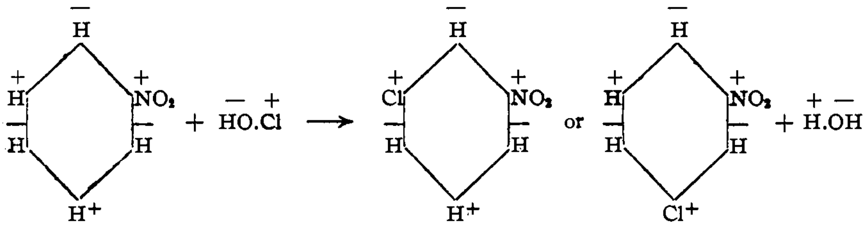


$$\overset{+\ \ -}{H\text{——}O}\overset{-\ \ +}{\text{——}N} = \overset{-}{HO}.\overset{+}{NO_2}$$

When, therefore, $\overset{+}{C_6H_5}.\overset{-}{Cl}$ is nitrated, *i. e.*, reacts with $\overset{-}{HO}.\overset{+}{NO_2}$, the positive nitro group replaces a positive hydrogen atom. Positive hydrogen atoms occupy positions ortho and para to the negative chlorine atom. Consequently the nitro radical must occupy positions either ortho or para to the chlorine atom in accordance with the following scheme:

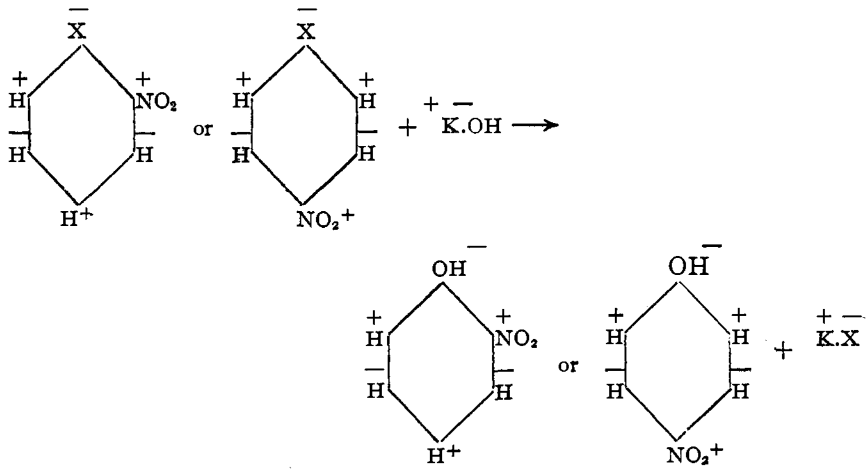


On the other hand, in the chlorination of nitrobenzene, since absolutely anhydrous chlorine does not react with anhydrous reagents, it follows that the substitution of chlorine in nitrobenzene may involve the formation of hypochlorous acid $(\overset{-}{HO}.\overset{+}{Cl})$ which in turn reacts according to the following scheme:

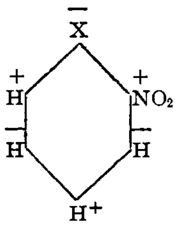


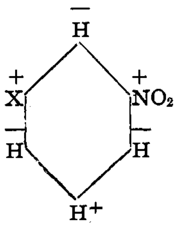
Thus when substituents are of the same sign or polarity they occupy positions which are meta to each other. If two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other. This principle may serve as the basis of a general rule for the determination of the positions of substituents in the benzene nucleus.

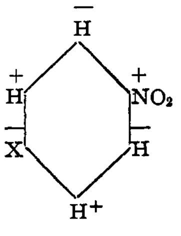
The proposed electronic formula for benzene, and the above principle of substitution applied thereto, indicate that the chlorine atom in ortho and in para chloronitrobenzene is negative while in meta chloronitrobenzene it is positive. Is there any experimental evidence to substantiate these electronic formulas of ortho, meta, and para chloronitrobenzenes? The experimental verification is presented by the apparently anomalous behavior of ortho, meta, and para, chloro- and bromonitrobenzenes when heated with potassium hydroxide. The ortho and para compounds, but not the meta, are found to exchange halogen for hydroxyl. Now the electronic formula of potassium hydroxide must be $\overset{+\quad-\quad-\quad+}{\text{K——O——H}}$ since in its aqueous solution the ions are $\overset{+}{\text{K}}$ and $\overset{-}{\text{OH}}$. Interaction with ortho and para chloro- and bromonitrobenzenes results in the exchange of the halogen atoms for the *negative* hydroxyl radical. Therefore, the halogen atoms must be negative also, the reactions taking place as follows. (X = Cl or Br):



On the other hand, since metachloro- and metabromonitrobenzene do not exchange their halogen atoms for the *negative* hydroxyl it follows that the halogen atoms in the meta compounds are not negative, and hence are assumed to function positively. All of these facts lead to the following electronic formulas for chloro-, bromo-, and hydroxynitrobenzenes (X = Cl, Br, or OH):

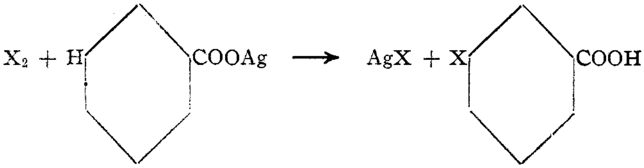






The same formulas have been derived through the application of the conception of positive and negative valences to the Brown and Gibson Rule. They are correlated to the electronic formula of benzene and afford an interpretation of the apparently anomalous behavior in the reactions just described.

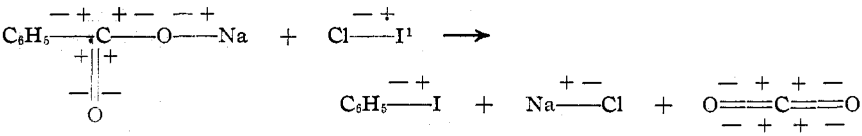
In this connection an interpretation of the action of the halogens, bromine and iodine, upon silver benzoate may be of interest. Silver benzoate reacts readily with liquid bromine, and violently with iodine at a temperature of 150°. The products are meta bromo- and meta iodobenzoic acids and silver bromide and iodide respectively: (X = Br or I)



Why does the halogen atom which enters the ring assume a position meta to the carboxyl in preference to an ortho or para position? According to the electronic conception of positive and negative valences the halogen molecule, X_2, undergoes dissociation yielding a positive and a negative halogen atom:

$$X_2 = X\overset{+\;-}{\text{——}}X \rightleftarrows \overset{+}{X} + \overset{-}{X}$$

The electronic formula of silver benzoate requires that the carboxyl radical be positive since it is a derivative of carbonic acid in which all of the four valences of the carbon atom function positively. In other words, the carbon atom of the carboxyl radical in benzoic acid is in the same state of oxidation as is the carbon atom in carbonic acid or its anhydride, $O\overset{-\;+}{\underset{-\;+}{=\!=}}C\overset{+\;-}{\underset{+\;-}{=\!=}}O$. Experimental evidence substantiating this assumption is afforded by the fact that iodine chloride and sodium benzoate interact giving iodobenzene, sodium chloride and carbon dioxide according to the following equation:



$$C_6H_5\overset{-\;+}{\text{——}}\underset{\substack{+\|+\\-\|-\\O}}{C}\overset{+\;-}{\text{——}}O\overset{-\;+}{\text{——}}Na + Cl\overset{-\;+}{\text{——}}I\text{[1]} \longrightarrow$$

$$C_6H_5\overset{-\;+}{\text{——}}I + Na\overset{+\;-}{\text{——}}Cl + O\overset{-\;+}{\underset{-\;+}{=\!=}}C\overset{+\;-}{\underset{+\;-}{=\!=}}O.$$

Since the carboxyl radical in benzoic acid is positive, the interaction

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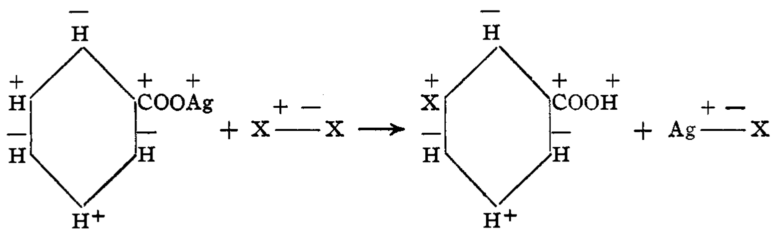
[1] The electronic formula for iodine chloride, $I\overset{+\;-}{\text{——}}Cl$, is evident from its interaction with potassium hydroxide yielding potassium chloride and potassium hypoiodite, thus:

$$2K\overset{+\;-}{\text{——}}O\overset{-\;+}{\text{——}}H + Cl\overset{-\;+}{\text{——}}I \longrightarrow$$

$$K\overset{+\;-}{\text{——}}Cl + K\overset{+\;-}{\text{——}}O\overset{-\;+}{\text{——}}I + H\overset{+\;-}{\text{——}}O\overset{-\;+}{\text{——}}H.$$

of the halogens, bromine and iodine, with silver benzoate must be represented by the following electronic formulas:



The positive silver must combine with negative halogen leaving the positive halogen to enter the ring. The positive hydrogen atoms of the ring occupy positions meta to the positive carboxyl group. Therefore, the entering positive halogen atom, in substituting a positive hydrogen atom, must likewise occupy a position meta to the positive carboxyl radical. This reaction substantiates the electronic formula for benzene. Furthermore, the dissociation of the halogen molecule into positive and negative parts, as indicated in the above equation, is a confirmation of the idea suggested at an earlier date by W. A. Noyes[1] that "If we suppose what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well may ionize into positive and negative parts."

Other stereochemical rearrangements, presented by Chattaway and Orton[2] in their study of the substituted nitrogen halides, have been interpreted in terms of positive and negative valences in a previous communication[3] further demonstrating that halogen atoms may function not only negatively but also positively.[4]

Reference may now be made to the differences in behavior of the carboxyl radicals in the benzene nucleus, some of which function negatively while others function positively. The anomalous behavior of the dihydro phthalic acids is worthy of note. Baeyer has shown that the $\Delta^{3,5}$, $\Delta^{2,4}$, and $\Delta^{2,6}$ acids when oxidized yield benzoic acid through the loss of one molecule of carbon dioxide. There has been much speculation as to why only one molecule instead of two molecules of carbon dioxide is removed

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[1] THIS JOURNAL, 23, 460 (1901).

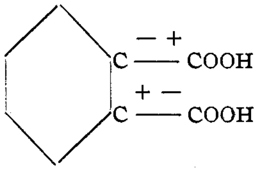
[2] *J. Chem. Soc.*, 75, 1046; *Ber.*, 32, 3572.

[3] Fry, THIS JOURNAL, 34, 667 (1912).

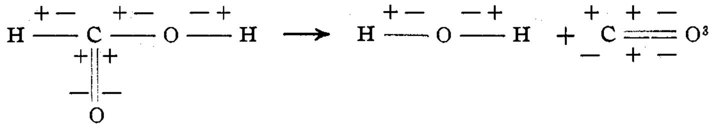
[4] The possibility of an electromer of the type $\overset{+\ -}{R.X}$ passing to an electromer of the type $\overset{-\ +}{R.X}$ is reviewed in the following paper (THIS JOURNAL). Detailed evidence of such changes is presented by L. W. Jones in the last number of the *Am. Chem. J.*, Dec., 1913.

from the acids in question.[1] The interpretation of this anomaly as presented in a previous paper[2] will now be briefly indicated since it is herewith to be extended to the interpretation of other anomalies manifested by certain substituted oxybenzoic acids.

The electronic formula of benzene requires that substituents occupying ortho positions to each other be of opposite polarity. Consequently in phthalic acid one carboxyl radical functions positively and the other negatively, thus

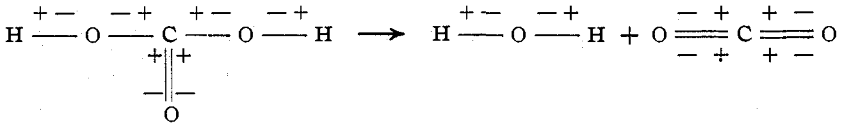


If reference be made to the electronic formulas of formic and carbonic acids, it is evident that the carboxyl radical in formic acid is negative $(\mathrm{H}\overset{+\ -}{\text{——}}\mathrm{COOH})$ while in carbonic acid it is positive, $(\mathrm{HO}\overset{-\ +}{\text{——}}\mathrm{COOH})$. Furthermore in formic acid three of the valences of the carbon atom are positive and one is negative. Accordingly formic acid on decomposition ordinarily yields carbon monoxide and water:



$$\mathrm{H}\overset{+\,-}{\text{——}}\underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H} \longrightarrow \mathrm{H}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H} + \overset{+}{\underset{-}{\mathrm{C}}}\overset{+\,-}{\underset{+\,-}{=\!=}}\mathrm{O}\;\text{[3]}$$

On the other hand, in carbonic acid and its anhydride each of the four valences is positive. Accordingly carbonic acid on decomposition yields water and carbon dioxide:



$$\mathrm{H}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H} \longrightarrow \mathrm{H}\overset{+\,-}{\text{——}}\mathrm{O}\overset{-\,+}{\text{——}}\mathrm{H} + \mathrm{O}\overset{-\,+}{\underset{-\,+}{=\!=}}\mathrm{C}\overset{+\,-}{\underset{+\,-}{=\!=}}\mathrm{O}$$

From the above it is evident that a carboxyl radical which is negative corresponds to the stage of oxidation represented by the carbon atom in formic acid, which does not lose carbon dioxide. On the other hand a carboxyl radical which is positive corresponds to the stage of oxidation represented by the carbon atom in carbonic acid, which very readily loses

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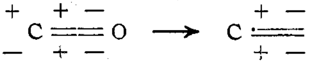
[1] Baeyer, *Ann.*, **269**, 178 (1892); Brühl, *J. prakt. Chem.*, [2] **49**, 229 (1894); Cohen, ’Organic Chemistry” (Longmans, Green & Co.), 1907, p. 461.

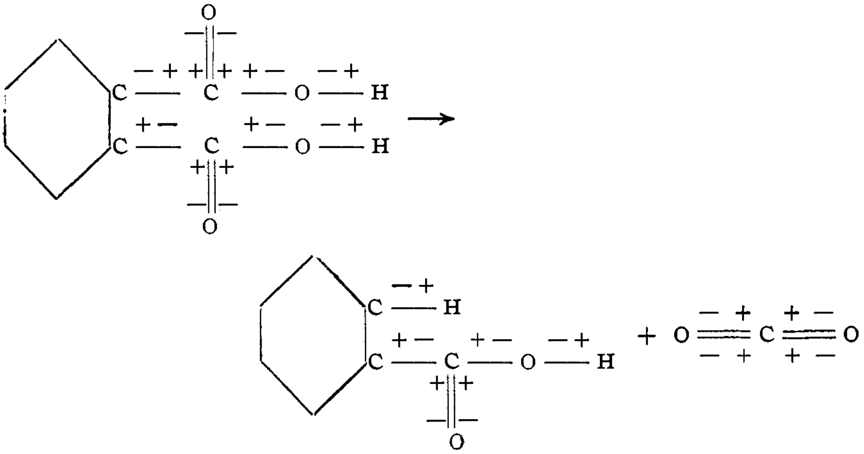
[2] Fry, THIS JOURNAL, **34**, 671 (1912).

[3] The free positive and the free negative valence of the carbon atom in carbon monoxide become neutral. In other words, carbon in carbon monoxide is divalent:



$$\overset{+}{\underset{-}{\mathrm{C}}}\overset{+\,-}{\underset{+\,-}{=\!=}}\mathrm{O} \longrightarrow \mathrm{C}\overset{+\,-}{\underset{+\,-}{=\!=}}\mathrm{O}$$

carbon dioxide. Therefore, dihydro phthalic acid, which embodies a negative carboxyl radical and a positive carboxyl radical, loses only one molecule of carbon dioxide, a result of the decomposition of the positive carboxyl radical as indicated in the following scheme:



This explanation may now be extended to the interpretation of many other anomalous phenomena involving the liberation of carbon dioxide from various substituted benzoic acids.

Cazeneuve[1] in a study of the decomposition of various hydroxybenzoic acids found that some of them readily lose carbon dioxide when heated with water or aniline, while others were quite stable. For instance, orthohydroxybenzoic acid (salicylic acid) when heated with aniline to 240° in a sealed tube gave phenol and carbon dioxide. Parahydroxybenzoic acid likewise gave carbon dioxide but the meta acid suffered no change. The instability of the ortho and the para acids and the stability of the meta acid may be interpreted in terms of the electronic formula of benzene and the polarity of the carboxyl radicals. These radicals in ortho and parahydroxybenzoic acids must function positively, *i. e.*, they correspond to the state of oxidation represented by carbonic acid and therefore may yield carbon dioxide. Furthermore, if the hydroxyl radical in the hydroxy benzoic acids is negative, then the electronic formulas for the ortho- and parahydroxybenzoic acids require that the carboxyl radicals be positive, while the carboxyl radical in the meta acid must be negative. The metacarboxyl radical being negative corresponds to the state of oxidation of formic acid and, therefore, does not lose carbon dioxide. The correlation of these phenomena with the conception of positive and negative valences is expressed in the following formulas for ortho-, para- and metahydroxybenzoic acids:

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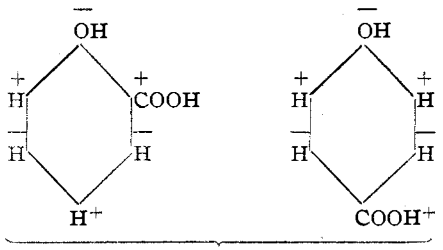
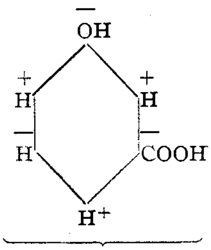
[1] *Bull. soc. chim.*, [3] 15, 7 (1896).



(unstable: lose carbon dioxide)



(stable)

From the above, a general conclusion may be drawn, namely, that *a carboxyl radical either ortho or para to a negative hydroxyl radical is positive and, therefore, unstable, yielding carbon dioxide when heated with water or aniline.* On the other hand, *a carboxyl radical meta to a negative hydroxyl radical is also negative and, therefore, stable, not yielding carbon dioxide when heated with water or aniline.*

The above conclusion receives remarkable confirmation by the recent and numerous experiments of Hemmelmayr[1] in an extensive research "Concerning the influence of the nature and position of substituents upon the stability of the carboxyl radical in the substituted benzoic acids." Cazeneuve estimated the relative stability of the carboxyl radicals by comparing temperatures at which different compounds eliminated carbon dioxide. Hemmelmayr's method is more comprehensive, in that he heated weighed quantities of various acids with either 50 cc. of water or 50 cc. of aniline and estimated quantitatively the amounts of carbon dioxide liberated. In this manner he experimented with thirty-nine differently substituted hydroxybenzoic acids. Their behavior in general conformed to the rule indicated above. In other words, an examination of the formula showed that every acid which contained a carboxyl radical either ortho or para to an hydroxyl radical yielded carbon dioxide. On the other hand, those acids in which the carboxyl group was neither ortho nor para but only meta to an hydroxyl radical did not yield carbon dioxide. Thirty-five of the thirty-nine variously substituted hydroxybenzoic acids conformed to this generalization. Among thirteen mono-, di-, and trihydroxybenzoic acids there was not one exception. Hence it must be concluded that the electronic formula of benzene and the conception of positively and negatively functioning carboxyl radicals afford an interpretation of the anomalous behavior of numerous and differently substituted hydroxybenzoic acids, some of which lose carbon dioxide while others do not.

While it is thus evident that positively functioning carboxyl radicals lose carbon dioxide when heated with water or aniline, nothing has been found in the literature which would indicate or explain the mechanism of these reactions.

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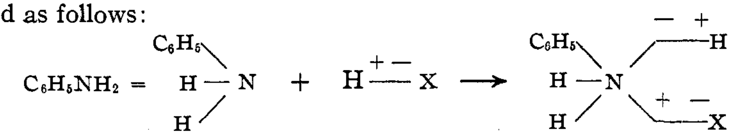
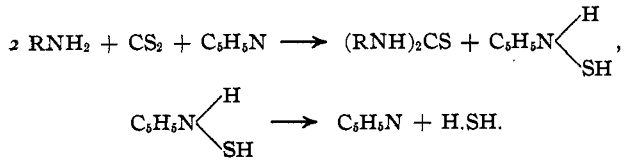
[1] *Monatsh.*, 34, 365 (1913).

In attempting to explain the action of water or aniline it should be noted that each of these reagents, which effect the elimination of carbon dioxide contains an unsaturated atom, *i. e.*, oxygen may increase its valence from two to four while nitrogen in aniline and other amines (or ammonia) may increase its valence from three to five. For instance, the combination of aniline with hydrogen halide $(\mathrm{H}\overset{+\quad-}{\text{——}}\mathrm{X})$ may be represented as follows:



Since Hemmelmayr has found that amines other than aniline effect the elimination of carbon dioxide it is advisable now to limit this explanation to the unsaturated state of the nitrogen atom in amines.

In a recent paper[1] I have shown that the unsaturated nitrogen atom in the amine, pyridine, lends itself to the elimination of hydrogen sulfide in a new reaction for the preparation of thiocarbanilides, according to the equations:



In other words pyridine combines with the elements of hydrogen sulfide forming the unstable pyridinium sulfide which, decomposing, regenerates the original pyridine and eliminates hydrogen sulfide. Analogously it may be assumed that an unstable addition compound of an amine and the oxybenzoic acid is formed which, decomposing, regenerates the amine and liberates carbon dioxide.

The validity of this assumption was put to an experimental test by employing pyridine as the amine and chlorocarbonic ethylester as an analogue of an hydroxybenzoic acid. The possibility of the elimination of carbon dioxide from chlorocarbonic ethylester is warranted, since all of the valences of its carbon atom are positive and so correspond to the state of oxidation of the carbon atom in carbonic acid and carbon dioxide. This follows from its interaction with water:

$$\mathrm{Cl}\overset{-\quad+}{\text{——}}\underset{\substack{+\|+\\ -\|-\\ \mathrm{O}}}{\mathrm{C}}\overset{+\quad-}{\text{——}}\mathrm{O}\overset{-\quad+}{\text{——}}\mathrm{C_2H_5}^{2} + \mathrm{H}\overset{+\quad-}{\text{——}}\mathrm{O}\overset{-\quad+}{\text{——}}\mathrm{H} \longrightarrow \mathrm{H}\overset{+\quad-}{\text{——}}\mathrm{Cl} + \mathrm{C_2H_5}\overset{+\quad-}{\text{——}}\mathrm{O}\overset{-\quad+}{\text{——}}\mathrm{H} + \mathrm{O}\underset{-\quad+}{\overset{-\quad+}{=\!=\!=}}\mathrm{C}\underset{+\quad-}{\overset{+\quad-}{=\!=\!=}}\mathrm{O}.$$

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[1] THIS JOURNAL, 35, 1539 (1913).

[2] Chlorocarbonic ethylester is very frequently but incorrectly called "chloroformic ethylester" which implies that it is a derivative of formic acid. If such were

When chlorocarbonic ethylester is dissolved in an anhydrous solvent (carbon tetrachloride, benzene, or toluene) the addition of a like solution of pyridine yields at once an extremely unstable addition-compound (white solid, not yet isolated) which spontaneously decomposes, liberating carbon dioxide and ethyl chloride. The following experiments were performed in order to determine quantitatively the extent of the decomposition of various amounts of chlorocarbonic ethylester by a fixed amount of pyridine.

3.95 grams of pyridine ($^1/_{20}$ mole) were dissolved in 25 cc. of absolute toluene, contained in a 200 cc. round bottomed flask suspended in a water bath. The flask was securely fitted to a dropping funnel (for the introduction of the chlorocarbonic ethylester) and to a long, upright spiral condenser. The upper end of the condenser was connected by glass tubing to a gas washing bottle containing toluene which was kept at a constant temperature of 0° (for the absorption of ethyl chloride) and saturated with carbon dioxide. The wash-bottle was in turn connected to U-tubes filled with soda-lime and accurately weighed for the absorption of carbon dioxide liberated in the reaction.

2.71 grams ($^1/_{40}$ mole) of chlorocarbonic ethylester dissolved in 10 cc. of toluene were admitted to the flask by way of the dropping funnel. The white, flaky solid which was formed immediately decomposed with such vigor that it became necessary to immerse the flask in cold water, and thereby control the rate of the elimination of carbon dioxide. The last traces of carbon dioxide had to be driven over by heating the reaction mixture and then drawing air through the entire apparatus. The increase in weight of the U-tubes due to the absorption of carbon dioxide was 0.9720 gram.

The above operation (addition of $^1/_{40}$ mole chlorocarbonic ethylester and its subsequent decomposition) was carried out three times in succession, thereby bringing into reaction $^1/_{40}$, $^2/_{40}$, and $^3/_{40}$ moles of the ester

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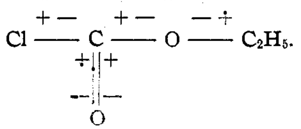
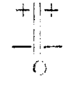
the case then its carbon atom must possess three positive valences and one negative valence in order that it correctly correspond to the state of oxidation of the carbon atom in formic acid. Its electronic formula would then be as follows:



$$Cl \overset{+\ -}{\text{——}} \underset{\substack{+\|+\\ -\|-\\ O}}{C} \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} C_2H_5.$$

This "electromer" if hydrolyzed could not yield carbon dioxide directly. The products would be hypochlorous acid $(H \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} Cl)$ and ethyl formate

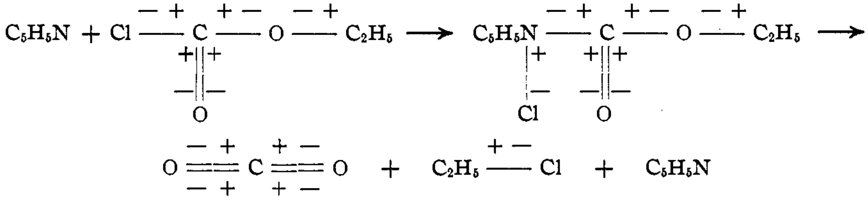


$$(H \overset{+\ -}{\text{——}} \underset{\substack{+\|+\\ -\|-\\ O}}{C} \overset{+\ -}{\text{——}} O \overset{-\ +}{\text{——}} C_2H_5).$$

with a fixed quantity ($^1/_{20}$ mole) of pyridine. Each addition was accompanied by an energetic liberation of carbon dioxide and ethyl chloride. The following table presents the molecular ratios of the interacting substances, the quantities employed, the amounts of carbon dioxide evolved and the corresponding percentages of the theoretical yields of carbon dioxide based upon the ratio $ClCO_2C_2H_5 : CO_2$:

Molecular ratios.	C_5H_5N. (Grams.)	$ClCO_2C_2H_5$. (Grams.)	CO_2. (Grams.)	Per cent. of theory.
2 C_5H_5N : 1 $ClCO_2C_2H_5$........	3.95	2.71	0.9720	88.36
2 C_5H_5N : 2 $ClCO_2C_2H_5$........	3.95	5.42	1.8960	86.18
2 C_5H_5N : 3 $ClCO_2C_2H_5$........	3.95	8.13	2.7305	82.74

The reaction mixture in the flask still contained pyridine which effected the decomposition of additional quantities of chlorocarbonic ethylester. Hence it must be concluded that the pyridine acts as a catalytic agent in effecting the elimination of carbon dioxide from the ester through the intermediate formation of an unstable addition compound. The reactions involved may be represented by the following equations:

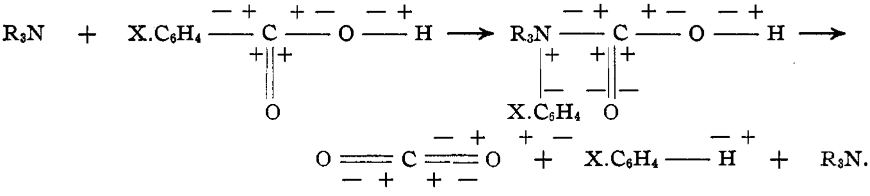


$$C_5H_5N + Cl \overset{-\;+}{-\!-\!-} \underset{\substack{+\|+\\ -\|-\\ O}}{C} \overset{+\;-}{-\!-\!-} O \overset{-\;+}{-\!-\!-} C_2H_5 \longrightarrow \underset{\substack{|+\\ |-\\ Cl}}{C_5H_5N} \overset{-\;+}{-\!-\!-} \underset{\substack{+\|+\\ -\|-\\ O}}{C} \overset{+\;-}{-\!-\!-} O \overset{-\;+}{-\!-\!-} C_2H_5 \longrightarrow$$

$$O \overset{-\;+}{\underset{-\;+}{=\!=\!=}} C \overset{+\;-}{\underset{+\;-}{=\!=\!=}} O + C_2H_5 \overset{+\;-}{-\!-\!-} Cl + C_5H_5N$$

I have found that amines, other than pyridine, also effect the elimination of carbon dioxide from chlorocarbonic methyl-, ethyl- and propylesters. Hemmelmayr has found that amines other than aniline effect the elimination of carbon dioxide from various hydroxybenzoic acids in which the carboxyl radicals have been shown to function positively. Therefore, equations perfectly analogous to those above may represent the action of an amine of the general formula R_3N upon an hydroxybenzoic acid (or any other substituted benzoic acid in which the carboxyl radical is positive) as follows:[1]

(R = alkyl, aryl, or H; X = OH or other substituent):



$$R_3N + X.C_6H_4 \overset{-\;+}{-\!-\!-} \underset{\substack{+\|+\\ \|\\ O}}{C} \overset{+\;-}{-\!-\!-} O \overset{-\;+}{-\!-\!-} H \longrightarrow \underset{\substack{|+\\ |-\\ X.C_6H_4}}{R_3N} \overset{-\;+}{-\!-\!-} \underset{\substack{+\|+\\ -\|-\\ O}}{C} \overset{+\;-}{-\!-\!-} O \overset{-\;+}{-\!-\!-} H \longrightarrow$$

$$O \overset{-\;+}{\underset{-\;+}{=\!=\!=}} C \overset{+\;-}{\underset{+\;-}{=\!=\!=}} O + X.C_6H_4 \overset{-\;+}{-\!-\!-} H + R_3N.$$

The formation of an intermediate unstable compound of the amine and the acid depends upon an increase in the valence of the nitrogen

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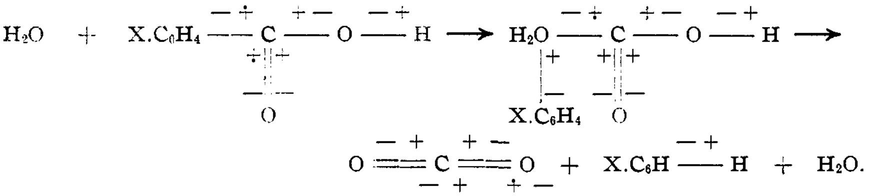
[1] Equations showing the formation of the amine salts of the acids have been omitted as they are not essential to the principal changes involved.

from three to five. Similarly, the action of water in effecting the elimination of carbon dioxide would depend upon the formation of an unstable oxonium compound through an increase in the valence of the oxygen atom from two to four as indicated in the following equations, which are perfectly analogous to those above:



Thus the electronic conception of positive and negative valences not only indicates the nature of the radicals which, through the action of amines or water, lose carbon dioxide but it also affords a possible interpretation of the way in which the reactions proceed. The theoretical deductions are based upon experimental facts and data afforded by the analogous action of pyridine upon chlorocarbonic ethylester.

In conclusion it may be remarked that the electronic conception of positive and negative valences and the electronic formula of benzene, afford explanations of certain anomalous properties and reactions which are generally classed as stereochemical problems. The possibility of interpreting some of these properties and reactions indicates that they are not necessarily anomalous or irregular. Hence it is hoped that a further extension of the principles and methods herewith presented may lead to the interpretation and solution of other problems.

The following article may be regarded as a continuation of the present paper, but only in so far as it relates to the electronic formula of benzene, which involves the question of the existence of negatively functioning hydrogen.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

POSITIVE AND NEGATIVE HYDROGEN, THE ELECTRONIC FORMULA OF BENZENE, AND THE NASCENT STATE.

BY HARRY SHIPLEY FRY.

Received December 15, 1913.

That a univalent atom, chlorine for example, may function either positively or negatively has been conclusively demonstrated from several different standpoints.[1] The other halogens, bromine and iodine, also have been shown to dissociate into positive and negative parts in their inter-

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[1] W. A. Noyes, THIS JOURNAL, **23**, 460 (1901); **35**, 767 (1913); Stieglitz, *Ibid.*, **23**, 796 (1901); Walden, *Z. physik. Chem.*, **43**, 385 (1903); Fry, *Ibid.*, **76**, 387, 395 (1911).