THE ELECTRON THEORY OF VALENCE AS APPLIED TO ORGANIC COMPOUNDS
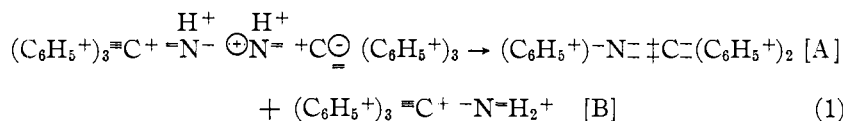
BY JULIUS STIEGLITZ

Since the writing of the preceding article (1917) by R. L. Brown and my-self on the molecular rearrangement of *sym.* *bis*-triphenylmethylhydrazine, considerable work has been done on the development of the electron theory of valence by G. N. Lewis, Langmuir, Kossel and W. A. Noyes, in addition to other authors. Of particular importance for our problem have been the opposing views as to the existence in organic compounds of "polar" valences or of "non-polar" valences, as defined by Lewis, by Bray and Branch[1] and by J. J. Thomson.[2] In the article by Brown and myself the conception of definite positive and negative charges on carbon, hydrogen, nitrogen and oxygen atoms in organic compounds has been used as in previous discussions of molecular rearrangements from this laboratory.[3]

In this article it is proposed to consider critically the value of the two theories, polar and non-polar, in the interpretation of the rearrangement of *bis*-triphenylmethylhydrazine and related compounds, as well as in following other types of reactions in organic chemistry, in which the writer has been actively interested.

I. From the point of view of polar valences the molecular rearrangement of the hydrazine would proceed as follows.

$$(C_6H_5{}^+)_3{\equiv}C^+ {=}N^- \overset{H^+}{\underset{}{\oplus}}N{=} {}^+C\underset{}{\ominus} (C_6H_5{}^+)_3 \rightarrow (C_6H_5{}^+)^-N{\equiv}{\ddagger}C{\equiv}(C_6H_5{}^+)_2 \; [A]$$

$$+ (C_6H_5{}^+)_3 {\equiv}C^+ {}^-N{=}H_2{}^+ \quad [B] \tag{1}$$

The final products are phenylimido-benzophenone (A) and triphenyl-methylamine (B). In this interpretation the source of instability or the "fault" in the original molecule is the nitrogen atom $^+N^=$ which needs 2 electrons in order to go over into its most stable form $N^{\equiv}$ as in ammonia. Whatever the mechanism of the rearrangement is, this nitrogen atom is *ultimately* found as $N^{\equiv}$ in triphenyl-methylamine (B) or in phenylimido-benzophenone (A). We have assumed as the most direct and simplest course that the "slip" starts with the capture of 2 electrons by $^+N^=$ from the neighboring carbon atom (the encircled charges $\oplus$ and $\ominus$ indicate the course of the slide of electrons), which necessitates the loss of a phenyl

[1] Bray and Branch, THIS JOURNAL, **35**, 1440 (1913). G. N. Lewis, *ibid.*, p. 1448; **38**, 762 (1916).

[2] Thomson, *Phil. Mag.*, **27**, 757 (1914).

[3] See literature references in *Proc. Nat. Acad. Sci.*, 1, 196 (1915) and THIS JOURNAL, **36**, 272 (1914), **38**, 2046 (1916), where references to previous articles are given. See also L. W. Jones, *Am. Chem. J.*, **50**, 440 (1913), etc.

group ($C_6H_5^+$) by the new positive corner of the methyl carbon atom and the capture of the phenyl group by the new negative charge on the nitrogen atom. It might well be possible that the slip starts with the capture of 2 electrons by $^+N^=$ from the neighboring *nitrogen* atom, leaving an unstable univalent nitrogen derivative $(C_6H_5^+)_3{\equiv}C^{+-}N$ which then rearranges as the result of the recapture of the lost electrons by the nitrogen atom from the neighboring carbon atom, phenylimido-benzophenone (B) resulting.[4]

In this interpretation two definite relations stand out. Without any *ad hoc* assumptions, we have, at first, an obvious *cause* for the molecular rearrangement in the unquestioned instability of $^+N^=$, containing only 6 valence electrons, as compared with $N^=$ in which the full complement of 8 electrons is found in the valence electron shell of the nitrogen atom. In the second place, in the rearrangement the one methyl carbon atom is very evidently *oxidized* by the loss of 2 electrons to the nitrogen. As a matter of fact in the reaction products phenylimido-benzophenone (A) is a derivative of a ketone, benzophenone $(C_6H_5)_2C{\ddagger}{=}O$, which it forms by hydrolysis, while the original compound is a derivative of an alcohol, triphenylcarbinol $(C_6H_5)_3C^{+-}OH$, and is indeed prepared from triphenylmethyl chloride $(C_6H_5)_3C^{+-}Cl$.

These two advantages—they are fundamental—are not found in the interpretation on the basis of the non-polar valence theory which follows.

II. Of the various theories of non-polar valence brought forward the author would incline to the type of non-polar valence first presented by Bohr[5] and to the somewhat similar views of G. N. Lewis.[6] We have Bohr's well-known conception of the hydrogen molecule as consisting of 2 positive atoms held together by 2 common electrons rotating in an orbit in a plane between the two atoms, which we may express as $\oplus : \oplus$. G. N. Lewis's views postulate a similar pair of electrons, but apparently these do not rotate (*i. e.*, they are essentially in fixed positions). Kossel[7] has applied similar views to other molecules, and the views of Lewis and Langmuir, as far as our present discussion is concerned, may be considered to express essentially the same fundamental conception. A pair of such binding electrons would be found, for instance, at each of the 4 valence positions, *i. e.*, the 4 tetrahedral corners of the Le Bel-van't Hoff carbon atom.[8]

Representing, as Lewis does, two such binding electrons by the symbol : we may also represent bis-triphenylmethylhydrazine as
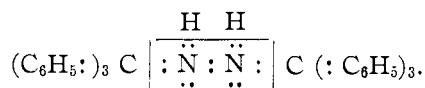
[4] See Stieglitz and collaborators, Ref. 3.

[5] Bohr, *Phil. Mag.*, **26**, 476, 857 (1913). See p. 874 in regard to the application of this conception to carbon valences.
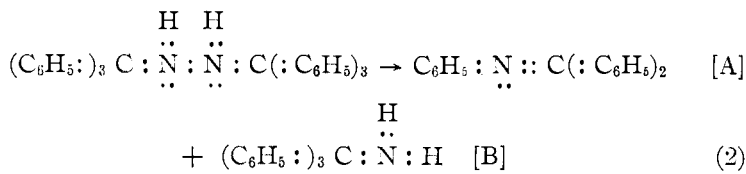
[6] Lewis, THIS JOURNAL, **38**, 762 (1916).

[7] Kossel, *Ann. Physik*, **49**, 229 (1916).

[8] Ref. 5, p. 874. Ref. 6, p. 780.

$$(C_6H_5:)_3 \; C \; \left| \; : \overset{\overset{H}{\cdot\cdot}}{N} : \overset{\overset{H}{\cdot\cdot}}{N} : \; \right| \; C \; (: C_6H_5)_3.$$

The following equation would express the rearrangement.

$$(C_6H_5:)_3 \; C : \overset{\overset{H}{\cdot\cdot}}{N} : \overset{\overset{H}{\cdot\cdot}}{N} : C(: C_6H_5)_3 \; \rightarrow \; C_6H_5 : \underset{\cdot\cdot}{N} :: C(: C_6H_5)_2 \quad [A]$$

$$+ \; (C_6H_5:)_3 \; C : \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} : H \quad [B] \tag{2}$$

An ammono-nitrogen atom of the type found in ammonia and the amines has either 3 extra electrons as expressed in $N \equiv (^+H)_3$ or there are 6 non-polar electrons binding the nitrogen to hydrogen and 2 non-active valence electrons as expressed by $H : \overset{\cdot\cdot}{\underset{\overset{\cdot\cdot}{H}}{N}} : H$. In either event, the valence shell would contain the octet of electrons, which represents a condition of stability. Now, in the hydrazine each nitrogen atom has its full octet of electrons as is seen in the above formula, and without some further assumption it is not at all evident why the molecule should be unstable and why it should undergo a rearrangement. It is true that the pair of nitrogen atoms, *if separated*, between them can contain 16 valence electrons whereas they hold jointly only 14 in the hydrazine, but individually each atom already has its full complement in the hydrazine and should be stable. In the rearrangement 2 electrons are supplied to the nitrogen by the migration of $:C_6H_5$ from a methyl carbon atom to one of the nitrogen atoms and we ultimately have the separate nitrogen atoms with the maximum number (16) of electrons, but from the valence theory alone it is not at all evident why the separated nitrogen atoms should represent a condition of greater stability.

Further, each of the methyl carbon atoms has its octet of valence electrons both before and after the rearrangement and it is not at all apparent, without further assumptions, that one of them has actually been *oxidized* (lost electrons) to form a derivative of benzophenone rather than of triphenylcarbinol.

It is quite evident that in these two respects of fundamental importance, in showing the source of the instability of the hydrazine and in expressing the intramolecular oxidation and reduction characteristic of the rearrangement, the polar valence theory is unqualifiedly superior, in the interpretation of the rearrangement, to the non-polar valence theory.

Similar relations could be used to express the molecular rearrangements of other compounds of this class, which have been studied in this laboratory, the halogen-amides, the hydroxylamine derivatives, the azides, the per-

oxides, etc. The interpretation from the point of view of polar valences would in every instance without any specific assumptions show that the cause of the rearrangement is to be found in an unstable atom (Cl^+, Br^+, $O^\pm$, etc.) which represents a fault and which by depriving some other atom of electrons in order to go over into the stable forms (Cl^-, Br^-, $O^=$) brings about as a sequel the shifting of groups. The interpretation with the aid of the non-polar valence theory would not reveal any fault in the molecules and would not express the net result of oxidation of some atom, by reduction of some other atom, which is an experimental fact of importance. It will not be necessary to discuss these other rearrangements in detail because the line of argument would follow closely that used in the above discussion.
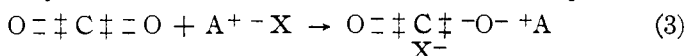
It is evident that while we can express the fundamental relations mechanically and arithmetically in the above reactions from the point of view either of polar or of non-polar valences as found in organic molecules, the question which must interest us most profoundly, namely, which method of expression represents better true relations, has been answered unequivocally in favor of the polar valence theory. In connection with still other fundamental reactions of organic chemistry, the writer wishes to explain here, as briefly and succinctly as possible, why he believes that the polar valence theory, as used originally by J. J. Thomson and later by Falk and Nelson, Jones, Fry, W. A. Noyes, the author himself and others,[9] gives a better representation of the facts of organic chemistry than the non-polar valence theory. It is to be explicitly understood, however, that this polarity is perhaps of a quite different order from the extreme polarity of an electrolyte such as sodium chloride.[10] Wherein the difference lies is a problem of atomistics and the writer himself does not care to advance any theory as to the difference. The insistence here is made on polarity as expressing a definite difference in electric charge between two linked atoms, one behaving as a positive, the other as a negative atom.

One will find such evidence in favor of polarity in numberless reactions which show the presence of unquestionable *directing forces*, which follow quite naturally from the polar valence forces without any further assumptions whatsoever, and for which the non-polar forces would demand some further specific interpretative assumptions. One might be inclined to consider whether the *reacting molecules* are the polar ones in these reactions —which unquestionably is the case—and whether the preponderating

[9] References are given in *Proc. Nat. Acad. Sci.*, Ref. 3.

[10] Cf. Lewis, Ref. 6. The writer's views approach those of this brilliant author except that for the reasons given in this article he cannot accept the view of actual, complete non-polarity, not to speak of a reversal of polarity (*e. g.*, $C^{++++}H^-_4$, Ref. 6, p. 182) and would emphasize the polarity of organic compounds, and the value of the conception in organic chemistry. In the interpretation of oxidation and reduction, the view of completely *polar* structures has very decided advantages [See below, and cf. Falk and Nelson, THIS JOURNAL, **36**, 209 (1916)].

mass of molecules are non-polar and inert, existing in equilibrium with the reacting polar molecules just as the ions, say, of acetic acid are in equilibrium with the large proportion of non-ionized acetic acid. That is a question indeed for physical investigation and its solution might bridge the gap between the opposing views. The impressive fact remains that most of the reactions that follow always go in only one way, and never in any other (cases when the directive forces act in two ways will be explicitly discussed). For instance, carbon dioxide, for which Thomson assumes non-polar structure, always absorbs reagents such as water, ammonia, metal alkyls, etc., in accordance with the well-known equation.

$$O \stackrel{..}{\stackrel{..}{\cdot}} C \stackrel{..}{\stackrel{..}{\cdot}} O + A^+ \, ^-X \rightarrow O \stackrel{..}{\stackrel{..}{\cdot}} \underset{X^-}{C} \stackrel{..}{\stackrel{..}{\cdot}} \, ^-O^- \, ^+A \qquad (3)$$

the positive component, H^+, Zn^{++}, Na^+, Mg^{++}, etc., invariably going to the negative oxygen, the negative component X^- invariably going to the positive carbon. For a non-polar union $O::C::O$ one would imagine that the planes of the orbits or positions of the electrons through collisions with other molecules and the vibrations of the atoms, would move[11] either closer to oxygen, leading to the polar structure $O\stackrel{..}{\cdot}C\stackrel{..}{\cdot}O$ (D) or closer to the carbon, leading to $O\stackrel{..}{\cdot}C\stackrel{..}{\cdot}O$ (E). In fact the breakdown of carbon dioxide under the bombardment of positive rays apparently according to both D and E, first led Thomson to consider carbon dioxide to be non-polar and to revise his earlier views of polar structure. But the chemical fact remains that *all* of the absorption reactions of carbon dioxide proceed strictly according to Equation 3 and never by the remotest chance do we seem to get a compound $O = C - OX$ such as $O = C - OCH_3$, or $O = C - OCH_3$

<center>A   Na   H</center>

a formate, by the action of sodium methide or zinc methide[12] on carbon dioxide. The formates are quite stable compounds and are obtained easily by absorption reactions of carbon monoxide through the latent valences of the bivalent carbon atom.

The same *one-sided* absorption is always shown by all $> C \stackrel{..}{\cdot} O$, $> C \stackrel{..}{\cdot} S$, $> C \stackrel{..}{\cdot} N^-$ etc. derivatives (aldehydes, ketones, esters, etc.) unless we deliberately first reduce the carbon atoms to the corresponding alcohols etc., by means of electrons from nascent hydrogen or some metal, from an electric current or some similar source.

Absorption by Olefins[13]

An illuminating behavior, in connection with the problem of polar *versus* non-polar valences, is shown in the absorption relations of such an

[11] Cf. Lewis, Ref. 6, p. 782.

[12] Stieglitz, "Qualitative Analysis," Century Co., 1912, Vol. I, p. 177. L. W. Jones, Ref. 3, p. 420.

[13] The views here presented were expressed by the author in addresses given at Johns Hopkins University and as retiring Vice-President of the Chemistry Division of

olefin as propylene. It behaves exactly as if by far the greater proportion of propylene or the by far more active part[14] has the definite polar structure

$$H_3C-\overset{H}{\underset{}{C}}\ddagger = \overset{H}{\underset{}{C}}H \quad [A]$$ (only the essential valences are indicated), per-haps in equilibrium[1] with a small fraction, or a sluggishly reacting fraction,

of the electromeric substance $CH_3C=\overset{H}{\ddagger}\overset{H}{C}H$ [B] or $H_3C.\overset{H}{C}\overset{H}{\mp}\overset{}{C}H$ [C]. The absorption of acids like hydrogen chloride, hydrogen bromide, etc., leads almost (but not quite[15]) exclusively to *iso*-propyl derivatives such as $(CH_3)_2CHCl$;[15] the absorption of hypochlorous acid, HOCl, on the other hand, carries the *positive* chlorine[16] to the outside carbon atom, and $CH_3CHOHCH_2Cl$ is formed.[17] Similar relations hold for the absorption by cinnamic acid, which lead to the formula $C_6H_5.HC\ddagger=CH.COOH$.

The small quantity of *normal* propyl chloride $CH_3CH_2CH_2Cl$ observed by Michael is best understood as indicating the presence of a small proportion of the electromer B, or possibly even C, as there is not the slightest indi-cation of any electromeric equilibrium $H^+Cl^- \rightleftarrows H^-Cl^+$. On the other hand, for such compounds as bromine chloride, bromine iodide, etc., we have every reason to consider that we must have equilibria, such as be-tween bromine chloride and chlorine bromide $Br^+Cl^- \rightleftarrows Cl^+Br^-$ (as well as Br:Cl) since both halogens have a very strong affinity for electrons, which must lead to an equilibrium condition.[18] As a matter of fact, we do get notable mixtures of such isomers as $CH_3CHCl.CH_2Br$ and $CH_3CHBr.CH_2Cl$ in such fair proportions as would be favored by the above equi-librium relation.[19]

the American Association for the Advancement of Science at Pittsburgh in 1917. Since then E. J. Cuy has published an excellent discussion of electron valences in carbon chains, which includes some of these relations [THIS JOURNAL, **42**, 503 (1920)]. Nelson and Falk discussed the same in 1910 (*ibid.*, **32**, 164) but the present writer's conclu-sions differ in some essential respects from those of these authors.

[14] There are of course, always two kinds of factors involved in the formation of definite products, mass action and velocity coefficients of reaction.

[15] The observation that a little propyl chloride is formed in the absorption of hydro-gen chloride is the basis of this conclusion. See A. Michael, *J. prakt. Chem.*, **60**, 286, 409 (1899) and Falk and Nelson, Ref. 13.

[16] Stieglitz, THIS JOURNAL, **23**, 796 (1901).

[17] When Cl$^+$ and Br$^+$ enter into combination with C$^-$, the combination is commonly followed by intramolecular oxidation and reduction to C$^+$Cl$^-$, C$^+$Br$^-$. Positive iodine has been recognized by Jones in one of the 4 iodine atoms in carbon tetra-iodide and Howell and Noyes [THIS JOURNAL, **42**, 99 (1920)] have found it in iodo-acetylene. Fry. [*ibid.*, **38**, 1328 (1916)] and Nicolet [*ibid.*, **43**, 2081 (1921)] have found evidence of positive halogen in certain benzene derivatives.

[18] Cf. Lewis, Ref. 6. Experimental work in the study of these equilibria has been started by A. T. McPherson in this laboratory.

[19] Michael, Ref. 15. Falk and Nelson seem to give propylene the structure [C] as the preferable structure on the basis of the character of these absorption products

The relatively inert element carbon seems to have no such outweighing preference either for negative charges (gain of electrons) as exists for chlorine and bromine or for positive charges (loss of electrons) as exhibited by metals, or sulfur and phosphorus, etc. Consequently it is to be considered that particular conditions, such as the presence of specific catalysts, may cause a shift of the valence electrons between carbon atoms (oxidation and reduction) and lead to derivatives of electromers, since we must conclude that such molecules will be rather sensitive to the net effect of the forces in the whole molecule, far more so than is the case with such extreme atoms as chlorine, bromine, sulfur, phosphorus, etc. Emphasis should be placed in a study of this character rather on simple, direct actions taking place under ordinary conditions.

The Crum Brown-Gibson Rule and the Structure of Benzene[20]

In the Crum Brown-Gibson[21] rule of substitution in the formation of benzene derivatives we have further most important evidence of the existence of powerful directing forces in organic compounds, which result in the ready formation of definite derivatives and automatically prevent the formation of isomers. Thus, as is well known, phenol reacts in the *ortho-ortho-para* positions, and nitrobenzene, benzoic acid, etc., in the *meta* positions. To Fry[22] belongs the credit of the first attempt to explain these relations with the aid of definite concepts of the electron theory of valence. But Fry's interpretation involves the assumption of the presence of negative hydrogen atoms in benzene, as expressed in the formula

$$\begin{array}{c} H^- \\ H^+ \overset{\displaystyle\bigcirc}{} H^+ \\ H^- \qquad H^- \\ H^+ \end{array}$$
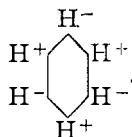
It is further assumed that only the positive hydrogen atoms react with such reagents as chlorine (Cl^-Cl^+), bromine, nitric acid, etc. Now, a negative hydrogen atom must be a powerful reducing atom, since without question the most stable form of hydrogen is H^+, and indeed metallic hydrides Na^+H^-, $Ca^+(H^-)_2$, etc., whose electrical structure follows from their ready hydrolysis to metallic hydroxide and hydrogen,[23] easily catch fire in

(Ref. 13, p. 1643). If that were the structure, hydrogen chloride and hypochlorous acid should yield large proportions of the isomeric absorption products. Such is not the case.

[20] This part of the report was presented before the Chemistry Division of the Pacific Coast Division of the American Association for the Advancement of Science at Berkeley, on August 5, 1921. See also Kharasch and Chalkley, THIS JOURNAL, **43**, 608 (1921).

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

[22] Fry, *Z. physik. Chem.*, **76**, 385 (1911). Presented before the Cincinnati Section of the American Chemical Society in January, 1908.

[23] Lewis and Bardwell have confirmed this conclusion by the electrolysis of sodium hydride (private communication).

the air as a result of the tendency of H^- to transfer its extra electrons to the oxygen of the atmosphere. No doubt the ionization of metallic hydrides brings out the maximum reducing power of negative hydrogen, but it would be illogical to consider that we have negative hydrogen in benzene without a trace of evidence of its presence,[24] shown in reducing power or instability. Benzene is eminently resistant to oxidation and extraordinarily stable. Furthermore, in the reaction of chlorine on benzene derivatives we are asked to believe that the reactive positive chlorine atoms, with an extraordinary tendency to absorb electrons, do not react with the negative hydrogen atoms, with their great tendency to release their extra electrons, for Fry's theory formulates the reaction between chlorine and phenol, for instance, as proceeding in the following way in order to account for the substitution in *ortho-ortho-para* positions:
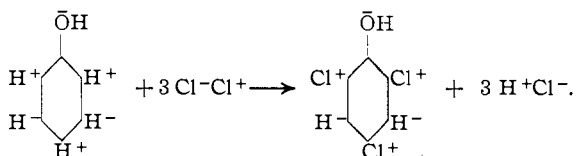
Finally, we have as yet no competent evidence of negative hydrogen attached to carbon in any other type of organic compound.

There is, however, an electrical basis for the Brown-Gibson rule of substitution which may be developed by the application to benzene derivatives of facts determined experimentally in the simple field of the aliphatic series of organic compounds and without a single *ad hoc* or specifically new assumption. The development of this interpretation[25] may well start with a consideration of the behavior of phenols. Phenols are in every respect the aromatic analogs of aceto-acetic ester:[26] they form the same type of deeply colored ferric salts; they form enol-keto tautomers, as is most clearly illustrated by the behavior of phloroglucinol

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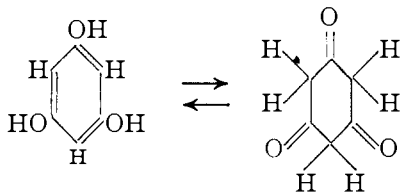
[24] Comparable with the ready evidence of the presence of positive chlorine, bromine, iodine, etc. (see below).

[25] Cf. Falk and Nelson, *School of Mines Quarterly*, **30**, 187 (1909), THIS JOURNAL, **32**, 1644 (1910), **33**, 1150 (1911); etc. See also Vorländer, *Ber.*, **52**, 263 (1919). Kharasch, Ref. 20.

[26] K. Meyer, *Ann.*, **398**, 51, 80 (1913). Meyer's views do not include any considerations of electrical valence forces.

about whose structure as a triphenol or triketone the usual controversy is to be found in the literature, resulting from the tautomeric behavior of the compound. For instance, phloroglucinol is soluble in alkali and forms ethers and esters—phenol characteristics—and it also forms a tri-oxime, a ketonic reaction. The alkali salts of phloroglucinol as well as of resorcinol when treated with ethyl iodide may be alkylated in such a way as to give $(C_2H_5)_2C$—$C=O$ derivatives,[27] the alkylation affecting the —CH_2— group between the carbonyl groups in the way that is so well known for the alkylation of aceto-acetic ester.

A minor point of difference between phenol and aceto-acetic ester is that it no doubt forms *para* as well as *ortho* tautomeric ketones, exactly as oxypyridine is known to form the pyridone tautomer,
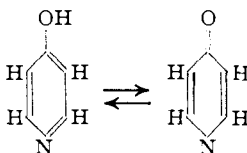
We have then for phenol the system[28]
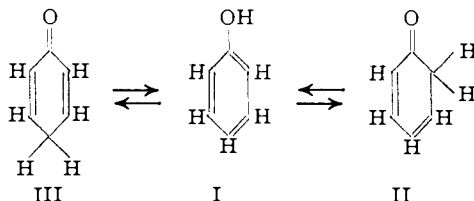
in which Structure I presumably is by far the most stable.

Now, the formation of ketonic tautomers by phenol, resorcinol, phloroglucinol, etc., means that the $C=O$ group has the electronic structure $C\ddagger\ddot{}O$ as in all ketones, and that consequently *the end of one of the double bonds of Formula I attached to the* $C-OH$ *carbon atom is positive.* The very fact of tautomerism rests in the equilibrium between the electrical forces
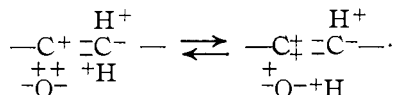
Further, there is a well-known noteworthy tendency of all atoms to become either wholly negative or wholly positive, intermediate forms being relatively unstable and tending to revert to the extremes. This is shown by such well-known reactions as the simultaneous formation of chlorides Me^+Cl^- and chlorates $Me^+{}^-O^-Cl\ddagger\ddagger^+O_2{}^-$ and perchlorates $Me^+{}^-O{}^-$

[27] Herzig and Zeisel, *Monatsh.*, 9, 217, 882 (1888); 11, 291 (1890).
[28] See below in regard to the oscillation of the double bond and the centric system.

Cl $^+$‡‡‡ O_3^- from hypochlorites Me$^+$O$^-$Cl$^+$; of sulfides and sulfates from sulfites, etc., all through intermolecular oxidation and reduction, *i. e.*, migration of electrons. These relations are of course in perfect harmony with the fundamental conceptions of Thomson, Lewis, Langmuir, and others in regard to the stability of the atoms provided with 8 electrons in their valence "shell." We can conclude, therefore, exactly as in the case of propylene, that both in acetoacetic ester and in phenol *both* of the bonds in the double bond of the enol are positive at the C—OH ends. Since in phenol the double bond oscillates (Kékulé, and confirmed by Fry), we have all four valences of the C—OH carbon atom as positive valences. The symmetry of the benzene nucleus having been amply demonstrated experimentally, we thus have for phenol

(IV).
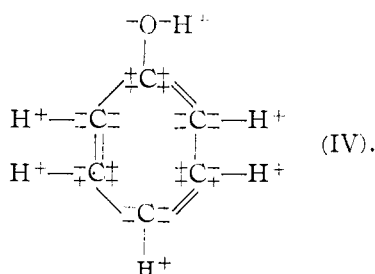
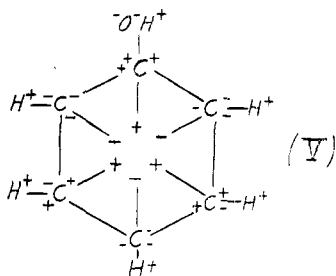It is to be distinctly understood that we have oscillations of the double bonds from side to side and that consequently the centric structure represents an intermediate position of the unsaturated valences.[29] For all we

(V)

know, this may represent the structure of by far the largest proportion of the molecules of a benzene derivative—but the *chemically active* molecules have the structure IV.

We are now prepared to understand why phenol gives substitution derivatives of the *ortho-ortho-para* series.

Kurt Meyer[30] in an excellent extended investigation has proved that bromination of aceto-acetic ester proceeds quantitatively by absorption of bromine by the enol double bond, followed by the loss of hydrobromic

[29] See especially the discussion of H. S. Fry, Ref. 22, on this point.

[30] Meyer, *Ann.*, **380**, 212 (1911); *Ber.*, **44**, 2718 (1911), etc.

acid to form a ketone (not directly a brominated enol). We may now express his results by using the electron valence structures,[31] as

$$—_+C\ddagger = \bar{\cdot}\dot{C}^-— + Br^-Br^+ \longrightarrow —_+C\ddagger—\bar{\cdot}\dot{C}^-—$$

with H^+ above, $^-O^-H^+$ below left, and $H^{+-}O^-$ Br^-Br^+ below right.

$$\longrightarrow \ ^{\cdot}C\ddagger—\bar{\cdot}\dot{C}^- + H^+Br^- \rightleftarrows —^+C\ddagger = \bar{\cdot}\dot{C}^+—$$

with H^+ above, $^-O^-$ Br^- below left, and Br^- above, $^-O^-H^+$ below right.
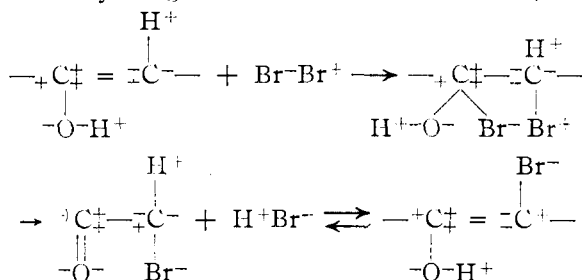
We may apply this proved course of the reaction for aceto-acetic ester without change[32] to the bromination of phenol:[33]

$$\text{[ring structure]} + Br-Br^+ \longrightarrow \text{[ring structure]} \longrightarrow$$

$$H^+Br^- + \text{[ring structure]} \rightleftarrows \text{[ring structure]} .$$
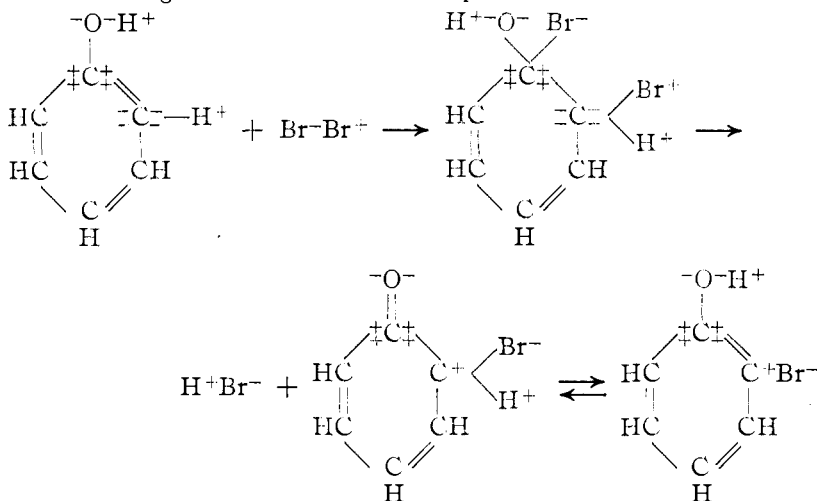
The second *ortho* position is brominated in exactly the same way.

For the *para* reactivity, we have to apply the facts discovered by Baeyer and Thiele which have been summarized in Thiele's theory of "conjugated double bonds" but which need no specific assumptions as to a special kind of double bond to understand their behavior.[34] The fact is simply that a pair of double bonds as in

$$\begin{array}{cccc} {}^+H & H^+ & H^+ & H^+ \\ | & | & | & | \\ —\bar{\cdot}\dot{C}\bar{\cdot} & \ddagger C\ddagger & \bar{\cdot}C\bar{\cdot} & \ddagger C^-— \\ 1 & 2 & 3 & 4 \end{array}$$

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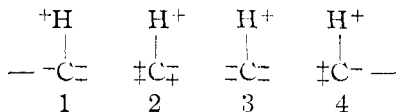
[31] Subsequently through intramolecular oxidation and reduction the bromine becomes negative and we have as usual C^+Br^-.

[32] Meyer, *Ann.*, **398**, 51 (1913).

[33] Only the essential changes are indicated to save printing.

[34] Cf. Falk and Nelson, Ref. 13, p. 1650.

is known to absorb hydrogen, halogen etc., at atoms 1 and 4 and not at 1 and 2, or 3 and 4. Now, in phenol (IV) we have such "conjugated" double bonds and bromine would accordingly be added in positions 1 and 4 to form[33]

Again, by loss of hydrogen bromide a ketone (*para*) is first formed, which reverts to the normal tautomeric enol, *para*-bromophenol (See I and III p.1301).

Similarly, in the nitration of phenol, we have absorption of HO^- (or an equivalent anion) and $^+N\ddagger\ddagger(O^-)_2$ at Positions 1 and 2, or 1 and 4, respectively, *ortho*- and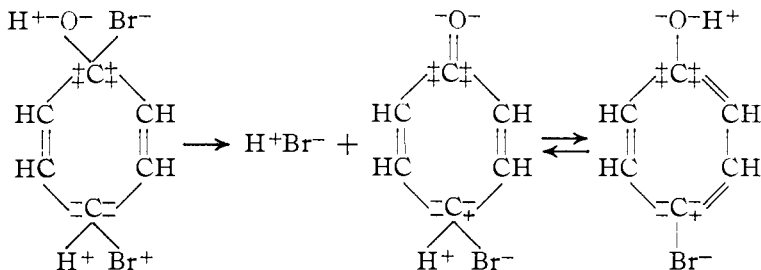 *para*-nitrophenol resulting. Nitric acid acts here characteristically through its *basic* ionization,[35] a view which is well confirmed by the use of conc. nitric acid, fuming nitric acid, and conc. sulfuric acid with nitric acid as the best nitrating reagents.

The important feature in the above formulation is to be found in the forces which lead to the location of the *negative ends* of the double bonds in the ring, to which the substituting positive atoms (Cl^+, Br^+, $^+NO_2$, etc.) ultimately go. Whether *simultaneous* additions of *both* components of an absorbed molecule ($Cl^{-+}Cl$, $HO^{-+}NO_2$, etc.) to the unsaturated carbon valences must always occur is doubtful and in fact unlikely, and whether the essential feature is not the attraction of the positive substituting group to the negative carbon valences irrespective of complete saturation is a question which will be subjected to further critical work in this laboratory. Kurt Meyer[36] to whom we owe the most profound experimental and theoretical work on this type of substitution has already uncovered at least one important instance where complete saturation, as it is formulated above, must occur. This is in the action of nitrous acid on the methyl ether of phenol, *para*-nitrosophenol being produced and the methoxyl group lost, according to
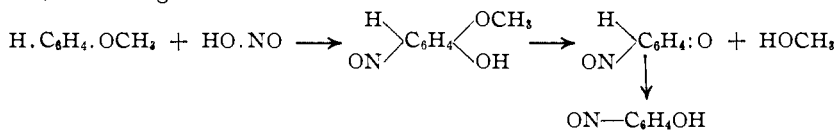
[35] Cf. Stieglitz, Ref. 12, pp. 288-9.
[36] Ref. 32, p. 80.

To what extent similar displacement of the original substituting group in benzene derivatives C_6H_5X takes place on further substitution, which addition to the positive and negative unsaturated valences obviously makes possible, is not well known and will be studied in this Laboratory.

The Crum Brown-Gibson rule of substitution for phenols, favoring *ortho-ortho-para* substitution, rests therefore on the electric structure, IV, of phenol which is here recognized as the favored one because the negative substituting group, $^-O^-$, develops two positive charges on the carbon atom holding it and these in turn favor complete positive character of the carbon atom in question, in conformity with the universal tendency of a charged atom to be positive or negative, a consequence of the structural relations of the atoms.

The other benzene derivatives C_6H_5X in which *ortho-ortho-para* substitution is favored, all have a negative X, as $\bar{N}H_2$, $\bar{C}l$, $\bar{B}r$, etc., which has, of course, the same effect as $\bar{O}H$.

As to the second group of benzene derivatives C_6H_5Y in which the formation of *meta-meta* derivatives occurs, we can obtain a similar electron valence basis for the rule by a study of nitrobenzene and its derivatives. From nitric acid $H^{+-}O^{-+}N^{\ddagger}_{\ddagger}(O^=)_2$ we obtain the positive nitro group $^+N^{\ddagger}_{\ddagger}(O^=)_2$. In accordance with this structure we have the well-known nitro-nitronic acid type of tautomerism, established by Hantzsch for phenylnitromethane and for nitrophenol, which we would express electronically for instance in
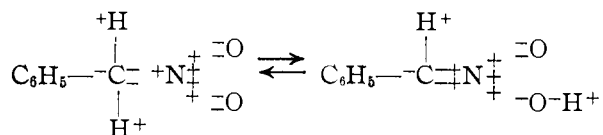
The analogous structure for *para*-nitrophenol is self-evident. It is clear from the nitronic acid formation that a nitro group favors the formation of negative carbon, exactly as oxygen, chlorine, etc., favor positive carbon. We have then as the stable form[37] of nitrobenzene and similar derivatives.

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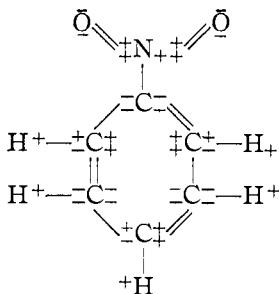
[37] The centric structure as given above is one of the modifications (tautomers) of this electronic structure and perhaps its most stable but *least reactive* one.

We can easily see that in further nitration, *meta*-dinitrobenzene would be the favored isomer[38] formed.
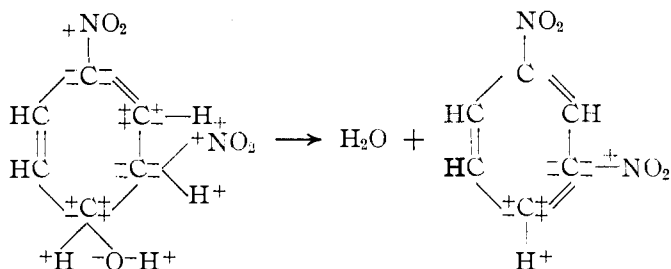
In the same way 1,3,5-trinitro-benzene would be formed. In the other benzene derivatives C_6H_5Y favoring *meta* substitution, Y is similarly a positive radical as found for $^+NO_2$.

In view of the character of the electrical forces involved, it should not be at all surprising that in more complex benzene derivatives we often have competing opposing forces of approximately similar orders of strength, and that mixtures of isomers result—as they always should when we deal with opposing forces of closely related orders of intensity: the well-known equilibrium between an organic acid and an alcohol, an ester and water is an instance of this kind, where the opposing forces are clearly of the same order and we can easily get in quantity derivatives either of the acid or ester, the alcohol or water. It is thought, therefore, that the true basis of the study of the rule of substitution from the point of view of the electronic structure of benzene is best found in the simplest derivatives of benzene. Once the structure is established, the more complex experimental results obtained for more complex derivatives should be used to throw light on the equilibrium relations involved.

Negative and Positive Halogen Atoms in Organic Compounds

Emphasis should be placed here again on the experimental relations for organic halogen derivatives, which were discussed by the author in a previous article.[39] In the alkyl halides, such as ethyl chloride, ethyl bromide and ethyl iodide we have (non-ionizing) compounds which react uniformly in accordance with the structure RC^+X^-; with water and alkalies, ammonia and amines, sulfides, alcoholates, we invariably have the negative X replaced by another negative atom as in $\overline{O}H$, $\overline{N}H_2$, $\overline{N}HR$, $\overline{O}R$, etc. We never

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[38] Only the essential changes are indicated; the others are given in preceding formulas. In place of OH^- an equivalent anion, *e. g.*, ONO_2^{--}, may be absorbed and split off again, *e. g.*, as HNO_3.

[39] *Proc. Nat. Acad. Sci.*, Ref. 3.

by any mischance get compounds **XOH, XNH₂, XNHR, XOR.** Jones has shown that in carbon tetra-iodide we have indeed one positive iodine atom, $(I^-)_3 \ddagger C^-I^+$, which easily reveals itself by forming HOI with water and by the ease with which carbon tetra-iodide is reduced to iodoform. The uniformly negative behavior of the halogen in alkyl halides $RH_2C^+X^-$ represents, therefore, as definite a guiding force in reactions as do the uniform charges on ionizable atoms in salts, acids and bases; and still alkyl halides are not ionizable, or are so slightly that one could not consider them electrolytes. Yet they show this concrete, specific behavior of polar charges—which proves that ionization and conductivity are not categorical tests for polar valence.

On the other hand, the acyl halogen amides of Hofman, the triarylmethylhalogen amines of the writer and his collaborators, behave in minute accordance with the electrical structure $RCO.HN^-(Hal^+)$ and $(Aryl)_3C.HN^-(Hal^+)$; hydrolysis forms $HOHal^+$, reduction with hydrogen iodide forms free iodine and the amides $RCONH_2$ and $(Aryl)_3CNH_2$. Hydroxylamine derivatives RCONHOH or RCONHOR, and $(Aryl)_3$-CNHOH or $(Aryl)_3CNHOR$, are not formed by hydrolysis, by treatment with alkali, alcohol or alcoholates.[40] The molecular rearrangements of these compounds find the most logical explanation in the presence of unstable position halogen atoms as "faults" in the molecule.[41] One cannot escape the fact that the polar structure expresses pointedly and succinctly the whole chemical behavior of these compounds. In exchange for this clean-cut, precise expression of the behavior of whole groups of compounds, one would have to assume *ad hoc* supposititious "tendencies" and give up every advantage of modern knowledge of valence over the old theory of structure and bonds.

Hydroxylamine Derivatives

The electrical structure of hydroxylamine[42] and its derivatives, $(H^+)_2{=}N^-$ $^+O^-H^+$ etc., again expresses perfectly the actual behavior of hydroxylamine and its derivatives. It forms salts exactly comparable with salts of ammonia with the analogous structure $H^+_3N^{\equiv}$; its positive hydroxyl group is not directly replaceable by $\overline{Cl}$, $\overline{Br}$, etc., as is the case for the hydroxyl group of bases, of alcohols (which are not *bases* but form oxonium salts[43]) of acids, etc. The positive hydroxyl group in hydroxylamines gives it oxidizing power, and represents a "fault" in the molecule of organic derivatives of hydroxylamine[42] which leads to their well-known rearrangement. Hydroxylamine has also reducing power in common with similar unstable molecules such as hydrogen peroxide, hypochlorous acid, hydrazines, etc. Most important of

[40] Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893).

[41] Stieglitz and collaborators, Ref. 3.

[42] Stieglitz, THIS JOURNAL, **36**, 272 (1914), and Jones, *ibid.*, **36**, 1268 (1914).

[43] Their behavior is often misrepresented as that of hydroxide bases.

all, the polar structure explains in a most beautiful fashion the occurrence as well as the chemical behavior of the isomeric derivatives discovered by Meisenheim and interpreted brilliantly by Jones.[44] It is true Michael[45] has attacked the interpretation of Jones and the writer's support of this interpretation but in doing so Michael has been obliged to make such extraordinary and impossible *ad hoc* valence assumptions that the writer has been quite content to rest the case and leave to critical chemists and the future the decision between the clean-cut, all inclusive presentation of Jones on the basis of polar valence, and the assumptions of his opponent.

The Structure of Acids. Oxidation and Reduction[46]

The whole behavior of organic acids and their derivatives is very accordingly understood on the basis of the electronic structure $RC \stackrel{\pm}{\mp} \stackrel{\pm}{=} \stackrel{O}{O} - H^+$.

Thus, the enol-tautomerism, *e. g.*, $RC = C \stackrel{H}{<} \begin{matrix} OH \\ OH \end{matrix}$ favoring chlorination in the α position, the absorption reactions of the $C \ddagger = O$ group (water, alcohols, sodium alcoholates, ammonia, magnesium alkylhalides, etc.) which differentiate the action of esters as compared with ethers R-O-R, are instances of this kind.

The structure also follows from the fact that electrical currents (a flow of electrons) can be obtained by oxidation cells in which alcohols or aldehydes are the sources from which electrons for the current are obtained,[47] producing acids. For instance,[48]

$$\stackrel{H^+}{\underset{H^+}{\ominus}} C \ddagger O \longrightarrow H^+ \oplus C \ddagger O + 2 \, \textcircled{e} + H^+$$
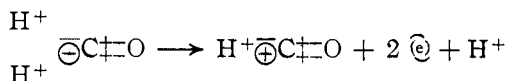
is the essential step in the oxidation of formaldehyde to formic acid. The other steps (union with ^-OH) are sequels.

Nevertheless, in recent years we have again and again proposals from the eminent leaders in the field of chemical atomistics, such as J. J. Thomson,[49] the founder of our modern school of thought, G. N. Lewis, Langmuir, etc., to the effect that acids have a non-polar structure to the extent that sulfur

[44] Ref. 42, p. 1284.

[45] Michael, THIS JOURNAL, **42**, 1232 (1920).

[46] This part of the present report was presented before the Chicago Section of the American Chemical Society in May, 1921. Cf. Chapters xiv and xv, in Vol. I of the author's "Qualitative analysis," Century, Co., **1912**.

[47] Stieglitz, *Science*, **27**, 774 (1908).

[48] The point where the electrons escape is indicated by $\ominus$. Cf. Stieglitz, Ref. 47 in regard to the intermediate formation of $H^+ \, \overset{+}{^-C} \, ^+ \, ^-OH$ which is the real tautomer $\overset{\ominus}{}$ losing electrons where they are *free* to escape (exactly as in the case of ions such as I^-, $S^=$, Fe^{++}, etc.).

[49] Ref. 2.

in sulfuric acid, phosphorus in phosphoric acid, etc., are bound to oxygen in a non-polar fashion.[50]   Indeed, in this the difference in the ionization of acids and bases is sought.[49]

Now, there are two fundamental sets of experimental facts of record which should be kept in mind in this connection, besides the above exposition of the polarity of organic acids.   The first of these is Faraday's observation[51] that electrolysis of very concentrated sulfuric acid deposits *sulfur* at the *negative* pole.   Helmholtz very properly considers that conclusive evidence of the positive character of the sulfur in sulfuric acid[51] and we would give it in accordance with his own clearly expressed views the structure

$$\begin{matrix} H^{+-}O^{-+} \\ H^{+-}O^{-+} \end{matrix} S \begin{matrix} {}^{+-}O \\ {}^{+-}O \end{matrix}.$$

The deposition of sulfur at the negative pole is another beautiful illustration of the power of *basic* ionization[52] of even our strongest oxygen acids.   This would be favored in concentrated acid solution.   Presumably there is sufficient ionized sulfur sulfate[53] $S \, {}^{++}_{++} \, (SO^{=}_4)_3$ formed to make the formation of sulfur in Faraday's experiment a perfectly normal action.   The *oxidizing* power of conc. sulfuric (and nitric) acids as against the much lower oxidizing power of the dilute acids is further evidence of polarity because it is essentially the exposed (ionized) positive charges of atoms which absorb electrons (oxidize) in intermolecular oxidation and reduction, as shown by oxidation and reduction potential studies.

The second experimental set of facts to which attention should be called in connection with the problem under discussion is found in the extremely interesting studies of Bird and Diggs[54] on the formation of oxidation-reduction cells with white phosphorus.   Not only does phosphorus produce a current (give up its electrons) exactly as any metal that is well known to form a current by the discharge of electrons from its atoms (*e. g.*, Zn ⟶ Zn^{++} + 2 ⓔ) but the potential is subject to the very equilibrium conditions which follow from the polar conception of phosphoric acid.   We have

$$P \rightleftarrows P^{+++++} + 5 \,ⓔ$$

and $\qquad P^{+++++} + 5 \, \bar{O} \, \overset{+}{H} \rightleftarrows O = {}^{+}_{+}P^{+}_{+} \, (^{-}O^{-}H^{+})_3 + H_2O$

It is evident that added acid, through the suppression of hydroxide ion should favor the presence of P^{+++}_{++} in solution and consequently reduce the potential, exactly as the presence of Cu^{++} in solution reduces the solution-tension potential of copper.   On the other hand, added alkali should sup-

[50] Cf. Lewis, Ref. 6, p. 778.

[51] Cf. Helmholtz, Faraday Lecture, *J. Chem. Soc.*, **39**, 277 (1881); see p. 290.

[52] Stieglitz, Ref. 12, pp. 283–289.

[53] Besides $(SO_2^{++})SO_{=4}$, comparable with uranyl nitrate $(UO_2)(NO_3)_2$, etc.

[54] Bird and Diggs, THIS JOURNAL, **36**, 1382 (1914).

press P_{++}^{++} and increase the potential.   Both of these consequences of the polar structure of phosphoric acid—and of its ionization as both acid and base—were confirmed experimentally by the work of Bird and Diggs.

The alternative hypothesis of non-polar union would be that phosphorus, in the face of its powerful tendency to discharge electrons, to be oxidized, resumes from, or shares with, oxygen electrons which oxygen itself has a tremendous tendency to absorb and hold, and would form[55] $O:P(:O^-H^+)_3$. This hypothesis is not only contradictory to the very obvious, powerful tendencies mentioned but fails to account for the equilibrium results of Bird and Diggs.   It seems to the author that the polar valence theory has the very decided advantage of summarizing the chemical behavior, without a single new assumption, in a very complete and definite way.

Of particular weight is the following further analogy.   It is well known that in the case of inorganic substances, oxidation (escape of electrons) occurs at ordinary temperature particularly readily where we have electrons *free* to escape, as in the case of the valence electrons of atoms (Zn, H *versus* H_2) or of ions (Fe^{++} *versus* $FeSO_4$, $S^=$ *versus* H_2S, etc.).   Reduction in the same way occurs where we have either exposed positive charges of ions (Ag^+ *versus* $Ag(CN)^-_2$, Cu^{++} *versus* $CuC_4H_2O_6^{--}$, etc.) ready to absorb electrons, or where we have exposed electron valence "shells" of free atoms (N *versus* N_2, O *versus* O_2) ready to absorb electrons.   Atoms in combination, it is well known, are far less active as oxidizing and reducing agents than in free atomic or ionic forms.[56]   In organic compounds we observe exactly the same fundamental characteristic[57]—an exposed free valence is far more reactive in discharging or absorbing electrons (being oxidized or reduced) than a valence bound by union with another atom. In organic compounds we have such exposed valences (comparable with inorganic ions and atoms) in the case of double bonds opening under the stress of the double bond union ($C_+^+ \bar{\cdot}C \rightleftarrows C^{+-}\underline{C}$), also for triple bonds, in the case of bivalent carbon atoms $RN = C$ and $H^{+-}C^{+-}OH$, of trivalent carbon

$(C_6H_5)_3C$, and of the more readily ionizable metal derivatives of carbon, ZnR_2, etc.   Such organic compounds may be used for the preparation of oxidation-reduction electrolytic cells, subject to exactly the same limiting conditions as inorganic compounds.   In either case only the exposed charges of a double bond, a methylene carbon atom, etc., or of an ionizable metal atom or a free ion (such as Fe, Fe^{++}, etc.) must be considered to be the sources from which electrons flow, or into which they enter, in oxidation and reduc-

[55] Lewis, Ref. 1, p. 778:   Only the essential valences are indicated.

[56] References and a detailed discussion are found in Chapters XIV and XV of the author's "Qualitative Analysis," 1912.

[57] Stieglitz, Ref. 47, p. 774; Ref. 12, p. 289; and *Proc. Inst. Med.*, Chicago, 1, 41 (1916–17).

tion. The free inorganic ions are known to be polar and there is no reason why their organic equivalents, the carbon valences which show exactly the same behavior in oxidation and reduction should not also have a similar electronic, *i. e.*, *polar*, structure.

There is ample further support of the important role played by polarity in the behavior of organic compounds, such as the difference in behavior of the odd and even numbered chains of carbon atoms in the case of such compounds as the dicarboxylic acids and similar derivatives but it has seemed best to confine this discussion to those groups of compounds in which the writer has been actively interested.[58]

We have thus seen that the polar version of the molecular rearrangement of *bis*-triphenylmethyl-hydrazine is from the point of view of the oxidation and reduction relations involved, far more direct and explicit than the non-polar version, although the latter could be used to arrive at the same net result arithmetically. Similarly, the electrolytic reduction of sulfuric acid to sulfur, the formation of phosphoric acid from phosphorus and of any organic acid from its aldehyde or alcohol in the development of an electric current in which phosphorus, aldehyde or alcohol, respectively, is used as the source of electrons, point unqualifiedly to polar valences rather than to non-polar union.

Similarly, the evidence of directing forces in the absorption by double bonds of organic compounds, in the formation of position isomers, in the occurrence of electromers as shown by L. W. Jones, all demand emphatically the application to organic molecules of polar valences produced by the shifting of electrons from one atom to another.

On the other hand, a difference in the properties of such extreme polar substances as sodium chloride, water, etc., and the corresponding properties of many polar organic compounds must be evident. Exactly wherein the difference lies—possibly expressed in the views of Bohr[5], Lewis[6] and Kossel[7]—is a subject of chemical and physical investigation in atomistics. Here it is sufficient to point out that it is unfortunate that one and the same word is used to express the two kinds of polarity. The attempt to escape from the resulting confusion of thought by emphasizing the non-polar character of organic compounds when they really show distinctly polar behavior has added confusion to confusion. Polarity exists wherever there is a difference in charge, positive and negative, between two atoms and it is so valuable a conception in the treatment of organic compounds that it must be clearly insisted upon. The author would suggest that in spite of the cumbersomeness of the term, Thomson's "intramolecular-ionization" as applied to sodium chloride, water and similar extreme polar compounds, does express exactly the presumable difference between the

[58] See also the persistent differentiation of nitrous acid nitrogen N^{+++} and ammono-nitrogen $N^{\equiv}$ in the diazo compounds, Stieglitz, THIS JOURNAL, **30**, 1798 (1908).

polarity of the extreme type represented by sodium chloride and the polarity of organic compounds, which is insisted upon in this discussion. Perhaps the use of Thomson's descriptive term for such extreme polar substances will give to organic chemistry the full value of polar conceptions and avoid confusion with the type represented by our common electrolytes.

Summary

The evidence in favor of the application of the theory of polar *versus* non-polar valences in organic compounds has been considered in various groups of derivatives, with the following results.

1. In the molecular rearrangement of a hydrazine $(C_6H_5)_3CNH.NH(C_6H_5)_3$ the theory of polar valence gives an evident cause for the rearrangement, revealing a "fault" in the molecule, and it also makes evident the intramolecular oxidation and reduction of certain atoms, which the experimental results demand. These are fundamental advantages of the theory of polar valences as against that of non-polar valences in carbon derivatives.

2. Exactly the same invaluable advantages are to be found in the theory of polar valences in the study of the analogous molecular rearrangements of chloro- and bromo-amides, of hydroxylamine derivatives, peroxides, etc.

3. In the wholly one-sided absorption reactions of carbon dioxide $O:C:O$ and of innumerable organic compounds containing unsaturated groups $C:O$, $C:S$, $C:N$, polar valences are recognized as the uniformly *directing forces*.

4. Similar directing forces are observed in absorptions by olefins in which polar valences exist in carbon-to-carbon unions. Exceptions to one-sided absorptions, as in the absorption of bromine chloride, are discussed and accounted for.

5. The Crum Brown-Gibson rule of substitution in the benzene series is developed as the result of a polar electronic structure for benzene, which does not require the assumption of negative hydrogen H^- (Fry) and is based on the application to benzene of results firmly established in the aliphatic series.

6. The different behavior of negative halogen (*e. g.*, in RX^-) and of positive halogen (*e. g.*, in $RNHX^+$) is emphasized as further important evidence favoring polar valences even in the absence of ionization.

7. Advantages of the polar structure for hydroxylamine and its derivatives are summarized.

8. Evidence of the complete polar structure of acids, such as sulfuric, phosphoric acids, and of the carboxyl group of organic acids, is found in:

(a) Faraday's observation of the deposition of sulfur at the negative electrode in the electrolysis of conc. sulfuric acid.

(b) The work of Bird and Diggs on the use of white phosphorus as the equivalent of a metal for the production of an electric current.

(c) The production of currents by the use of organic compounds as the source for the escape of electrons in oxidation-reduction cells.

9. It is pointed out that in the oxidation and reduction of organic compounds at ordinary temperature the same general laws hold as for inorganic compounds, namely, that *exposed* valences in organic compounds on double and triple bonds, in bivalent and trivalent carbon, etc., are the common seat of oxidation and reduction reactions, especially at ordinary temperature, exactly as the exposed valences of free ions, free atoms, etc., of inorganic compounds have been found to be.

10. While polarity in organic compounds is insisted upon as giving us an invaluable guide in following organic reactions, it is pointed out that the polarity need not be of the extreme character shown by common salts but may very well be of the character proposed by Bohr, Lewis and Kossel, where the transfer of electrons from atom to atom is not as complete as in the case of common electrolytes. Polarity exists, nevertheless, and the application of the theory of polar valence represents a decided advance in the interpretation of reactions of organic compounds.

CHICAGO, ILLINOIS

THE SOL-GEL EQUILIBRIUM IN PROTEIN SYSTEMS[1]

BY ROBERT HERMAN BOGUE[2]

Introduction

The significance of a transitional temperature in gelatin solutions recently has been receiving much attention from chemists. In a general sense it has long been recognized that whereas very dilute solutions (1.0%) of pure gelatin would gel at low temperatures (10°), yet that above certain temperatures, roughly placed at about 35°, gelation would not take place at any concentration. Exceedingly viscous solutions might be obtained, but the ability of these to congeal to a jelly was not observed above this temperature.

In a sense, the melting point of a gelatin or glue has been taken as the critical temperature, as is the case with crystalloids, but melting point is not at all easily obtained or even defined when such substances as gelatin are under consideration. Many attempts have been made to determine this property, but none of them may be regarded as absolute melting-