

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 98]

## ELECTRON DISPLACEMENT IN CARBON COMPOUNDS IV. DERIVATIVES OF BENZENE

BY HOWARD J. LUCAS

RECEIVED MARCH 8, 1926

PUBLISHED JULY 6, 1926

The Lewis theory of molecular structure<sup>1,2</sup> has been of great service in the field of inorganic chemistry. The development of a rational procedure by which the properties of carbon compounds can be related to this theory is one of the pressing problems of organic chemistry. In this paper it will be shown that using the dynamic models of molecules the screening effect<sup>3</sup> of electrons provides a mechanism for the phenomenon of electron displacement<sup>1,4</sup> and that by the application of the principles of electron displacement to the Pauling<sup>5</sup> structure of benzene derivatives it is possible to explain their chemical properties and the phenomena of substitution.

**The Screening Effect of Electrons.**—We shall accept as self-evident truths the following postulates.

*Postulate I.* The effective nuclear charge of any atomic nucleus is greatest for the innermost orbit of electrons and least for the outermost orbit.

*Postulate II.* In any atom the inner electrons act as screens between the nucleus and outer electrons and thus decrease the effective nuclear charge for outer electrons; they are said to exert a screening effect upon the latter.

*Postulate III.* In any one atom the innermost electrons exert the largest screening effect and the outermost electrons the smallest screening effect.

*Postulate IV.* The screening effect of an electron in a given shell towards other electrons is not a constant; it is least towards innermost electrons and greatest towards outermost electrons.

These four postulates have been shown to be reasonable theoretically from classical electrostatic considerations, and have been substantiated by physicists in their researches in the field of atomic structure and spectral lines.

The assumption is now made that the relationships which hold between the nucleus of an atom and its electrons also hold between the nucleus of an atom in a compound and the shared electrons in the valence shell of the atom. In order to show how a change in the effective nuclear charge of

<sup>1</sup> (a) Lewis, *THIS JOURNAL*, **38**, 762 (1916). (b) "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., 1923.

<sup>2</sup> Langmuir, *THIS JOURNAL*, **41**, 868, 1543 (1919); **42**, 274 (1920); *J. Ind. Eng. Chem.*, **12**, 385 (1920); *Nature*, **105**, 261 (1920); *Science*, **54**, 59 (1921).

<sup>3</sup> Sommerfeld, "Atomic Structure and Spectral Lines," Translated by Brose, E. P. Dutton and Co., 1923, p. 73.

<sup>4</sup> (a) Lucas and Jameson, *THIS JOURNAL*, **46**, 2478 (1924). (b) Lucas and Moyses, *ibid.*, **47**, 1459 (1925). (c) Lucas, Simpson and Carter, *ibid.*, **47**, 1462 (1925).

<sup>5</sup> Pauling, *ibid.*, **48**, 1132 (1926).

an atom produces electron displacement about other atoms through the mechanism of the screening effect, it is desirable to adopt the view that the shared electrons which constitute a bond are moving in elliptical orbits which inclose the nuclei they join. This is an extension of the Bohr theory of electron orbits and has been made by others.<sup>5,6</sup>

**Displacement of Electron Orbits.**—Now if in methane,  $\text{CH}_4$ , one of the hydrogen atoms is replaced by a radical of high electron attraction,<sup>7</sup> R, the orbits joining C to R (Fig. 1) will presumably be pulled out in the direction of R and consequently the electrons will be in the neighborhood of C for a shorter time than they were when the hydrogen atom was present. The pulling away of these orbits from the carbon nucleus leaves it with a

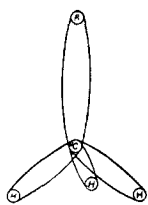


Fig. 1.—Probable enlargement of electron orbits in  $\text{CH}_3\text{R}$ , when R has a high electron attraction.

larger effective nuclear charge than before, since the more remote average positions of the electrons decrease their screening effect towards the other electrons, a result which follows from Postulate III. Therefore the orbits of the other three electron pairs will be contracted and the electrons drawn more closely to the carbon nucleus. Since the three pairs of orbits are symmetrical with respect to the carbon nucleus, orbital displacement will be distributed equally among them when they all inclose, as in this case, the same other atom.

If the radical has an electron attraction which is less than that of hydrogen the orbits of the electrons which bind it to carbon will be displaced towards the latter with a consequent decrease in its effective nuclear charge. The other three electron pairs will therefore be displaced away from the carbon nucleus.

Displacement of electron orbits is, therefore, a necessary consequence of the extension of the Bohr theory to the shared electron bond. It is evident that this displacement may be transmitted from atom to atom with decreasing intensity, since usually the effect is divided between two or more atoms. The view that in molecules the atoms tend to become alternately polarized<sup>8</sup> cannot be reconciled with the accepted postulates.

In order to indicate relative orbital positions conveniently we shall use

<sup>5</sup> W. A. Noyes, *THIS JOURNAL*, **39**, 879 (1917). Knorr, *Z. anorg. allgem. Chem.*, **129**, 104 (1923). Højendahl, *J. Chem. Soc.*, **125**, 1381 (1924).

<sup>7</sup> It is well to distinguish between electron affinity and electron attraction. A substance which tends to appropriate electrons of other substances, and which is therefore an oxidizing agent, may be said to have a high electron affinity. An atom or radical which exerts a strong pull on the shared electron pair joining it to some other atom may be said to have a high electron attraction. Thus, the presence in a molecule of a group possessing high electron attraction may give to the molecule a high electron affinity.

<sup>8</sup> Cuy, *THIS JOURNAL*, **42**, 503 (1920). Hanke and Koessler, *ibid.*, **40**, 1726 (1918). Lapworth, *J. Chem. Soc.*, **121**, 416 (1922). Kermack and Robinson, *ibid.*, **121**, 427 (1922). Allsop and Kenner, *ibid.*, **123**, 2296 (1923).

the symbols previously proposed<sup>4c</sup> for static models, namely,  $\circ\text{---}$ ,  $\text{---}\circ\text{---}$ ,  $\text{---}\circ\text{---}$ . The small circle in each case represents two electrons, and the circle is placed nearer to an atom the more strongly the electrons are held by that atom.

**Electron Displacement in Benzene Derivatives.**—In Pauling's model of the benzene molecule (Fig. 2) each closed curve represents a bond which results from the revolving of two electrons in elliptical orbits about the two nuclei of the atoms they join. The electrons constituting the bonds which join each carbon atom to hydrogen and to adjacent carbon atoms move in smaller orbits called  $\lambda$  orbits, and the electrons which join each carbon atom to its *para* carbon atom move in larger orbits called  $\mu$  orbits.

If now a radical R of high electron attraction (a so-called negative group) such as  $\text{NO}_2$  replaces one of the hydrogen atoms of benzene, the resulting electron displacement will be transmitted throughout the molecule and will influence the position of all the other electrons in the molecule. It is proposed to show that the electrons in the C—H bonds suffer different degrees of displacement, and that this difference in degree of electron displacement corresponds to a difference in the degree of reactivity of the *ortho*, *meta* and *para* positions.

Now, in the Pauling formula there is a direct connection to the *ortho* and *para* positions, but not to the *meta*. It is reasonable to infer, then, that any displacement of electrons at the carbon atom C-1 will influence directly the *ortho* and *para* carbon atoms and only indirectly the *meta*. Therefore we may conclude that the *meta* carbon will be influenced least by the original electron displacement, and that the *ortho* and *para* carbon atoms will be influenced more.

If Postulate IV is true the substituent group will cause a greater change in the effective nuclear charge of the carbon atom C-1 with respect to  $\mu$  electrons than with respect to  $\lambda$  electrons, since  $\lambda$  electrons screen the outer  $\mu$  electrons more than they screen the other  $\lambda$  electrons. Thus the  $\mu$  electrons are affected more by the substituent group than the  $\lambda$  electrons. On the other hand, the  $\mu$  electrons are not able to change the effective nuclear charge of a carbon atom with respect to other  $\lambda$  electrons as effectively as  $\lambda$  electrons. Accordingly one is unable to say *a priori* that the *para* carbon atom will be influenced more strongly than an *ortho*, since

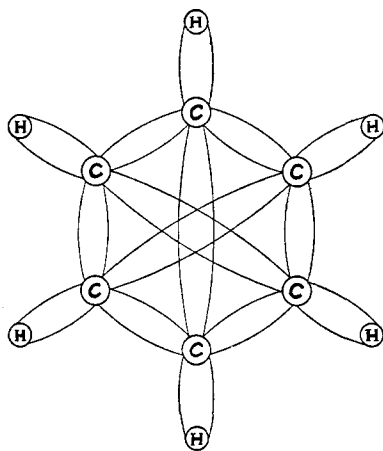


Fig. 2.—The Pauling structure for benzene. Each closed curve represents two electron orbits. The *para* bonds are  $\mu$  orbits, the others are  $\lambda$  orbits.

at the present time we have no quantitative measurements of these phenomena. Now many of the properties of benzene derivatives and most of the phenomena of substitution can be rationally explained if the *para* position is the one which is more strongly influenced; we shall accordingly make that assumption. *In general then the substituent influences the para carbon most, the ortho carbon atoms somewhat less, and the meta carbon atoms least of all.*

Thus the substituted radical R of high electron attraction increases the effective nuclear charges of the carbon atoms of the benzene ring in the order *para* > *ortho* > *meta*. Now the electrons joining these carbon atoms to the hydrogen atoms will be attracted by the former in proportion to the magnitude of these effective nuclear charges, and the magnitudes of these forces are again in the order *para* > *ortho* > *meta*. Fig. 3 shows the relative positions which the electrons or rather the orbits of the electrons have assumed under the influence of the forces now existing in the molecule.

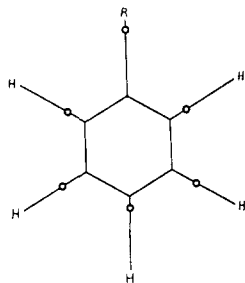


Fig. 3.—Displacement formula for  $C_6H_5R$ . This shows the relative positions of the electrons when R has a high electron attraction.

in benzene. The *meta* hydrogen atoms in  $C_6H_5R$  are, however, negative in relation to the *ortho* and *para* hydrogen atoms. This may be represented by the polarity formula shown in Fig. 4. This formula should not be interpreted as indicating that the hydrogen in the *meta* position is negative but only that it is less positive than the other hydrogen atoms.

Now when a group of low electron attraction (a so-called positive group) such as  $NH_2$  takes the place of a hydrogen atom, electron displacement is towards the ring carbon and is transmitted to the other positions by the mechanism discussed above, with the result that the opposite effect is produced around the ring, in this case the *para* hydrogen being most negative, the *ortho* next and the *meta* least (Fig. 5). Relative to the *ortho* and *para* hydrogens the *meta* is now less negative (Fig. 6), a relationship opposite to that which results when the substituent has a high electron attraction.

It is interesting to point out that Formulas 4 and 6 resemble those proposed by Fry,<sup>9</sup> but with this difference, that whereas the principle of electron displacement demands that nitrobenzene resemble Fig. 4 and aniline

<sup>9</sup> Fry, "Electron Conception of Valence," Longmans, Green and Co., 1921. Also numerous journal articles.

**Polarities of the Hydrogen Atoms.**—Compared to the hydrogen atoms of benzene, all of the hydrogen atoms in  $C_6H_5R$  where R has a high electron attraction are positive, since all of the electrons in  $C_6H_5R$  lie closer to the carbon atoms than do those

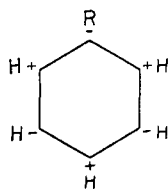


Fig. 4.—Polarity formula corresponding to 3. This indicates that the *meta* hydrogen atoms are the least positive.

Fig. 6, Fry assumes that nitrobenzene has the latter structure and aniline the former. However, the displacement Formulas 3 and 5 are much to be preferred to the polarity formulas.

**Electron Attraction of Radicals.**—It is necessary that we have some means of determining the relative electron attraction of radicals. Many chemists regard  $\text{NO}_2$ ,  $\text{COOH}$ , and similar groups as negative and  $\text{NH}_2$ ,  $\text{CH}_3$ , etc., as positive, expressions which, in terms of the theory here presented, mean the possession of electron attractions greater than hydrogen and less than hydrogen, respectively. A strongly negative group usually causes an increase in the ionization constant of an acid and a decrease in that of a base when it is substituted for a hydrogen atom, and a positive group usually brings about the opposite result. There are many groups, however, which produce one effect in one compound, and an opposite effect in another. Such an anomalous behavior is no doubt associated with electrostatic effects operating across space between the substituent and the carboxyl group, a result which may at times outweigh the effect produced by displacement along the chain of atoms. Thus Spiers and Thorpe<sup>10</sup> have shown that the degree of ionization of substituted glutaric acids increases as the carboxyl groups are brought closer together in space.

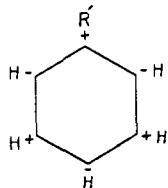


Fig. 6.—Polarity formula corresponding to 5. This indicates that the *meta* hydrogen atoms are the least negative.

In order to obtain a measure of relative electron displacements from data on ionization constants we must select compounds in which the substituents are so far removed that steric influences can be neglected. Since in *para* substituted benzoic acids the carboxyl and the substituent are far apart in space, it seems reasonable to assume that any change in the ionization constant must result from electron displacement, which in turn is presumably proportional to the electron attraction of the substituent. In Table I are listed the ionization constants of some *para* substituted benzoic acids.

The positions of most groups in this table conform to our accepted notions of relative negativity and positivity, since  $\text{NO}_2$  causes the largest increase, and  $\text{NH}_2$ ,  $\text{NH}(\text{CH}_3)$  and  $\text{N}(\text{CH}_3)_2$  cause the largest decreases in the ionization constant. The position of hydroxyl is unexpected, since it is usually considered to be negative. However, the positive character of this group becomes more evident when it is noted that the halogens, carboxyl and sulfonic acid increase the electrode potentials of quinol-

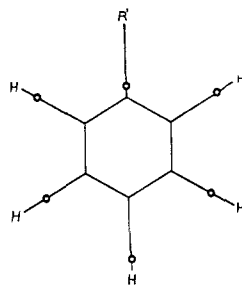


Fig. 5.—Displacement formula for  $\text{C}_6\text{H}_5\text{R}'$ . This shows the relative positions of the electrons when  $\text{R}'$  has a low electron attraction.

<sup>10</sup> Spiers and Thorpe, *J. Chem. Soc.*, 127, 538 (1925).

TABLE I  
IONIZATION CONSTANTS OF PARA SUBSTITUTED BENZOIC ACIDS<sup>11</sup>

Substituent	NO <sub>2</sub>	SO <sub>2</sub> NH <sub>2</sub>	COOH	Cl	Br	H	NHCOCH <sub>3</sub>	
K <sub>A</sub> × 10 <sup>5</sup>	40.1	26	13	9.3	6.6	6.6	5.2	
Substituent	OC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	OCOCH <sub>3</sub>	OCH <sub>3</sub>	OH	NH <sub>2</sub>	NH(CH <sub>3</sub> )	N(CH <sub>3</sub> ) <sub>2</sub>
K <sub>A</sub> × 10 <sup>5</sup>	5.1	4.5	4.2	3.2	2.9	1.2	0.9	0.9

quinone cells and alkyls, phenyl, methoxyl and hydroxyl decrease the electrode potentials.<sup>12</sup> Now, the *para* bonds are ruptured in the oxidation of quinol to quinone, and the more difficult this process becomes the greater should be the value of the free energy decrease and, therefore, of the electrode potential. The ease with which a *para* bond can be broken should vary inversely with the effective nuclear charges of the ring carbon atoms, and these vary directly with the electron attraction of the substituent. The positive character of hydroxyl is also shown by the fact that the additive power of CO, which is greatest when combined with negative radicals,<sup>13</sup> is much less when it is joined to CH<sub>3</sub>, OR, NH<sub>2</sub> and OH.<sup>14</sup>

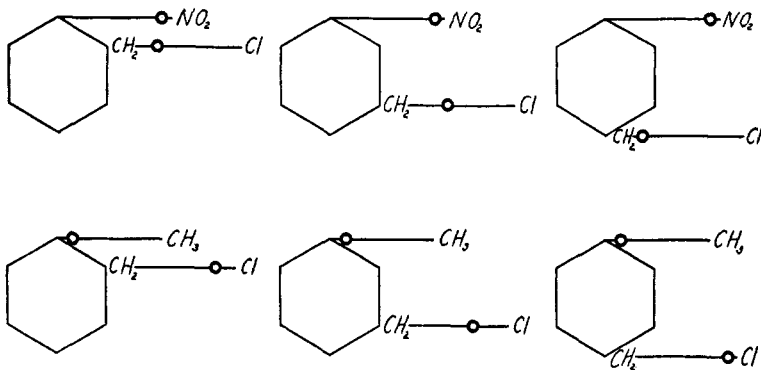


Fig. 7.—Displacement formulas for substituted benzyl chlorides. These show the relative polarities of the chlorine atoms.

**Alternation in Reactivity.**—The relative reactivities of a group X in  $C_6H_4^RCH_2X$  and  $C_6H_4^{R'}CH_2X$  can be predicted on the basis of relative electron displacements. Thus if X is Cl, R is NO<sub>2</sub> and R' is CH<sub>3</sub>, the relative polarities of the chlorine atoms are given by the formulas shown in Fig. 7. Since the most negative halogen is hydrolyzed the most easily, the order of hydrolysis rate should be *p*-CH<sub>3</sub> > *o*-CH<sub>3</sub> > *m*-CH<sub>3</sub> > H > *m*-NO<sub>2</sub> >

<sup>11</sup> Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," Van Nostrand Co., 1914. The constants of other *para* substituted benzoic acids are now being determined.

<sup>12</sup> Clark, *Chem. Reviews*, **2**, 163 (1925).

<sup>13</sup> Stewart, *J. Chem. Soc.*, **87**, 186 (1905).

<sup>14</sup> Vorländer, *Ann.*, **341**, 9 (1905).

$o\text{-NO}_2 > p\text{-NO}_2$ . Now this is exactly the order found by Olivier,<sup>15</sup> whose results accordingly strongly support the displacement theory. Likewise chlorine, which is less negative than nitro should produce an effect intermediate between hydrogen and nitro, which it does, although the order is  $p\text{-Cl} > o\text{-Cl} > m\text{-Cl}$  instead of  $m\text{-Cl} > o\text{-Cl} > p\text{-Cl}$ , as one would predict.

The hypothesis of electron displacement likewise accounts for the relative reaction rates of substituted benzyl bromides,<sup>16</sup> and does so more satisfactorily than the hypothesis of alternate polarity.

**Substitution Reactions.  $\mu$  Electrons not Involved.**—Reactions of substitution in the benzene ring are usually brought about by an oxidizing agent such as chlorine, bromine, iodine, nitrous acid, nitric acid, concd. sulfuric acid, etc. It has been pointed out<sup>4c</sup> that in the case of aliphatic hydrocarbons substitution proceeds most rapidly at the point where the attraction of carbon for electrons is least, that is, when the hydrogen atoms are the most negative. In the case of benzene derivatives it is necessary first of all to consider whether the electrons of the outer  $\mu$  orbits or those of the inner  $\lambda$  orbits are the more easily appropriated by the reagent. It seems reasonable to think that in reactions of substitution a molecule of the reactant must approach close to a molecule of the aromatic compound before it can attract electrons. Now although the  $\mu$  electrons are in outer orbits as far as the carbon atoms are concerned, it is probable that the reactant cannot approach as closely to them as to the  $\lambda$  orbits which inclose the hydrogen nuclei because the ring of six carbon nuclei would strongly repel the nucleus of any atom except the very lightest when it approached the side of the benzene compound where the  $\mu$  orbits are exposed, whereas the proton would not exert such a strong repulsion if the reactant should approach the edge where the  $\lambda$  orbits are exposed. Therefore the process of substitution would presumably involve the  $\lambda$  electrons and not the  $\mu$  electrons.

Since benzene may be converted to cyclohexane by reduction with hydrogen and to hexabromocyclohexane by adding on bromine, it is evident that under favorable conditions the  $\mu$  electrons may be involved in chemical reactions.

**Relative Reactivities of the Ortho, Meta, and Para Positions. Rules of Substitution.**—The degree to which a substituting reagent reacts with the  $\lambda$  electrons of a C—H bond depends upon the strength of the attraction exerted upon these electrons by the particular carbon atom. Compared to  $\text{C}_6\text{H}_6$  these forces are greater in  $\text{C}_6\text{H}_5\text{R}$  (R having a high electron attraction) and their strengths are in the order *para* > *ortho* > *meta*,

<sup>15</sup> Olivier, *Rec. trav. chim.*, **41**, 301 (1922).

<sup>16</sup> Lapworth and Shoesmith, *J. Chem. Soc.*, **121**, 1391 (1922). Shoesmith, Hetherington and Slater, *ibid.*, **125**, 1312 (1924). However, electron displacement does not account for the relative reactivities of nitrochlorobenzenes.

while in  $C_6H_5R'$  ( $R'$  having a low electron attraction) they are less and in the order *meta* > *ortho* > *para*. By the deductive method we are led to the following statements.

I. Substitution reactions will, in general, be slower with  $C_6H_5R$  than with  $C_6H_6$ .

II. Formation of the *meta* isomer will predominate in reactions with  $C_6H_5R$ , since the *meta* positions are the most reactive.

III. In the absence of steric effects, the *ortho* isomer will exceed the *para* in reactions with  $C_6H_5R$ , since there are two *ortho* positions to one *para* and the *ortho* positions are the more reactive.

IV. Substitution reactions will, in general, be faster with  $C_6H_5R'$  than with  $C_6H_6$  and  $C_6H_5R$ .

V. Formation of the *ortho* and *para* isomers will predominate over the *meta* in reactions with  $C_6H_5R'$  since the *meta* positions are the least reactive.

VI. The quantities of the *ortho* and *para* isomers formed in reactions with  $C_6H_5R'$  may be almost equal since the one *para* position is more reactive than either of the two *orthos*.

VII. The directive power of a substituent varies in the direction opposite to its electron attraction since, in general, the rate of reaction (upon which the directive power is dependent) itself varies in the direction opposite to the electron attraction of the substituent.

In the main these deductions correctly represent the facts of substitution as they have been elucidated by many workers, especially Holleman and his students. The following exceptions should be noted, however: (a) when  $R$  is halogen the main products are *ortho* and *para*, not *meta*, as predicted; this is discussed below; (b) often the amount of *para* exceeds the *ortho* when the *meta* is the main product; this may result from steric hindrance; (c) the directive power does not vary strictly inversely with the electron attraction of the substituent; otherwise, the order would be  $NH_2 > OH > CH_3 > \text{halogen}$ , whereas according to Holleman it is  $OH > NH_2 > Cl > I > Br > CH_3$ . But since the directive power of an *ortho-para* substituent is greater than any *meta*, since also in the *meta* directive group the order agrees with the prediction, that is  $COOH > SO_3H > NO_2$ , and since even in the *ortho-para* directive group the two which exert the strongest directive influence have the lowest electron attraction, it is reasonable to think that there is a fundamental relationship between directive power and electron attraction.

It is instructive to point out here that the *ortho-para* directive power of a group may be decreased by changing hydrogen atoms in the group to radicals of higher electron attraction, and that the *meta* directive power of some other group may be decreased by changing hydrogen atoms in the group to radicals of lower electron attraction. Thus, the *ortho-para* directive  $CH_3$  is changed to the *meta* directive  $CCl_3$  when all of the hy-







sideration of its electron attraction, it is probable that its *ortho-para* directive power is due to the tendency of the reagent to appropriate its unshared electrons rather than those of the ring. Such an explanation may in part account for the great difference in the directive influence of  $\text{NO}_2$  and  $\text{NO}$  which are *meta* and *ortho-para* directive, respectively,<sup>23</sup> although the greater electron attraction of  $\text{NO}_2$  is an important factor. Also the difference between  $\text{NH}_2$  and  $\text{NH}_3^+$  (present in salt of amines) which are *ortho-para* and *meta*<sup>24</sup> directive, respectively, may in part be due to the presence of unshared electrons in the  $\text{NH}_2$  although here also the relative electron attraction must be considered. The introduction of  $\text{H}^+$  into  $\text{NH}_2$  would increase the electron attraction of the group as a whole because of the pull exerted by the additional hydrogen nucleus.<sup>25</sup>

That a reaction may proceed by the reagent appropriating unshared electrons on the substituent already present, followed by the migration of a radical to the *ortho* or *para* position, is an assumption which agrees with the views of Karrer<sup>26</sup> in regard to the method by which diazonium salts couple with ethers and with tertiary amines. The splitting off of alkyl groups during these coupling processes necessitates only that the alkyl group instead of hydrogen drop off from the oxygen or nitrogen atom, as the case may be. Since the splitting off of methyl in the reaction of nitrous acid with phenylmethyl ether to produce *p*-nitrosophenol<sup>27</sup> may proceed in the same way, we need no longer consider this reaction as evidence in support of the view that the reagent adds to a double bond of the benzene ring.<sup>28</sup>

The orienting influence of substituents in the benzene ring seems to depend upon two factors, namely, electron attraction and the presence of unshared electrons on the atom joined to ring carbon. If the electron attraction is greater than hydrogen and unshared electrons are absent, the *meta* position is entered; if slightly greater than hydrogen and unshared electrons are present, the *ortho-para* position is entered; if less than hydrogen, the *ortho* and *para* positions are taken whether there are unshared electrons on the atom joined to ring carbon or not. It is significant that the most strongly directive groups contain such electrons.

### Summary

The Lewis theory of molecular structure promises much in the way of explaining the chemical properties of carbon compounds. It must be

<sup>23</sup> Ingold, *J. Chem. Soc.*, **127**, 513 (1925).

<sup>24</sup> Vorländer, *Ber.*, **52B**, 263 (1919).

<sup>25</sup> Compare Latimer and Rodebush, *THIS JOURNAL*, **42**, 1425 (1920). Lewis, Ref. 1b, p. 141.

<sup>26</sup> Karrer, *Ber.*, **47**, 1275 (1914).

<sup>27</sup> Meyer, *Ann.*, **398**, 80 (1913).

<sup>28</sup> Stieglitz, *THIS JOURNAL*, **44**, 1304 (1922).

interpreted in the light of physical principles which include the screening effect. By extending the Bohr concept of elliptical orbits to shared electrons it follows that a displacement of an orbit in one part of a molecule causes displacement of the other electron orbits in the same general direction. When these concepts are applied to the Pauling model of benzene, we obtain displacement formulas of benzene derivatives which indicate the relative attractive forces between the carbon nuclei and the electrons in the respective carbon-hydrogen bonds. These formulas account for the relative reactivities of substituted benzyl chlorides and bromides and for the phenomena of substitution.

A measure of the relative electron attractions of radicals is given by the ionization constants of *para* substituted benzoic acids.

PASADENA, CALIFORNIA

---

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 180]

## THE ULTRAVIOLET ABSORPTION SPECTRA AND THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDROGEN BROMIDE AND IODIDE

BY HAROLD C. TINGEY<sup>1</sup> AND ROSCOE H. GERKE

RECEIVED MARCH 8, 1926

PUBLISHED JULY 6, 1926

The purpose of this investigation was to study the ultraviolet absorption spectra of the hydrogen halides during photochemical decomposition in order to test the validity of two alternative mechanisms which have been suggested to explain the existing experimental facts.

Before the quantum theory of band spectra of molecules had received its great development Warburg<sup>2</sup> suggested the following mechanism, which was in accord with his experimental observations. The absorption of a quantum of ultraviolet light decomposed a single hydrogen halide molecule into atoms which later reacted with another hydrogen halide molecule in such a manner as to produce one hydrogen and halogen molecule. More recently Stern and Volmer,<sup>3</sup> in view of the recent developments on the theory of band spectra have assumed that the absorption of the radiation did not produce direct photochemical decomposition, but that it did produce an excited molecule which would, upon collision with another hydrogen halide molecule produce one hydrogen and halogen molecule. With the aid of the quantum theory of band spectra<sup>4</sup> it is possible to

<sup>1</sup> From the Doctor's Dissertation of Harold C. Tingey, Massachusetts Institute of Technology.

<sup>2</sup> Warburg, *Sitzb. preuss. Akad. Wiss.*, **1916**, 314; **1918**, 300.

<sup>3</sup> Stern and Volmer, *Z. wiss. Phot.*, **19**, 275 (1920).

<sup>4</sup> Sommerfeld, "Atomic Structure and Spectral Lines," translated from third German Edition by Henry L. Brose. E. P. Dutton and Company, New York, 1923.