

1934

## Thiele's Theory of Partial Valency in Terms of Electrons

Francis Earl Ray  
*University of Cincinnati*

Copyright ©1934 Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

---

### Recommended Citation

Ray, Francis Earl (1934) "Thiele's Theory of Partial Valency in Terms of Electrons," *Proceedings of the Iowa Academy of Science*, 41(1), 157-160.

Available at: <https://scholarworks.uni.edu/pias/vol41/iss1/43>

This Research is brought to you for free and open access by the Iowa Academy of Science at UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact [scholarworks@uni.edu](mailto:scholarworks@uni.edu).

## THIELE'S THEORY OF PARTIAL VALENCY IN TERMS OF ELECTRONS

FRANCIS EARL RAY

Scientific theories generally have a long and difficult road to travel before gaining acceptance. It is, therefore, somewhat surprising to find that Thiele's theory of partial valency gained such ready recognition. This was undoubtedly due to the fact, as the saying goes, that it filled a long felt want. As time went on and chemists learned more about valence there arose a tendency to question the existence of such a thing as a "partial" valence. But as no alternative explanation was forthcoming to explain the phenomena that Thiele's theory explained so well, no great inroads were made against his hypothesis.

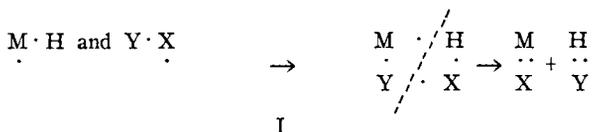
As long as the ordinary carbon to carbon valence was considered a single bond, it *was* difficult to picture a "partial" bond. It is only when we consider the electron nature of the bond that the full justification of Thiele's theory becomes plain.

According to the modern electron theory the ordinary single bond between carbon atoms consists of a *pair* of electrons shared equally by the two atoms. If, under the influence of the reagent, this bond is loosened and momentarily exists as a single electron bond, we have an excellent picture of a "partial valence." The object of this paper is to point out this new justification of an old theory.

This partial valence consisting of less than the normal number of electrons then is the type of reaction that is involved in substitutions. In the non-ionic reaction



the first stage is the activation of the molecules with the formation of partial valences.

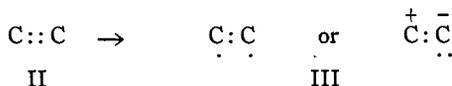


These now join through partial valences and then separate as indicated by the dotted line to form the new compounds, I. At no

time is any atom entirely free. This is the distinction between ionic and non-ionic reactions.

When we examine the electronic arrangement of the double bond we perceive the cause of its reactivity.

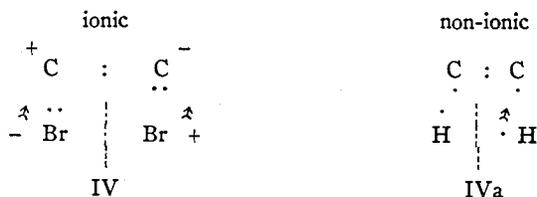
The ethylenic double bond consists of four electrons, II. When the molecule is activated two of these electrons are freed to unite with the reagent, as in III.



Note that two electrons forming a regular bond remain between the carbon atoms. Less energy is required in this case than when a single electron bond is formed. This accounts for the ease with which the double bond reacts.

Let us now suppose that a molecule of halogen is reacting with this compound. It will be remembered that when bromine reacts with sodium hydroxide two compounds are formed, NaBr and NaOBr. That is to say the bromine molecule splits into one positive and one negative bromine atom. In terms of electrons this means that one atom has both the valence electrons and is, of course, negative.

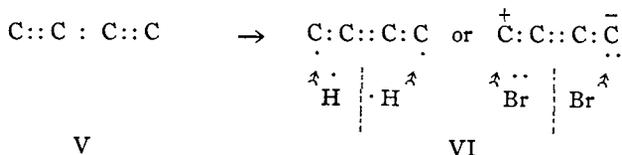
This negative atom is consequently attracted to the carbon which is without electrons while the other bromine goes to the carbon with the two free electrons, IV.



If the addendum is non-ionic it first joins by single electrons as previously described, IVa.

It is, perhaps, in the conjugated system that the most important application of the original theory is found and it is to such a system that we will now apply these newer ideas.

The electronic arrangement of the conjugated system is shown in V. The reagent causes a probable shift of electrons, as in VI.

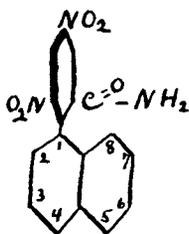


The halogen can then add to the 1-4 positions in the manner previously described.

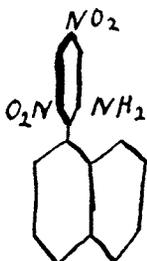
If it be objected that such a shift of electrons is improbable, one might cite the transformation of beta-gamma unsaturated acids into alpha-beta unsaturated acids under the influence of bases and other reagents. In fact it is hard to see how any reaction can take place between compounds unless there is a mutual displacement of electrons. ¶

These ideas have been used in the author's classes for several years. It was, however, extremely gratifying to learn of the beautiful experimental demonstration of the correctness of the partial valency theory by E. S. Wallis and W. W. Moyer.<sup>1</sup>

Professor Wallis and his assistant used, in this research, the optically active amide of 3, 5-dinitro-6- $\alpha$ -naphthylbenzoic acid,



VII



VIII

VII. This compound exists in two optically active forms because the two ortho groups on the benzene ring ( $\text{NO}_2$  and  $\text{CO-NH}_2$ ) restrict the free rotation of the rings by coming in contact with the 8-carbon atom of the naphthalene ring. When this compound is submitted to the Hofmann hypobromite reaction the  $\text{CO}$  is eliminated and the amino group becomes attached directly to the benzene ring, VIII.

If, in this operation, the  $\text{CO-NH}_2$  group momentarily leaves the benzene ring, the rings would be free to rotate and an optically *inactive* compound would result. Professor Wallis found that the Hofmann rearrangement did *not* racemize the compound but gave an amine with a high rotation. His conclusion is that the migrating radical was never entirely free from the benzene ring.

If one might be permitted to make the obvious extension of Professor Wallis's conclusions it would be: at all times during the reaction some part of the migrating radical was connected by a partial valence to the benzene ring.

Excellent evidence for the existence of single electron linkages is given by N. V. Sidgwick in his comprehensive work, *The Electron Theory of Valency*.<sup>2</sup> In more recent work Pauling<sup>3</sup> offers

<sup>1</sup> Wallis, E. S. and Moyer, W. W., *J. Am. Chem. Soc.*, 55, 2598 (1933).

<sup>2</sup> Sidgwick, N. V. *The Electron Theory of Valency*. Oxford University Press. (1929).

<sup>3</sup> Pauling, L. J. *Amer. Chem. Soc.*, 53, 3225 (1931).

physical data as evidence for the existence of both single and triple electron bonds. Perrin and Ramart-Lucas<sup>4</sup> have used single electron linkages in their interpretation of reaction mechanisms.

This conception of partial valency is useful because it not only shows the similarity of organic to inorganic chemistry but also indicates the reason for the slow reactivity of many organic compounds and the production of by-products by pointing out the essential difference between ionic and non-ionic reactions.

---

<sup>4</sup> Perrin, *Compt. rend.* 185, 557 (1927). Ramart-Lucas, *Ibid.*, 185, 561, 718 (1927).

DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CINCINNATI,  
CINCINNATI, OHIO.