

Bond Orbital Theory of Chemical Reactivity

by

Kang Yang* and Taikyue Ree**

(Received on Jan. 7, 1964)

反應性的 結合 Orbital 理論

梁 岡* · 李 泰 圭**

(1964. 1. 7 受理)

要 約

結合 오비탈을 線型式으로 連結하여 分子 오비탈을 만드는 方法(linear combination of bond orbitals method, LCBO 法)을 應用하여 할로겐화메탄($\text{CH}_n\text{X}_{4-n}$)과 이를 攻擊하는 原子 (或은 自由基) A 와의 抽出反應(abstraction reaction $\text{CH}_n\text{X}_{4-n} + \text{A} \rightarrow \text{CH}_n\text{X}_{3-n} + \text{XA}$)에 對한 反應性을 研究하려는 것이 이 論文의 目的이다. 이 反應의 活性化 에네르기 ϵ 를 計算하려고 다음과 같은 假定을 하였다. 「 $\text{CH}_n\text{X}_{4-n}$ 分子가 活性化複合物로 變할 때 그의 反應性 結合(reactive bond) C-X 에 있는 두 電子는 完全히 이 分子의 他 σ 電子系로부터 分離된다.」 이런 모델은 재미있는 直感的인 觀念을 導引하게 되니 即 反應性結合과 그의 周圍에 있는 化學結合과의 相互作用에 依하여 σ 電子系의 反應性이 左右된다는 것이다. 著者들의 理論的 計算에 依하면 ϵ 는 다음 式으로 表示된다.

$$\epsilon = \xi + \sum_{i=1}^3 \eta_{C-i, C-4} \quad (1)$$

Subscript C-i ($i=1, 2, 3$)는 C와 原子 i ($i=\text{H, Cl, Br, F, } \dots$)間的 化學結合을 表示하며 C-4 ($4=\text{Cl, Br} \dots$)는 反應性結合을 가르킨다. ξ 는 上述한 바와 같이 完全分離狀態에 있는 C-4 結合과 攻擊原子 A 間的 假想的 反應의 活性化 에네르기이며 $\eta_{C-i, C-4}$ 는 C-4와 그의 周邊結合 C-i 間的 相互作用에 依하여 安定化되는 에네르지를 表示한다. 結合強도와 兩立하는 η 值을 選出하여 (1)式에 代入하면 次式이 誘導된다.

$$\epsilon = \xi + N\eta_{C-H, C-4} \quad (2)$$

N은 $\text{CH}_n\text{X}_{4-n}$ 分子中에 있는 C-4 以外의 C-H 及 C-F 結合들의 總數이다. 實驗值의 ϵ 를 N에 對하여 圖示하면 $\text{CH}_n\text{Cl}_{4-n} + \text{H} \rightarrow \text{HCl} + \text{CH}_n\text{Cl}_{3-n}$, $\text{CH}_n\text{X}_{4-n} + \text{Na} \rightarrow \text{NaCl} + \text{CH}_n\text{Cl}_{3-n}$, $\text{CH}_n\text{X}_{4-n} + \text{Na} \rightarrow \text{NaBr} + \text{CH}_n\text{Cl}_{3-n}$ 反應系들에 對하여 좋은 直線을 주니 (2)式이 實驗과 一致한다는 것이다.

Abstract

The linear combination of bond orbitals method is used to investigate the reactivity of halomethanes in abstraction reactions by atoms. The activation energy is evaluated on the assumption that, in an activated complex, two electrons in a bond to be broken become completely isolated from the rest of the σ -electron systems. Such a model leads to an intuitively attractive concept that the interactions between the reactive bond and the neighboring bonds govern the reactivity of σ -electron systems. The resulting equation for the activation energy, ϵ , is:

* Radiation Laboratory Continental Oil Company Ponca City, Oklahoma, U. S. A.

** Department of Chemistry, University of Utah, Salt Lake City, Utah, U. S. A.

$$\epsilon = \xi + \sum_{i=1}^3 \eta_{C-i, C-4}$$

Here, subscript C-4 indicates the bond to be broken, while C-i represents the other three bonds surrounding the reactive bond; ξ is the activation energy of a hypothetical reaction of an isolated C-4 bond and an attacking atom; and $\eta_{C-i, C-4}$ stems from the stabilizing interaction of C-4 bond with neighboring C-i bonds. A choice of η' , consistent with bond strength data simplifies the above equation to a form

$$\epsilon = \xi + N\eta_{C-H, C-4}$$

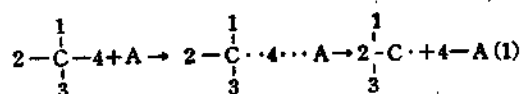
where N denotes the number of C-H plus C-F bond in halomethanes. In agreement with this equation, experimental ϵ -values increase linearly with increasing N.

I. Introduction

The reactivity of conjugated molecules in radical and ionic reactions is often examined⁽¹⁾ on the basis of the localization energy theory⁽²⁾, according to which energy required for localizing a π -electron or electrons at the reaction center plays a decisive role in determining reaction rates. Various successful examples^{(3) (4)} indicate that the activated complex invoked here has a plausible structure. As it stands now, the localization energy theory is capable of treating π -electron reactivities only. An extension to σ -electron cases is important, particularly in view of the fact that a unified theory is urgently needed to understand the reactivity of chemical compounds in general. The present paper attempts such an extension⁽⁵⁾ by taking as a specific example the abstraction reaction involving halomethanes. The activated complex to be employed has essentially the same structure as in the π -electron reactions. Because of the difference between the electron mobilities of the two systems, however, it is necessary to employ entirely different basis orbitals in representing overall molecular eigenfunctions.

I. Activated complex

Schematically, the abstraction reactions may be written as



where i (=1, 2, 3, and 4) denotes either hydrogen or halogen atoms. As the attacking species A approaches the reaction center, C-4 bond becomes weaker. In the vicinity of transition state where this reactive bond is at the verge of breakdown, two electrons in it become nearly uncoupled. When this happens, the unshared electron close to the carbon atom resides in an orbital

having nearly $2p\pi$ character which, because of symmetry property, interacts negligibly with the rest of σ -electron systems. These intuitions suggest an activated complex having a structure in which two electrons in a bond to be broken become isolated from the rest of σ -electron systems.

To evaluate the energy of such a structure, it is necessary to presume a reasonable molecular eigenfunction. For this we recall that, in contrast to the π -electron systems where electron densities tend to spread all over the molecular framework, the mobility of σ -electrons is mostly confined within the vicinity of a single bond. This suggests the use of an orbital strongly localized in each single bond. Such an orbital is called a bond orbital⁽¹⁾ and has been successfully employed in the quantum mechanical investigation of paraffins.^{(6) (7)} Denoting the bond orbital of C-i bond as ϕ_{C-i} , we then represent the molecular orbital of halomethane in the initial state as follows:

$$\phi = \sum C_i \phi_{C-i} \quad i=1, \dots, 4 \quad (2)$$

At the transition state, C-4 bond is missing; and the summation goes only up to 3:

$$\phi = \sum C_i \phi_{C-i} \quad i=1, 2, 3 \quad (3)$$

It is important at this point to realize that the number of allowed energy levels in the variation treatment is the same with the number of basis functions in the molecular orbital; thus the use of bond orbitals leads to the completeness to the molecular orbital theory of π -electrons where a common practice of using atomic orbitals results in the occupation of only a half of the allowed levels. This fact drastically simplifies the eigenvalue evaluation in the σ -electron case. In fact, all of our forthcoming conclusions concerning the structural factors governing chemical reactivity also stem directly from this use of bond orbitals. To emphasize these facts, the present use of

bond orbitals in investigating elementary reactions is called bond orbital theory of chemical reactivity.

III. Activation energy evaluation

In the evaluation of eigenvalues associated with (2) and (3), there appear various matrix elements for which the following standard notation is employed:⁽⁷⁾

$$\alpha_i = \int \phi_{C-i} H \phi_{C-i} d\tau$$

$$\beta_{ij} = \int \phi_{C-i} H \phi_{C-j} d\tau$$

$$S_{ij} = \int \phi_{C-i} \phi_{C-j} d\tau$$

The subscripts i and $C-i$ are used interchangeably to denote the corresponding quantities for $C-i$ bond. These matrix elements may be expressed in terms of α_{C-H} , β_{C-H} , $C-H'$, and α_{C-H} , $C-H'$, which are the corresponding elements in unsubstituted methane, by using the usual following approximations:⁽²⁾

$$\bar{\beta}_{ij} = \beta_{ij} / \beta_{C-H, C-H'} = S_{ij} / S_{C-H, C-H'}$$

$$\alpha_i = \alpha_{C-H} + h_i \gamma$$

where

$$\gamma = \beta_{C-H, C-H'} - S_{C-H, C-H'} \alpha_{C-H}$$

and h_i is a constant determined by the relation $(\alpha_i - \alpha_{C-H}) / \gamma = h_i$. We define X as follows:⁽²⁾

$$\frac{(\alpha_{C-H} - E) / (\beta_{C-H, C-H'} - S_{C-H, C-H'} \alpha_{C-H})}{= X / (1 - S_{C-H, C-H'} X)} \quad (4)$$

i. e., $X = (\alpha_{C-H} - E) / (\beta_{C-H, C-H'} - E S_{C-H, C-H'})$, E being the energy of the system; then the secular equation resulting from the application of the variation principle to ϕ given by (2) becomes:

$$\begin{vmatrix} \delta_i X + h_i & \bar{\beta}_{12} & \bar{\beta}_{13} & \bar{\beta}_{14} \\ \bar{\beta}_{12} & \delta_2 X + h_2 & \bar{\beta}_{23} & \bar{\beta}_{24} \\ \bar{\beta}_{13} & \bar{\beta}_{23} & \delta_3 X + h_3 & \bar{\beta}_{34} \\ \bar{\beta}_{14} & \bar{\beta}_{24} & \bar{\beta}_{34} & \delta_4 X + h_4 \end{vmatrix} = 0 \quad (5)$$

where

$$\delta_i = 1 - S_{C-H, C-H'} h_i$$

From (4),

$$E_k = \alpha_{C-H} - \frac{X_k}{1 - S_{C-H, C-H'} X_k} \gamma = \alpha_{C-H} - \gamma [X_k + S_{C-H, C-H'} X_k^2 + \dots]$$

Where X_k denotes one of the four roots of (5). Since all four energy levels are doubly occupied, the ground state, E_0 , for the halomethane becomes:

$$E_0 = 8\alpha_{C-H} - 2\gamma (\sum X_k + S_{C-H, C-H'} \sum X_k^2 + \dots) \quad (6)$$

The symmetric functions $\sum X_k^n$ are related to the coefficients of a polynomial,⁽⁸⁾

$$a_0 X^4 + a_1 X^3 + a_2 X^2 + a_3 X + a_4 = 0$$

(resulting from the expansion of (5)) by the equations:

$$\sum X_k = -a_1/a_0$$

$$\sum X_k^2 = (a_1^2 - 2a_0 a_2) / a_0^2$$

When these coefficients are evaluated, E_0 becomes

$$E_0 = 8\alpha_{C-H} + 2\gamma \sum_{i=1}^4 \left(\frac{h_i}{\delta_i} - S_{C-H, C-H'} \frac{h_i^2}{\delta_i^2} \right) - 4S_{C-H, C-H'} \gamma \sum_{i>j}^4 \frac{(\bar{\beta}_{ij})^2}{\delta_i \delta_j} \quad (7)$$

where the terms depending on the second and higher powers of $S_{C-H, C-H'}$ are neglected. The corresponding equation for the energy, E_n , associated with (3) is:

$$E_n = 6\alpha_H + \alpha_C + \alpha_4 + 2\gamma \sum_{i=1}^3 \left(\frac{h_i}{\delta_i} - S_{C-H, C-H'} \frac{h_i^2}{\delta_i^2} \right) - 4S_{C-H, C-H'} \gamma \sum_{i>j}^3 \frac{(\bar{\beta}_{ij})^2}{\delta_i \delta_j} \quad (8)$$

where the term $\alpha_C + \alpha_4$ represents energy of the two electrons in $C-4$ bond at the transition state.

In the above discussion, the $C-4$ bond is presumed to be completely isolated at the transition state from the rest of σ -electron system. Strictly speaking, this is only true at the final stage of reactions; and in an actual case, some interaction is expected to operate between the $C-4$ and remaining σ -electron system even at the transition state. Because of this effect, experimental activation energy, ϵ , is usually lower than $E_n - E_0$ as indicated below:⁽⁴⁾

$$\epsilon = a(E_n - E_0) - b \quad (9)$$

where a and b are constant expressible in terms of potential parameters involved in the reaction.

The use of (7) and (8) into (9) gives:

$$\epsilon = \xi + \sum_{i=1}^3 \eta_{C-i, C-4} \quad (10)$$

where

$$\xi = a \left(\alpha_C + \alpha_4 - 2\alpha_{C-H} - 2\gamma \frac{h_4}{\delta_4} + 2\gamma S_{C-H, C-H'} \frac{h_4^2}{\delta_4^2} \right) - b$$

$$\eta_{C-i, C-4} = a \left(4S_{C-H, C-H'} \frac{\gamma}{\delta_4} \right) \left(\frac{\bar{\beta}_{i4}^2}{\delta_i} \right)$$

Equation (10) indicates that activation energy is governed by two quantities, ξ and η . The former represents the activation energy of a hypothetical reaction of A with the $C-4$ bond, which is completely isolated from any molecular environment. The other term, η , stems from the fact that in actual reactions the $C-4$ bond resides in a molecular environment, hence it undergoes interactions with a neighboring bond. For the reaction to take place, an extra amount of energy must be supplied to overcome such an interaction. For example, $\eta_{C-1, C-4}$ represents this extra energy coming from the interaction between $C-1$ and $C-4$ bonds.

W. Comparison with experiments

An insight concerning the relative magnitude of various $\eta_{C-H, C-4}$ may be obtained from some thermodynamic data. With a slight modification, the present method is also applicable in treating bond energy data. (9) For example, it can be shown that

$$\frac{3}{2}(\eta_{C-H, C-Cl} - \eta_{C-F, C-Cl}) = D(CH_3-Cl) - D(CF_3-Cl)$$

and

$$\frac{3}{2}(\eta_{C-H, C-Br} - \eta_{C-Cl, C-Br}) = D(CH_3-Br) - D(CCl_3-Br)$$

The first ΔD is nearly zero, (10) while the second is as high as 19 kcal/mole. (11) This indicates that $\eta_{C-H, C-4}$ is about the same as $\eta_{C-F, C-4}$ but much larger than $\eta_{C-Cl, C-4}$. In consistency with these considerations, we select the following simple η :

$$\eta_{C-H, C-4} = \eta_{C-F, C-4} \gg \eta_{C-X', C-4}$$

where X' denotes Cl or Br atoms. Then, (10) takes a simple form:

$$\epsilon = \xi + N\eta_{C-H, C-4} \quad (11)$$

where N denotes the number of C-H plus C-F bonds in halomethanes. In a series of similar reactions in which both the attacking species and the atom to be abstracted remain constant, ξ as well as $\eta_{C-H, C-4}$ may

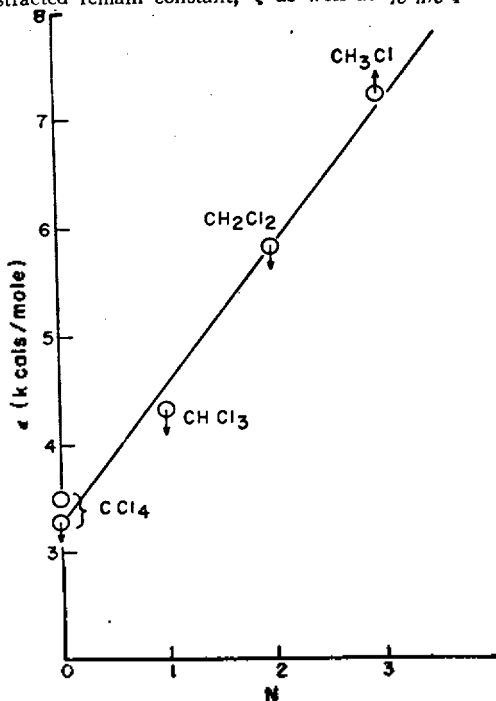
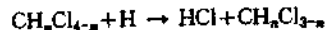


Fig 1. Activation energy ϵ for the reactions: $CH_nCl_{4-n} + H \rightarrow HCl + CH_nCl_{3-n}$ as a function of the number, N , of C-H bonds in halomethane.

be considered constant. Then, (11) predicts that ϵ should increase linearly with increasing N .

Figure 1 demonstrates this linearity for these reactions:



Downward and upward arrows here are, respectively, used to indicate the data (12) (13) reported to be the maximum and the minimum.

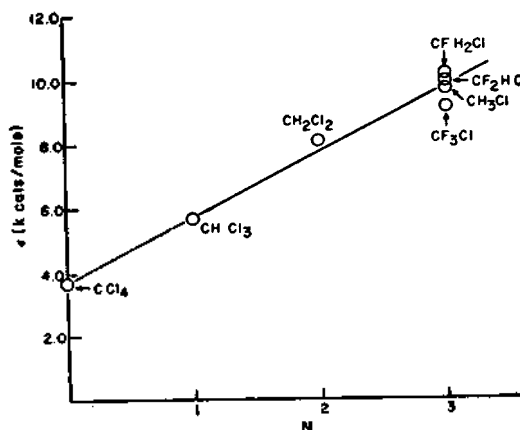
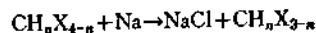


Fig 2. Activation energy ϵ for the reactions: $CH_nX_{4-n} + Na \rightarrow NaCl + CH_nX_{3-n}$ a function of the number, N , of C-H plus C-F bonds in halomethane.

Figure 2 shows the linearity for the reactions:



where X indicates halogen atoms. The activation energies of the reactions, which are shown in Figure 2, are evaluated by the following procedure: the difference, $\Delta\epsilon$, in the activation energies for CH_nX_{4-n} and for CH_3Cl is first estimated by using an expression:

$$\Delta\epsilon = -RT \ln(k'/k_0)$$

after making proper corrections for the symmetry change and assuming pre-exponential factors to be the same; the relative rates for CH_nX_{4-n} and CH_3Cl , k'/k_0 , are taken from the results of diffusion flame technique. (14) (15) (As to the absolute rates, a recent investigation indicates (16) that some corrections are necessary to these data; however the relative rates are not likely to be affected significantly.) The $\Delta\epsilon$ thus estimated is converted to ϵ using the information: (10)

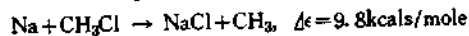
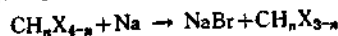


Figure 3 shows the same linearity for the reactions:



Here, values are similarly estimated from the data in the references. (15) (17)

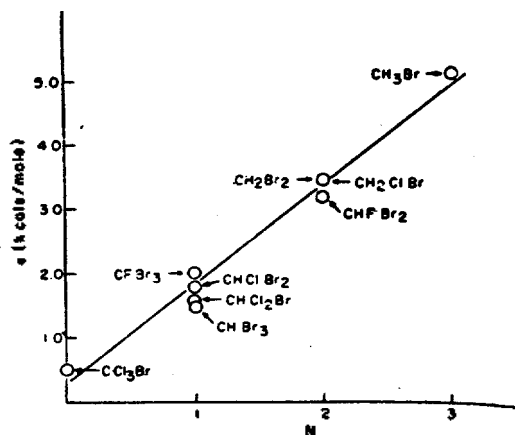


Fig 3. Activation energy ϵ for the reactions:
 $\text{CH}_n\text{X}_{4-n} + \text{Na} \rightarrow \text{NaBr} + \text{CH}_n\text{Cl}_{3-n}$
 as a function of the number, N, of C-H
 plus C-F bonds in halomethane.

In all three cases, (11) agrees well with experimental data. It is indeed gratifying to observe that activation energy is expressible as a linear function of whole numbers.

The present method may be refined by carrying out theoretical calculations of the two parameters, ξ and γ . Such an investigation, currently being planned at the University of Utah, is expected to provide a further insight on the structural factors which govern σ -electron reactivities.

References

- 1) For a recent review see: (a) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, 1959, and (b) T. Fueno, *Ann. Rev. Phys. Chem.*, **12**, 303 (1961).
- 2) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
- 3) C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).
- 4) K. Yang, *J. Am. Chem. Soc.*, **84**, 3795 (1962); also see various references quoted in this paper.
- 5) A preliminary account of the present approach has been described in the following papers:
 - (a) K. Yang, *J. Phys. Chem.*, **67**, 1562 (1963).
 - (b) K. Yang, *J. Chem. Phys.*, **38**, 2586 (1963).
- 6) G. G. Hall, *Proc. Roy. Soc. (London)*, **A205**, 541 (1951).
- 7) R. D. Brown, *J. Chem. Soc.*, 2615 (1953).
- 8) H. W. Turbull, "The Theory of Equations," Oliver and Boyd, Edinburgh, 1946.
- 9) T. Ree, to be published.
- 10) J. F. Reed and B. S. Rabinovitch, *J. Phys. Chem.*, **61**, 598 (1957), and references quoted there.
- 11) M. Szwarc, *J. Chem. Phys.*, **18**, 1660 (1950), and references quoted there.
- 12) E. Cremer, J. Curry, and M. Polany, *Z. Physik Chem.*, **B 23**, 445 (1933).
- 13) J. E. Vance and W. C. Bauman, *J. Chem. Phys.*, **6**, 811 (1938).
- 14) W. Heller and M. Polany, *Trans. Faraday Soc.*, **32**, 633 (1936).
- 15) J. N. Haresnape, J. M. Stevels, and E. Warhurst, *Trans. Faraday Soc.*, **36**, 465 (1960).
- 16) J. F. Reed and B. S. Rabinovitch, *J. Phys. Chem.*, **59**, 261 (1955).
- 17) E. Warhurst, *Quart. Rev.*, **5**, 44 (1951).