

A Qualitative Valence-Bond Approach to Organic Reactivity

ADDY PROSS* and SASON S. SHAIK*

Department of Chemistry, Ben Gurion University of the Negev, Beer-Sheva, Israel

Received November 12, 1982 (Revised Manuscript Received June 2, 1983)

Sophisticated molecular orbital programs that can calculate both molecular structure and reaction profiles efficiently are now readily available. As a result, the literature of the last decade abounds with such applications. However, these quantitative methods do not, on their own, satisfy the chemist's need to understand. In order to understand a particular chemical phenomenon, the chemist needs a simple qualitative model that may be utilized to rationalize, as well as predict, experimental and computational data. For problems of molecular structure, the qualitative model is frontier molecular orbital (FMO) theory.¹ As a result, conformational problems and questions concerning substituent effects on structure, for example, are now relatively well-understood.

Application of FMO theory to problems of reactivity, however, is less straightforward—this, despite the considerable success in explaining reactivity trends in many systems. The main problem here appears to be that within the physical organic chemistry framework, FMO theory does not clarify the mechanism of barrier formation nor does it lead to a qualitative description of the reaction profile. This is because the FMO approach by its very design is not strictly suited to studying problems of reactivity. Certainly one can look at the key orbital interactions that take place as two molecules approach. But as the molecules react, old bonds are broken and new bonds are formed. As a consequence, the original orbitals undergo tremendous modification. One therefore should not expect to extrapolate too much information about the transition state of a reaction by a study of the frontier orbitals of reactants—both structural and electronic changes that have taken place may be too drastic.

The purpose of this Account is to describe a method that attempts to overcome this difficulty by examining the *entire* reaction profile of a given reaction. The model, which we term the valence-bond configuration mixing (VBCM) model,^{2,3} shows how a reaction profile can be qualitatively built up from its constituent configuration building blocks in precisely the same way as atomic orbitals, or group molecular orbitals, may be utilized to build up the molecular orbitals of a molecule.^{1f,g} In this sense we would suggest that the VBCM model constitutes a dynamic analogue of FMO. Thus,

Addy Pross received his B.Sc. and Ph.D. degrees from Sydney University. After postdoctoral positions at Kings College, London, and the Hebrew University, Jerusalem, he was appointed to the Department of Chemistry, Ben Gurion University where he holds the position of Associate Professor. His current research interests include applications of qualitative VB and MO theory to mechanistic organic chemistry and the elucidation of transition-state structure and its application to general problems of organic reactivity.

Sason S. Shaik. Born Bagdad 1948. Ph.D. 1978, University of Washington. A Fulbright Scholar in the U.S. (1974-1979). Sason Shaik is an applied theoretical chemist interested in the construction of unifying concepts for problems of structure and reactivity. His current research involves reactivity of organic molecules, organic conductors, inorganic polymers, and solid-state chemistry. Shaik has been at Ben Gurion University since 1979/80 where he is a Senior Lecturer of Chemistry.

whereas FMO applications are most readily applied to *static* situations where the interacting groups are stationary with respect to one another, CM theory may be applied to *dynamic* situations where molecules are reacting and, therefore, both intermolecular and intramolecular processes are constantly changing along the reaction coordinate.^{2,3} We believe, therefore, that the VBCM approach may be usefully applied to problems of chemical reactivity and, in terms of our main interest, organic reactivity, so that application of the theory can provide the organic chemist with a conceptual framework on which much of his empirical and intuitive understanding may be attached. No doubt, the reader may recognize many of the principles underlying our approach. It constitutes a natural evolution of the continuing interest in the makeup of potential energy surfaces. Of particular importance is the pioneering work of Bell^{4a} and Evans and Polanyi^{4b} that defines the mechanism of barrier formation. Other contributions that have relevance to our work are mentioned in ref 4.

The essence of the approach is simple: to define in some qualitative fashion the reaction profile for any organic reaction. If we know how to define the reaction profile for a given reaction, then we have an important

(1) For reviews on the FMO method, see: (a) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley-Interscience: New York, 1976. (b) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Top. Curr. Chem.* 1977, 70, 1. (c) Klopman, G., Ed. "Chemical Reactivity and Reaction Paths"; Wiley-Interscience: New York, 1974. (d) Hudson, R. F. *Angew. Chem. Int. Ed. Engl.* 1973, 12, 36. (e) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975. (f) Hoffmann, R. *Acc. Chem. Res.* 1971, 4, 1. (g) Hoffmann, R. *Science* 1981, 211, 995.

(2) For a theoretical analysis of the VBCM model, see: Shaik, S. S. *J. Am. Chem. Soc.* 1981, 103, 3692.

(3) For recent applications of the VBCM model, see: (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* 1981, 103, 3702. (b) Pross, A.; Shaik, S. S. *Ibid.* 1982, 104, 187. (c) Pross, A.; Shaik, S. S. *Ibid.* 1982, 104, 1129. (d) Shaik, S. S.; Pross, A. *Ibid.* 1982, 104, 2708. (e) Shaik, S. S. *Nouv. J. Chim.* 1982, 6, 159. (f) Pross, A.; Shaik, S. S. *Tetrahedron Lett.* 1982, 5467. (g) Pross, A., submitted for publication. (h) Shaik, S. S.; Pross, A. *Bull. Soc. Chim. Belg.* 1982, 91, 355. (i) McLennan, D. J.; Pross, A. *J. Chem. Soc., Perkin Trans. 2*, in press. (j) Shaik, S. S. *J. Am. Chem. Soc.* 1983, 105, 4359.

(4) The following is a (necessarily incomplete) list of contributions to the qualitative understanding of the makeup of potential energy surfaces for organic reaction: (a) Bell, R. P. *Proc. R. Soc. London, Ser. A* 1936, 154, 414. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* 1938, 34, 11. (c) Laidler, K.; Shuler, K. E. *Chem. Rev.* 1951, 48, 153. (d) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969. (e) Nagakura, S. *Tetrahedron, Suppl.* 2 1963, 19, 361. (f) Longuet-Higgins, H. C.; Abrahamson, E. W. *J. Am. Chem. Soc.* 1965, 87, 2045. (g) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970. (h) van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* 1969, 91, 6042. (i) Michl, J. *Top. Curr. Chem.* 1974, 46, 1. (j) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* 1975, 8, 41. (k) Salem, L.; Leforestier, C.; Segal, G.; Wetmore, R. *J. Am. Chem. Soc.* 1975, 97, 479. (l) Fukui, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: Heidelberg, 1975. (m) Epiotis, N. D.; Shaik, S.; Zander, W. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980. (n) Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* 1980, 102, 6218. Warshel, A. *Acc. Chem. Res.* 1981, 14, 284. (o) Epiotis, N. D. "Theory of Organic Reactions"; Springer-Verlag: Heidelberg, 1978.

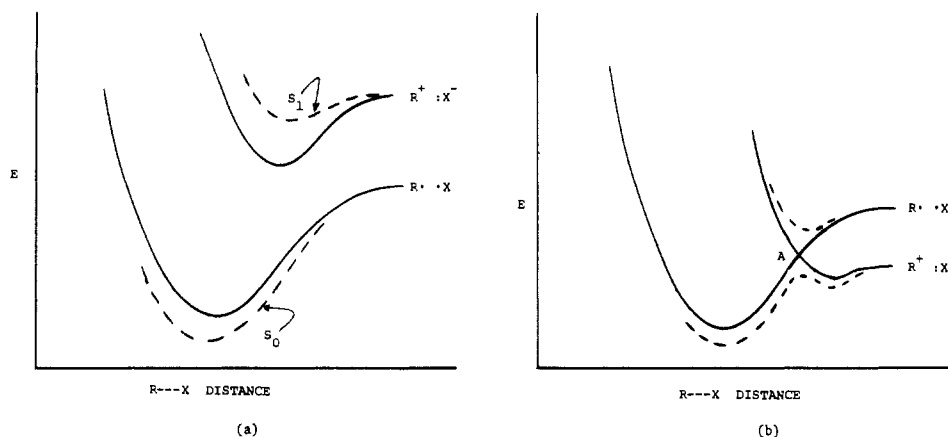


Figure 1. Energy diagram of Heitler–London, $R\cdot X$, and zwitterionic, $R^+ :X^-$, configuration curves (bold lines) as a function of $R\cdots X$ distance. State curves obtained after mixing are indicated by broken lines (a) in the gas phase (no avoided crossing) and (b) in solution (when $R^+ :X^-$ is strongly stabilized, leading to an avoided crossing).

basis for understanding that reaction. We should then be able to offer answers to questions such as:³ Is an intermediate likely to be formed in a given reaction? How will substituents affect the rate of the reaction? What effect will substituents have on the mechanism of the reaction? What is the structure of the transition state and what mechanistic significance may be attached to linear free energy proportionality constants, such as the Brønsted parameter, α ?^{3g}

These are evidently far-reaching questions, and we do not suggest that absolute answers can be provided to all of these. It is simply unreasonable to expect that a simple qualitative model of organic reactivity can reproduce the quantum mechanical complexity that is the basis for most of chemistry. Nevertheless, we believe this qualitative quantum mechanical model neatly fits into the chasm separating “hard” theory and the experimental world and can provide chemists with a sound and intuitive framework for understanding general reactivity problems.

Theory

The key element of the model is to seek out a simple quantum mechanical description of the reaction profile. The first step in achieving this goal is to choose a basis set of configurations that constitute the building blocks from which the entire reaction profile is generated. Once chosen, the energy of the configurations are plotted as a function of the reaction coordinate and then mixed quantum mechanically so as to generate the reaction profile. Before we apply the model to a particular reaction, let us exemplify the approach using a simple reaction—the formation of a polar covalent $R-X$ bond from the two radicals $R\cdot$ and $X\cdot$. The aim is to specify how the energy and character of the $R-X$ bond vary as a function of the reaction coordinate (in this case the $R\cdots X$ distance). This analysis generates a reaction profile for a simple combination reaction and, as such, illustrates the principles required to apply the method to more complex reactions.

We first set up all possible valence-bond configurations of $R-X$ and examine the way their energy depends on the $R\cdots X$ bond distance. For the $R-X$ bond the two most important electronic configurations are $R\cdot X$ and $R^+ :X^-$ (and to a lesser extent $R^- :X^+$). These two forms are pictorial representations of the electronic wave functions that place the two electrons in the system.

Thus $R\cdot X$ represents a Heitler–London type wave function (eq 1) in which one electron is associated with

$$R\cdot X = 2^{-1/2}\{(R\cdot\uparrow\downarrow X) \leftrightarrow (R\cdot\downarrow\uparrow X)\} \quad (1)$$

R and one is associated with X , while $R^+ :X^-$ represents the zwitterionic form, in which both electrons are associated with the atom, X . The way in which the energy of these two configurations vary as a function of the $R-X$ distance is illustrated by the bold lines in Figure 1a. At all points along the $R\cdots X$ axis, the $R\cdot X$ configuration is the most stable one.

The key that forms the basis for this entire Account is that an improved wave function describing the actual $R-X$ bond-dissociation profile may be obtained by taking a linear combination of these two valence-bond configurations. The higher energy zwitterionic form mixes⁵ into the low-energy covalent form in a stabilizing manner to generate the ground state of the $R-X$ bond, S_0 (eq 2a), while the low-energy covalent form mixes into the high-energy ionic form in a destabilizing way to generate the first excited state of the $R-X$ bond, S_1 , which, within the two configuration-approximation, is given by eq 2b.

$$(R-X)_{S_0} \approx (R\cdot X) + \lambda(R^+ :X^-) \quad (2a)$$

$$(R-X)_{S_1} \approx (R^+ :X^-) - \lambda'(R\cdot X) \quad (2b)$$

These *state* curves are shown as the dotted lines of Figure 1a. Thus, just as in qualitative MO theory a delocalized molecular orbital is generated through the mixing of two or more atomic orbitals, the states of the $R-X$ bond at any $R\cdots X$ distance may be obtained by the quantum mechanical mixing of higher energy zwitterionic VB forms and the lower energy Heitler–London form.⁵ The S_0 curve correctly predicts that the polar covalent bond becomes increasingly less polar during $R-X$ bond extension till finally the two radicals $R\cdot$ and $X\cdot$ are formed.

The above analysis of $R-X$ bond dissociation was applicable to the gas phase, and the question now arises how this picture is modified if the bond dissociation is performed in solution. In the gas phase, at infinity, $R\cdot X$ is more stable than $R^+ :X^-$. This is because $I_R - A_X > 0$ (I_R is the ionization potential of R , A_X is the electron affinity of X), a typical figure for $C-Cl \sim 6$ eV.

(5) The two configurations mix via the resonance integral β_{RX} since they are mutually related by a single $R \rightarrow X$ electron shift.^{2,3} β_{RX} is proportional to the $R-X$ overlap.

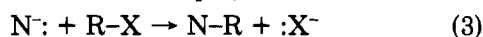
Solution, however, strongly stabilizes the $R^+ : X^-$ configuration and reverses the stability order. This is illustrated in Figure 1b and provides an example of curve crossing. Due to this curve crossing the effect of R-X stretching is predicted to lead to the formation of solvated R^+ and X^- and not to $R\cdot$ and $X\cdot$.^{4m,n,o} Thus, as the R-X bond is stretched, its energy increases till the point is reached where covalent and ionic configurations are of the same energy (position A, Figure 1b). At that point, rather than continue along the covalent curve, which increases the energy even further, there is a configuration switch to the more stable ionic configuration curve that then leads to ions. At the intended crossing point there occurs what is termed an avoided crossing.^{4k} This is a direct consequence of the mixing of the two configurations (as discussed earlier) and is indicated by the dotted lines. Thus the dissociation of R-X in solution involves the avoided crossing of $R\cdot X$ and $R^+ : X^-$ configurations. Note also that $R\cdot X$ switches over to $R^+ : X^-$ through a single-electron transfer (from R to X). Thus the gas-phase and solution dissociation of an R-X bond, the simplest type of reaction, provides a clear illustration of the basic ideas associated with the VBCM model.

An important conclusion of this discussion is that the main descriptor of *stable* organic two-electron bonds is the Heitler-London (H-L) covalent form, while the other VB forms can, at best (Figure 1b), describe potential intermediates. It is clear then that *breaking of a bond during a reaction must be attended by the disappearance of the specific H-L form of that bond from the wave function of the reaction complex. Symmetrically, formation of a new bond must be attended by an appearance of that specific H-L form of the new bond within the wave function of the reaction complex.* It is this simple yet powerful principle that lends the VB approach its scope and practicality in the quest for conceptualizing reaction profiles.

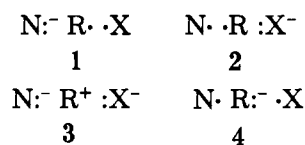
Let us now apply this qualitative VB approach to a simple organic reaction—aliphatic nucleophilic substitution.^{3a,c-j} Our goal is to show how the entire range of aliphatic nucleophilic substitution reactions may be related to one another mechanistically, to show in simple quantum mechanical terms when intermediates are likely to be generated, how new insights into these reactions are provided, and how certain general aspects of reactivity may be explained in a straightforward manner with use of the VBCM model. Applications of the model to elimination reactions,^{3b} proton transfer,^{3c} and rate-equilibrium relationships^{3g} have recently appeared.

Nucleophilic Substitution

In order to study the reaction profile for a nucleophilic substitution reaction (eq 3), we must first choose



our basis set of configurations. In VB terminology, this means rearranging the four key electrons that govern the chemical reaction in all possible, energetically sensible forms. These are indicated in 1-4. Configuration



1 is termed the reactant configuration because it is the major descriptor of the reactant molecules. Stated in words, the wave function represented by 1 places an electron pair on the nucleophile, an odd electron on R, and a spin-paired odd electron on X. Note that 1 contains within it the H-L form of the RX bond. Mathematically it may be described by

$$2^{-1/2} \{ |\Phi_N(1)\Phi_N(2)\Phi_R(3)\Phi_X(4)| - |\Phi_N(1)\Phi_N(2)\Phi_R(3)\Phi_X(4)| \} \quad (4)$$

However, we feel secure in the belief that the pictorial representation, 1, is both simpler and more comprehensible to the general chemical community than eq 4, and, therefore, we will describe all further wave functions in the pictorial manner.

A second configuration, 2, is termed the product configuration since it is the major descriptor of the product molecules (i.e., N-R and X^-). Note that 2 contains within it the H-L form of the N-R bond. Thus 1 and 2 are the two key configurations from which the reaction profile is generated and involve the switching of an $R\cdot X$ bond pair to an $N\cdot R$ bond pair. There are, however, two additional configurations, 3 and 4, termed the carbocation and carbanion configurations, respectively, which may also play a role in certain cases. Thus configurations 1-4 are the set of basis configurations from which, in principle, all nucleophilic substitution reactions, including S_N1 , S_N2 , and radical anion pathways, may be understood. Before we see how this is done, let us summarize the rules that govern the configuration mixing model.^{3b}

Rules for Determining the Reaction Profile and the Nature of the Transition State

1. The reaction profile is generated from a linear combination of VB configurations. Two key configurations are those describing reactants and products. Additional configurations are obtained by seeking out chemically "sensible" intermediates.

2. The change in energy of any configuration along the reaction coordinate is governed by the electron distribution within that configuration. Thus, the interaction between A and X in the species AX is attractive for $A \cdot \uparrow \cdot X$ but repulsive for $A \cdot \uparrow \uparrow \cdot X$, $A \cdot : X$, and $A : X$. Interaction between the forms $A : X$ and $A \cdot X$ is stabilizing, however, and may lead to a stable three-electron bond.

3. The reaction mechanism and hence the reaction coordinate will, themselves, be governed by the nature of the configurations from which the profile is built up. Thus, for example, a large contribution of the carbocation configuration will endow the entire reaction coordinate with S_N1 character.

4. The character of the transition state will reflect the extent to which the configurations mix into its wave function. Thus, in general, the transition state will be endowed with the characteristics of the configurations of lowest energy in the vicinity of the transition state.

5. An intermediate is likely to be formed in a reaction whenever the configuration describing that intermediate is similar or lower in energy than reactant and product configurations in the region of the transition state.

6. Stabilization of any key configuration with respect to the reactant configuration is likely to lead to stabilization of the transition state and a corresponding rate enhancement.

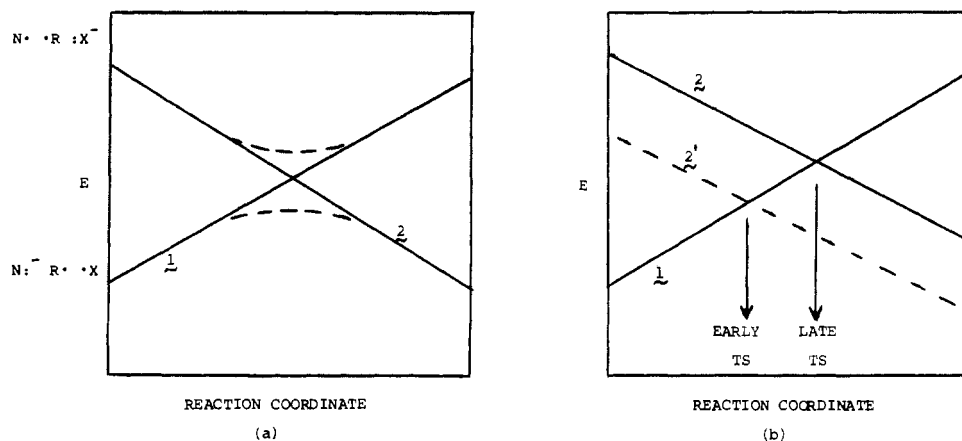


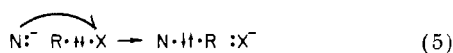
Figure 2. (a) Generation of a simplified reaction profile from reactant, 1, and product, 2, configurations. Broken lines denote avoided crossing (i.e., the reaction profile after configuration mixing). (b) The effect of stabilization of 2 ($2 \rightarrow 2'$) by (for example) a substituent effect. Arrows indicate the positions of the TS. The TS for $2'$ is earlier than that for 2. Avoided crossings are deleted for clarity.

Let us now examine a simple S_N2 reaction profile, such as for methyl derivatives.

Simplified S_N2 Profiles. Methyl Derivatives

For conceptual purposes, the S_N2 reaction profile for methyl derivatives may be considered to be built up from just two configurations, the reactant configuration, 1, and the product configuration, 2. These are illustrated in Figure 2a.^{3c,g} Configuration 1 increases in energy along the reaction coordinate because a favorable $R \cdot X$ interaction is broken while an unfavorable $N: \cdot R$ interaction is generated (rule 2). Configuration 2 decreases in energy for the opposite reasons—a favorable $N \cdot R$ interaction is formed while an unfavorable $R \cdot X^-$ interaction is released. Thus we can see that the reaction may be most simply built up by just two configurations and that two is the least number of configurations that is necessary in order to generate a TS higher in energy than either reactants or products. The barrier comes about through the avoided crossing of the reactant, 1, and product, 2, configurations. It can be seen therefore that *reaction profiles of concerted pathways will be generated by the crossing of electronic curves that contain the Heitler–London forms of the bonds that interchange during the reaction.*

The first conclusion that derives from this simple picture is that S_N2 reactions really involve a *single-electron shift*. The only electronic change that is required to convert 1, the primary VB form describing reactants, to 2, the primary VB form describing products, is a *single-electron shift* from N to X (eq 5).



This picture, very much at variance with the conventional view, has recently been supported by Flesia^{6a} and others.^{6b,7} In the conventional view, S_N2 substitution is classified as a *two-electron process* in contrast to the electron-transfer pathway,⁸ in which a *single-electron transfer* is proposed. Our view would be that both S_N2 and electron-transfer pathways involve a

single-electron shift and that the difference between these two pathways depends on what transpires *after* that shift. Let us consider this point in more detail.

The experimental criterion for distinguishing between the so-called one- and two-electron processes rests on the detectability of free radicals. Accordingly, it is generally held that a chemical reaction that involves single-electron transfer should result in the experimental detection of unpaired electrons. A “two-electron” process on the other hand maintains two spin-paired electrons that remain coupled at all times: no free radicals are generated.

This classification of substitution reactions as either one- or two-electron processes, while specifying whether radicals are involved or not, does tend, however, to obscure the similarities between the two processes. This is because we feel that single electron shift processes in which no free radicals are generated are possible. In fact, we believe the S_N2 process as represented in eq 5 provides just such an example. Single-electron shift from the nucleophile into the $R-X$ bond leads to the generation of the species $N \cdot (R \cdot X)^-$.^{9a} The primary VB contributor that describes $(R \cdot X)^-$ is $R : X^-$, with a repulsive force acting between R and X (rule 2). Since R· and N· remain spin paired at all times, however, no radicals will necessarily be formed. The possible detection of radicals will depend entirely on the time scale for the various steps. If coupling of the electron pair $N \uparrow R \downarrow$ takes place synchronously with the single-electron shift, no radicals will be detected *because none are formed*: through a single-electron shift an $R \uparrow X \downarrow$ spin pair has been directly converted to an $N \uparrow R \downarrow$ spin pair (eq 5).

The fundamental mechanistic difference between the so-called one- and two-electron processes focuses, therefore, not on *how many* electrons have been transferred but whether *after* the single-electron shift takes place an intermediate is formed or not. Any factor capable of *delaying* $N \cdots R$ coupling after the

(6) (a) Flesia, E., unpublished, quoted in ref 6b. (b) See also, Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 1.

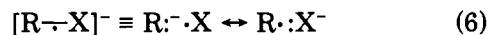
(7) For an early report see, Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* 1973, 95, 8203.

(8) (a) Bunnett, J. F. *Acc. Chem. Res.* 1978, 11, 413. (b) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 734. (c) Rossi, R. A. *Acc. Chem. Res.* 1982, 15, 164.

(9) (a) In MO terms the electron transfer takes place into the σ^*_{R-X} orbital. Thus the species $(R \cdot X)^-$ may be approximated in MO terms as $\cdots \sigma^*_{R-X}, \sigma^*_{R-X}$, while in VB terms it may be represented by eq 6. (b) We note that an electron-transfer reaction can arise also when the $N: / RX$ pair is a *very good donor-acceptor pair*. In such a case the crossing of the curves will occur very “early” and the $N \cdot (R \cdot X)^-$ pair will be separated by a large distance—a factor that ultimately leads to the intervention of radical ions and/or radicals. For electron-transfer reactions between simple alkyl iodides and, e.g., hydrides, see, e.g., Ashby, E. C.; DePriest, R. N.; Goel, A. B. *Tetrahedron Lett.* 1981, 22, 1763.

electron shift has taken place may lead to the actual generation of radical intermediates. Two major reasons that are likely to delay $N\cdots R$ coupling, leading to free-radical formation, may be noted.

(a) If after single-electron shift from N to RX a stable radical anion $[R\cdots X]^-$ is generated, then $N\cdots R$ coupling is weak. This will occur if R is of similar electron affinity to $X^{3d,e}$ so that the radical anion can now be described by *two* resonance forms (eq 6) and not mainly



by $R\cdot X^-$.^{9b} For this reason $[CH_3\cdots Cl]^-$ (described primarily by $R\cdot X^-$) spontaneously decomposes to $CH_3\cdot$ and Cl^- , while $[CF_3\cdots Cl]^-$ and $[(CF_3)_3C\cdots I]^-$ are delocalized (described by eq 6) and have finite lifetimes.^{10a} This also explains why CCl_4 undergoes electron-transfer reactions^{10b} rather than nucleophilic substitution.

Alternatively, if the electron shift takes place into some low-lying orbital, other than σ^*_{R-X} ,^{9a} then dissociation of the radical anion $[R\cdots X]^-$ will be delayed since the electron has then to relocate into the σ^*_{R-X} orbital. This appears to be the major reason for observation of the $S_{RN}1$ mechanism. For most $S_{RN}1$ substrates electron transfer appears to take place into a low-lying π^* orbital, followed by its relocation into the σ^*_{R-X} orbital.⁸ This generation of a low-lying π^* orbital appears to be the primary role of the NO_2 group, which dominates so much of organic electron-transfer chemistry.⁸

(b) If after single-electron shift the resultant nucleophile radical, $N\cdot$, is either sufficiently delocalized or sterically hindered to delay the coupling to $R\cdot$, then free radicals may also be detected. *In other words, any factor associated with N or R that interferes in the $N\cdots R$ coupling process may delay the coupling sufficiently to enable free-radical detection,^{9b} leading to an electron-transfer process.*

Thus in our view the fundamental difference between so-called one- and two-electron processes is whether after single-electron shift, intermediate radicals are formed or synchronous electron coupling takes place. Cases where other intermediates are formed will be discussed subsequently.

Charge Development and the Reaction Coordinate

The second striking conclusion that derives from this simple picture is that charge development and geometric progression along the reaction coordinate are *not* necessarily related.^{3f} Specifically, for a nucleophilic substitution reaction (eq 3) charge development of approximately 0.5 is expected at the TS because ψ_{TS} (eq 7) is composed of a linear combination of 1 and 2 in

$$\psi_{TS} = \frac{1}{\sqrt{2}}\{(N\cdots R\cdots X) + (N\cdot R\cdots X^-)\} \quad (7)$$

equal amounts.¹¹ The equality derives from the fact that at the intended crossing point 1 and 2 are isoenergetic and therefore contribute equally to the

(10) (a) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* 1980, 102, 2860.
(b) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* 1978, 43, 1985.

(11) The slight mixing in of "intermediate" configurations, the carbanion ion configuration, $N\cdots R^+X^-$, and the carbanion configuration, $N\cdot R\cdots X^-$, will modify the value of 0.5 but will not change the equality of 1 and 2. See footnote 7 of ref 3f.

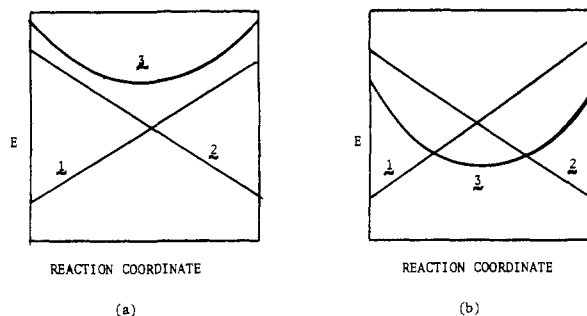


Figure 3. (a) Reactant (1), product (2), and carbocationic (3) configurations for an S_N2 reaction involving a moderately stable R^+ . Note the proximity of the three configurations near the intersection point. (b) The same three configurations for a case where R^+ is very stable. Note that 3 crosses the two H-L configurations below the intersection point, leading to intermediate formation. The actual profiles arise through the mixing of the configurations as in Figure 2a.

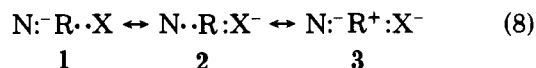
ground-state reaction profile (eq 7).¹¹

The important point is that the above conclusion holds *regardless of the position of the transition state along the reaction coordinate.*^{3f,11} Making the nucleophile more powerful, or replacing the leaving group by a better one, may lead to a lowering of the energy of configuration 2 relative to 1. This is indicated in Figure 2b by the broken line. Of course, the transition state is now "earlier" in accord with the Bell-Evans-Polanyi principle;^{4a,b} however the electron shift also takes place "earlier", so that the transition-state charge is not directly related to the position of the transition state along the reaction coordinate and in any event is certainly *not* expected to be a linear function of the geometric change along that coordinate.

Thus, the intuitive idea that early transition states have reactant-like charge distributions while late transition states have product-like charge distribution appears to lack a theoretical basis. Our simple quantum mechanical model illustrates that charge development in the TS is governed by the charge distributions within the configurations describing that TS. This, of course, means that for certain reactions charge development in the TS may be *unrelated* to reactant and product charge distributions altogether and such a phenomenon will be most pronounced when "intermediate" configurations mix in strongly into the TS but not into reactants and products. Let us now illustrate how this takes place.

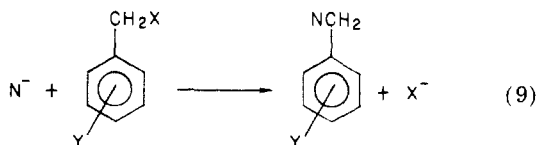
Effect of Secondary Configurations. Benzyl Derivatives

If an S_N2 reaction is undertaken on a system RX where R^+ is moderately stable, e.g., $R = \text{benzyl}$, then the configuration diagram will be that shown in Figure 3a. From the figure it is apparent that the TS for the reaction will take on the character of $N\cdots R^+X^-$ (3) in addition to that of 1 and 2. This is because in the TS region all three configurations are of similar energy. Thus the TS may be described by the resonance forms:



Clearly, then, though the reaction is defined here as a one-step concerted process, there is some excess carbocationic character in the TS (due to $N\cdots R^+X^-$), and this means that substituent effects on R are likely

to have significant effects on rates (due to the substituent effect on R^+ within 3) and only a small effect on equilibria (which is governed by 1 and 2). This means for cases in which an "intermediate" configuration mixes significantly into the TS of a concerted one-step reaction that rates may not correlate with equilibria or, if they do, that the Brønsted parameter, α , may be greater than 1.^{3g,12} This is precisely the situation that is observed for S_N2 reactions on benzyl derivatives (eq 9). Whereas rates are highly sensitive



to the substituent Y, equilibria are less so; in fact, for the identity exchange reaction ($N = X$) the equilibrium constant is 1 for all Y's. It is apparent therefore that for such systems rates and equilibria are not related in the usual Brønsted fashion.^{3g}

The unusual reactivity patterns of benzyl systems,¹³ long of interest to physical organic chemists, now become more coherent. The mechanistic diversity of benzyl derivatives, the nonlinear Hammett plots, and the variable transition-state structures may be understood in terms of the VBCM model. The factor that sets benzyl derivatives apart from other substrates is the fact that four configurations may be utilized to describe their reactions. In addition to reactant and product configurations, 1 and 2, both carbocation and carbanion configurations, 3 and 4, may play an important role in benzyl substitution. This is because electron-releasing substituents (e.g., OCH_3) will stabilize 3, while electron-withdrawing substituents (e.g., NO_2) will stabilize 4.

The U-shaped Hammett plots can now be simply understood in terms of these four configurations. Substitution of an electron-releasing group on the aromatic ring has the effect of stabilizing 3, leading to rate enhancement (rule 6). Substitution of an electron-withdrawing group has a destabilizing effect on 3, a factor that on its own would lead to a reduction in rate. Of course, such a behavior pattern would be likely to lead to a linear Hammett plot. However, an electron-withdrawing substituent will have a stabilizing effect on 4 so that again rate enhancement may occur with respect to the unsubstituted benzyl derivative. With both electron-releasing and -withdrawing substituents liable to generate rate enhancements, nonlinear Hammett plots are to be expected.

The accepted TS structures of the substituted benzyl derivatives is in accord with these ideas. For example, the TS for substitution on a *p*-methoxybenzyl derivative is expected to be represented by eq 8, i.e., the significant involvement of 3, in addition to 1 and 2. 3 is expected

(12) Pross, A. *Tetrahedron Lett.* 1983, 835.

(13) (a) Ko, E. C. F.; Parker, A. J. *J. Am. Chem. Soc.* 1968, 90, 6447. (b) Young, P. R.; Jencks, W. P. *Ibid.* 1979, 101, 3288. (c) Westaway, K. C.; Ali, S. F. *Can. J. Chem.* 1979, 57, 1354. (d) Thorstenson, T.; Eliason, R.; Songstad, J. *Acta Chem. Scand., Ser. A.* 1977, 31, 276. (e) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* 1979, 101, 3295. (f) Hill, J. W.; Fry, A. *J. Am. Chem. Soc.* 1962, 84, 2763. (g) Ballistreri, F. P.; Maccarone, E.; Mamo, A. *J. Org. Chem.* 1976, 41, 3364. (h) Hudson, R. F.; Klopman, G. *J. Chem. Soc.* 1962, 1062. (i) Grimsrud, E. P.; Taylor, J. W. *J. Am. Chem. Soc.* 1970, 92, 739. (j) Friedberger, M. P.; Thornton, E. R. *Ibid.* 1976, 98, 2861. (k) Westaway, K. C.; Waszczylo, Z., submitted for publication.

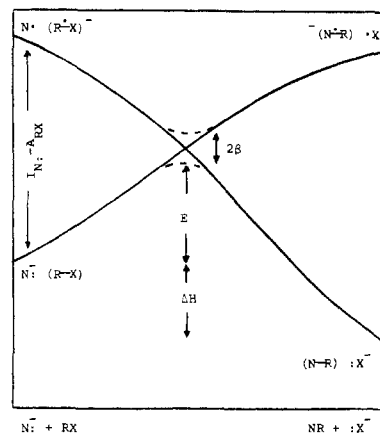
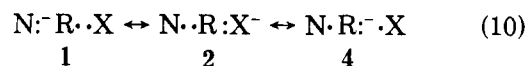


Figure 4. State correlation diagram for an S_N2 reaction. The lower states are ground states of reactants and products, while the upper states are the corresponding charge transfer states. β is the degree of avoided crossing. E is the reaction barrier.

to lead to a "loose" TS (little $N\cdots R$ and $R\cdots X$ bonding) and positive charge development on C_α . For substitution on a *p*-nitrobenzyl derivative, however, the TS is expected to be represented by eq 10, where 4 is now the



major "intermediate" configuration. 4 will lead to a "tight" TS with negative development on C_α . These ideas are consistent with available experimental data^{13a} and were recently also couched by us in MO terms.^{3a}

What happens if the intermediate configuration for a given reaction is strongly stabilized? In such circumstances a situation illustrated in Figure 3b is obtained. One can see that an *actual* intermediate is formed due to the overwhelming influence of the intermediate configuration at some central point of the reaction coordinate. For the case where the intermediate configuration is $N: R^+ : X^-$, 3, then the intermediate is seen to be an ion-pair species $R^+ : X^-$ (which incidentally was generated in Figure 1b during $R-X$ dissociation in solution) and which may also possess some nucleophilic solvation. This represents the S_N1 end of the substitution spectrum. Thus the entire spectrum of nucleophilic substitution reactions may be generated—from S_N1 with carbocationic intermediates through S_N2 , where no intermediates are generated, and finally to electron-transfer pathways, where a radical anion intermediate is generated.

The above discussion is consistent with views recently expressed by Jencks¹⁴ who has proposed that concerted pathways are followed when potential intermediates are too high in energy to be formed along the reaction pathway. Our analysis is in agreement with this view: concerted pathways are enforced when intermediate configurations are too high in energy to affect the reaction pathway—a stepwise reaction pathway, if available, will be energetically more favored than a concerted one.

State Correlation Diagrams. Barrier Heights in S_N2 Reactions

In order to discuss reaction barriers one needs to convert the qualitative scheme discussed above into a

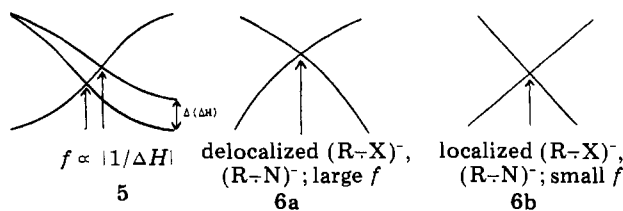
(14) Jencks, W. P. *Acc. Chem. Res.* 1980, 13, 161.

more quantitative form. By mixing the carbocationic ($N^+R^+X^-$) and the carbanionic (N^-R^-X) configurations into the two ground and two excited configuration anchor points of Figure 2a, we generate anchor states for the intersecting curves.^{3d,e,j} The resulting diagram, shown in Figure 4, is a state correlation diagram with two ground and two excited states. The two ground states involve the usual R-X and R-N polar two-electron bonds, while the two excited states are charge-transfer states of reactants and products. This state correlation again merely reflects the fact that the S_N2 transformation involves a single-electron shift attended by bond reorganization. The charge-transfer state of the reactants, $[N^-(R^+X)^-]$, is the unique excited state that contains within it the electronic image of the product ($N^+R^-X^-$). This means that as the geometry changes along the reaction coordinate, this excited state is stabilized and correlates with the product. Thus, this correlation involves breaking of an $(R^+X)^-$ three-electron bond¹⁵ and generation of an N-R two-electron bond. Symmetric arguments apply to the other correlation line [$-(N^+R^-)X \rightarrow N^-(R^+X)$]. It is evident from Figure 4 that the barrier for the forward reaction (E) is always a fraction (f) of the energy gap $I_N - A_{RX}$ between the intersecting curves, or quantitatively:

$$E = f(I_N - A_{RX}) - \beta \quad (11)$$

I_N is the ionization potential of the nucleophile (N^-), A_{RX} is the electron affinity of the substrate, and β is the avoided crossing constant.^{3d,e,j} These two factors reflect the dual nature of the transformation—the gap accounts for the electron shift aspect, while f accounts for the bond-reorganization aspect along the reaction coordinate.

For a given energy gap the size of f depends on the forms of the curves as a function of the characteristic molecular distortions along the reaction coordinate (e.g., $f = 0.25$ for two parabolas; $f = 0.5$ for two straight lines having equal slopes, etc.). f is dominated mainly (but inter alia^{3d}) by two electronic effects; the reaction enthalpy ΔH (Figure 4) and the degree of delocalization of all the species in the charge transfer state, i.e., N^- , X^- , $(R^+X)^-$, and $(R^-N)^-$. The magnitude of ΔH determines the extent of the “pull down” effect on the lower part of the product curve, so that as the reaction becomes more exothermic a smaller fraction of $I_N - A_{RX}$ enters the barrier, i.e., f gets smaller (per a given gap) as shown in 5.



For a given gap and ΔH , the size of f is determined by the steepness of descent of the charge-transfer states toward the crossing point. This depends on the strength of the $N^-(R^+X)^-$ and $X^-(R^-N)^-$ couplings as a function of the molecular distortions along the reac-

tion coordinate. When the two odd electrons of the charge-transfer states are delocalized away from the reaction atomic centers, these couplings are weak and the curves descend gradually, causing a higher fraction, f , of the gap to enter the activation barrier. This effect of delocalizing the odd electrons in the charge-transfer states on the size of f is shown in 6a vs. 6b.

These considerations lead us to anticipate two types of reactivity patterns: one dominated by variations in the gap of the intersecting curves and, hence, responding to the donor-acceptor abilities of the reactants, while the other is dominated by variations in the f factors, thus responding to the degrees of delocalization of N^- , X^- , $(R^+X)^-$, and $(R^-N)^-$ or to the reaction exothermicity (ΔH).

Note that the model contains the predictions of FMO¹ theory through the donor-acceptor relationship between the reactants (the HOMO-LUMO energy gap) but does offer some additional insights. For identity S_N2 reactions $X^- + CH_3-X \rightarrow X-CH_3 + :X^-$, f (eq 11) depends mainly on the degree of delocalization of the three-electron bonds. When in a series of reactions the $(CH_3^+X^-)$ species are delocalized approximately to the same extent, the intrinsic barriers will respond to the donor-acceptor ($I_X - A_{CH_3X}$) abilities of the reactants. Such is the case for the halide exchange reactions ($X^- = F^-, Cl^-, Br^-, I^-$)¹⁶ where the best donor-acceptor pair (I^-/CH_3I) reacts the fastest.^{16c} On the other hand, whenever the $(CH_3^+X^-)$ species are heavily delocalized,^{16d} f is large and the intrinsic barriers will be large even if the reactants comprise a good donor-acceptor pair. Such is the case for the exchange reactions of, e.g., H^- , HO^- , CH_3O^- , CH_3S^- .¹⁶ Thus, not only does eq 11 establish a direct link to the Marcus equation,¹⁷ it also provides a rationale for variations of intrinsic barriers in S_N2 .^{3d,e,16}

For nonidentity S_N2 reactions the model anticipates that S_N2 reactivity in a reaction series (N^-/RX) will increase as the reactant pair becomes a better donor-acceptor pair (small $I_N - A_{RX}$) and/or as the reaction becomes more exothermic. This trend will be maintained if and only if, the changes in the series do not involve great changes in the delocalization of the three-electron bonds of $(R^+X)^-$ and $(R^-N)^-$ and of X^- and N^- . Such changes will modify the “pull down” effect of ΔH and will offset the improvement of the donor-acceptor abilities of the reactants, leading to rate retardation.

Thus eq 11 and its more explicit version (ref 3d, eq 29), incorporate the Bell-Evans-Polanyi rate principle,^{4a,b} but they also predict under what conditions this principle is likely to break down. As a general guideline, the increased delocalization of N^- , X^- , or the three-electron bonds is predicted to impair S_N2 reactivity. This appears to be one of the reasons¹⁸ behind the re-

(15) (a) Pauling, L.; Wilson, E. B. Jr. “Introduction to Quantum Mechanics”; McGraw-Hill: New York, 1935. (b) For a detailed description of three-electron bonds, see Harcourt, R. D., *Lect. Notes Chem.* 1982, 30, 1. See Chapter 21 for a similar description of the S_N2 transition state.

(16) (a) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* 1980, 102, 5993. (b) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* 1981, 103, 7694. (c) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* 1978, 16, 85. (d) The delocalization of $(R^+X)^-$ is roughly inversely proportional to the electron affinity difference $A_X - A_R$ and to the number of identical C-X linkages accessible for delocalization.

(17) Marcus, R. A. *Annu. Rev. Phys. Chem.* 1964, 15, 155.

(18) (a) Shaik, S. S. *J. Am. Chem. Soc.* 1983, 105, 4359; *Nouv. J. Chim.* 1983, 7, 201. (b) Shaik, S. S. *J. Am. Chem. Soc.*, in press.

duced S_N2 reactivity of CH_2X_2 , CHX_3 , and CX_4 relative to CH_3X ($X = Cl, Br, I$).¹⁹

In this manner the correlation diagram model provides insight into S_N2 reactivity. Reactivity patterns arise from the gap-slope interplay, which in turn stem from the interplay between the electron-shift and bond-reorganization aspects of the chemical transformation. Other reactivity problems such as solvent effect^{18b} on rates, nucleophilicity, leaving-group ability, and reactivity-selectivity patterns seem also to fall under the sovereignty of the model and are now under further study.

Concluding Remarks

The VBCM model provides a framework for conceptualizing reactivity trends through an understanding of the makeup of reaction profiles. The model borrows its strength from the same philosophy inherent in the fragment MO approach—that the whole may be understood by reconstruction from its parts.^{1f,g} As such the fundamental rule is striking in its simplicity. Reaction profiles may be built up from a linear combination of VB configurations. When at least one reactant is a closed shell molecule, the reaction profile for the concerted pathway may be generated through the mixing of just two configurations—those representing the Heitler-London VB forms of the bonds that interchange during the reaction (e.g., Figures 2, 4). The secondary VB configurations (e.g., 3, 4) will mix-in in proportion to their relative stabilities and thereby endow the TS with a variable character, thus generating the mechanistic spectra for each reaction type (e.g., tight and loose S_N2 transition states). The secondary configurations also provide the stock of possible reaction intermediates as they cross the two principle curves

below their intersection point (e.g., Figure 3b). Thus, the secondary configurations determine the extremes of the mechanistic spectrum for each reaction type (e.g., S_{N1} , S_{RN1}).

In constructing reaction profiles, one can either use the explicit VB approach (e.g., Figure 2a) starting with the primary configurations and then mix in the secondary configurations (rules 1-6). Alternatively, one can anchor *all* the configurations in electronic states of reactants and products and thereby generate state correlation diagrams (e.g., Figure 4). The selection of the unique anchor excited states for the correlation diagram is described in detail in ref 2 and 3a,h and requires knowledge of MO-VB correspondence. As a rule, *an excited state of the reactants will correlate with the ground state of the products if the major (or only) constituent of its electronic wave function contains spin-paired odd electrons in symmetry-matched reactant orbitals, per each new intermolecular bond that is formed during the reaction.* The argument is symmetric for the unique excited state of the products that correlates with the ground state of the reactants (see Figure 4).

The choice of approach depends on the kind of insight one wishes to gain. For example, the explicit VB approach provides a more immediate insight regarding TS structure and charge distribution, while the state correlation diagram yields more quantitative information about reaction barriers and reveals the preferred stereochemical course of the reaction (e.g., the Walden inversion in S_N2). When properly utilized, however, both approaches, which are mutually related as localized-delocalized bonding pictures, lead to the same conclusions.^{2,3a} Thus VBCM theory constitutes a *single* framework capable of handling a wide range of reactivity phenomena. We would hope therefore that application of this theory may provide a means for building on existing knowledge and lead to a more fundamental understanding of organic reactivity as a whole.

(19) (a) Hine, J. *J. Am. Chem. Soc.* 1950, 72, 2438. (b) Hine, J.; Dowell, A. M., Jr. *Ibid.* 1954, 76, 2688. (c) Hine, J.; Thomas, C. H.; Ehrenson, S. J. *Ibid.* 1955, 77, 3886. (d) Hine, J.; Ehrenson, S. J.; Brader, W. H., Jr. *Ibid.* 1956, 78, 2282.

The Partnership of Gas-Phase Core and Valence Photoelectron Spectroscopy

WILLIAM L. JOLLY

Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Received January 12, 1983 (Revised Manuscript Received May 23, 1983)

Around 1970 a great surge of activity in photoelectron spectroscopy occurred, because of the availability of improved instrumentation and because of optimism regarding the usefulness of the technique.^{1,2} Many

William L. Jolly received his Ph.D., based on research in thermodynamics under Prof. W. M. Latimer, in 1952 at the University of California in Berkeley. He then began teaching as an Instructor at Berkeley and is now a Professor at the same institution and is a Principal Investigator in the Lawrence Berkeley Laboratory. For many years his research involved the synthesis and characterization of inorganic compounds. In recent years he has concentrated on the application of X-ray photoelectron spectroscopy to inorganic and organometallic systems.

chemists had the impression that valence-shell photoelectron spectra (usually obtained by ultraviolet photoelectron spectroscopy, or UPS) directly give information about the bonding or antibonding character of molecular orbitals. It was also commonly believed that

(1) Siegbahn, K.; et al. "ESCA. Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy"; Almqvist and Wiksells: Uppsala, 1967; Siegbahn, K.; et al. "ESCA Applied to Free Molecules"; North-Holland: Amsterdam, 1969.

(2) Turner, D. S.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: London, 1970.