Molecular Orbital Correlation Diagrams, Mobius Systems, and Factors Controlling Ground- and Excited-State Reactions. II

Sir:

In the preceding communication of this series we noted that the concept of Möbius systems can be extended to many molecular species including those involved in terminal cyclization of polyenes. In addition we presented a simple mnemonic device for deriving the MO energies of cyclic Möbius systems and for drawing correlation diagrams for the polyene cyclizations.

Where the reactant and product MO's are known and the reacting system maintains some symmetry one may use the noncrossing rule to correlate reactant and product MO's as is implicit in literature efforts.[1,2] For simple cyclic closures the mnemonic[3] is available.

However, if the reacting system lacks symmetry, another method is needed. One can calculate the MO energy change as a ground-state[4] or photochemical[5] reaction proceeds.

An alternative and analytic method is presently suggested. It can be shown that at points along the reaction coordinate where two energy levels intersect, all $n - 1$ minors of the secular determinant vanish.[6a] A necessary and sufficient condition is obtained when all the symmetrical minors are zero.[6b] The latter criterion is equivalent to saying that each submolecule obtained by deleting one atom from the species will at a crossing point have one MO energy equal to that of the crossing MO's of the parent species. The procedure determines not only where along the reaction route a crossing (*i.e.*, degeneracy) occurs but also which levels cross. When no degeneracy is found anywhere between reactant and product, MO's can be correlated in order of increasing energy.

One example is provided by the butadiene to cyclobutene closure. Regular geometry is not assumed, and variable resonance integrals (Figure 1) are used in the π electron approximation. The symmetrical minors of the secular determinant for **1** are $X^3 - (\omega^2 + \gamma^2)X$, $X^3 - (\gamma^2 + \delta^2)X$, $X^3 - (\omega^2 + \epsilon^2)X$, and $X^3 - (\delta^2 + \epsilon^2)X$.

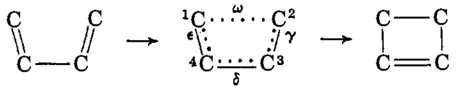

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Figure 1.

Each minor is zero for $X = 0$ indicating a crossing at this energy. Crossings are also seen at $X = \pm\sqrt{\gamma^2 + \omega^2}$ but γ^2 must equal ϵ^2 and $\omega^2 = \delta^2$. Setting minor $A_{12} = 0$, we obtain for this crossing that $\omega = -\delta$ if $\gamma = +\epsilon$. Also from $A_{12} = 0$ we see $\omega = \gamma\epsilon/\delta$ for the crossing at $X = 0$. Thus a single sign inversion (Möbius) leads to a crossing of ψ_1 and ψ_2, while Hückel closure gives crossing of ψ_2 and ψ_3. We note (i) agreement with the circle mnemonic, (ii) crossing of levels not differing in symmetry (*i.e.*, **1** being trapezoidal), being reminded that the noncrossing rule is not inviolate,[7] and (iii) that the present treatment detects such violations. The method may prove useful for detecting the geometric requirement for crossing and for ascertaining lack of crossing for the purpose of drawing correlation diagrams where no symmetry exists. For larger systems a computer is needed.

It seems likely that such crossing points are significant in organic photochemistry, since ground- and excited-state energy surfaces meet and the transition probability for electron demotion is enhanced. These may provide a route for conversion of excited-state reactant to ground-state product.[8]

Finally, in connection with MO prediction of reactions, we wish to point out that exceptions will occur where the over-all energy change will not follow that of the highest filled MO. One example is the π-π^* excited state of cyclohexadienones where the total β,β bond order is slightly negative,[9] showing an over-all antibonding tendency; however, the highest occupied MO is β,β bonding.[9]

A second example of interest is the 1,5 bonding of 1,3,5-hexatrienes, a process which occurs with frequency in photochemistry.[10] Reference to Table I shows this type of bonding to be the second most energetically favored. It may be seen that the bonding

Table I. Energy Change and Highest Occupied MO Bonding as a Function of Type of Bonding of Hexatriene in Ground and Excited States

Type of bonding[a]	Ground state		Excited state	
	Energy change[b]	Overlap of HOCMO[c]	Energy change[b]	Overlap of HOCMO[c]
1,6-Hückel	−1.01	Bonding	+0.10	Antibonding
1,6-Möbius	+0.06	Antibonding	−0.83	Bonding
1,5-Hückel	−0.48	Bonding	−0.50	Bonding
1,5-Möbius	−0.48	Antibonding	−0.50	Antibonding
1,3-Hückel	−0.56	Antibonding	−0.30	Antibonding
1,3-Möbius	−0.56	Bonding	−0.30	Bonding

[a] 1, r bonding assumed equal to that of adjacent olefinic orbitals. [b] Energies in $|\beta|$. [c] Highest occupied MO.

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(1) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) *ibid.*, **87**, 2511 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (d) *ibid.*, **87**, 4388 (1965); (e) *ibid.*, **87**, 4389 (1965).

(2) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2046 (1965).

(3) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966).

(4) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(5) H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963).

(6) (a) The proof is simply that the rank of the secular determinant becomes $n - 2$ at the point of single degeneracy and all $n - 1$ subdeterminants become zero by definition. (b) The sufficiency of using the symmetrical minors derives from a theorem of L. Kronecker, *J. Rein. Angew. Math.*, **72**, 152 (1870).

(7) Note G. Herzberg and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **35**, 77 (1963).

(8) (a) *Cf.* E. Teller, *J. Phys. Chem.*, **41**, 109 (1937), for some related views. (b) At a point of degeneracy Jahn-Teller vibrations may be available with the correct symmetry (or geometry) to increase a radiationless transition probability which is electronically low.

(9) (a) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964); (b) H. E. Zimmerman, *Pure Appl. Chem.*, 493 (1964).

(10) (a) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); (b) W. G. Dauben and P. Baumann, *Tetrahedron Letters*, 565 (1951); (c) W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965); (d) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Am. Chem. Soc.*, **86**, 2660 (1964); (e) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, **235**, (1964); (f) W. G. Dauben, and P. Baumann, *Tetrahedron Letters*, 565 (1961); (g) W. G. Dauben, Abstracts, 19th National Organic Symposium, Columbus, Ohio, June 1965, p 30; (h) J. Meinwald, A. Eckell, and K. L. Erickson, *J. Am. Chem. Soc.*, **87**, 3532 (1965); (i) the authors in ref 1d and e explicitly depicted the reaction as involving initial 1,5 bonding; (j) it should be noted that added driving force is obtained by a concerted 4,6 bonding and that a 4,6 bond appears in all the products except that of ref 10a.

or antibonding properties of the highest occupied MO are not a helpful guide to the over-all energy change, and, in general, one cannot depend on the HOCMO predicting the over-all bond order or energy change on bonding.[11] A safer approach is the consideration of bond order[9,12] and energy change.[4,5]

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[11] (a) In the case of 1,5 bonding of hexatriene the total bond order prior to molecular change is zero and is of no help. Subsequent to slight molecular change the bond order is helpful. (b) It can be shown that for a system of p orbitals arranged so that alternating atoms are starred except for two adjacent starred positions, the Möbius and Hückel versions will have energy levels which are mirror images of one another, and coefficients are simply related.

[12] H. E. Zimmerman, Abstracts, 17th National Organic Chemistry Symposium, Bloomington, Indiana, June 1961, p 31.

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The Reactivity of Electrons Produced in the γ-Radiolysis of Aliphatic Alcohols[1]

Sir:

The reactions of solvated electrons with aromatic hydrocarbons in aqueous solution conform to the general pattern of bimolecular nucleophilic substitution, SN2.[2] The solvated electron is an important intermediate in the radiolysis of alcoholic solutions,[3-9] and it would be of interest to determine whether this species fits a pattern similar to that of the hydrated electron, and if so, the influence of the change in solvent on reactivity.

It has been demonstrated[9] that nitrous oxide is a specific scavenger for solvated electrons produced in the radiolysis of 2-propanol solutions, and a convenient method for determining the reactivity of solute substrates has been suggested.[9] This method involves the measurement of the yield of molecular nitrogen, $G(N_2)$, in competitive experiments in which a solution of nitrous oxide and the substrate is irradiated. The difference between $G(N_2)$ and the nitrogen yield in the radiolysis of a solution containing the same concentration of nitrous oxide alone, $G(N_2)_0$, gives a measure of the electrons scavenged by the substrate, and hence its reactivity relative to nitrous oxide. Such competitive experiments have now been carried out with a number of monosubstituted benzenes in 2-propanol and methanol,[10] and the results are listed in Table I.

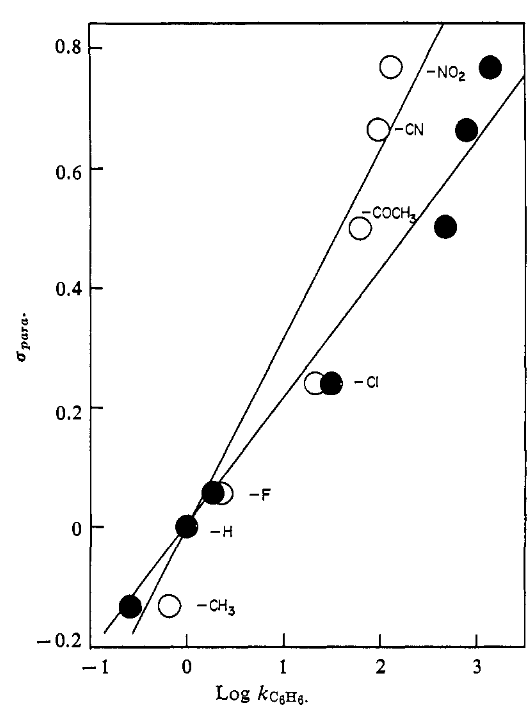

Figure 1. Plot of Hammett σ_{para} functions[11] *vs.* log $k_{C_6H_6}$ values obtained in 2-propanol and methanol. ○, 2-propanol; ●, methanol.

In Figure 1 the logarithm of the rate constants of the monosubstituted benzenes normalized to that of benzene, log $k_{C_6H_6}$, are plotted against the respective Hammett σ_{para} functions.[11] A satisfactory linear correlation is obtained in both solvents. This result is in accord with the rate-determining step in the reaction of the solvated electron with aromatic compounds being the localized attack on the aromatic nucleus.[2] The ρ value for the reaction in 2-propanol and methanol is 3.1 and 4.7, respectively.

Table I. Reactivity Relative to Nitrous Oxide of Monosubstituted Benzenes in 2-Propanol and Methanol

Aromatic substrate	$k_{N_2O}{}^a$ 2-Propanol	$k_{N_2O}{}^a$ Methanol
Toluene	1.4×10^{-2}	7.2×10^{-4}
Benzene	2.1×10^{-2}	2.9×10^{-3}
Fluorobenzene	5.0×10^{-2}	5.9×10^{-3}
Chlorobenzene	5.4×10^{-1}	9.5×10^{-2}
Acetophenone	1.7	1.8
Benzonitrile	1.9	2.1
Nitrobenzene	2.3	4.1

^{a} Reactivity relative to nitrous oxide.

The energy of an electron in a dipolar medium involves the term $(1/D_{op} - 1/D_s)$,[12] where D_{op} and D_s are the optical and static dielectric constants, respectively. D_{op} generally has values near unity, so that as D_s increases the energy of the solvated electron decreases. The static dielectric constant at room temperature of 2-propanol and methanol are 19 and 33, respectively,[13] and the hypsochromic shift observed

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(1) This work was performed during the tenure of an Israel Atomic Energy Commission Fellowship.

(2) M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).

(3) J. H. Baxendale and F. W. Mellows, *ibid.*, **83**, 4720 (1961).

(4) G. E. Adams and R. D. Sedgwick, *Trans. Faraday Soc.*, **60**, 865 (1964).

(5) J. J. J. Myron and G. R. Freeman, *Can. J. Chem.*, **43**, 381 (1965).

(6) E. Hayon and M. Moreau, *J. Phys. Chem.*, **69**, 4053 (1965).

(7) I. A. Taub, D. A. Harter, M. C. Sauer, and L. M. Dorfman, *J. Chem. Phys.*, **41**, 979 (1965).

(8) H. Seki and M. Imamura, *Bull. Chem. Soc. Japan*, **38**, 1229 (1965).

(9) W. V. Sherman, *J. Phys. Chem.*, **70**, 667 (1966).

(10) Full details of the radiolysis of the nitrous oxide–methanol system will be published elsewhere.

(11) The σ values are those given in the review by H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

(12) J. Jortner, *Radiation Res. Suppl.*, **4**, 24 (1964), and references quoted therein.

(13) F. Buckley and A. A. Maryott, National Bureau of Standards Circular 583, U. S. Government Printing Office, Washington, D. C., 1958.