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Excited State Energy Distribution and Redistribution and Chemical Reactivity; Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman* and I. V. Alabugin

Department of Chemistry, University of Wisconsin,
1101 University Avenue, Madison, Wisconsin 53706

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Four decades ago one of us presented a means of relating, qualitatively, the structures of electronically excited states to many of the known organic reactions.[3] We now describe a method of predicting excited-state reactivity more generally.[4]

A particularly intriguing but elusive problem is how excitation energy is distributed in electronic excited states, particularly those exhibiting photochemical reactivity. Using modern quantum mechanical wavefunctions, the present paper not only provides an answer to this question but also provides a method for predicting photochemical reactivity.

In very early efforts[5] we reported the use of a "ΔD Matrix" (also termed Δp Matrix) which gives the change in electron densities and bond orders at different molecular sites as a result of electronic excitation. The promise was the ability to predict the molecular consequences of electronic excitation as well as being able to predict and understand photochemical reactions in general. These early studies were limited to the use of a truncated system of basis orbitals, these being in chromophores and bonds involved in a given reaction. However, now with the Weinhold Natural Hybrid Orbitals (NHOs)[6] being available in Gaussian98,[7] it is possible to determine the validity of the concept in virtually any electronically excited state of interest using any of the quantum mechanical methods capable of affording density matrices for ground and excited singlet and triplet electronic states. We define our ΔD matrix elements as in eq 1.

$$\Delta D_{\mathrm{rt}} = D^{*}_{\mathrm{rt}}S^{*}_{\mathrm{rt}} - D^{\circ}_{\mathrm{rt}}S^{\circ}_{\mathrm{rt}} \qquad (1)$$

Here, the D^{*}_{rt} refers to the excited-state density and D°_{rt} refers to the ground state. The S_{rt} terms are overlap integrals to adjust for distance effects and to maintain proper relative orbital signs. Thus, ΔD might be properly termed an "overlap density matrix"; *r* and *t* designate a pair of orbitals.

The idea is that, where a ΔD element (e.g., ΔD_{rt}) is negative, that bond not only is weakened in the excitation process but also is generated by Franck−Condon vertical excitation in a nonminimum geometry with an accumulation of vibrational as well as electronic energy.[8] There may be some bonds which have positive ΔD elements and are stabilized and strengthened, but they will necessarily be fewer, since the molecular electronic energy has risen.[9] Also, the ΔD method gives changes in one-center electron densities, and this portion of our concept has been of value in the literature.[10]

The ΔD method not only predicts the occurrence of photochemical reactions but also subtleties such as regioselectivity. Some reactions considered are (a) the Norrish Type I and its regioselectivity,[11a] (b) the Yates ring-strained ketone to carbene ring expansion,[11b] (c) the cyclopropyl ketone ring opening reactions and regioselectivity,[11c] (d) the Norrish Type-II reaction,[11d] (e) the butadiene to cyclobutene disrotatory transformation,[11e] (f) Type-B bicyclic transformations,[11f] (g) p_y-orbital hydrogen abstraction,[11g] (h) the α-expulsion reaction of α-substituted ketones,[11h] (i) meta-electron transmission,[11i] (j) the photoracemization of optically active biphenyls,[11j] and (k) the di-π-methane rearrangement.[11k]

The results are outlined qualitatively in Chart 1 and quantitatively in Supporting Information. In Chart 1, each reactant has bonds of interest designated as markedly dissociative, less dissociative, or unreactive. Bonding tendencies between nonadjacent orbitals also are included. One finds that the bonds becoming most antibonding, as indicated by possessing most negative ΔD elements and having the most concentrated excitation energy, are indeed the ones breaking experimentally in the primary photochemical process.

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* To whom correspondence should be addressed. Phone: (608) 262-1502; Fax: (608) 262-0381. E-mail: zimmerman@chem.wisc.edu.

(1) This is Paper 256 of our general series.

(2) For Paper 255, see: Zimmerman, H. E.; Alabugin, I. V.; Chen, W.-C.; Zhu, Z. *J. Am. Chem. Soc.* **1999**, *121*, 11930−11931.

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(4) The publications in ref 3 outlined for the first time the reaction mechanisms of most of the photochemical reactions known at that time; these mechanisms were based on the three-dimensional electronic structures of the reactants. Theory was provided which was based on control of excited-state reactions by energetics. In the intervening years there has been a myriad of publications, including our own, dealing with the treatment of individual reactions as well as general theory regarding what controls organic photochemistry.

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(6) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218. (b) Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(7) *Gaussian98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998. Note that the NBO analysis is also available in earlier versions (e.g., *Gaussian92* and *Gaussian94*).

(8) While local accumulation of electronic excitation is readily seen, vibrational excitation is less obvious. That vertical excitation leads to a vibrational level above zero is seen by the transition from equilibrium S_0 geometry to a nonoptimal bond order in S_1 or T_1 and thus a nonequilibrium bond geometry.

(9) Computational detail and numerical results are given in Supporting Information.

(10) For example, note: Head-Gordon, M.; Grafia, A. M.; Maurice, D.; White, C. A. *J. Phys. Chem.* **1995**, *99*, 14261−14270.

(11) The following lists original references as well as subsequent reviews: (a) Ciamician, G. P.; Silber, P. *Chem. Ber.* **1908**, *41*, 1071. Also see refs 3(a) and 3(b). For a review, note: Gilbert, A., Baggott, J., Eds.; Essentials of Molecular Photochemistry; Blackwell Scientific Publications: Cambridge, MA, 1991; pp 288−301. (b) Yates, P. *Pure Appl. Chem.* **1968**, *16*, 93−113. Morton, D. R.; Lee-Ruff, E.; Southam, R. M.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 4349−4357. (c) Zimmerman, H. E.; Hixson, S. S.; McBride, E. F. *J. Am. Chem. Soc.* **1970**, *92*, 2000−2015. (d) See ref 3(a); Wagner, P. J.; Keiso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500−7506. Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1−52. (e) *The Conservation of Orbital Symmetry*; Woodward, R. B., Hoffmann, R.; Verlag Chemie: Weinheim (Germany), 1970. Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395−396. Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564−1565. (f) Zimmerman, H. E.; Grunewald, J. O. *J. Am. Chem. Soc.* **1967**, *89*, 3354−3356. Zimmerman, H. E.; Nasielski, J.; Keese, R.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895−4903. Zimmerman, H. E.; Sebek, P. *J. Am. Chem. Soc.* **1997**, *119*, 3677−3690. (g) See refs 3(a) and 3(b); Kasha, M. In *Light and Life*; McElroy, W. D., Glass, B., Eds.; Johns Hopkins Press: Baltimore, MD, 1961; p 31. Wagner, P. J.; Park, B. *Org. Photochem.* **1991**, *11*, 227−336. (h) See refs 3(a) and 3(b); Iwasaki, S.; Schaffner, K. *Helv. Chim. Acta* **1968**, *51*, 557−561. Zimmerman, H. E. *Tetrahedron* **1963**, Suppl. 2, *19*, 393−401. (i) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915−922. Zimmerman, H. E. *J. Phys. Chem. A* **1998**, *102*, 5616−5621. (j) Zimmerman, H. E.; Crumrine, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 498−506. (k) Zimmerman, H. E.; Binkley, R. W.; Givens, R. W.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932−3933. Zimmerman, H. E. *Org. Photochem.*; Padwa, A., Ed.; Marcel Dekker, Inc., New York, 1991; pp 1−36. (l) See refs 3(a) and 3(b); Zimmerman, H. E. Some Theoretical Applications to Organic Chemistry. In *Modern Electronic Structure Theory and Applications in Organic Chemistry*; Davidson, E., Ed.; World Scientific Publishing Co.: 1998.

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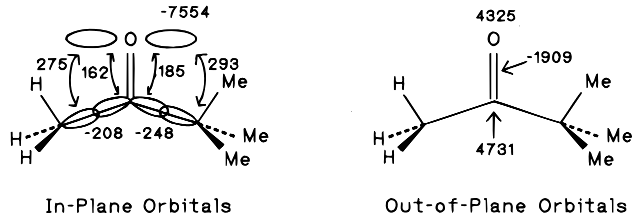
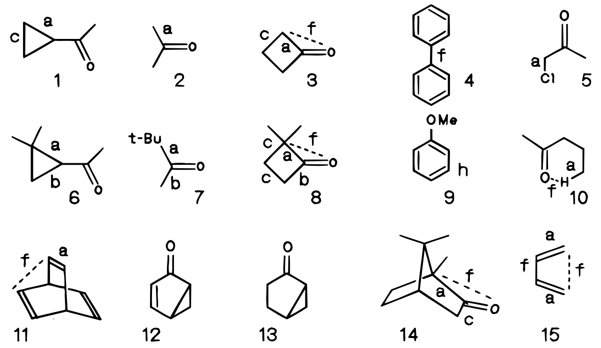


Figure 1. ΔD Matrix values for orbital pairs in methyl *tert*-butyl ketone. Values are expanded by 10 000.

Chart 1. Assorted Organic Photochemical Reactants and Two-Center ΔD Values[a]



[a] Key: (a) largest negative ΔD; (b) lesser negative ΔD; (c) very small ΔD, nonbreaking bond; (f) large positive ΔD, bond forming; (h) increased one-center ΔD.

Thus, the reactants listed in Chart 1 have known photochemistry. For each there is bond scission or formation or both in the primary photochemical step. Chart 1 designates the largest negative ΔD element by a, the next most negative element by b, zero elements by c, and positive ΔD elements by f. In one case, a one-center ΔD value is given, designated by h. For example, in the case of the photolysis of cyclopropyl methyl ketone (**1**) where the triplet is known[12] to undergo fission of the α,β bond from the $n-\pi^*$ state, the most negative element corresponds to this bond with a value of −184 while the p_y (lone pair) has a ΔD element showing loss of 0.8465 electron, as expected in n−p* excitation. For the methyl dimethylcyclopropyl ketone **6**, the preferential reaction is opening of the more substituted three-ring bond,[12] corresponding to a in Chart 1. Figure 2 in Supporting Information illustrates the source of reactivity differences between the bicyclo[3.1.0]enones **12** and their saturated counterparts **13**. Each bonding change corresponds to a known molecular reaction.[11f,13]

One particularly interesting example is that of 2,2-dimethylcyclobutanone (**8**) where not only is a negative acyl carbon to a dimethyl carbon ΔD element found but additionally there is a strongly positive ΔD between the p_y orbital and the dimethyl carbon atom, signifying a bonding interaction. This bears on the controversy in the Yates Ring Expansion to give carbenes[11b] where there is experimental evidence of stereospecificity which suggests a concerted mechanism rather than a two-step Norrish Type-I fission to acyl odd-electron and saturated carbon odd-electron centers which then subsequently combine. Also, the reaction regioselectivity, in which it is the more substituted carbonyl to α carbon bond which is severed, is suggested by the relative magnitude of negative ΔD elements (i.e., a vs b).

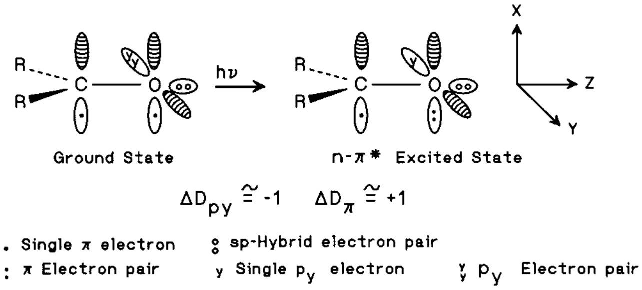


Figure 2. Change in p_y and π electron density on $n-\pi^*$ excitation.

The expulsion of substituents α to a carbonyl group is a process known in organic photochemistry,[11h] and indeed, it is an α carbon to Cl bond in α-chloroacetone which has a negative ΔD value.

Figure 1 deals with the Norrish Type-I reaction and gives the values for the occurrence and regioselectivity of methyl *tert*-butyl ketone. Additionally, loss of p_y and π densities as well as the increase in one-center carbonyl carbon and oxygen densities are given. Similarly, the regioselectivity of the Norrish Type-I reaction of camphor,[14] including the ring-expansion to afford a carbene, is in accord with the ΔD elements (*a* vs *b* and a positive *f*).

The initial bridging in the di-π-methane rearrangement of barrelene[11k] is also accounted for (i.e., prediction of transannular bridging with a positive *f* and loss of π bonds with negative *a* values).

The disrotation of butadienes is predicted with a positive *f* (structure **15**); a negative value would have predicted conrotation. Loss of two π bonds (ΔD *a*) and formation of the new π bond (ΔD *f*) are calculated.

The known[11j] photoracemization of chiral biphenyls results from the enhanced ΔD between phenyl rings which leads to ring planarization.

It has been noted that $n-\pi^*$ reactivity arises in two ways (see Figure 2),[11l] (i) from involvement of the singly occupied p_y orbital and (ii) from behavior of the electron-rich, "radical-anion like" π system. The ΔD analysis presented above includes both effects. The "p_y-orbital effect" is seen in the Norrish Type-II (**10**),[3,11i] the Norrish Type-I, the ring expansion in the cyclobutanones (**3** and **8**), and camphor (**14**). The "electron-rich π^* effect" is found in the three-ring opening of the cyclopropyl ketones (cases **1**, **6**, **12**, and **13**) and α expulsion (case **5**). $\pi-\pi^*$ excited states (e.g., **11** and **15**) exhibit parallel effects.

Also of interest, the one-center ΔD elements for the p_y orbital invariably are less than unity due to delocalization of the "electron hole" into the σ framework.

Finally, in basing predictions on the primary photochemical process, we are not considering energy barriers[3] or conical intersections[15] subsequently encountered by the reacting excited state. It has been noted that both factors are important, but without the primary process there is no reaction.

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