A New Theoretical Approach in Photochemistry.   Minimization of Excited State–Ground State Surface Separation by Selected Molecular Deformation. Vibrational Dissipation of Local Contributions to Excitation Energies

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Summary   A new method is described for prediction of photochemical reactions by determining which molecular motions convert electronic into vibrational energy and thus minimize excited state–ground state energy separation; the method works generally on a large variety of photochemical reactions, and on the more limited set

subject to orbital control, it affords predictions consistent with the Woodward–Hoffmann and Zimmerman Möbius–Hückel methods.

In the preceding communication[1] we introduced a ΔP matrix, each element, ΔP_{rt}, of which indicates the extent of electronic excitation at that site in the molecule. The matrix can be utilized to determine which overlaps need to be diminished, by molecular twisting or stretching, and which overlaps need to be increased by molecular compression in order to bring the excited and ground state hypersurfaces closer. Where a ΔP_{rt} element is negative, the molecule must be twisted or stretched at site r,t to decrease this overlap. If the element is positive, then bond tightening is required. The assumption is that approach of the potential enery surfaces will be needed for reaction.[2]

The method works qualitatively as well as quantitatively, and it fits a remarkably wide range of photochemistry. A few selected examples are given here. The first is the treatment of the n–π^* hydrogen abstraction reaction of ketones (Figure 1). For simplicity we use qualitative

FIGURE 1. Hydrogen abstraction from a C–H bond.

MO's.[3] The reaction is depicted early along the reaction co-ordinate, and the MO's in the p_y plane are allyl-like with a shifted node. That ΔP_{12} is positive is seen from the increase in this bond order on excitation. This suggests that increasing 1,2 overlap will help bring the excited- and ground-state surfaces together. The negative ΔP_{23} predicts weakening of this C–H bond. Both these molecular changes do occur during reaction. This process can be considered to provide a mechanism of converting electronic excitation into vibrational energy, since to dissipate local electronic excitation energy contributions molecular geometry is modified.

Another case of interest is the Norrish type I fission of ketones (Figure 2). The positive ΔP_{12} predicted corresponds to formation of a new C–O π bond and the negative

FIGURE 2. Type I fission of ketones.

ΔP_{23} leads to disengagement of the alkyl radical. This is the molecular and electronic mechanism we proposed many years ago[4] and the commonly accepted electronic mechanism.[5]

A third example is the expulsion of substituents α to n–π^* carbonyl groups (Figure 3).[6] The orbital array is a butadiene-like string of four orbitals and the qualitative
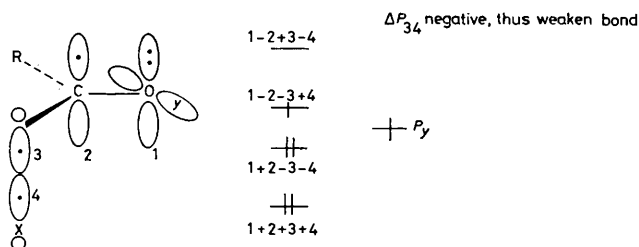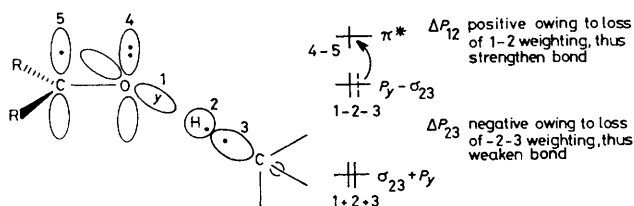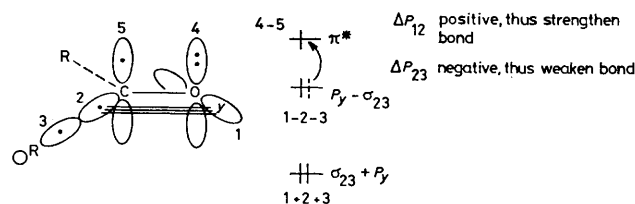
FIGURE 3. α Expulsion in the n-π^* excited state.

MO's[3] shown result. Here the bond (i.e. 3,4) bearing the departing species X has a negative ΔP and the expulsion is predicted.

A very simple example is the case of polyenes. In the case of butadiene, excitation is from an MO of the form $1 + 2 - 3 - 4$ to an MO of form $1 - 2 - 3 + 4$. A negative ΔP_{12} and a positive ΔP_{23} suggests terminal bond twisting.[7]

Examples treated by the Woodward–Hoffmann[8] or Zimmerman Möbius–Hückel[9] methods can also be treated by the present method. For example, the case of excited butadiene is shown in Figure 4 where preferential top–top (disrotatory) overlap is predicted.
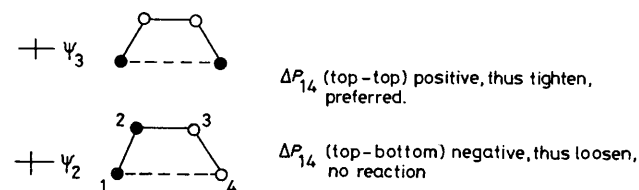
FIGURE 4. Prediction of disrotatory, or top–top, closure in butadiene.

The method presented can be used with better wavefunctions but the utility arises from its operation with qualitative MO's. Where all the basis orbitals are of the same variety, minimum risk in using ΔP_{rt} values, uncorrected for slightly differing overlaps and s-characters is incurred.

The treatment is tantamount to determining modes of converting electronic into vibrational energy. Consider an optimum geometry suggested by the ΔP_{rt} values for the excited state. Decay to the ground state at this point

leads to a geometry unfavourable for this new electronic makeup; *i.e.* a vibrationally 'hot' ground-state is generated.[†]

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[†] One can conceive of an example where the two surfaces approach one another but only with excessive energy increase of both. Thus there is a caveat to be considered, namely that the predicted excited state energy change not be excessively energy demanding.

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