Electronically Excited Species in Organic Photochemistry; A Reply

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RECENTLY a Communication[1] appeared criticising both the "polar state" representation (*i.e.* $C^+–C{=}C–O^-$) by Chapman[2] and the earlier suggestion of Zimmerman[3] for depicting excited states of unsaturated ketones. The Communication overlooked original literature except for that summarized in one text cited. As a result the author was led to erroneous conclusions.

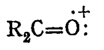
Chapman's polar state representation was criticised in that it predicts an electron deficient β-carbon for the n–π^* excited state of an unsaturated ketone while the β-carbon is known to be electron rich. However, it has never been clarified whether the "polar state" is meant to represent an actual electronic excited state (*e.g.* a π–π^* singlet) or instead as a hypothetical and convenient structure.

Taylor's suggestion was to write the bonding π-electron framework in ordinary resonance terms as a series of contributing structures and to indicate the antibonding electron of the n–π^* excited state outside a bracket without specifying its distribution [as (It)]. Attention was then focused on the distributed positive charge [as in (II t)].

Our representation (Iz) and (IIz) was criticized on the grounds (*inter alia*) that unnecessary care was taken to avoid violating the octet rule, that the structures imply the absence of π-bonds (as in Iz), and that electron demotion in dienone transformations must precede skeletal rearrangement in our scheme.

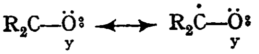
These points reply to this Communication:

(1) Our notation does *not* preclude demotion after rearrangement to the excited state of product as an *a priori* possibility. We discussed this point[4,5] and noted that our mechanistic steps were written separately for convenience yet might prove to be merged. Our further studies on the question, however, established the chronology as involving



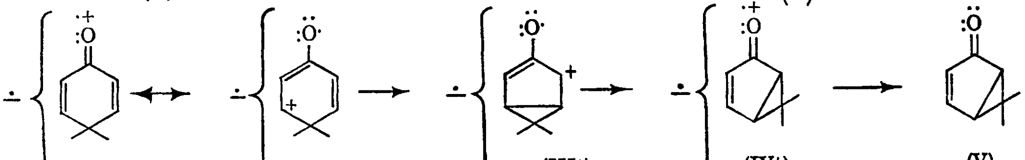
$R_2C{=}\overset{\cdot+}{O}{:}$

(It)



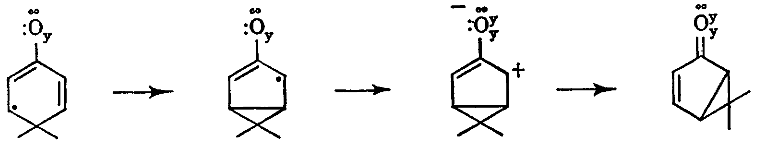
$R_2C\text{—}\ddot{O}{:}_y \longleftrightarrow R_2\dot{C}\text{—}\ddot{O}{:}_y$

(Iz)



(IIt) (IIt) (IIIt) (IVt) (V)

Equation It; the Taylor modification, as applied to the Type A rearrangement of dienones



(IIz) (IIIz) (IVz) (V)

Equation Iz; the original formulation of the dienone rearrangement

demotion with loss of electronic excitation prior to complete rearrangement. The sequence is shown in equation Iz. Thus we presented evidence[4-7] that zwitterions [*e.g.* (IVz)] are in fact intermediates in the dienone and bicyclic ketone rearrangements.

(2) The representation offered in the literature criticism[1] focuses attention on the positive charge distribution and shows this charge distributed among the carbonyl carbon and β-carbons [*e.g.* structure (IIt)]. Emphasis then is placed on this electron deficiency in the rearrangement. Our study of electron densities in the n–π^* excited state[8] showed the β-carbons and the carbonyl carbon to be especially electron rich, not poor.

(3) The $\beta\beta$-bonding signified in the bracket of equation (Iz) would not be expected for the positive system within the bracket; we showed[8] the bonding π-M.O.'s, as presented in the ground state in the bracket, would not be readily transformed into a $\beta\beta$-bridged species. It is the contribution of the singly-occupied antibonding MO which makes the $\beta\beta$-bond order positive and $\beta\beta$-bonding energetically favourable. Our molecular orbital treatment of the dienone[4,9,10] made this point clear and deals with the role of the antibonding electron in a more definite fashion than the dot outside the bracket notation.

(4) When the electron outside the bracket [as in (IIt)] is considered most heavily localized at the carbons indicated as positive within the bracket, one then has the heaviest contributors in resonance language, and the structures are those [*e.g.* (II z)] we suggested[3-6,8-10] as the more important resonance contributors.

(5) Focusing attention on the positive charge distribution within the bracket (*i.e.* that of the ground state π-electron population) suffers from Taylor's own criticism of the Chapman representation.

(6) Taylor suggests that more than eight electrons may be associated with a carbon atom if antibonding orbitals are utilized. This is erroneous as long as one does not invoke d-orbitals. That this is true may be seen by considering the extreme case where *all* antibonding M.O.'s are occupied in an N-atom molecule. The π-electron density, q_r, at any one carbon atom r is then $q_r = 2\sum\limits_{k}^{N} C_{rk}^2$ [*i.e.* summed over all M.O.'s (the k's)]. But the matrix $[C_{rk}]$ is orthonormal and the summation $\sum\limits_{k}^{N} C_{rk}^2 = 1$; therefore the π-electron density is $q_r = 2$ at the atom. With three sigma bonds and a contribution of two π-electrons at each such atom, one has reached only the usual octet limit.

(7) Our representation, originally due to Wheland[11] but used by us to represent three dimensional structures (see ref. 3) and applied to photochemistry, does not imply the absence of π-bonds if one recognizes that the moiety $\dot{C}\text{–}\ddot{C}$ includes a full π-bond and half an antibond. Hence this is not a weakness.

(8) The literature rearrangements are not uniquely described by the proposed[1] notation. We have discussed one of these in part[12] and the remainder may be similarly accommodated. These reactions do not provide relevant evidence.

In summary, the criticism seems to have arisen from overlooked literature. Where one needs a quantitative picture of an excited state reacting, the M.O. representation should be used. Then bond orders,[8–10] change in energy as the molecule is deformed towards product,[10] or excited-state charge densities[3] may be used. For qualitative purposes either a M.O. treatment[3,4,6,8,9,13] or the resonance approach suggested by us may be used.

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