

## Hybridization as a metric for the reaction coordinate of the chemical reaction. Concert in chemical reactions\*

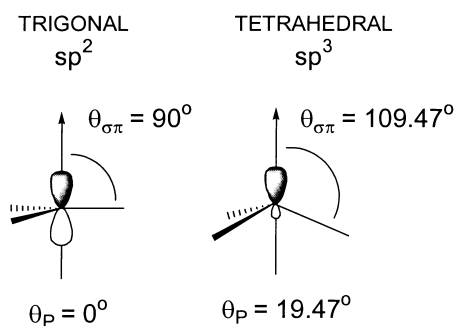
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**Abstract:** We have introduced hybridization as the unifying metric for the degree of structural progress in organic reaction processes. In the present paper we show how the hybridization metric may be applied to other atoms in the reacting molecule to provide information on bond-making and bond-breaking and the degree of concertedness in chemical reactions.

The study of chemical reactions is probably the most important facet of chemistry. Considering the maturity of the subject, it is surprising to find that there has been no universal scale for the progress of chemical reactions that allows comparisons to be drawn even among those reactions that simply involve the formation and cleavage of carbon-carbon bonds.

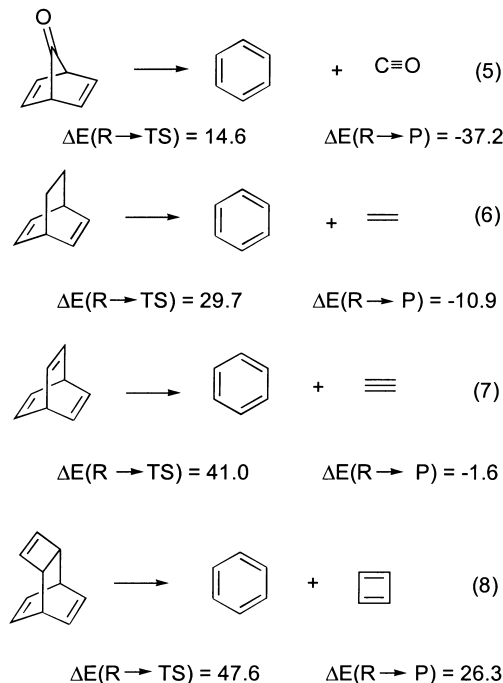
Most previous attempts to quantify reaction progress have relied on some function of the interatomic distances that suffer a significant change during the chemical transformation; while this approach is suitable for controlling the position of a structure on the potential surface, it is less useful as an indicator. We have recently introduced hybridization (with scaling based on the pyramidalization angle), as the general metric for reaction progress and as the universal reaction coordinate of the chemical reaction [1]. In most cases it is possible to associate an *ideal* initial and final hybridization with the atoms that are involved in the bond forming and breaking in chemical reaction processes, and together these provide well defined boundary conditions for the reaction metric (Fig. 1). The most common reaction processes involve conversions among  $sp^2$  and  $sp^3$  hybrids in the reacting atoms. By use of the  $\pi$ -orbital axis vector (POAV) analysis it is possible to solve analytically for the intermediate hybridizations [2,3], and thus a general metric may be obtained for almost any organic reaction process. The hybridization metric is structurally based, and is valid for the reactants, products, transition states and intermediates of many organic reaction processes. By adopting this reaction metric, it is possible for the first time, to apply the Hammond postulate in a quantitative manner across a variety of reactions [1].



**Fig. 1** Virtual boundary conditions for the interconversion of trigonal and tetrahedral carbon atoms along the hybridization reaction coordinate.

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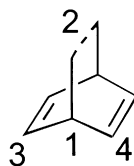
We illustrated the method with a series of simple reverse Diels–Alder cycloaddition reactions of varying exothermicity. The structures and energies of reactions (5–8, Scheme 1) were calculated along the dissociation pathways using the B3LYP/6-31G\* method. [4–7]. The energies of the products and transition states (kcal/mol), relative to the reactants are reproduced above (the results are in good agreement with prior high level calculations) [8–10]. This allowed the first general, quantitative test and verification of the Hammond Postulate [11]. We adopt as a modern statement [12] of the Hammond Postulate: ‘The structure of a transition state resembles the structure of the nearest stable species. Transition states for endothermic steps structurally resemble products, and transition states for exothermic steps structurally resemble reactants.’ While the Hammond postulate depends on the structural evolution of reactants to products along a reaction coordinate, the nature of the essential structural characteristic(s) was previously undefined.



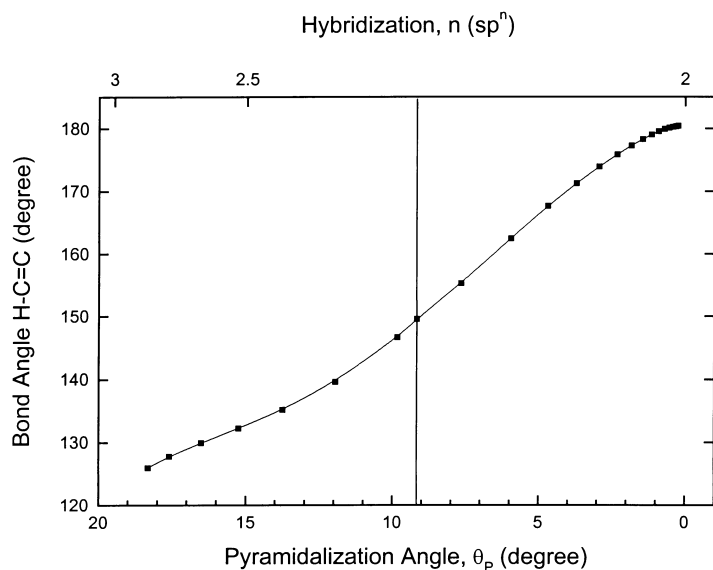
**Scheme 1** Reactions (5–8).

In the previous work we used the change in pyramidalization and hybridization ( $sp^3 \rightarrow sp^2$ ) of the bridge carbon atoms (C1) as the reaction coordinate (Fig. 2) [1]. The carbon atoms at C2 also suffer a change in hybridization, and while it is not immediately obvious from the reactants and products, the same is true for the carbon atoms at C3. In the present work, we investigate the changes in hybridization of these secondary carbon atoms (Figs 3–8), as they provide another indication of reaction progress. As before, we use the pyramidalization angle ( $\theta_p$ ) (bottom axis), and POAV1 hybridization (top axis) [2,3] at C1 as the reaction coordinate. In POAV1 theory the  $\pi$ -orbital axis vector is defined as that vector which makes equal angles ( $\theta_{\sigma\pi}$ ) to the three  $\sigma$ -bonds at a conjugated carbon atom, and the pyramidalization angle is obtained as  $\theta_p = (\theta_{\sigma\pi} - 90^\circ)$  (Fig. 1). In Fig. 3, we plot the bond angle change of the leaving group ( $H-C\equiv C-H$ , C2 in Fig. 2) against the pyramidalization angle for carbon atom 1 (Fig. 2), in reaction (7). There is a strong correlation, but it is not a straight-line relationship. This is probably because the two axes represent different hybridization changes [ $sp^3 \rightarrow sp^2$  ( $x$ -axis) and  $sp^2 \rightarrow sp$  ( $y$ -axis)], although they both describe the rehybridization accompanying the breaking of the same  $\sigma$ -bond. A more stringent test is provided by reaction (6) where the rehybridizations at carbon atoms C1 and C2 are the same ( $sp^3 \rightarrow sp^2$ ). In this situation, we would expect that the extent of reaction progress would be about the same when measured using either atom (C1 or C2). As may be seen in Fig. 4, this turns out to be the case, and there is a very good straight-line relationship between the two measures. Thus the hybridization reaction coordinate displays the necessary invariance to be a robust measure of reaction progress across a broad range of organic reactions

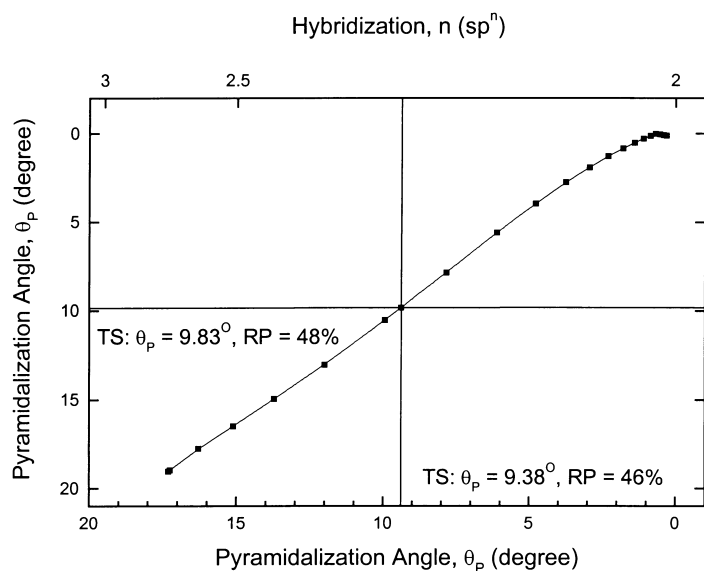
In Fig. 5–8, we show the pyramidalization angles at carbon atom C3 (C4), as a function of the



**Fig. 2** Numbering system for the carbon atoms in the molecules in reactions (5–8). While it is clear that C1 ( $sp^3 \rightarrow sp^2$ ) and C2 undergo a change in hybridization during the course of the reactions, this is also true for C3 and C4 which undergo a reversible rehybridization (see text).

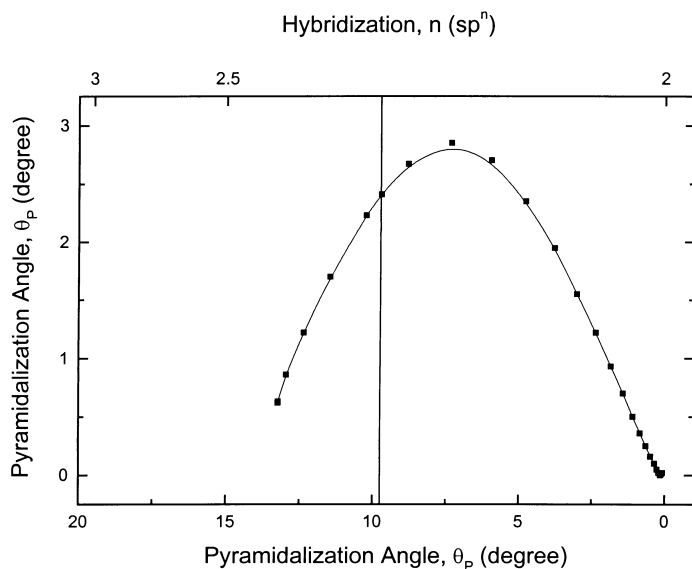


**Fig. 3** Plot of pyramidalization angle at C1 (Fig. 2) ( $x$ -axis), against bond angle at C2 in bridge group ( $y$ -axis) for reaction (7). The vertical line represents the position of the transition state on the horizontal axis.

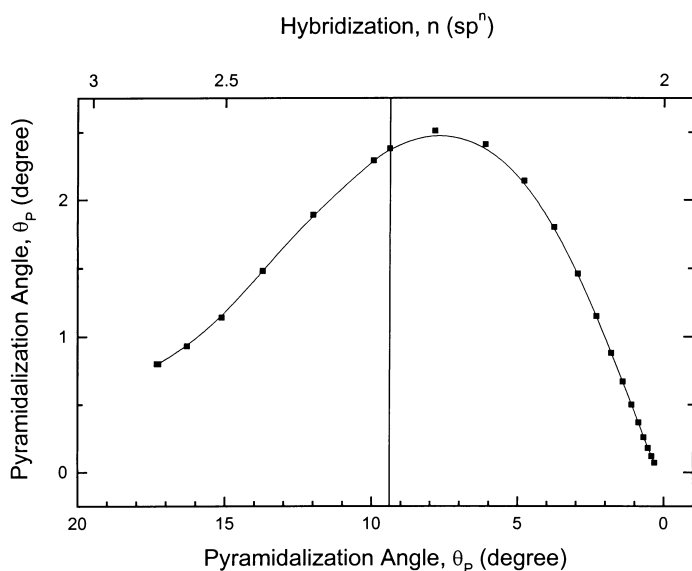


**Fig. 4** Plot of pyramidalization angle at C1 (Fig. 2) ( $x$ -axis) against pyramidalization angle at C2 in bridge group ( $y$ -axis) for reaction (6). The lines represent the position of the transition state.

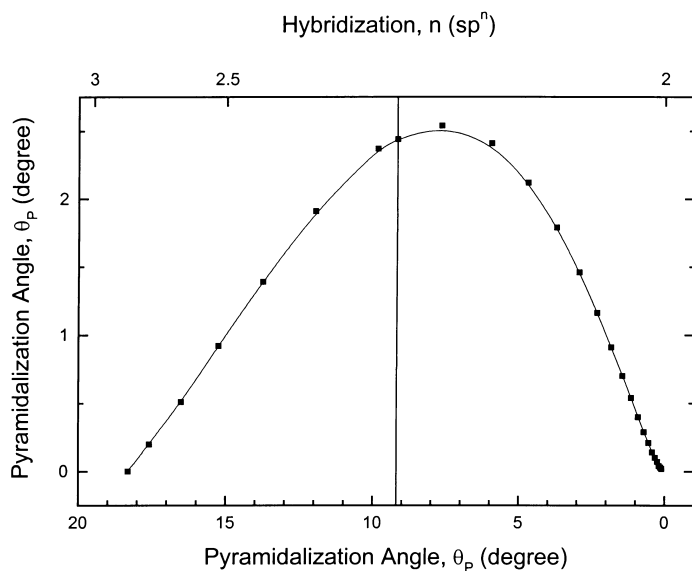
pyramidalization angles at C1. This analysis provides a new approach to concert in chemical reactions. Carbon atom C3 is only remotely involved in the chemical reaction, and the overall hybridization change is very small [analytically zero in the case of reaction (6)]. Nevertheless this atom is involved in the bond forming process as the isolated double bond becomes part of the benzene ring (aromatizes). During the reaction, the bond between C1 and C2 is broken, while  $\pi$ -bonds form between atoms C1 and the C3; thus C1 seeks to adopt a hybridization that maximizes bonding with both C2 and C3. As this compromise is not fully efficient, C3 rehybridizes during the course of the reaction in order to help develop the forming bond. This process is reminiscent of the behavior of the conjugated carbon atoms in the static structures of the bridged-annulenes that rehybridize in order to maintain overlap with the sterically constrained bridge carbon atoms [2,3]. In the present case it provides a unique approach to concertedness [13] in chemical reactions. The atoms C3 are solely involved in the bond-making part of the reaction, and thus by using them as an indicator of reaction progress we can divide the reaction between bond-making and bond-breaking components.



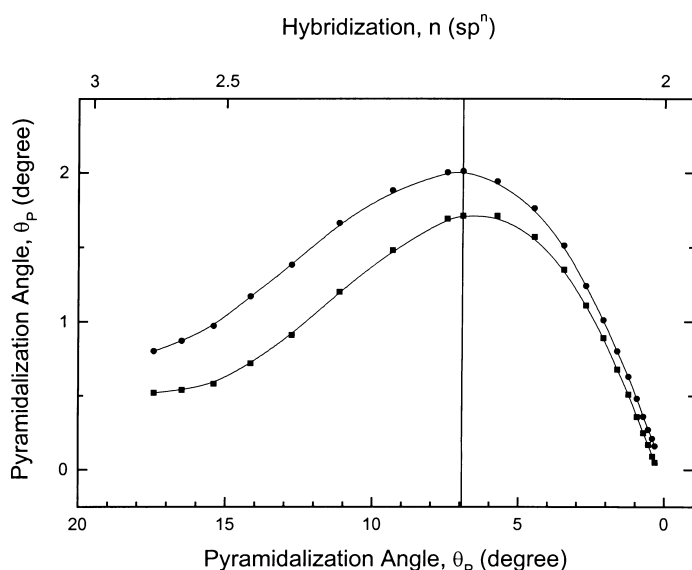
**Fig. 5** Plot of pyramidalization angle at C1 (Fig. 2) ( $x$ -axis) against pyramidalization angle at C3 ( $y$ -axis) for reaction (5). The vertical line represents the position of the transition state.



**Fig. 6** Plot of pyramidalization angle at C1 (Fig. 2) ( $x$ -axis) against pyramidalization angle at C3 ( $y$ -axis) for reaction (6). The vertical line represents the position of the transition state.



**Fig. 7** Plot of pyramidalization angle at C1 (Fig. 2) ( $x$ -axis) against pyramidalization angle at C3 ( $y$ -axis) for reaction (7). The vertical line represents the position of the transition state.



**Fig. 8** Plot of pyramidalization angle at C1 (Fig. 2) ( $x$ -axis) against pyramidalization angle at C3 and C4 ( $y$ -axis) for reaction (8). The vertical line represents the position of the transition state.

The vertical line in Fig. 5–8 denotes the position of the transition state (TS) on the horizontal ( $x$ -axis), and it is immediately apparent that the TS occurs at different stages in the evolution of the pyramidalization angle at C3. In the most exothermic case (Fig. 5), the TS is attained well before the maximum rehybridization at C3. This is because the reaction is dominated by the energy release associated with the departure of the CO group, and the reaction energy begins to fall before the bond making is fully developed. In the case of Fig. 8, however, the maximum in the rehybridization at C3 occurs at the TS, because this endothermic reaction is energetically disfavored, and more bond making is required in the TS for the reaction to proceed.

It is clear that the rehybridization metric for reaction progress [1], brings a valuable new perspective to many aspects of the study of chemical reactions.

## ACKNOWLEDGEMENTS

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