Reply to Comment "Electronic Reorganization in 1,3-Dipolar Cycloaddition of Fulminic Acid to Acetylene"

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Leroy et al.[1] were indeed the first to suggest mechanism II (see schemes in Comment by Nguyen et al.[2]) on the basis of a study of the evolution of restricted Hartree−Fock (RHF) Boys-localized MOs (LMOs) along the intrinsic reaction coordinate (IRC) for the 1,3-dipolar cycloaddition of fulminic acid to ethyne. However, the applicability of the RHF wave function to chemical reactions is limited by its closed-shell nature. While this wave function can describe reasonably well "heterolytic" mechanisms, characterized by the movement of electron pairs, such as the one for the 1,3-dipolar cycloaddition of fulminic acid to ethyne, limitations of its construction do not allow it to accommodate also "homolytic" mechanisms, exemplified by the spin-coupled (SC) description of the Diels−Alder reaction (see ref 1). Without results for a range of systems, it is difficult to make reliable a priori predictions as to whether a reaction is going to follow a "heterolytic" or "homolytic" mechanism.

An unprejudiced strategy could be to use a wave function that allows both, such as a SC or a complete active space self-consistent field (CASSCF) construction. In ref 1, the reacting system had no choice but to follow the heterolytic mechanism (II), while in ref 3, the outcome could have been *any* of the mechanisms: such a "decision" was left to the variational procedure used to optimize all components of the very compact SC wave function. Of course, the outcome was not what we had expected, but we have checked our calculations very carefully and, indeed, have subsequently found an analogous heterolytic mechanism for the gas-phase 1,3-dipolar cycloaddition of diazomethane to ethene.[4] Of course, we never "assign" any particular center as a new bond donor or acceptor: we simply report the changes in orbital shapes, orbital overlaps, and mode of spin coupling observed in "modern valence bond" calculations along the entire reaction path.

The weights of even the most important configurations within the configuration interaction−localized molecular orbitals−complete active space (CI−LMO−CAS) wave functions tend to be fairly small. In the case of the 1,3-dipolar cycloaddition of fulminic acid to ethyne (see ref 5 and structures therein) configurations 18 and 16, which are used to deduce the electronic reaction mechanism, have weights that never exceed 0.28 and 0.16, respectively. A third configuration (21) of a similar weight was not discussed, probably because it does not carry information about the mechanism.

As a rule, the SC wave function accounts for more than 90% of the correlation energy of a "N in N" CASSCF wave function over the whole IRC of a pericyclic reaction by making use of just *one* product of N singly occupied active orbitals. The overlap between the SC and CASSCF wave functions is even higher (often more than 0.99). It is this proximity between the two wave functions that justifies the use of changes to orbital shapes, orbital overlaps, and mode of spin coupling in order to describe the electronic mechanism of a chemical reaction. In a sense, we are faced with choosing between mechanism II, which is backed by more than 90% of the CASSCF wave function, and mechanism III, which has behind it a much smaller proportion. Further studies of pericyclic reactions using modern quantum chemical methods would certainly be very useful.

References and Notes

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