

Letters

An Idea Whose Time Has Come?

In the December 1999 issue of this *Journal*, author David Lewis proposes a nine-category classification of organic electrophilic–nucleophilic reactions based on the bonding and symmetry characteristics of the reactants' frontier orbitals (1). In support of this proposal, I would like to point out that others have suggested closely related classifications in the past. Indeed, an identical classification (see table) appeared 20 years ago as the basis of a book-length monograph on the Lewis acid–base concepts (2), as well as in numerous review articles dealing with the same subject (3–6). This classification was, in turn, largely anticipated by the work of Robert Mulliken and Günther Briegleb on the classification of molecular charge-transfer complexes, which had appeared almost 30 years earlier (7–9). As noted in the article by Lewis, organic electrophilic and nucleophilic reactions are special cases of Lewis acid–base interactions and were treated as such using frontier orbital theory in the monograph in question.

Of special relevance is the fact that interactions involving antibonding acceptor LUMOs and/or bonding donor HOMOs need not necessarily result in bond rupture, as implied in Lewis's table. If the degree of interaction is weak enough, a donor–acceptor addition complex will result instead in which one or more bonds within the acceptor and/or donor species are elongated or weakened relative to the isolated reactants. Even when the degree of interaction is strong enough to lead to bond rupture within the original species, the initial stage of the reaction can still be thought of as a weak donor–acceptor complex (10).

Also of interest to chemical educators is Viktor Gutmann's introduction of the acronyms "EPA agent" and "EPD agent" as abbreviations for the terms "electron-pair acceptor" and "electron-pair donor", respectively (11). Adoption of these terms would eliminate the objectionable anthropomorphisms of the electrophilic–nucleophilic terminology currently used by organic chemists, on the one hand, and the confusion resulting from the overuse of the acid–base terminology by inorganic chemists, on the other.

Not only is it possible to talk about n-EPD species, σ^* -EPA species, $\sigma \cdot \pi^*$ -EPDA interactions, etc., the terminology is easily extended to include reactions involving free radicals, which interact via singly occupied MOs or SOMOs. Radicals simultaneously function as both electron donors and electron acceptors or as EDA agents and may be further classified as n-EDA agents, π -EDA agents, σ^* -EDA agents, etc., depending on the bonding and symmetry properties of the SOMO in question.

Finally, it should be noted that BF_3 is a π^* -EPA agent rather than an n-EPA agent (or an a-EPA agent in Lewis's symbolism) as stated in the article. This is a result of back-donation between the boron atom and the three fluorine ligands (12). In keeping with this, the B–F bond lengths found in EPD– BF_3 complexes are always longer than those found in the isolated BF_3 molecule.

		Acceptor Orbital			
		n	a		
			σ^*	π^*	
Donor Orbital	n	n - n	n - σ^*	n - π^*	
	b	σ	σ - n	σ - σ^*	σ - π^*
		π	π - n	π - σ^*	π - π^*

Table 4.3 from ref 2, illustrating the nine-category classification of donor–acceptor interactions: n is nonbonding, b is bonding, and a is antibonding. Lewis uses "a" instead of "n" to denote a nonbonding acceptor orbital.

Literature Cited

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The author replies:

I was not aware of Dr. Jensen's monograph, and from his discussion it is clear that much of what appears in my paper also appears in his monograph. More importantly, the fact that neither I nor the original reviewers of the manuscript knew of these papers by Jensen surely reinforces one of the central theses of my paper—that unoccupied orbitals as the major arbiters of reactivity have been long ignored by the organic chemistry community when we teach introductory organic chemistry courses. I view his work as a

Letters

welcome addition to the list of literature citations already present in the paper itself.

The discussion in this paper was largely restricted to organic *reactions*, where the interaction between HOMO and LUMO is large and where movement of electrons into an antibonding LUMO will be accompanied by bond rupture. However, it is recognized that less significant interactions between filled orbitals and antibonding orbitals does not necessarily lead to bond rupture. *Ab initio* calculations of the ethane molecule, for example, show that the C–C bond distance is shorter and the C–H bond distance is longer in the staggered conformation than in the eclipsed conformation, which would be expected if there were a small degree of π delocalization of electron density from the C–H σ orbital to the vicinal C–H σ^* orbital in the staggered conformation, thus strengthening (shortening) the C–C bond and weakening (lengthening) the C–H bonds. This argument was set forth in the paper itself during the discussion of $\sigma + \sigma^*$ overlap.

Likewise, Jensen's point about extending this discussion to free radicals is well taken, although I chose not to address this subject in the paper. In similar vein, the point made in his final paragraph is correct: it is known that BF_3 has π backbonding between the boron and the halogens. However, it is not essential to invoke this set of orbitals to rationalize the reactivity of BF_3 , whose Lewis acidity (but not detailed structure) is adequately rationalized on the basis of an empty 2p orbital on boron. (Fortunately, the paper also used the second step of the $\text{S}_{\text{N}}1$ reaction involving a *tert*-butyl cation as an example of this type of reagent, and in this case there is no such π backbonding possible except for hyperconjugation.)

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