Electron Reorganization in Chemical Reactions. Structural Changes from the Analysis of Bond Order Profiles

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The applicability of bond order profiles as a new tool for the interpretation and the visualization of electron reorganization during chemical reactions is examined, with emphasis on (i) the sensitivity to the particular choice of the definition of bond order, (ii) the sensitivity to the quality of the computational methods used, comparing HF and post-HF (MP2, SC and CASSCF) levels of theory, and (iii) the possibility of a mechanistic interpretation of bond order profiles in terms of the Hammond postulate. The systems studied are the dissociation of molecular hydrogen, the conrotatory ring opening of cyclobutene to *cis*-butadiene, and the s + s Diels−Alder cycloaddition reaction of butadiene and ethene.

Introduction

Chemistry is a science of molecular change, and understanding the structural transformations that accompany the conversion of reactants into products is one of its ultimate goals. Much effort has of course been devoted to elucidating factors governing the course of chemical reactions. Although it is true that a great deal of qualitative understanding was already provided by classical structural theory,[1] the contemporary understanding of the principles governing chemical reactivity is closely tied with the progress of chemical theory.

Theoretical descriptions of chemical reactivity tend to rely on Eyring's theory of absolute reaction rates,[2] with its idea of the transition state as a saddle point on the potential energy surface (PES). Another important theoretical characteristic closely related to the concept of the PES is the tenet of the intrinsic reaction coordinate, IRC,[3] as the minimum energy path connecting the transition state with the energy minima characterizing the reactants and products. Based on such concepts, the standard quantum chemical description of chemical reactivity typically starts with the calculation of the geometries, energies, and wave functions of decisive critical species lying on the IRC of a given reaction.

Although it is true that very important information about chemical reactions can be obtained in this way, and also from dynamics calculations run on the computed PES, it is nevertheless true that purely numerical approaches are not completely satisfactory from the chemical point of view. The reason is that chemists usually think of molecules and reactions in terms of classical concepts of bonds, bond orders, valences, Lewis structures, and so on, whose relation to "high accuracy", but abstract, quantum chemical descriptions is not immediately obvious. An important task for chemical theory thus consists of designing appropriate auxiliary tools that allow us to transform quantum chemical descriptions into a language closer to classical chemical thinking. An important example in this respect is the introduction of the quantum chemical definition of bond order,[4−25] which is the theoretical counterpart of the classical concept of bond multiplicity. Several reports were published in recent years, in which such approaches were used for the interpretation and visualization of electron reorganization in the course of chemical reactions by monitoring the variation of bond orders or other related quantities, such as valences, along the reaction path. Such dependencies, known as bond order (BO) profiles, have been investigated by various groups.[26−39] The most important conclusion of such studies is that the breaking of disappearing bonds is often synchronized with the formation of new ones—the phenomenon anticipated on the basis of an empirical rule known as the BEBO relationship.[40−42]

Another important observation reported in those studies concerns the empirical finding that the position of the transition state, which is intuitively considered as a species in which the bonding pattern changes from the one corresponding to the reactants to that characteristic of the products, is often localized in the vicinity of the inflection point on the bond order profiles.[27,29,30] One aim of the present study is to address this empirical observation in more detail.

In addition to examining two genuine chemical reactions, we report here the analysis of bond order profiles for the simplest bond-breaking process, namely, the dissociation of the H_2 molecule. Such a process is interesting because despite the absence of any special point on the corresponding potential energy curve, the bond order profile shows one of the same features as for ordinary chemical reactions, namely, the existence of an inflection point or even abrupt changes at the internuclear distance, R, at which the electron reorganization is occurring most rapidly. We then examine the utility of BO profiles for two representatives of the broad class of symmetry-allowed gas-phase pericyclic reactions: the conrotatory ring opening of cyclobutene to *cis*-butadiene and the s + s cycloaddition of butadiene to ethene (Diels−Alder reaction). As is well-known, the theoretical description of multibond processes can be very sensitive to the quality of the computational methods used, and

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it could be somewhat naïve to expect realistic results at the HF level. Instead, we mostly examine results of CASSCF and MP2 quality.

Theoretical Section

Bond orders represent the theoretical counterpart of the classical concept of bond multiplicity, and their variation along the reaction path allows one to visualize the more abstract "electron reorganization" in terms that are closer to classical chemical thinking. The introduction of the concept of bond order can be traced back to Pauling[4] and to Coulson,[5] but these early definitions were restricted mainly to π-electron aromatic systems. The need to generalize the idea of bond order beyond the scope of such a restricted class of systems stimulated the systematic effort of many groups and a plethora of definitions of bond order has been proposed.[4−24] The definition most widely used in the analysis of bond order profiles is due to Mayer,[11−13] who defined the bond order between atoms A and B as

$$B_{AB}^{M} = \sum_{\mu \in A} \sum_{\nu \in B} [(\mathbf{P}^{\alpha}\mathrm{S})_{\mu\nu}(\mathbf{P}^{\alpha}\mathrm{S})_{\nu\mu} + (\mathbf{P}^{\beta}\mathrm{S})_{\mu\nu}(\mathbf{P}^{\beta}\mathrm{S})_{\nu\mu}] \quad (1)$$

in which $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ are spin-dependent one-particle density matrixes, $\mathbf{S}$ is the overlap matrix, and μ and ν are label basis functions. In the case of closed-shell systems at the SCF level of the theory, this definition reduces to the well-known Wiberg-indices,[6] which were generalized for nonorthogonal basis sets by Giambiagi and co-workers,[9] and also to the so-called effective pair populations.[20] There is now a relatively broad consensus that Wiberg indices represent the "best" definition of bond order at the SCF level of the theory. However, satisfactory descriptions of chemical reactivity usually involve going beyond the scope of the SCF approximation, so that reliable applications of bond order profiles depend crucially on the appropriate generalization of the bond order concept to correlated, post-HF levels.

One of the simplest possibilities is, of course, the straightforward use of formula 1, which, for the case of singlet states, reduces to what could be called the "generalized" Wiberg index:

$$B_{AB}^{W} = \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{PS})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \quad (2)$$

in which $\mathbf{P}$ is the total (spinless) one-particle density matrix corresponding to the correlated wave function.

This straightforward approach was recently reconsidered by various authors, and several alternative definitions of correlated bond orders were proposed.[16−19,21−24] Most, such as the definitions of Cioslowski[17] and of Fulton,[16] also rely only on knowledge of the (correlated) first-order density. Given that most of the existing studies of BO profiles are based on bond orders derived from the first-order density, we confine ourselves in the present study to definitions of this type. We note, however, also the proposal to use the so-called "fluctuation" bond order, which is defined in terms of the two-particle density matrix.[21−25]

Not only do numerical values of individual bond orders often differ quite considerably between different definitions, but so do the shapes of the corresponding bond order profiles. Such a situation is, of course, rather unsatisfactory and it casts doubt on the whole approach. One aim of the present study is to compare different definitions of BO profiles, and related quantities, so as to check to what extent the particular choice can affect or bias the mechanistic picture that emerges. In addition we compare results obtained with HF and post-HF (MP2, SC, and CASSCF) wave functions. The main emphasis is to assess the extent to which differences reflect direct changes to the quality of the wave function, as opposed to the indirect effects of changes to the geometries.

In the first part of this study, we compare the following definitions of bond order:

(i) the generalized Wiberg index (eq 2) as the representative of the approach that has been most often used in previous studies of bond order profiles and

(ii) the Cioslowski covalent bond order,[17] defined according to

$$B_{AB}^{C} = \sum_{i} n_i^{2} \langle i|i\rangle_A \langle i|i\rangle_B \quad (3)$$

which was originally introduced within the framework of AIM theory.[43] For the sake of consistency with the Wiberg definition, we used here a simplified approach in which the integrals over atomic basins were replaced by an appropriate Mulliken-like approximation:

$$\langle i|i\rangle_A = \sum_{\mu \in A} \sum_{\nu} c_{\mu i} c_{\nu i} S_{\mu\nu} \quad (4)$$

A specific feature of this particular bond order is that molecular orbitals i and the occupation numbers n_i entering into definition 3 are not in fact the usual natural orbitals and occupation numbers but are obtained from them by applying the so-called isopycnic transformation, which leaves invariant the first-order density matrix.[44] Values of Cioslowski bond orders are not invariant with respect to transformations of the orbital set.

We also examine here the quantity Ω, defined according to

$$\Omega = \int\int \rho(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}',\mathbf{r})\, \mathrm{d}\mathbf{r}'\, \mathrm{d}\mathbf{r} = \mathrm{Tr}[(\mathbf{PS})(\mathbf{PS})] \quad (5)$$

We have previously used the dependence of Ω on internuclear distance, R, to monitor the dissociation of chemical bonds.[45] This quantity is closely related to the so-called density of unpaired electrons $U(\mathbf{r})$ (eq 6), originally introduced by Takatsuka[46] and more recently explored by others:[47−51]

$$U(\mathbf{r}) = 2\rho(\mathbf{r},\mathbf{r}) - \int \rho(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}',\mathbf{r})\, \mathrm{d}\mathbf{r}' \quad (6)$$

Of course, $\mathrm{Tr}(\mathbf{U})$ is simply $2N - \Omega$, where N is the number of electrons.[46−51]

Results and Discussion

1. Dissociation of Molecular Hydrogen. The dissociation of H_2 represents the simplest example for testing various definitions of correlated bond order and their eventual impact on the picture of electron reorganization accompanying such a process. The main goal of this part of the study was to investigate the extent to which the interpretation can be affected by the particular choice of definition. For this purpose, various BO profiles, and related quantities, are depicted in Figure 1. These were generated from correlated first-order densities calculated from CASSCF(2,2) wave functions in a 6-311G** basis using the Gaussian98 program.[52]

It is clear that the numerical values, as well as the forms of the associated bond order−bond length dependencies, differ considerably. Nonetheless, the two BO curves display a common feature, in the sense that the inflection point for the Wiberg definition of bond order occurs at the same internuclear distance as the sharp drop in the analogous dependence for the Cioslowski bond order. This is clear not only from visual inspection of the figures but also from numerical differentiation. Additionally, as is shown in Figure 1c, the so-called localization index, introduced some time ago by Cioslowski,[44] also shows

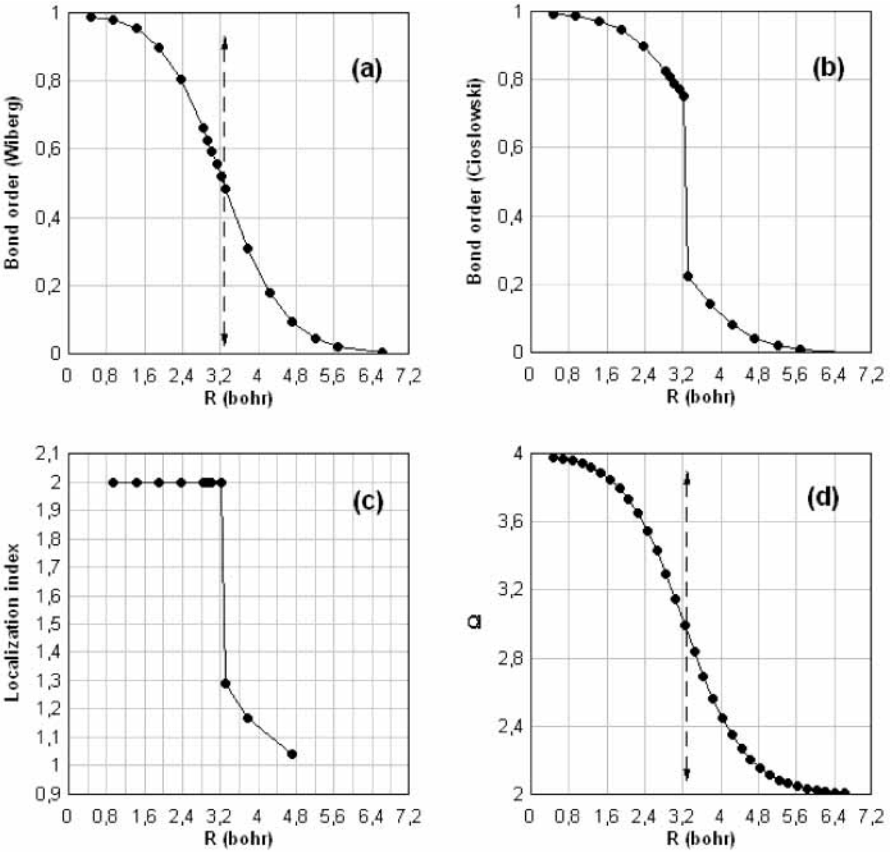

Figure 1. *R* dependence of bond orders and other quantities for the dissociation of H_2, derived from CASSCF(2,2) wave functions with a 6-311G** basis. (a) Generalized Wiberg bond order; (b) Cioslowski covalent bond order; (c) Localization index; (d) Ω. Further details are provided in the text. The vertical dotted lines in frames (a) and (d) identify the position of the point of inflection, as determined by numerical differentiation.

a similar dramatic drop at essentially the same distance, and this may even be interpreted as the actual splitting of H−H bond. The *R* dependence of Ω for the dissociation of H_2 is depicted in Figure 1d. Yet again, the position of the inflection point coincides with those in the BO profiles. An alternative definition of bond order proposed by Fulton[16] was found to be somewhat more linear in this region, but numerical differentiation again placed the inflection point at the same value of *R*.

The problem of generalizing the concept of bond order beyond the scope of the HF approximation was recently addressed by various authors,[18,22,24] without leading to any definitive answer. It is a general observation that there is considerable scatter in the values from different definitions and so it has proved difficult to attribute much physical or chemical meaning to correlated bond orders. Such a situation is more than a little disappointing, given that HF values of bond orders (Wiberg indices[6,9−13]) are known to more or less coincide, at least for stable molecules close to equilibrium geometries, with classical bond multiplicities. This fortunate coincidence is somewhat accidental and, apparently, it is related to the remarkable parallel between the Lewis electron pair model and the pairing of electrons with opposite spin due to Fermi correlation.[23,53] The inclusion of Coulomb correlation in post-HF treatments partially destroys the ideal pairing suggested by the Lewis model, and it leads to significant changes to the values of correlated bond orders.

Although the different definitions of bond orders, and related quantities, certainly lead to numerical values which differ considerably from case to case, we find in the present work that the positions of the inflection points are practically invariant. This observation is important because it implies that the particular choice of definition might not be so important after all. Provided that sufficiently reliable computational methods are used, it is possible that practically any of the existing definitions could be used to construct a useful BO profile.

2. Thermally Allowed Conrotatory Ring Opening of Cyclobutene to *cis-Butadiene*. As a second example we examine BO profiles for a genuine chemical reaction, namely, the thermally allowed gas-phase conrotatory ring opening cyclobutene to *cis*-butadiene. An extensive theoretical study of the reaction mechanism of this pericyclic process was performed some time ago by Spellmayer and Houk,[54] who reported a systematic investigation of the effect of electron correlation on the geometries and energetics. A comparison was made of various semiempirical and ab initio methods at HF and post-HF (MP2, TCSCF) levels of theory. A general conclusion was that geometrical parameters were reproduced reasonably well by nearly all the methods, but that the accurate calculation of activation energies and reaction energies requires a realistic treatment of electron correlation.

Our main goal in investigating this reaction was to examine the extent to which BO profiles based on generalized Wiberg indices (eq 2) are sensitive to the quality of the wave functions from which they are derived. There are two key aspects to consider, namely, the effect of the geometry changes between IRCs calculated with different approaches and the effect of using different wave functions along the same IRC. We use the notation *x*/*y* to denote a BO profile calculated with method *x* along an IRC generated with method *y*. Calculations were performed by using PCGamess[55] (HF) and Gaussian98[52] (MP2, CASSCF(4,4)) with a 6-31G* basis. The resulting CASSCF/CASSCF and MP2/MP2 profiles are shown in Figure 2, in which negative IRC values are toward products and positive values toward reactants, so that the ring opening runs from right

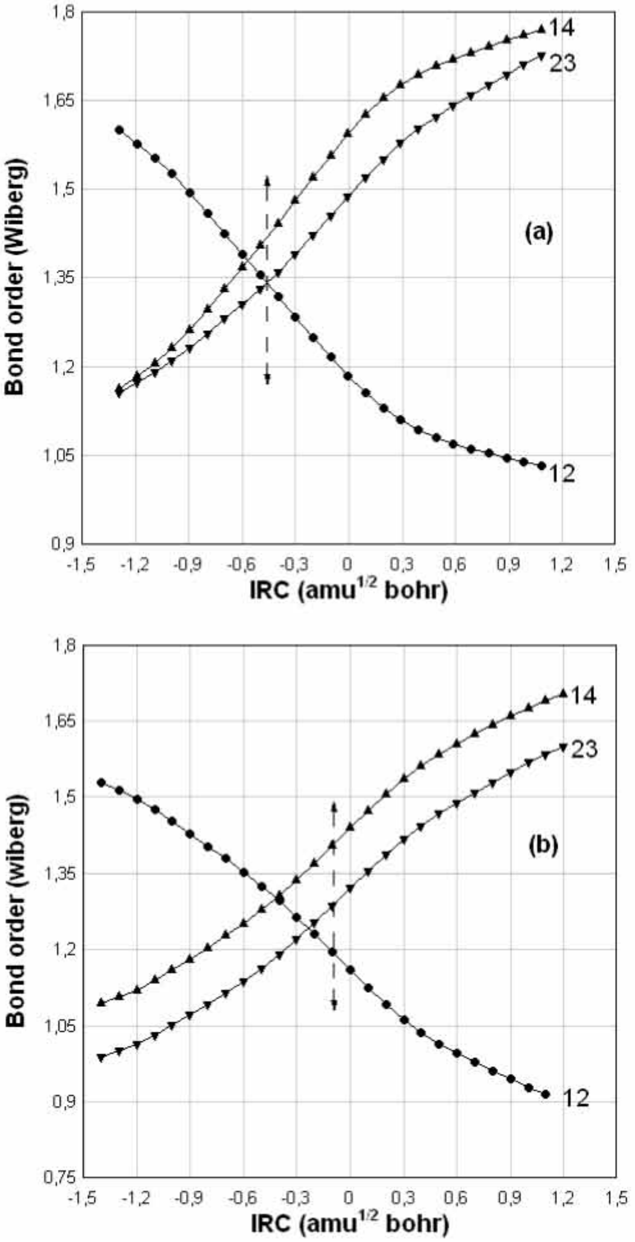

Figure 2. Bond order profile calculated at (a) CASSCF/CASSCF and (b) MP2/MP2 levels of theory for the gas-phase symmetry-allowed conrotatory ring opening of cyclobutene to *cis*-butadiene. The atoms are numbered sequentially clockwise, such that the value of B_{23}^{W} (which has been increased by unity, so as to put it on the same scale as the others) corresponds to the σ bond being broken. Negative IRC values are toward products and positive values toward reactants, so that the ring opening runs from right to left. The vertical dotted lines identify the vicinity of the points of inflection, as determined by numerical differentiation.

to left. The atoms are numbered sequentially clockwise, such that the value of B_{23}^{W} (which has been increased by unity, so as to put it on the same scale as the others) corresponds to the σ bond being broken. The vertical dotted lines identify the vicinity of the points of inflection, as determined by numerical differentiation.

The various BO profiles all show that the weakening of old bonds in the reactant is accompanied by a complementary strengthening of new bonds in the product, as expected, but the inflection points are not located at the transition state. The most dramatic shifts are observed for the CASSCF/CASSCF case (Figure 2a), for which all the inflection points are localized on the IRC in the vicinity of -0.45 amu$^{1/2}$ bohr (rounded to the nearest 0.05). This result is entirely consistent with a previous modern valence bond study, based on spin-coupled (SC) theory,[56,57] in which it was found that the most rapid changes to the wave function took place in this same region of the IRC. A SC wave function for a system with N active electrons closely resembles the corresponding many-configuration “N electrons in N orbitals” CASSCF(N,N) wave function, but it is much more compact, and it is easy to interpret in terms of changes in the shapes of nonorthogonal orbital and the modes of spin coupling.[58,59]

In the case of the dissociation of molecular hydrogen, the R dependence of bond orders, and related quantities, could be used to monitor the splitting of the H−H bond. The situation with chemical reactions is of course usually more complex, simply because of the active involvement of more than one bond. Moreover, especially in the case of allowed pericyclic processes, the splitting of old bonds strongly benefits from the concert with the formation of new ones, so that none of the chemical bonds are actually completely split near the transition state. The question thus naturally arises as to what physical or chemical meaning is to be attributed to the inflection points on the BO profiles in such a case. The answer to this question is that the position of the inflection point on the IRC coincides with the region along the IRC in which the bonding pattern undergoes the fastest change from the one characteristic of the reactants into the one corresponding to products. Such a structural change is often intuitively expected to take place at the transition state but, as has been shown here, this is not necessarily the case. For some systems, the shifts of the inflection points away from the transition state can be quite considerable.

In the present case, the shift in the positions of the inflection points on the CASSCF/CASSCF bond order profiles (Figure 2a) is toward the negative side of the IRC, which is in the direction of products. Such a shift implies that the transition state, characterized by an IRC value of zero, falls into the region where the electronic structure is still characteristic of the bonding pattern of the reactant, cyclobutene. In another words, the electronic structure of the transition state can be expected to be more “similar” to that of cyclobutene than to that of the product, *cis*-butadiene. This is of course a specification which very closely resembles the language of the Hammond postulate,[60] which characterizes the structure of transition states in terms of the overall exo- or endothermicity of the reaction. Taking into account that the reaction written in the direction cyclobutene → *cis*-butadiene (which runs from right to left in the figures) is exothermic, the Hammond postulate predicts the transition state to be “reactant-like”. It is evident that the classification of the transition state resulting from the analysis of CASSCF/ CASSCF bond order profiles is in accord with the expectations of this postulate. In this connection it is, perhaps, fair to say that the possible connection of these two concepts was already mentioned in earlier studies[28−31] but that the straightforward relation between the position of the inflection point and the nature of the transition state is explicitly formulated for the first time here. The Hammond postulate has of course proved very useful, especially in organic chemistry, but it is important to note that many systems are known which show intermediate or even anti-Hammond behavior. One such example is the Diels−Alder reaction,[61] which we consider later. For such systems, we do not expect any relation between the position of the inflection point and the overall exo- or endothermicity, but we do expect that the position of the inflection point will still correspond to the region in which electron reorganization is occurring most rapidly.

Returning to the ring opening of cyclobutene to butadiene, inspection of Figure 2b shows that there is a smaller shift toward the same (negative) side of the IRC for the MP2/MP2 profiles, which have inflection points in the vicinity of −0.10 amu$^{1/2}$ bohr. On the other hand, the analogous MP2/CASSCF profiles exhibit inflection points near −0.25 amu$^{1/2}$ bohr, so that only some of the difference between CASSCF/CASSCF and MP2/MP2 can be attributed to geometric changes. To investigate this further, we considered HF values along these two IRCs. In the case of HF/CASSCF, the inflection points are in practically the same location (−0.45 amu$^{1/2}$ bohr) as for the CASSCF/CASSCF profiles. On the other hand, the HF/MP2 inflection points are shifted to positive values, +0.25 amu$^{1/2}$ bohr, which makes us a little suspicious of the utility of the geometries along the IRC calculated at the MP2 level. Finally, we also examined HF/HF profiles, despite our expectations that an IRC calculated at such a low level might not be too reliable. Unlike HF/MP2, the inflection points are again on the negative side of the IRC (−0.15 amu$^{1/2}$ bohr).

Comparing all of these various calculations, we conclude that the main effect on the position of the inflection points of including mostly nondynamical correlation via the CASSCF method is indirectly, via the geometries, rather than directly from the wave function itself. On the other hand, there appears to be both a direct and an indirect (i.e., geometric) effect of including mostly dynamical correlation via the MP2 method.

Close inspection of Figure 2a shows that the shapes of the B_{12}^{W} and B_{14}^{W} profiles (for π bonds) are practically the same, essentially being mirror images of each other. On the other hand, the corresponding SC/CASSCF curve for the σ bond (B_{23}^{W}) is slightly different, suggesting that the making/breaking of the π bonds initially lags behind the breaking of the σ bond. Nonetheless, the fastest changes in all of these bonds occur in the same region of the IRC. This distinction between σ and π bonds is not apparent in the MP2/MP2 profiles (see Figure 2b), suggesting that all of the bond making and breaking is strictly in concert. Further calculations, such as CASPT2 or CASSCF-MRCI, that incorporate dynamical correlation with a multiconfiguration reference function would be required to settle which of these two scenarios is the more accurate qualitative description.

3. Symmetry-Allowed (s + s) Diels−Alder Addition of Ethene to Butadiene. As a further example, we examined the preferred concerted reaction mechanism[62] of another pericyclic process, namely, the symmetry-allowed gas-phase 4s + 2s cycloaddition of ethene to butadiene, which represents the simplest example of the broad family of Diels−Alder reactions. The choice of computational methods was motivated by the possibility of direct comparison with our previous studies,[63,64] in which analysis of changes to the spin-coupled (SC) wave function along the CASSCF(6,6) IRC suggests that the system passes through a structure, at or very close to the transition state, that has certain similarities to the aromatic ring in benzene. For the sake of comparison with previous studies,[63,64] we used the same 4-31G basis.

The resulting SC/CASSCF bond order profile is depicted in Figure 3, in which negative IRC values are toward products and positive values toward reactants, so that the cycloaddition reaction runs again from right to left. The atoms are numbered sequentially clockwise, with 1−4 on butadiene and 5−6 on ethene, so that B_{16}^{W} corresponds to one of the newly formed σ bonds in cyclohexene. The value of B_{16}^{W} has been increased by unity, so as to put it on the same scale as the others. The vertical dotted lines identify the vicinity of the points of inflection, as determined by numerical differentiation.

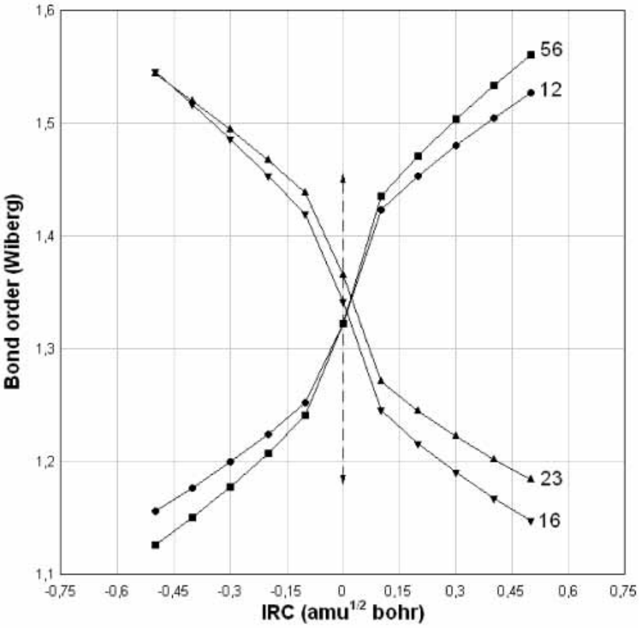

Figure 3. Bond order profile calculated at the SC/CASSCF level of theory for the gas-phase symmetry-allowed s + s Diels−Alder cycloaddition of ethene to butadiene. The atoms are numbered sequentially clockwise, with 1−4 on butadiene and 5−6 on ethene. The value of B_{16}^{W} (which corresponds to one of the newly formed σ bonds in cyclohexene) has been increased by unity, so as to put it on the same scale as the others. Negative IRC values are toward products and positive values toward reactants, so that the cycloaddition reaction runs from right to left. The vertical dotted lines identify the vicinity of the points of inflection, as determined by numerical differentiation.

It is clear from Figure 3 that the SC/CASSCF bond order profiles for all disappearing and newly formed bonds have much the same shape and that they do indeed exhibit a point of inflection that is again at or very close to the transition state, as we might have anticipated from the previous studies,[63,64] which showed that this is in the region along the IRC in which the bonding pattern undergoes the fastest change. As was mentioned earlier, this is a system that is already known not to show Hammond behavior, according to which the transition state should be cyclohexene-like. We also ran HF calculations along the same IRC, and found the positions of the inflection points in the HF/CASSCF profiles to be practically indistinguishable from those observed in Figure 3.

Despite our serious reservations about the validity for this system of an IRC calculated at just the HF level, we also examined the HF/HF bond order profiles. For the bonds being broken (C_1C_2 and C_5C_6), the inflection point is near −0.15 amu$^{1/2}$ bohr, and for those being formed (C_2C_3 and C_1C_6) it is near −0.30 amu$^{1/2}$ bohr, suggesting[27−29] some asynchronicity in the splitting and formation of different bonds. Comparison with the HF/CASSCF profile, which shows much the same inflection points as SC/CASSCF, leads us to believe that the shifts seen at the HF/HF level are nothing more than artifacts arising from calculating the IRC at such a low level of theory. In the case of the positions of the points of inflection, we observe that the main effect of including mostly nondynamical correlation via the SC or CASSCF methods is indirectly, via the geometries, rather than directly from the wave function itself, just as in the case of the conrotatory ring opening of cyclobutene to *cis*-butadiene. Our findings cast serious doubts on the utility of previous studies of BO profiles that followed multibond reactions along IRCs that were calculated only at the HF level of theory.

Conclusions

We find for the process of dissociating H_2 that although different definitions of bond orders, and related quantities, based on the first-order density lead to numerical values which differ considerably from case to case, the positions of the inflection points are practically invariant. Of course, to be sufficiently reliable, bond order (BO) profiles for chemical reactions need to be calculated at a post-HF level of theory that can describe properly the making and breaking of chemical bonds. In particular, the geometries along an IRC calculated at the HF level are somewhat unlikely to be realistic.

The positions of the inflection points on the BO profiles coincide with the critical structure at which the bonding pattern is changing most rapidly from the one characteristic of the reactants into the one corresponding to products. In general, such a geometry need not correspond to that of the transition state. The shifts of the inflection points with respect to the position of the transition state may be interpreted in terms of the Hammond postulate except, of course, for reactions that do not show Hammond behavior.

For the chemical reactions studied here, in which the splitting of old bonds is accompanied by the concerted formation of new ones, the main effect on the positions of the inflection points due to the inclusion of mostly nondynamical correlation, via a SC or CASSCF treatment, is mostly indirect, via the geometries. At least for the cyclobutene to *cis*-butadiene reaction, the inclusion of mostly dynamical correlation, via MP2, has both direct and indirect effects on the positions of the inflection points. Further studies with highly correlated treatments based on multiconfiguration reference functions would seem worthwhile, in this context.

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