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THE PARENT DIELS-ALDER CYCLOADDITION REACTION: A DFT STUDY OF THE CONCERTED AND STEPWISE MECHANISMS

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RESUM

S'han dut a terme càlculs amb la teoria del funcional de la densitat (aproximació local) per tal de localitzar les estructures de transició corresponents als mecanismes de reacció concertat i per etapes de la reacció de Diels-Alder entre l'1,3-butadiè i l'etilè. Els resultats teòrics permeten concloure que l'estructura de transició que porta a un intermedi amb un sol enllaç entre diè i dienòfil (procés per etapes) està 11 kcal mol^{-1} per sobre de l'estructura de transició sincrònica concertada. Per tant, podem predir que la reacció tindrà lloc a través d'un procés concertat. A diferència del que havia succeït amb càlculs CASSCF previs, el nivell de teoria emprat en aquest treball sí que coincideix amb els resultats experimentals.

RESUMEN

Se han llevado a cabo cálculos con la teoría del funcional de la densidad (aproximación local) con el fin de localizar las estructuras de transición correspondientes a los mecanismos de reacción concertado y por etapas de la reacción de Diels-Alder entre el 1,3-butadieno y la molécula de etileno. La principal conclusión que se deduce de los resultados teóricos es que la estructura de transición que lleva a un intermedio con un único enlace formado entre dieno y dienófilo (proceso por etapas) está 11 kcal mol^{-1} por encima de la estructura de transición sincrónica concertada. A diferencia de lo que se obtiene con la metodología CASSCF, el presente nivel de teoría coincide con los resultados experimentales.

ABSTRACT

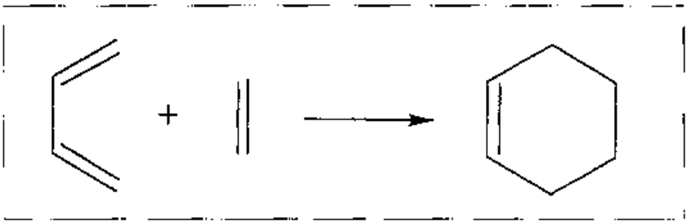
Local density functional calculations with the 6-31G* basis set have been performed to locate transition structures for the concerted and the stepwise mechanisms of the Diels-Alder reaction between 1,3-butadiene and ethylene. Theoretical results lead to the conclusion that the stepwise transition structure leading to an intermediate with a single bond joining diene and dienophile lies 11 kcal mol^{-1} above the concerted synchronous transition structure. Therefore, the reaction is predicted to take place through a concerted process. Unlike earlier CASSCF calculations, the present level of theory agrees with experimental evidence.

Keywords: 1,3-butadiene, concerted mechanisms, density functional theory, Diels-Alder cycloaddition reactions, ethylene.

INTRODUCTION

The Diels-Alder reaction between 1,3-butadiene and ethylene (Scheme 1) is the most widely used and best known pericyclic reaction. It was discovered in the

1920s by Otto Diels and Kurt Alder (1) and soon became a very useful tool in synthetic organic chemistry (2). Noteworthy, the mechanism of this reaction has always been the subject of interesting controversies.



Scheme 1

Although it was originally considered to be a 'no mechanism' process, nowadays it is understood in terms of aromatic transition structures, this proposal being consistent with both experimental and computational evidence. At least two mechanisms are possible in the Diels-Alder reaction (Figure 1). The reaction may take place in a concerted fashion, with partial formation of the two new bonds in the single transition state. If both bonds are formed to exactly the same extent in the transition state, this is called a synchronous concerted reaction; otherwise, it is asynchronous. The other extreme is a stepwise process, involving first the formation of an intermediate with a single bond formed between diene and dienophile; subsequent formation of the second bond gives the cycloadduct. Either step may be rate determining, and such an intermediate may be either diradical or zwitterionic.

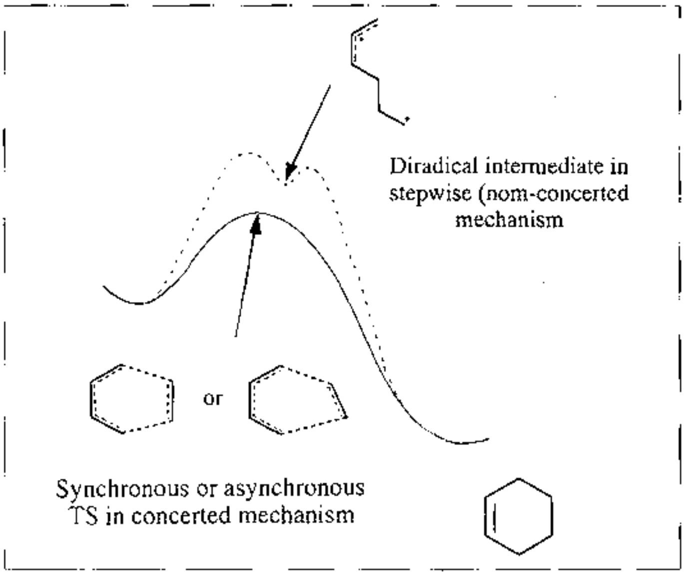


***Figure 1** Energy versus reaction coordinate diagram for concerted and stepwise mechanisms of the Diels-Alder reaction.*

Regarding experimental studies, the first transition state model was proposed in 1935 by Wasserman (3), who postulated a concerted transition state, with forming C-C bond distances of 2.0 Å. Ionic intermediates and transition states were also invoked in the early days to explain the regioselective formation of certain products (3,4). Later, Woodward and Katz came up with a nice mechanistic analysis based on a study of what we now consider a Cope rearrangement (5). Thus, they considered the transition state that interconverted the studied structures to be related to the Diels-Alder transition state. The formation of a single bond between the diene and the dienophile was assumed to be the rate-controlling step, while the other forming bond was barely beginning to form in the transition state (5). On the contrary, Dewar reported some observations which provided strong evidence for the one-step mechanism for the Diels-Alder reaction and suggested symmetric cyclic transition states (6). A mechanistic study of Houk et al. (7) proved that no long-lived diradical intermediate can be formed.

As far as computational studies are concerned, the tools of quantum chemistry have been applied to this reaction during the last two decades. Despite the remarkable advances in the experimental studies of the transition states of simple chemical reactions (8), the only way to obtain detailed information on the geometries of transition states of complex processes is the use of quantum mechanical calculations (9,10). As methods and computers have been improved, better accuracy has been achieved; nevertheless, different methods yield different answers. This has lead to heated arguments among theoreticians and mistrust of some calculations by many experimentalists. Pioneering work using semiempirical methods predicted a two-step mechanism, the symmetrical concerted path (C_s transition structure) being much higher in energy. On the contrary, the first *ab initio* calculations performed on the parent Diels-Alder reaction showed that the synchronous concerted pathway was favored. Several insights were offered into this dichotomy between *ab initio* and semiempirical techniques.

More than ten years ago, new *ab initio* calculations were performed using analytical first- and second-derivative techniques (11). The synchronous concerted mechanism was found, and the saddle point was proven to be a transition structure with one negative force constant (imaginary vibrational frequency). Dewar's new semiempirical method (AM1) also predicted a concerted, synchronous transition structure for the butadiene-ethylene reaction (12). This conclusion is now known to be true at the many *ab initio* levels studied (13,14). Most methods yield virtually superimposable synchronous transition structures; however, the energetics are very sensitive to the level of calculation. By 1986, experimental and theoretical evidence converged on the synchronicity of the parent reaction. To determine how much higher the diradical mechanism is, multiconfiguration SCF techniques were used (15,16). The synchronous concerted mechanism was predicted to be favored by 6 kcal mol^{-1} with inclusion of dynamic correlation energy (17). This is in good agreement with experimental estimates of 2-7 kcal mol^{-1}

Nevertheless, the investigation of transition states of chemical processes like the Diels-Alder reaction is still an open area. Recently, new methodologies have appeared which are waiting to be tested in different chemical areas. Thus, it is interesting to study how reliable modern computational implementation techniques of quantum chemistry such as density functional theory (DFT) (18-23) are when studying the butadiene-ethylene reaction (24). Thus, the first goal in this paper consists of investigating which is the best mechanism predicted by the local density approximation (LDA). The second purpose is to quantify how accurate this approximation can be as compared to post-Hartree-Fock methodologies. Interestingly, *ab initio* RHF and MCSCF calculations predict a symmetric transition structure for a route with no intermediates, whereas *ab initio* UHF calculations predict a two-step mechanism involving a diradical intermediate (14).

COMPUTATIONAL DETAILS

DFT calculations within the local density approximation (LDA) were performed using the GAUSSIAN 94 program (25), with the Slater exchange functional (27) and the Vosko, Wilk and Nusair correlation functional (27) (SVWN). Reactants were located through full geometry optimizations. Further, transition states were located in the full potential energy hypersurface and characterized by the existence of a single negative eigenvalue of the Hessian matrix. The basis set employed was the 6-31G* due to Pople and co-workers (28), usually used in studies of moderately large organic molecules.

RESULTS AND DISCUSSION

We begin this section with a brief description of the optimized geometries. The study of the two possible mechanisms proposed for the butadiene-ethylene accounts for the central part of the discussion. Finally, a comparison between DFT results and previous post-HF calculations is made.

A. Molecular structures

Figure 2 shows the reactants and transition structures of the butadiene-ethylene reaction according to SVWN/6-31G* full-optimizations. Analytical Hessian calculations and harmonic vibrational frequency analyses show that both **2** and **3** are actual transition structures (only one imaginary frequency: -288.5 cm^{-1} for **2**, and -280.9 cm^{-1} for **3**). Several interesting features of these transition structures are summarized here. In **2** the angles of attack are approximately tetrahedral, so that butadiene and ethylene do not approach each other in parallel planes, but instead the planes are tilted with respect to each other. The out-of-plane bending of the hydrogens at C_2 and C_3 of the diene is quite remarkable, since these hydrogens are nearly coplanar with the attached and germinal carbons in both reactant and product. This pyramidalization of the orbitals on C_2 and C_3 occurs in order to maximize overlaps of the p orbitals at these carbon atoms with the orbitals of forming C⋯C bonds (29). The forming σ-bond in **3** calculated at the SVWN/6-31G* level is 0.08 Å shorter than the corresponding length obtained at CASSCF/6-31G* level (17).

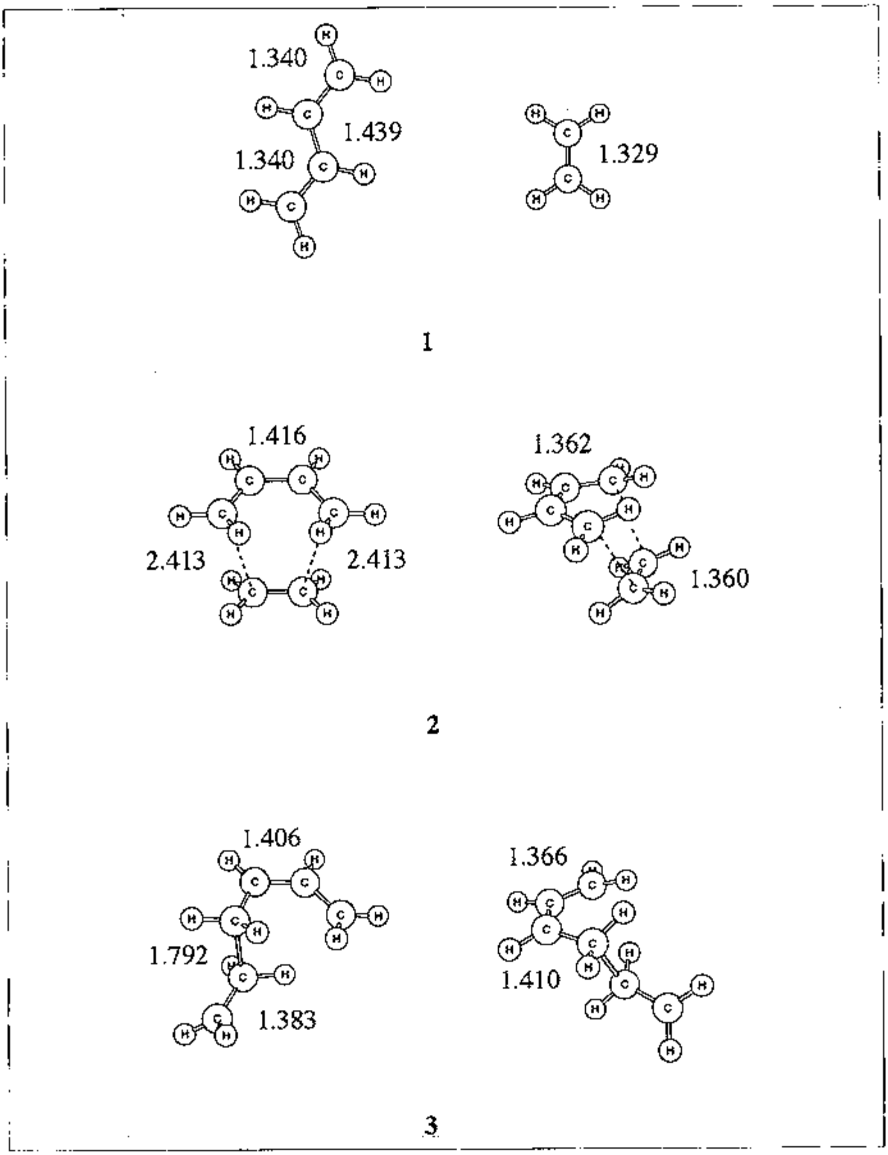


Figure 2. Optimized geometries for the reactants (above), the concerted transition structure (middle), and the stepwise transition structure (below). Bond lengths in Å

B. Concerted versus stepwise mechanisms

Previous studies indicated that there is a very small potential energy barrier, if any at all, for the closure of biradical intermediate when the radical centers are in a conformation where interaction is possible. Neither an asynchronous transition structure nor a biradical minimum are found when the methylene radical center in **3** is rotated syn-gauche to the allyl moiety. That is, when the two radical centers are located near each other, the only stationary points found are **2** and cyclohexene. As reported by Li and Houk (17), MCSCF optimizations starting from the UHF biradical in the syn-gauche conformation led to the boat cyclohexene, whereas a transition structure search at the CASSCF level starting with the UHF syn-gauche transition structure collapsed to the concerted synchronous transition structure **2**. There is no asynchronous concerted transition state but a vibrationally excited synchronous transition state. The only stepwise mechanism of the parent Diels-Alder reaction involves formation of an intermediate in the rate-determining step which is followed by rotation involving a second barrier accompanied by collapse with no further barrier to cyclohexene. Although we have not investigated this portion of the potential surface in detail, the fact that **1** is a minimum along with the well-known values of rotational barriers in hydrocarbons lead to this conclusion.

Molecule	ΔE^{a}	$\Delta E_{t}^{a,b}$	$\Delta H^{a,c}$	ΔS^{d}	$\Delta G^{a,c}$
1	0.0	0.0	0.0	0.0	0.0
2	1.9	5.0	4.5	-39.6	16.3
3	13.3	15.9	15.3	-40.5	27.4

[a] In kcal mol^{-1}
[b] Including ZPE and thermal corrections
[c] At 298.15 K
[d] In e.u.

Table 1. LDA calculated relative energies and entropic contributions for the Diels-Alder reaction of butadiene with ethylene.

As shown in Table 1, the concerted transition structure **2** is clearly more stable than **3**. This indicates that, at the present level of theory, the reaction is predicted to take place in a concerted fashion. The stepwise process is much less favourable because it involves a transition structure higher in energy by several kcal mol^{-1}.

C. DFT versus other post-HF methodologies

The correlation energy is especially important in the transition states because partially formed and partially broken bonds have larger correlation errors than fully formed bonds (14). Thus, the comparison will be made with regard to transition structures.

At the CASSCF/6-31G* level, the concerted transition structure **2** has been reported to be lower in energy than the stepwise transition structure by 1.9 kcal mol^{-1}. But regarding the CASSCF/6-31G* energy surface, the stepwise pathway is 0.5 kcal mol^{-1} below the concerted one, after adding zero-point energy (ZPE) corrections. The calculated activation entropy of the concerted transition structure **2** is 8 e.u. more negative than that of the stepwise transition structure, which favors the stepwise pathway in terms of lower activation free energy. Therefore, calculations at the CASSCF/6-31G* level predict a favorable stepwise pathway for the Diels-Alder reaction of butadiene with ethylene, which is in disagreement with experimental evidence.

To reproduce the correct behaviour, it is necessary to use more expensive techniques including dynamical correlation energy, such as QCI. Thus, it has been reported that single point energy calculations at the RQCISD(T)/6-31G* level with the CASSCF/6-31G* geometries predict the concerted transition structure **2** to be 10 kcal mol^{-1} more stable than the stepwise transition structure **3**. This RQCISD(T) method with a single determinant wave function offers a substantial improvement of the calculated relative energies as compared to RHF, CASSCF and MP2/MP4 methods, and can be taken as reference.

Regarding our LDA results, the concerted transition structure **2** is lower than the transition structure **3** by 11.4 kcal mol^{-1}. Unlike CASSCF calculations, when ZPE and thermal corrections are taken into account here, **2** is still more stable than **3** (by 10.9 kcal mol^{-1}). The calculated activation entropy of the concerted transition structure **2** is ca. 1 e.u. less negative than that of the stepwise transition structure, which slightly favours the concerted pathway in terms of lower activation free energy (11.1 kcal mol^{-1}).

These results provide interesting insights into the correlation energies of different species evaluated by means of different procedures. The concerted transition state may be considered to be more unsaturated than the transition state leading to an intermediate. That is, the concerted transition state has two partial σ-bonds, both quite long [LDA, 2.4 Å; QCI, 2.2 Å (17)], while the transition state leading to a diradical or zwitterionic intermediate has only one partial σ-bond, which is more fully formed [LDA, 1.8 Å; QCI, 1.8 Å (17)]. This is probably the reason why dynamical correlation energy, calculated either by QCI or by DFT, corrects the energy of the concerted transition state more than the energy of the stepwise transition state.

CONCLUSIONS

From a qualitative point of view, the calculations carried out at the DFT level of theory are reliable enough to offer a conclusive distinction among various mechanisms of the butadiene-ethylene reaction, and correctly predict their relative stability according to experimental data. When DFT calculations performed at the simple LDA level are compared to post-HF methodologies, it is found that they are quite advantageous because, without being so much expensive, they are able to yield accurate predictions as well. Both the QCI and DFT results (17) predict that the concerted pathway is lowest in energy, and indicate that other levels of calculation such as MCSCF (which do not include dynamical correlation energies) are not suitable since they overestimate the stability of biradical species relative to closed-shell species.

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