



Femtosecond dynamics of retro Diels–Alder reactions: the concept of concertedness

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Abstract

Using femtosecond-resolved mass spectrometry in a molecular beam, we report real-time studies of the retro Diels–Alder reactions of cyclohexene, norbornene and bicyclo[2,2,2]oct-2-ene. The experimental results and theoretical calculations elucidate the influence of conical intersections on ground-state reaction trajectories. We address the issue of concertedness on the actual time scale of the nuclear motion. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

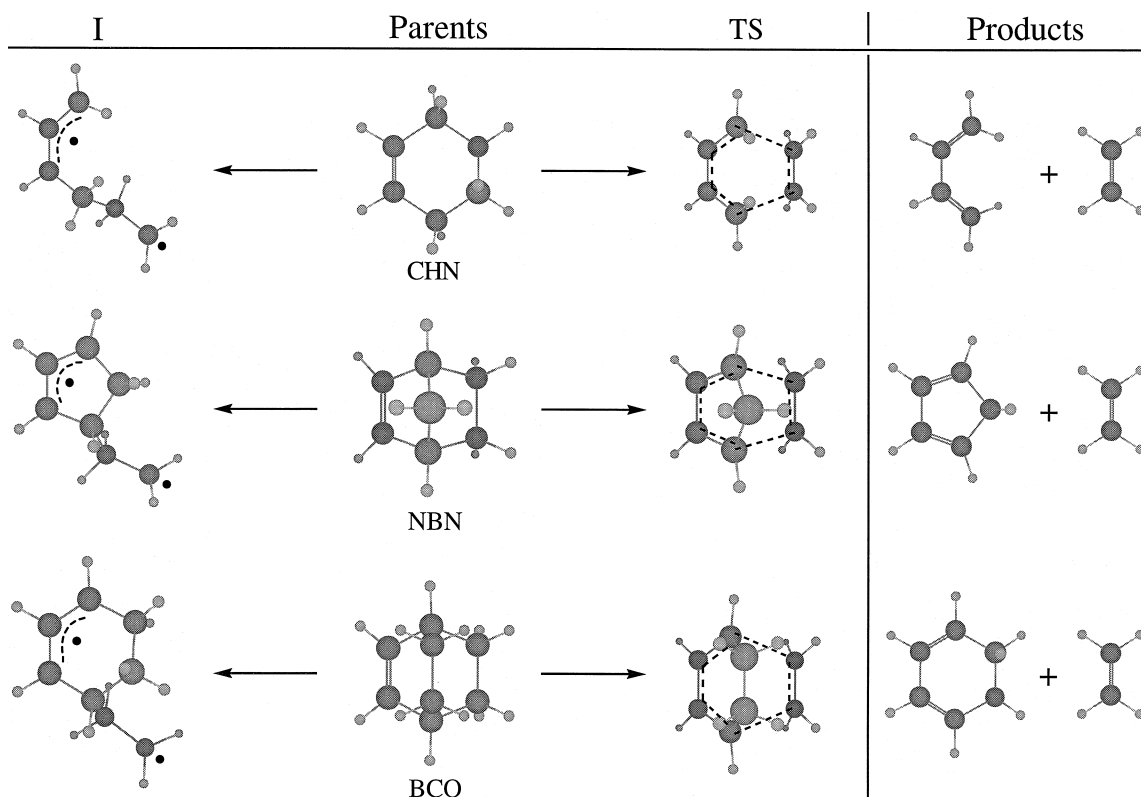
The Diels–Alder (DA) reaction, discovered in the 1920s [1,2], has become one of the most widely used methods in synthetic organic chemistry. The addition of ethylene to butadiene to form cyclohexene (CHN) is a well-known example (for a review, see Ref. [3]). Although the conservation of orbital symmetry [4,5] makes definite predictions regarding concertedness, the issue of concerted [6] vs. stepwise [7] mechanisms has been the subject of numerous studies and controversy [6–8]. Recent theoretical work, based on ab initio and density functional theory (DFT) calculations, has shown that the transition state (TS) located on the ground-state potential energy surface (PES) for the concerted reaction path is only a few

kcal/mol lower in energy than that for the stepwise path [9–11].

Earlier, we investigated the retro DA femtosecond (fs) reaction dynamics of norbornene (NBN) and norbornadiene and suggested that both concerted and stepwise trajectories are involved in the reaction [12]. In a recent comprehensive theoretical study by Wilsey et al. [13], the concerted and stepwise pathways were related to molecular structural changes and details of the PES for this 2 + 4 type reaction. For 2 + 2 addition reactions, the diradical species was experimentally observed, indicating a non-concerted pathway [14,15]. For the retro DA reaction of CHN, using photofragmentation translational spectroscopy in a molecular beam, a concerted dissociation path was suggested by Lee and coworkers [16].

In this Letter, we examine the fs dynamics of three systems: CHN, the classic Diels–Alder system, bicyclo[2,2,2]oct-2-ene (BCO), and, for comparison, NBN (Scheme 1). Fs-time-resolved mass spectrometry was employed to probe the dynamics. Theoretical

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Scheme 1. Molecular structures of parents, concerted transition states (TS), diradical intermediates (I), and the retro DA reaction products.

calculations of the ground-state PESs were performed, using the hybrid DFT approach.

2. Experimental and results

The experimental setup has been detailed elsewhere [17]. Briefly, the output of a colliding-pulse, mode-locked oscillator was amplified by a four-stage dye amplifier, pumped by a Nd:YAG laser. The output, after recompression by a four prism pair, was an 80 fs width (Gaussian) pulse. The pulse was split to provide the pump and probe beams. For the pump, the 615 nm output was frequency doubled. The probe beam was passed to a computer-controlled translation stage for the time delay. The time zero was measured in situ [17,18]. The two beams were spatially combined and were focused onto the supersonic molecular beam containing a time-of-flight mass spectrometer. By gating the signal due to a

particular ion, the temporal evolution of each species was measured. The excitation [19] involves a two-photon process ($E = 186$ kcal/mol), and the available energy is $E - D$, where D is the C–C bond energy.

Fig. 1A, B, and C show the fs mass spectra of CHN, NBN, and BCO, respectively. For CHN, there are three major peaks. The intense peak at 82 amu fits the signal of the parent or the diradical species after β -cleavage. The peaks at 67 amu and 54 amu represent the ion signals corresponding to the parent minus 15 (methyl group) and parent minus 28 (equivalent to an ethylene molecule) mass, respectively. The 94 amu signal of NBN represents the parent molecule or equivalent mass species (β -cleavage diradical) and the 66 amu signal corresponds to the parent minus 28 mass. The mass spectrum of BCO is also characterized by two peaks corresponding to the parent or β -cleavage intermediate (108 amu) and the parent minus 28 mass (80 amu).

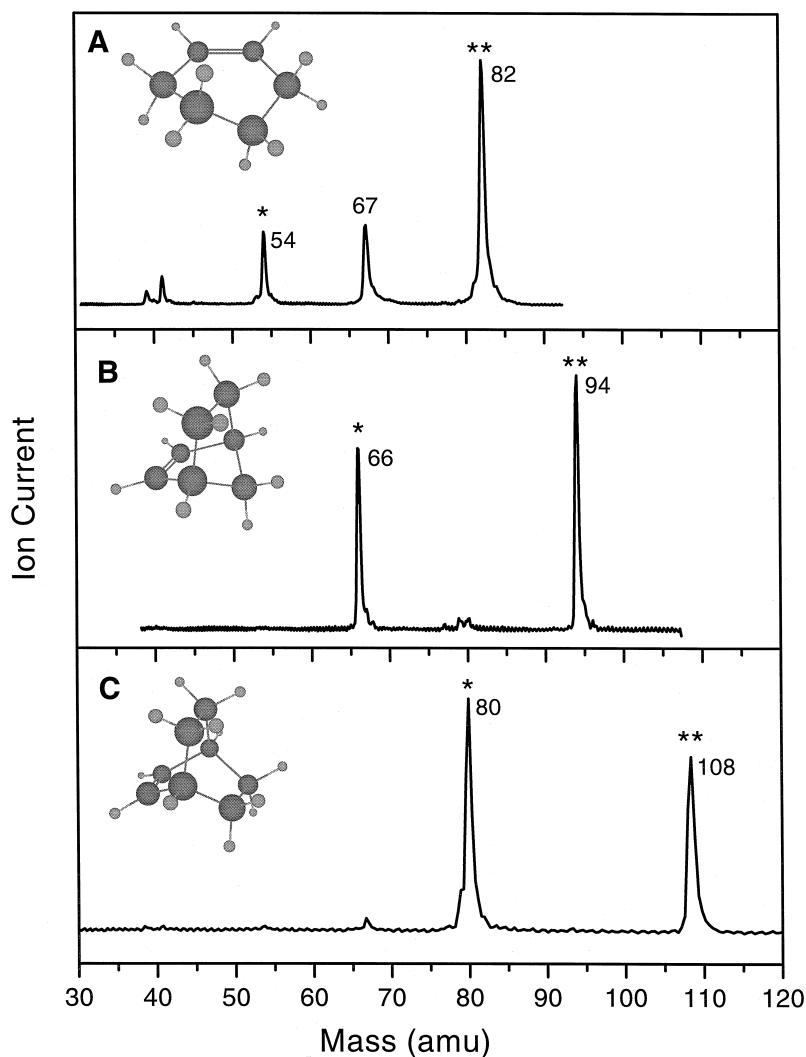


Fig. 1. The mass spectra obtained with fs pulses: the parent peaks (***) and fragment peaks (*) are marked: (A) cyclohexene (CHN); (B) norbornene (NBN); (C) bicyclo[2,2,2]oct-2-ene (BCO). The molecular structures are displayed on the left.

The fs transients of CHN, NBN, and BCO are shown in Fig. 2A, B, and C, respectively. All transients were described by a rise and decay component. The results are summarized as follows: (i) CHN: the precursor signal (82 amu) rises in less than 10 fs and decays in 225 ± 20 fs; the fragment signal (54 amu) rises in 15 ± 10 fs and decays in 150 ± 15 fs. (ii) NBN: the precursor signal (94 amu) rises in less than 10 fs and decays in 190 ± 10 fs while the fragment signal (66 amu) rises in 30 ± 15 fs and decays in 230 ± 30 fs. (iii) BCO: the precursor

signal (108 amu) also rises in less than 10 fs and decays in 190 ± 10 fs while the fragment signal (80 amu) rises in 15 ± 10 fs and has a similar decay time as the parent (185 ± 10 fs).

3. Discussion

3.1. Concerted vs. non-concerted pathways

The above results indicate several important points. First, the transient of the reaction fragment is

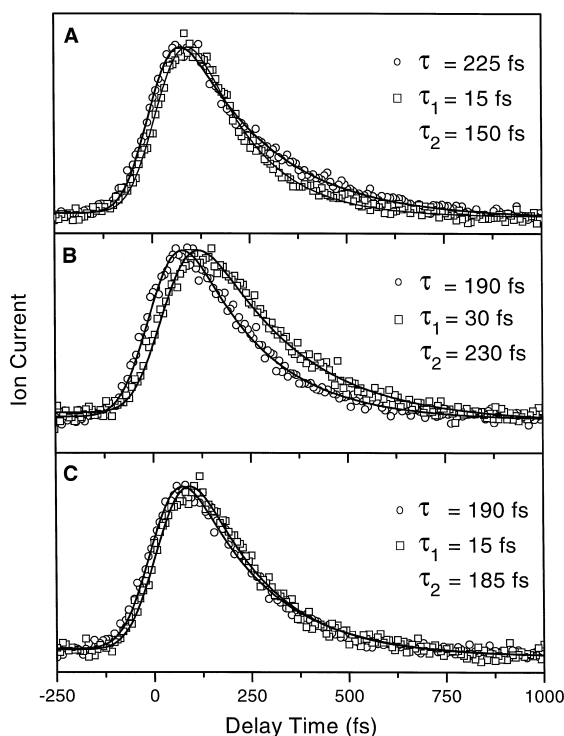


Fig. 2. fs transients of the parents (\circ) and the fragments (\square): (A) CHN; (B) NBN; (C) BCO. τ , τ_1 and τ_2 are defined in the dynamics model (see text).

different from that of the parent, indicating the distinct dynamics of the neutrals, i.e., not due to fragmentation of the parent ion. Second, the fragment signal appears within 10 to 30 fs, inconsistent with the decay of the parent signal in 190 to 230 fs. Third, the fragment transient decays in ~ 150 –230 fs, instead of building up with time and reaching a plateau, indicating that they are not final products (Scheme 1). These observations support the idea that the parent and the fragment transients are from different trajectories, as pointed out in our previous communication [12]. As discussed below, the transient of the parent mass reflects the dynamics of the intermediates taking part in the stepwise reaction path. The transient of the fragment reflects those trajectories following a rather concerted, asynchronous reaction path. Therefore, both concerted and stepwise trajectories can be rationalized through the direct observation of the fs dynamics of fragment and parent species.

We illustrate such concepts by considering the possible trajectories of the reaction. Fig. 3 is a representation of the two-dimensional ground-state PES of CHN. Both pure concerted (synchronous) ($R_1 = R_2$, dashed line) and stepwise ($R_1 \neq R_2$, solid lines) reaction paths are shown. Many more trajectories, partly concerted and stepwise in nature, are possible. Evidence for the existence of these so-called transient configurations has been shown both experimentally [20] and theoretically [21] for an ABA system involving three atoms with well-defined PES topology for the breakage of two bonds. For organic reactions with many degrees of freedom one must consider the nature of the initial wave packet and how it propagates to the reactive coordinate(s).

Normally at high energies the initial state involves either a σ^* type promotion or a π^* one. For the former, the breakage of a C–C bond is due to direct repulsion with the diradical structure being formed typically in 10 s of fs. We note that the strict correlation rules for σ and σ^* orbitals of H_2 will be relaxed in polyatomics due to the topology of the system [22]. If, however, the π system is involved, the energy can be lowered considerably through conical intersections (CI) which are much more probable at high energies; the π^* is lowered while the π is increased in energy as the reaction coordinate changes. This simple description on the basis of σ or π interaction is the origin of ground-state thermal chemistry for many systems when molecules are photolyzed at high energies [23]. The CIs (funnels) are an effective means of populating the ground state, and, in fact, experiments in this laboratory have provided evidence for such dynamics on the fs time scale [18,24,25]. Recent CASSCF calculations of NBN by Wilsey et al. [13] revealed the existence of an S_0/S_1 CI corresponding to a molecular configuration which is highly asymmetrical and diradicaloid in nature. Based upon the similarity of the electronic structure of the molecules under investigation, surface crossing point(s) on the PES for CHN and BCO are also anticipated.

The dynamics can now be elucidated. The wave packet in Fig. 3 proceeds directly in the concerted and non-concerted channels, following the description of trajectories given in Ref. [21]. Under σ^* type excitation, both trajectories must be considered. On the other hand, if the CI is reached, as in NBN, then

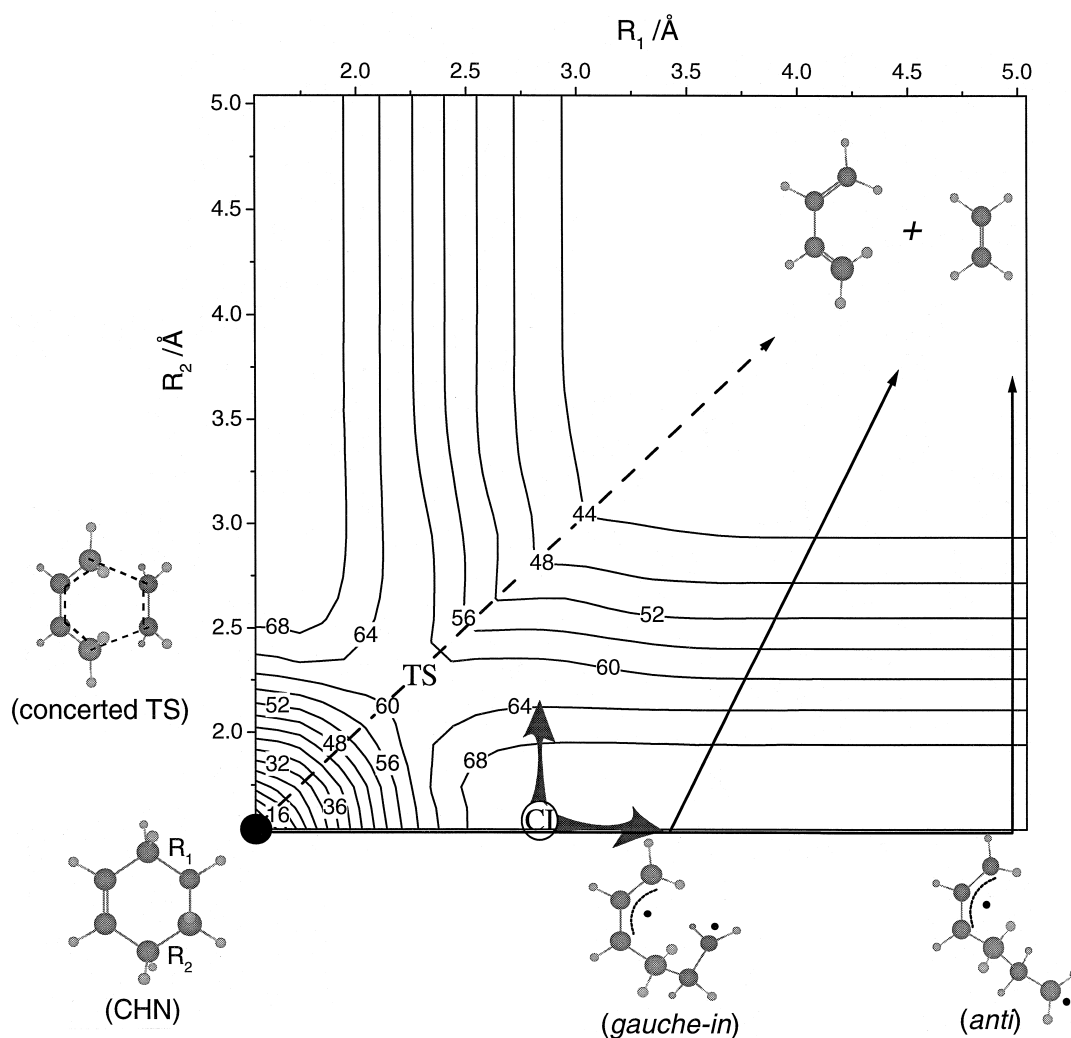
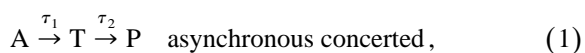


Fig. 3. Representative two-dimensional PES of CHN with contour values representing the relative energies in kcal/mol. R_1 and R_2 are the coordinates defined by the β -CC bond cleavages. Note that the molecular structures involved are not planar and that the multidimensionality of the PES is not shown; i.e. the reaction coordinate does not only involve the lengthening of the β -CC bonds but also other degrees of freedom such as rotations. The initial wave packet in the Franck–Condon region is shown on the lower left corner. The dashed trace represents a concerted reaction path whereas the solid one follows a stepwise reaction path. The projection of a conical intersection as predicted for NBN [13], is also indicated. The heavy arrows represent possible initial directions of the trajectories funneling from CI.

funneling will lead to two types of trajectories, the diradicaloid type and the concerted-asynchronous type (Fig. 3). Starting from this particular point on the ground-state surface, the trajectories spread out on the PES. Those trajectories crossing or following the concerted-like reaction path can be probed by the ionizable species of the fragment mass, whereas those following a stepwise reaction path are observed on the parent mass signal.

3.2. Dynamics model

Based upon the mechanism of the previous section, we consider the trajectories for the following two steps:



Reactions (1) and (2) describe the concerted and stepwise retro DA reaction mechanism, respectively. In reaction (1), A represents the particular population of excited parent molecules which leads to those ground-state transient configurations (T) following

asynchronous concerted pathways on their way to the final products (P). τ_1 is the time constant for the wave packet moving from A to T, which may involve two different dynamical processes: (i) direct bond breakage on a repulsive excited-state surface

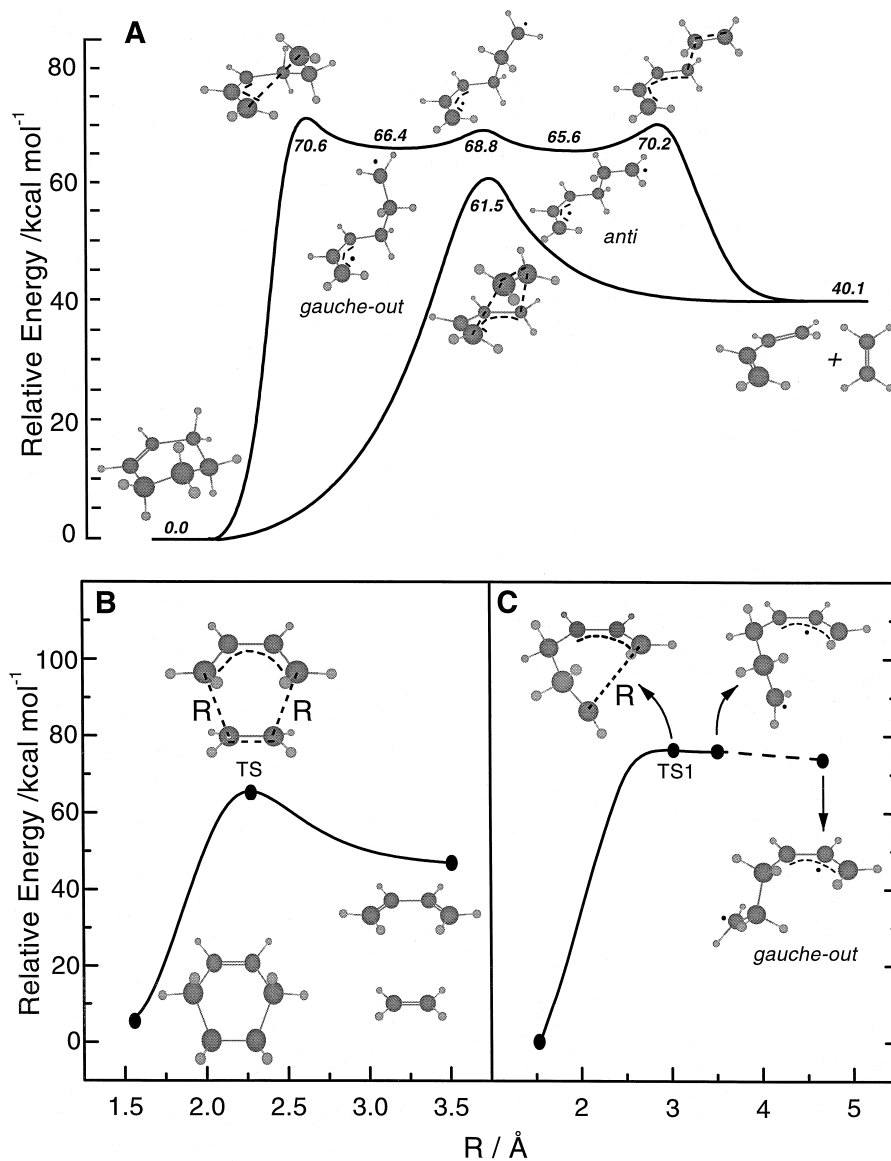


Fig. 4. (A) Ground-state PES of CHN performed at the B3LYP/6-31G(d) level of theory and including zero-point energy (ZPE) corrections. (B) Minimum energy pathway (MEP) with C_s symmetry predicted by intrinsic reaction coordinate (IRC) calculations along the synchronous concerted reaction coordinate (R). (C) MEP predicted by IRC calculations for the first β -CC bond-cleavage process along the stepwise reaction path. Due to the flatness of the PES, the IRC calculations stopped at a point corresponding to the geometry shown in the upper right part of the figure. Optimization of this geometry leads to a *gauche-out* diradical intermediate. Note that both MEPs shown in (B) and (C) represent 'classical' potential energies without ZPE corrections.

after a $\pi\text{-}\sigma^*$ type transition ($\tau_1 \leq 10$ fs); (ii) searching for and funneling through the CI after a $\pi\text{-}\pi^*$ type transition ($\tau_1 > 10$ fs). τ_2 reflects the ground-state, asynchronous concerted dynamics of the transient species to form final products. For reaction (2), A' represents the population of excited parent molecules leading to ground-state diradicaloid inter-

mediates (I), which are characterized by a local minimum on the ground-state PES. These intermediates follow a stepwise reaction path leading to final products (P). τ' represents the time it takes from A' to I via either a repulsive excited-state surface or a CI (in both cases, $\tau' \leq 10$ fs). τ' is expected to be very short because both processes lead directly to the

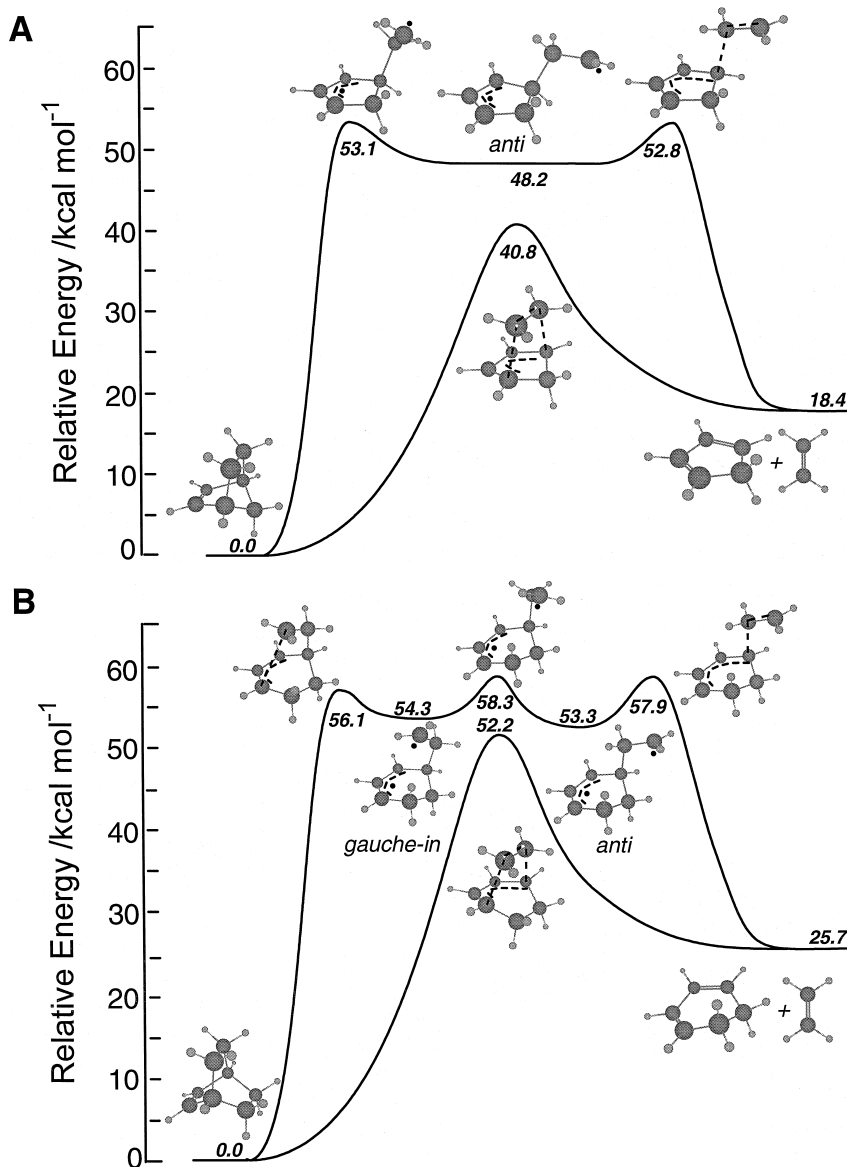


Fig. 5. Ground-state PES of (A) NBN and (B) BCO performed at the B3LYP/6-31G(d) level of theory and including ZPE corrections. Both concerted and stepwise reaction paths are shown.

diradicaloid intermediates. τ is thus the lifetime of I following the stepwise reaction path to form P on the ground-state PES.

The concerted path of the retro DA reaction has several interesting features. We compare the concerted-path trajectories of CHN and NBN: the former disappears in 150 fs whereas the latter does so in 230 fs, even though the energy barrier of the concerted TS of CHN is ~ 20 kcal/mol higher than that of NBN, due to the larger ring-strain energy of the latter (Figs. 4 and 5). This behavior suggests that the dynamics are not controlled by the energetics of the barriers and that the concerted TS is not effectively involved, either because of the repulsive force in the excited state σ bonds or the location of the CI, which is close to the diradicaloid intermediate (Fig. 3). Thus, the nuclear rearrangements and electronic hybridization are key factors in the dynamics on the fs time scale. Along the concerted reaction path, the nuclear motion of the 54 amu species of CHN involves only rotations about the terminal carbons for the final formation of butadiene. For NBN, in addition to these motions, the formation of planar cyclopentadiene involves the bending of the additional CH_2 -group (bridgehead). The butadiene formation along the concerted reaction path should hence be faster than that of cyclopentadiene, as observed here.

Although the nuclear motion of the 80 amu species of BCO involves one more CH_2 group, compared to NBN, we observed faster dynamics for BCO along the concerted reaction path. One also notices that both parent and fragment transients of BCO are very similar for the decay component but slightly different for the rise component (Fig. 2C). This observation suggests that both stepwise and concerted trajectories in BCO are strongly coupled, which can be rationalized in terms of the topological features of the PES (Fig. 5B). The difference in potential energy between the concerted and stepwise reaction paths of BCO is small, e.g., 1.1 kcal/mol between the concerted TS and the stepwise I. Such stepwise-concerted coupling should be much weaker for the NBN reaction because the energy difference between both reaction paths (7.4 kcal/mol) is much more pronounced than that of BCO (Fig. 5).

Regarding the stepwise reaction path, the intermediate decay time (τ) of CHN (225 fs) is longer than

that of NBN and BCO (190 fs). Based upon the PESs shown in Figs. 4 and 5 and the excitation energy (186 kcal/mol), the available internal energies for the CHN, NBN, and BCO diradicaloid intermediates are 120, 138, and 133 kcal/mol, respectively. However, as shown elsewhere the energy factor is not the dominant force driving the dynamics when the PES with respect to different conformations is rather flat (entropy effect) [15,26]. Indeed, the CHN diradical has a flexible open-chain structure, in contrast to the NBN and BCO diradicals with their more rigid closed-ring moiety. Such increased entropic configurations lead to a longer lifetime for the CHN intermediate. The almost size-independent dynamics for all the parent diradicals studied also indicates that the second β -CC bond-cleavage process is non-statistical, i.e., the redistribution of the available energy is highly directed into the bond-breakage process [27].

4. Potential energy surfaces

The ground-state PESs were characterized using the B3LYP hybrid functional [28,29] and the 6-31G(d) basis set. The reactants, diradical intermediates, TSs, and products were fully optimized. Frequency calculations were performed for all optimized species in order to determine the nature of stationary points and to obtain zero-point energy (ZPE) corrections. To confirm that the TS is the correct saddle point connecting two local minima, intrinsic reaction coordinate (IRC) calculations were further performed [30,31]. The restricted method was used for all closed-shell species while we employed the unrestricted method for the open-shell species [32]. All calculations were carried out using GAUSSIAN 94 [33].

4.1. PES of CHN

Both concerted and stepwise reaction paths of CHN on the ground-state PES are shown in Fig. 4A. First, the results indicate that the energy of the TS in the concerted path is lower by 4.1 kcal/mol than that of the intermediate in the stepwise path. Second, the diradical type intermediates are located on a flat region of the PES (rotation about the single CC

bonds is nearly free), with an energy barrier of ~ 5 kcal/mol for both β -CC bond-breaking processes. In addition to reproducing the results of Houk and coworkers [9] using the same DFT approach, we have performed more extended calculations as discussed below.

The IRC calculations for the minimum energy pathway (MEP) of the concerted reaction path (Fig. 4B) show that although both the reactant and the product have C_2 symmetry, they are connected through a MEP with C_s symmetry. The C_2 MEP involving a half-chair TS is much higher in energy (~ 50 kcal/mol) than that of the C_s MEP [11], which is fully consistent with the description of the Woodward–Hoffmann rules for the symmetrical DA reactions [4,5]. This was further examined by recent high-level ab initio calculations based on the spin-coupled valence-bond approach which revealed that the electronic structure of the concerted TS is highly aromatic, resembling that of benzene [34].

The first step involved in the stepwise mechanism of the retro DA reaction is a simple β -CC bond-breaking ring-opening process. Such a process is expected to have a small reverse energy barrier owing to the stabilization by allylic resonance and the release of ring strain. However, recent DFT studies did not describe this process due to the difficulty of locating a TS on a near flat surface [3,9]. We have found a MEP corresponding to such process, as shown in Fig. 4C. The MEP describing the ring-opening process is characterized by a saddle point (TS1) – the two carbon atoms involved in the β -CC bond cleavage are separated by 2.95 Å – which lies 70.6 kcal/mol above the CHN minimum. The C_2 CHN minimum was obtained by following the IRC starting from TS1 towards the reactant side. Following the MEP to the other side, a *gauche-out* diradical intermediate was obtained after reoptimization of the IRC end point geometry (upper right structure in Fig. 4C).

The *gauche-out* intermediate may easily rotate about the second β -CC single bond to form other conformers, like *anti* and *gauche-in*. Following this rotational path, the *anti* intermediate was obtained with a relative energy of 65.6 kcal/mol. However, there was no evidence for a stable *gauche-in* structure using the theory currently studied, as pointed out previously [3,9]. The lack of a stable *gauche-in*

intermediate suggests that there is no pronounced energy barrier between the stepwise pathway involving the *gauche-in* intermediate and the concerted reaction path on the global ground-state PES. Finally, the reaction path in the stepwise mechanism may follow the second β -CC bond-breakage reaction coordinate to form the final products from either the *gauche-out* or *anti* intermediate, with an energy barrier calculated to be 5.5 (not shown) and 4.6 kcal/mol, respectively.

4.2. PES of NBN

The ground-state PES of NBN is shown in Fig. 5A. These results reproduce the recent calculations by Wilsey et al. [13] at the same level of theory. The energies of both concerted and stepwise paths are ~ 20 kcal/mol lower than those of CHN due to the larger strain energy for NBN. The concerted TS lies 7.4 kcal/mol below its *anti* diradical intermediate. Again, no stable *gauche-in* diradical intermediate was successfully located on the stepwise reaction path for reasons similar to those given for CHN.

4.3. PES of BCO

Both concerted and stepwise mechanisms for BCO (Fig. 5B) were studied using the similar strategy as for CHN and NBN. The concerted TS with C_s symmetry is located 52.2 kcal/mol above the BCO minimum. For the stepwise reaction path, the most striking feature is that a stable *gauche-in* diradical intermediate was successfully located using the current DFT approach. This *gauche-in* intermediate, with a relative energy of 54.3 kcal/mol, has an energy barrier of 1.8 kcal/mol for ring closure. Attempts to stretch the second β -CC bond of the *gauche-in* intermediate to obtain the bond-breaking TS were not successful and eventually a concerted TS was obtained. The rotational barrier for the *gauche-in* intermediate forming the *anti* intermediate with 53.3 kcal/mol is calculated to be 4.0 kcal/mol. The second β -CC bond cleavage of the *anti* intermediate forming the final products (1,3-cyclohexadiene and ethylene) on the stepwise reaction path requires 4.6 kcal/mol, which is exactly the same value predicted for both CHN and NBN. It is worth noting that the energy difference between the

concerted TS and the *anti*-intermediate is only 1.1 kcal/mol.

5. Concluding remarks

Time scales of nuclear motion are crucial to distinguishing between concerted and stepwise reaction mechanisms. If the rotational motion of the entire molecule is invoked as a clock, this rotation, which takes a few ps, will make a reaction involving multiple bond breakages or formations (< 1 ps) appear to be concerted. However, as pointed out elsewhere [24,35], the correct criterion must address the nuclear motions in relation to the time scale of the reaction coordinate. Only when real-time dynamics of the intermediate is available can we address such a concept of concertedness.

The measured ~ 200 fs reaction time indicates the presence of intermediate structure capable of vibrating many times before bond breakage; the time for C–C vibration is ~ 30 fs. Use of the operational limit of transition-state theory will imply the absence of such intermediates. Furthermore, these time scales of the nuclear motion are of underlying importance for the stereochemistry of the reaction. The retention of the stereochemistry in the Diels–Alder reaction is a direct consequence of the femtosecond dynamics. As discussed elsewhere [15], the specific bond breakage time and the rotation time of the bond involved are the determining factors.

Acceptance of one mechanism over the other has to be handled with extreme care. The reaction trajectories on the global ground-state PES need to be considered in order to relate the topology and energetics to the dynamics. The reaction does not only follow the pure stepwise and concerted trajectories, but the trajectories involve many other transient configurations determined by the topology of the PES. However, in general we identified two major pathways with simple predictions based on TS locations. We suggest that both trajectories are present and that the asymmetry of the molecular structure, the location of the transition state(s) and the barrier height are the controlling factors for the bifurcation of trajectories involving diradicaloid and concerted transition-state structures.

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