

Femtosecond dynamics of hydrogen elimination: benzene formation from cyclohexadiene

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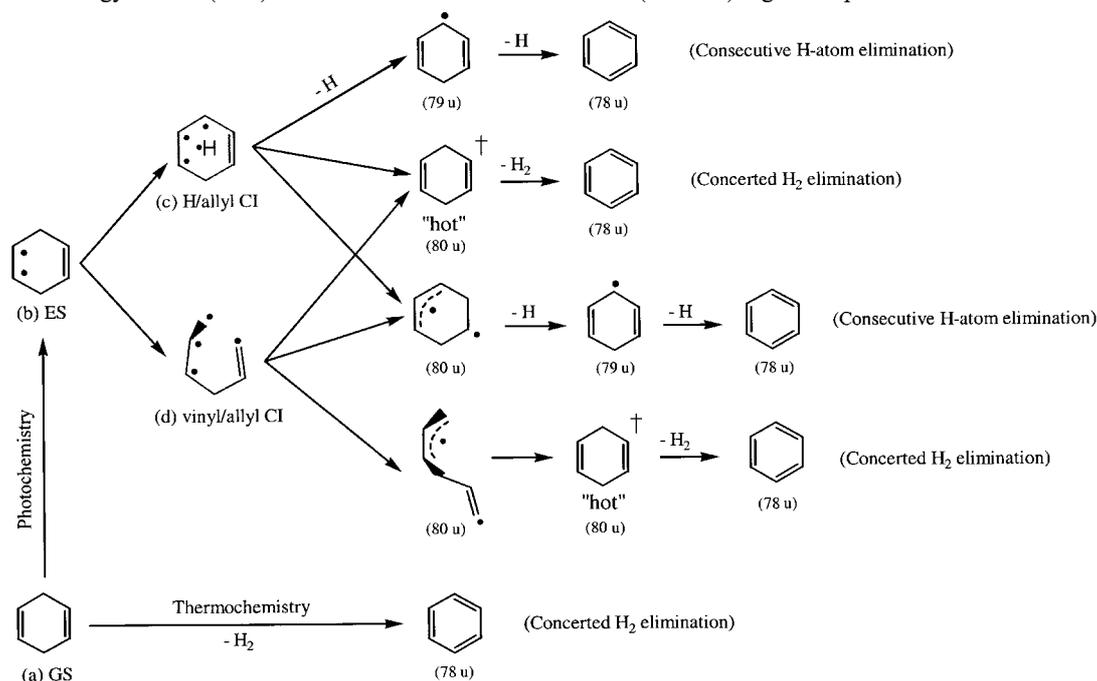
Using femtosecond-resolved mass spectrometry in a molecular beam, we report real-time study of the hydrogen elimination reaction of 1,4-cyclohexadiene. The experimental observation of the ultrafast stepwise H-elimination elucidates the reaction dynamics and mechanism. With density-functional theory (ground-state) calculations, the nature of the reaction (multiple) pathways is examined. With the help of recent conical-intersection calculations, the excited-state and ground-state pathways are correlated. From these experimental and theoretical results we provide a unifying picture of the thermochemistry, photochemistry and the stereochemistry observed in the condensed phase.

1. Introduction

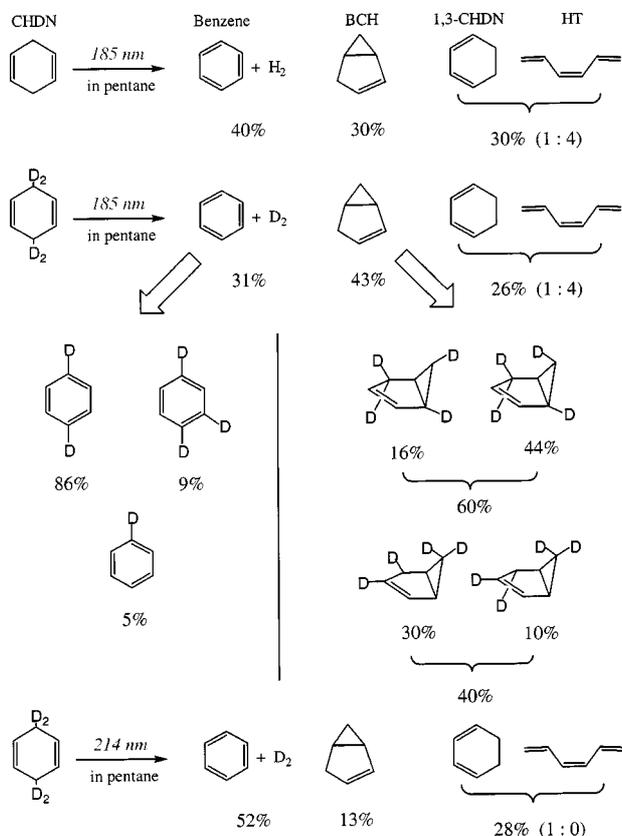
In complex reactions, product formation comprises multiple pathways which may involve transition states and transient intermediates with lifetimes vastly different from the rotational and vibrational periods. In this laboratory, we have studied the elementary dynamics of these transition states and intermediates with femtosecond (fs) time resolution in a number of complex reactions. These include: α -cleavage reactions of linear^{1,2} and cyclic ketones,^{3–5} β -cleavage dynamics in cyclic ethers,⁶ nitrogen extrusion reactions^{5,7} and retro-Diels–Alder reactions and H-shift reactions.^{8,9} The studies of the fs dynamics of these radicaloid (diradicaloid) intermediates are critical for the understanding of the stereochemistry and for the reaction mechanism—the concerted or consecutive nature of the reaction and the multiple pathways possible on the global potential energy surface (PES).

Hydrogen elimination is common in organic chemistry, and one of the classic examples known is the reaction of 1,4-cyclohexadiene (CHDN) to form benzene and molecular hydrogen; the major reaction products both by thermolysis^{10–13} and photolysis.^{14–20} Two general mechanisms are possible, one involves a concerted release of molecular hydrogen in a one-step process and the second is a consecutive elimination of two hydrogen atoms (Scheme 1). The consequence of each on stereochemistry is dramatic, as discussed below.

Lee and co-workers¹⁶ have studied the photochemistry of CHDN using photofragmentation translational spectroscopy in a molecular beam at a total energy of 147 kcal mol⁻¹ (193 nm). In their time-integrated investigation, the signal at 79 u, which corresponds to the intermediate with the mass of one hydrogen atom less than the parent molecule (80 u), was not observed. However, the successful simulation of the observed 78 u (benzene) signal required the involvement of both the



Scheme 1 Concerted and consecutive hydrogen elimination.

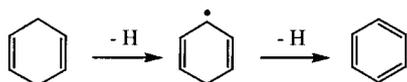


Scheme 2 Stereochemistry in solution—experimental results.¹⁵

concerted H₂-elimination and the stepwise H-elimination processes. They suggested that H₂ moves away from the transition state complex with a helicopter type motion^{17,18} and that this concerted H₂-elimination process occurs on the nanosecond time scale. From the infrared-multiphoton dissociation (IRMPD) studies of CHDN, both Lee and co-workers¹⁶ and Kumar *et al.*¹⁹ concluded that the concerted H₂-elimination process occurs on the ground-state PES.

In the condensed phase, there are other products formed. In addition to benzene, a considerable amount of 1,3-cyclohexadiene (1,3-CHDN), bicyclo[3.1.0]hex-2-ene (BCH) and 1,3,5-hexatriene (HT) have been observed.¹⁵ Srinivasan *et al.* have thoroughly studied the organic photochemistry of CHDN in pentane solutions and compared its reactivity with 1,4-cyclohexadiene-3,3,6,6-d₄ (CHDN-d₄).¹⁵ Scheme 2 shows an overview of the product branching ratios and the stereochemistry of CHDN and CHDN-d₄. Their study revealed a number of important points concerning the isotope effect and the stereochemistry. First, when photolyzed at 185 nm, CHDN produces relatively more benzene than BCH, but for CHDN-d₄ this tendency is reversed. Second, by careful product analyses, *via* NMR spectroscopy, the authors clarified the presence of four BCH stereoisomers with different product yields. Third, the photochemistry of CHDN-d₄ involves three different isomers of benzene in different yields, *i.e.*, 86% of benzene-1,4-d₂ (bzn-d₂), 9% of benzene-1,2,4-d₃ (bzn-d₃) and benzene-d₁. Finally, when photolyzed at 214 nm, the product yields are much different from those at 185 nm, which demonstrates a strong wavelength dependency of the chemistry.

In this paper, we report real-time studies of the hydrogen-atom elimination of CHDN using fs resolved mass spectra and transients. The presence of H one-step elimination as an intermediate, hitherto unobserved, supports the consecutive elimination on the femtosecond time scale:



We also report calculations of the ground-state PES, obtained using density functional theory (DFT), in order to compare with the different experimental results. Recent high-level *ab initio* calculations of Wilsey and Houk²¹ have found two conical intersections (CI), which as described below are important for the different excited-state pathways. The experimental and theoretical findings are related to the stereochemistry of the intermediates and provide quantification of the product branching ratios observed in condensed phases.

II. Methodology: experimental and theoretical

The fs laser and molecular beam apparatus have been described in detail elsewhere.²² Briefly, the output of a colliding-pulse, mode-locked oscillator (CPM) was amplified in a four-stage dye amplifier, pumped by a Nd:YAG laser. The output, after recompression by a four prism pairs, was a 80 fs width (Gaussian) pulse with an intensity of $\sim 200 \mu\text{J pulse}^{-1}$ at 615 nm. The pulse was split to provide the pump and probe beams. For the pump, the 615 nm output was frequency doubled by a potassium dihydrogen phosphate (KDP) crystal to give a 307 nm pulse which was isolated by a band-pass filter. The probe beam, 615 nm, was passed to a computer-controlled translation stage for the time delay with respect to the pump beam. The instrumental response function was determined by the *in situ* measurement.^{22,23} The CHDN sample (97%) was obtained from Aldrich and the mass spectrum confirms the purity (Fig. 1). In order to avoid the formation of clusters, CHDN was cooled to -15°C and the pulse valve was operated at 100°C . The excitation is at $E = 186 \text{ kcal mol}^{-1}$.²⁴

Fig. 1A shows the fs mass spectrum of CHDN. The main peak corresponds to the parent mass (80 u). The peaks at 79 and 78 u correspond, respectively, to those species with one and two hydrogen atoms less. The transients of these mass signals are shown in Fig. 1B (80 and 79 u) and Fig. 1C (80 and

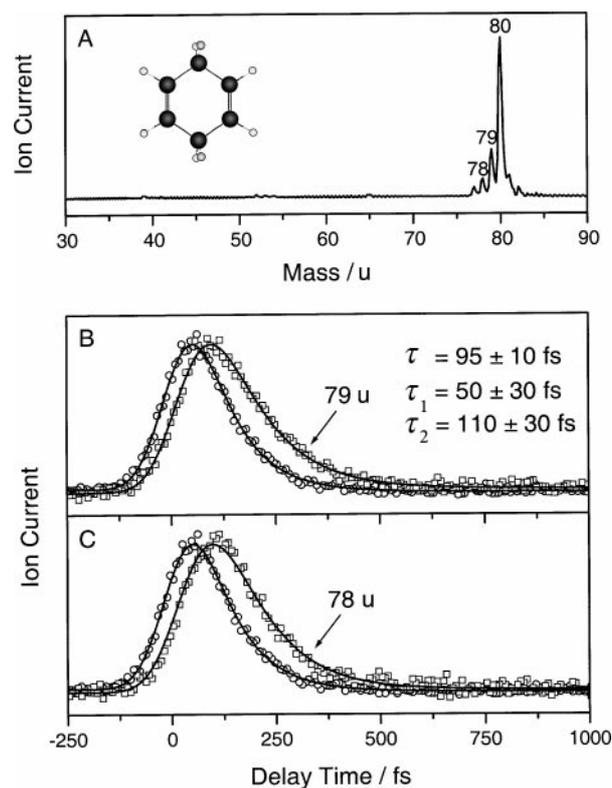


Fig. 1 (A) Femtosecond mass spectrum of CHDN. (B) Parent (○) and 79 u (□) transients. (C) Parent (○) and 78 u (□) transients. The theoretical fits are represented as solid curves in (B) and (C) with the fitted time constant τ representing the decay time of the parent, and τ_1 and τ_2 the rise and decay times of the intermediate species.

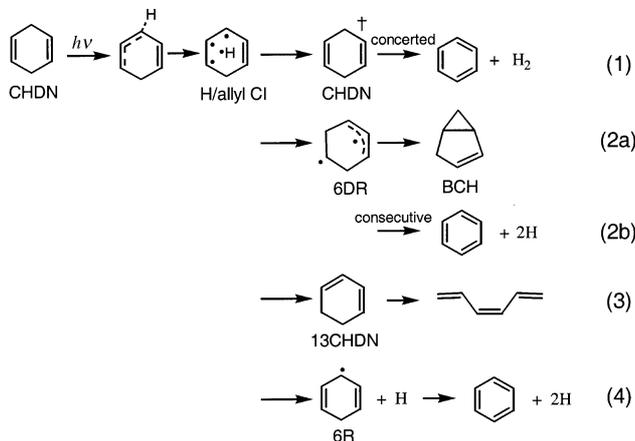
78 u). The transient for 80 u decays in $\tau = 95 \pm 10$ fs and is distinct from the intermediates. The transients of the 79 and 78 u species are similar. They are characterized by a rise time of $\tau_1 = 50 \pm 30$ fs and a decay time of $\tau_2 = 110 \pm 30$ fs. The common dynamics observed for both 79 and 78 u species indicates that the 78 u signal is due to ion fragmentation from the 79 u species.

The ground-state PES of CHDN is characterized by the B3LYP hybrid functional,^{25,26} with the 6-31G(d) basis set.²⁷ The reactants, diradical intermediates, transition states 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 corrections. The restricted B3LYP/6-31G(d) method was used for all closed-shell species and the unrestricted method for open-shell species. To confirm that the TS is the correct saddle point connecting two local minima, intrinsic reaction coordinate (IRC) calculations were further performed. Based upon the linear response theory for the time-dependent (TD) DFT calculations,²⁸ the vertical electronic excitation spectrum of CHDN (D_{2h} symmetry) was predicted using the B3P86 hybrid functional^{25,29} and a 6-311++G(d,p) basis set at the ground-state equilibrium geometry. All calculations were carried out using GAUSSIAN 94 and 98 packages.³⁰

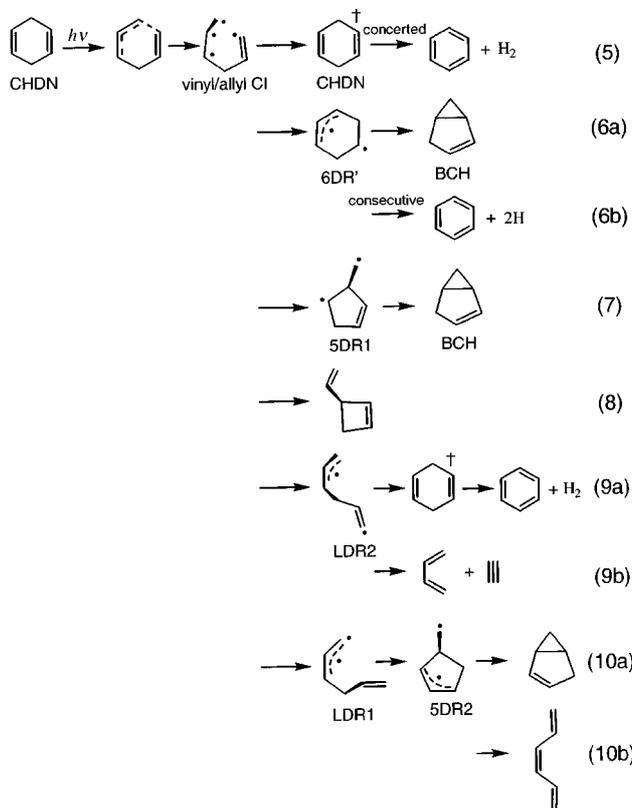
Based upon the time-dependent DFT calculations, which will be detailed elsewhere, the excitation after absorbing two photons at 307 nm ($186 \text{ kcal mol}^{-1}$) involves only the B_{1g} state (a $\pi\text{-}\pi^*$ type transition, $172 \text{ kcal mol}^{-1}$), provided the molecule maintains a center of inversion. Vibronic coupling can also allow for the excitation of the allowed B_{3u} state (a $\pi\text{-}\pi^*$ type transition, $180 \text{ kcal mol}^{-1}$),²⁴ via a bending motion. The latter case may involve a very important dynamical effect on the excited-state PES, which facilitates the conical intersection (CI) and the funnel through such CI to reach the ground-state PES.

III. Discussion

The results obtained from recent high-level *ab initio* calculations²¹ indicate that for CHDN there are two types of S_0/S_1 CI involved. The H/allyl CI has a nearly planar six-membered ring structure with an H atom bridged across three carbons above the plane. On the other hand, the vinyl/allyl CI has an open-chain, asymmetrical and bent structure. Following these CIs to the ground state, several reaction channels may be predicted, as shown in Schemes 3 and 4. We suggest that the driving force for leading to a particular CI should be related to the excitation wavelength (see below), and the preference is determined by the vibrational motion of the molecule in the initial excited state. For example, the asymmetrical CH bending/stretching motion could lead to the H/allyl CI whereas the initially favored out-of-plane bending motion would facilitate the vinyl/allyl CI.



Scheme 3 Possible reaction channels involving H/allyl CI.



Scheme 4 Possible reaction channels involving vinyl/allyl CI.

Since the CI is an effective mean of populating the ground state, the reaction products and branching ratios on the ground-state PES are conditioned by the trajectories initiated by the funneling and the topology of the PES. The fs dynamics of CI in a number of systems has recently been reported from this laboratory.^{7,9,23} Scheme 1 describes the most important elementary steps involved in concerted/consecutive hydrogen elimination processes based on our theoretical and experimental findings. Upon excitation of CHDN (a), the structure (b) is on its way to the conical intersection, which is either a H-bridged four-center radical species (c), H/allyl CI or a CC-cleaved four-center radical species (d), vinyl/allyl CI. The conventional wisdom is that the excitation species (b) converts into a hot ground state of CHDN, followed by hydrogen molecule elimination. However, we found that the CIs are crucial in populating the hot ground state of the diradical species, which proceeds to eliminate hydrogen by consecutive or concerted routes (Scheme 1). Our results explain the stereochemistry, branching of products, energetics, and significantly the formation of three- and five-membered ring bi-cyclic compounds¹⁵ from structures (c) and (d). The ultrafast stepwise H-elimination mechanism is detailed in the following sections.

A. Consecutive H- and concerted H₂-elimination

1. Consecutive H-elimination. The transient of the 79 u species is different from the parent one: ion fragmentation of the 80 u species is not dominant. Therefore, the dynamics of the 79 u species demonstrate the existence of a consecutive reaction channel for H-elimination at our excitation energy. Unlike the internal conversion picture, the species at the CI structure (c) or (d) will funnel in within a vibrational period (10–100 fs)^{5,9,31–34} to form the 79 u species, the hot CHDN molecule, or the diradical intermediates (Scheme 1). The most efficient way to eliminate the first H atom is to funnel through the H/allyl CI, directly forming the 79 u species in the observed ~ 50 fs and then the species eliminates the second H

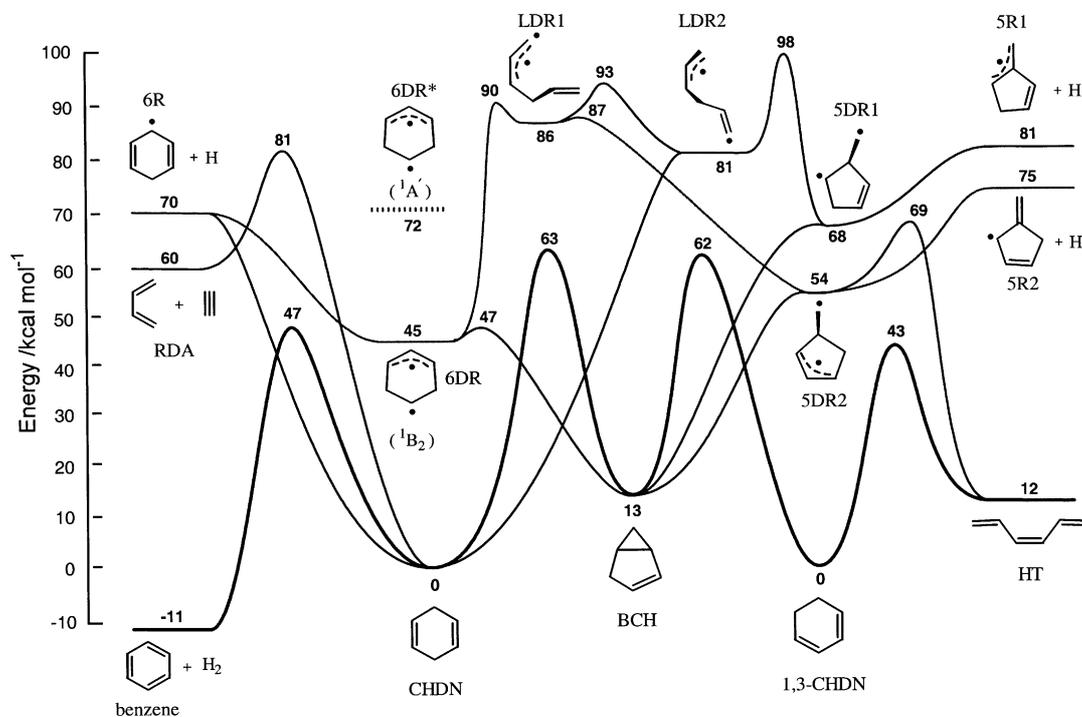
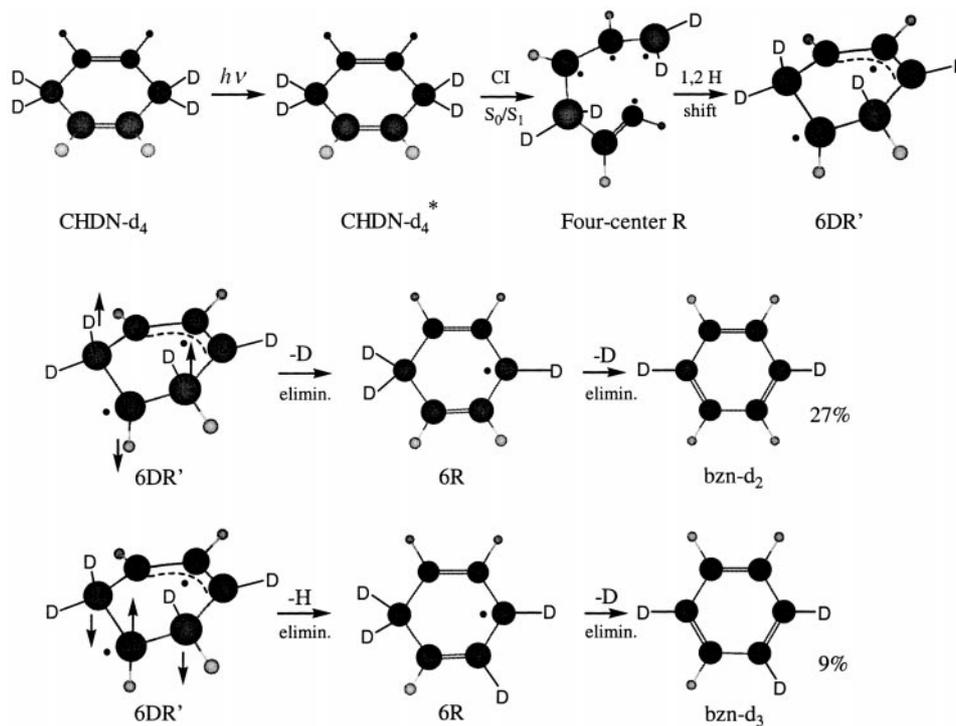


Fig. 2 Ground-state potential energy surface (PES) calculated at the B3LYP/6-31G* level of theory for various reaction paths of CHDN including (di)radical intermediates and reaction products with labels as indicated (see text for detail).

atom to form benzene in ~ 110 fs. Alternatively, the excited molecule may form the six-membered ring diradical intermediate *via* either the H/allyl or the vinyl/allyl CI and then two H atoms are eliminated in a stepwise manner. Since the vinyl/allyl CI, characterized by a non-planar open-chain structure, is relevant to interpret the product yields and stereochemistry observed in solution,¹⁵ we discuss the possible consecutive H-elimination channels involving this CI in the following.

The details of the calculation of the ground-state PES are shown in Fig. 2. The driving force from the vinyl/allyl CI may lead to the formation of a linear diradical intermediate (LDR1) through a hydrogen atom migration, and the six-membered ring diradical intermediate (6DR) is formed *via* a

ring closure process [reaction (6a)]. Following the IRC path from the ring-closure side of the transition state (a saddle point between LDR1 and 6DR), the geometry optimization process along this reaction path was not successful after $\text{IRC} > 5.1 a_0 u^{1/2}$. The corresponding structure at this point (labeled as 6DR' with relative energy of 49 kcal mol^{-1}) is depicted in Scheme 5 and the dynamics of the stepwise H-elimination are shown in the same scheme. 6DR' is highly bent and its structure elucidates the ultrafast H-elimination dynamics. The highly bent structure is specific in its motions which prefer the formation of bzn-d_2 , as opposed to bzn-d_3 . This is consistent with the stereochemistry observed in solution and this feature will be further discussed in section B.

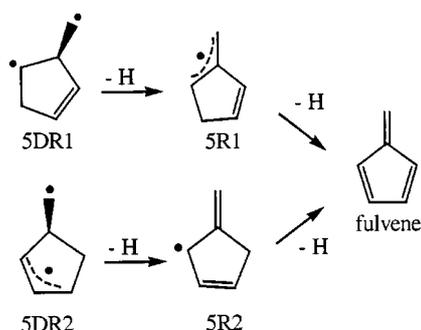


Scheme 5 Stepwise H-elimination: dynamics and structures.

The energetics of the consecutive H-elimination processes on the ground-state PES can now be considered. The release of one hydrogen atom from the ground-state 6DR to form cyclohexadienyl radical (6R) requires 25 kcal mol⁻¹ (Fig. 2), and the energy barrier for the release of a second hydrogen atom to form benzene is 26 kcal mol⁻¹, according to our DFT predictions (not shown). However, the first excited state of 6DR (labeled as 6DR*), located only 27 kcal mol⁻¹ above 6DR and its structure (*C_s* symmetry), is bent and characterized by two elongated C–H bonds ($R_1 = 1.123 \text{ \AA}$) on the tertiary carbon atoms. Therefore, both energetic and structural considerations favor the consecutive channel for the six-membered ring diradical intermediates (6DR, 6DR' and 6DR*). The concerted H₂ elimination is not favorable *via* a six-membered ring diradical because this mechanism does not fulfill the Woodward–Hoffmann symmetry rules.³⁵

Other channels could also account for the formation of the 79 u species involving the vinyl/allyl CI. First, after funneling through the CI, the molecule may close the ring to form hot CHDN, which might subsequently lose the H atom forming 6R (bond energy = 70 kcal mol⁻¹). However, in light of the substantial difference in the energy barrier between the concerted (47 kcal mol⁻¹) and the stepwise (70 kcal mol⁻¹) mechanism, the latter is very unlikely. Moreover, the aforementioned IRMPD experiments^{16,19} indicate the absence of the 6R intermediate in the ground-state chemistry of CHDN, suggesting that the concerted H₂ elimination channel prevails once “hot” CHDN is formed [reactions (1), (5) and (9a)].

Second, the vinyl/allyl CI structure may also lead to the formation of a five-membered ring diradical (5DR1, Fig. 2), which, besides the barrier-free formation of BCH, may release hydrogen from the tertiary carbon atom (bond energy = 13 kcal mol⁻¹), forming a five-membered ring radical (5R1, Fig. 2). The subsequent release of a second hydrogen atom would form fulvene:



However, this reaction channel is not favored for the following three reasons: (i) The formation of fulvene + 2H is highly endothermic by 46 kcal mol⁻¹ (not shown in Fig. 2). (ii) The second H-elimination process does not relate dynamically to the first one and a much longer lifetime for 5R1 is anticipated due to substantial energy redistribution. (iii) The lack of the corresponding deuterated products in the CHDN-d₄ photolysis in solution.¹⁵ Third, another five-membered ring 79 u radical species (5R2) may be produced from 5DR2, losing a second hydrogen atom to form fulvene. Due to similar reasons as given for 5R1, the ultrafast release of a second hydrogen atom is not likely to occur.

2. Concerted H₂-elimination. As demonstrated in Schemes 3 and 4, hot CHDN can be populated by reactions (1), (5) and (9a). Due to the large difference in the energy barrier between the concerted release and consecutive release from “hot” CHDN, the concerted channel is favored. In an early *ab initio* study, the energy barrier for the concerted H₂ elimination of CHDN was reported to be 60.1 kcal mol⁻¹.³⁶ We calculated a value of 46.8 kcal mol⁻¹ and the experimental value is 43.8 kcal mol⁻¹.¹² According to the Woodward–Hoffmann rules,³⁵

the concerted H₂ elimination is a fully symmetry-allowed process on the ground-state PES. Our experiments show relatively very small contribution of the 78 (80–2) u (Fig. 1). The ns time-resolved study of the photodissociation of CHDN by Cromwell *et al.*¹⁸ indicates that the rate constant for the concerted H₂ elimination is on the order of 0.5 ns⁻¹ at a total energy of 135 kcal mol⁻¹ (212 nm). The evidence of wavelength dependency and stereochemistry found in solution (see below) suggests that the concerted H₂-elimination channel at 212 nm^{17,18} is dominated by reaction (1) (Scheme 3). It is interesting to note that the structure of CI is highly asymmetrical and the H₂ elimination from hot CHDN through the helicopter-type motion should be controlled by IVR. Therefore, much slower dynamics is observed for the concerted channel.

B. Wavelength dependency, stereochemistry and isotope effect

As mentioned in the Introduction and summarized in Scheme 2, the condensed-phase studies of Srinivasan *et al.* revealed the rich stereochemistry of CHDN-d₄.¹⁵ Guided by our theoretical work and that of Wilsey and Houk²¹ in what follows, we provide a description of the reaction mechanism which rationalizes the reported¹⁵ wavelength dependency, stereochemistry and isotope effect of the CHDN photochemical reactions in the solution phase.

1. Wavelength dependence of the product branching ratios.

Photolysis of CHDN-d₄ in solution¹⁵ shows that the product yields at 185 and 214 nm are strikingly different (Scheme 2): the ratio of benzene to BCH is 0.7 : 1 at 185 nm, but dramatically increases to 4 : 1 at 214 nm. Furthermore, the excitation at 185 nm yields 1,3-CHDN and HT in a 1 : 4 ratio, while at 214 nm the amount of HT is negligible. This behavior can be explained with our findings.

The above evidence suggests that the photochemistry of CHDN at 185 nm may be dominated by vinyl/allyl CI whereas at 214 nm it may be dominated by D/allyl CI. If the vinyl/allyl CI is dominant (Scheme 4), HT can only be produced by reaction (10b), and 1,3-CHDN can then be formed afterward with an energy barrier of 31 kcal mol⁻¹ (Fig. 2). This is consistent with the observed branching ratio at 185 nm (1,3-CHDN : HT = 1 : 4, Scheme 2). However, if the D/allyl CI is dominant (Scheme 3), HT will be produced after 1,3-CHDN is formed [reaction (3)]. The interconversion from 1,3-CHDN to HT involves a high-energy barrier (43 kcal mol⁻¹) and is endothermic by 12 kcal mol⁻¹ (Fig. 2). Therefore, it is consistent with the observed product branching ratio at 214 nm (1,3-CHDN : HT = 1 : 0, Scheme 2). Note that the channel for the secondary photochemical reaction involving the formation of HT through VUV photolysis of 1,3-CHDN is negligible.¹⁸ Furthermore, the results obtained from the TDDFT calculations have shown that the absorption at 185 nm corresponds to a B_{3u} state (a π–π* type transition), whereas the excitation at 214 nm corresponds to a B_{1u} state (a π–3s Rydberg type transition). Thus, the π–π* transition may initiate a relevant out-of-plan bending motion to facilitate the excited molecule reaching the vinyl/allyl CI. The π–3s transition, which contains significant σ*(CD) character, would probably favor a C–D bending/stretching motion, which guides the excited molecule following the appropriate reaction path to the D/allyl CI.

The photolysis of CHDN-d₄ at 214 nm may produce cyclohexadienyl-d₃ radical (6R-d₃) from a direct D-elimination process along the repulsive excited-state PES. The 6R-d₃ intermediate may lead to bzn-d₂ by eliminating the second D atom, or it may abstract a D or H atom from the solution to form 1,3-CHDN-d₄ or 1,3-CHDN-d₃, respectively, after an appropriate electronic resonance rearrangement. If the excited molecule follows the reaction path through D/allyl CI to the ground state, deuterated benzene may also be

formed by reactions (1), (2b), and (4), but BCH can only be produced *via* reaction (2a). Once the elimination of a D atom has taken place through either the D/allyl CI or the excited-state repulsive PES, to form a 6R radical (Scheme 1), this would not lead to direct BCH formation, but rather to benzene and 1,3-CHDN formation. This mechanism explains the relatively low yield of BCH and high yield of benzene and 1,3-CHDN, produced at longer wavelengths.

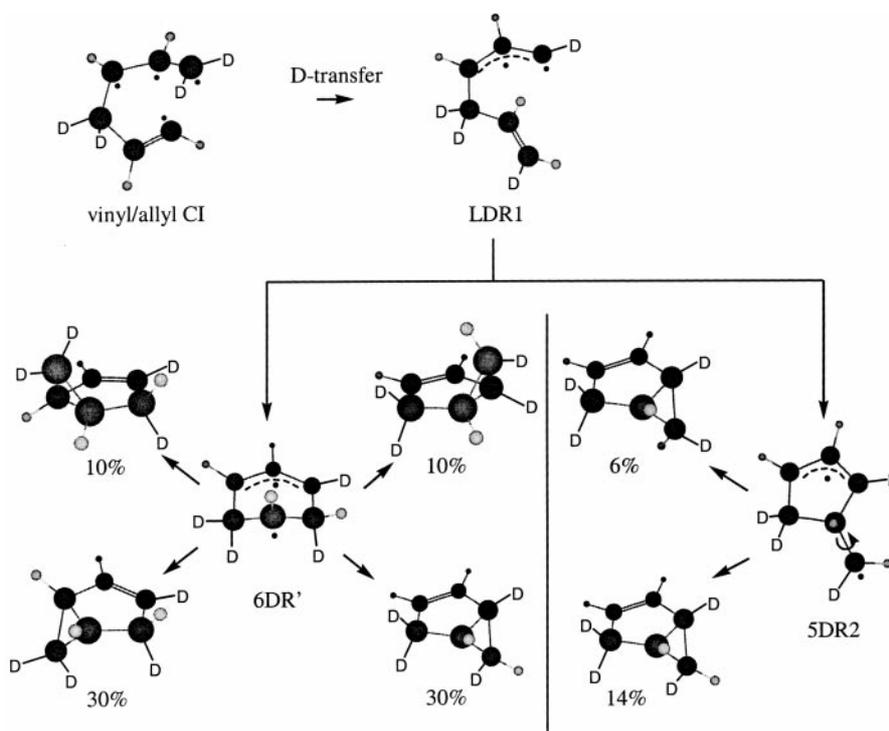
2. Stereochemistry of benzene formation. The photochemistry of CHDN-d₄ at 185 nm involves three benzene isomers: the main fraction (86%) is bzn-d₂; bzn-d₃ represents 9% of the total benzene population and a small fraction (5%) contains benzene-d₁. The presence of a considerable amount of bzn-d₃ suggests that the concerted D₂-elimination is not the only reaction path. According to the above discussion regarding the wavelength dependence, the vinyl/allyl CI may be involved at 185 nm. Scheme 5 gives the mechanistic details which quantitatively explain the observed trends. From the dynamics view discussed in Section A, the vibrational motion of the bent carbon skeleton (6DR'), combined with the increased length of the C–H (or C–D) bonds, favors the ultrafast consecutive channel. The nuclear motions could lead to different deuterated benzenes. The formation of bzn-d₂ (Scheme 5) is expected to be favored upon the formation of bzn-d₃, as this vibrational motion favors the release of two D atoms which are initially in “axial” position. The predicted 3 : 1 ratio of bzn-d₂ over bzn-d₃ is based upon the product yields and the stereochemistry of BCH formation, which involves the same 6DR' intermediate (see below). However, if the D-elimination is dominated by the D/allyl CI, then the following is predicted: either the equal yield for both bzn-d₂ and bzn-d₃ [reaction (2b)] or the preference for bzn-d₂ [reaction (4)]. The formation of a trace amount of bzn-d₁ is probably the result of D–H exchange in solution.

3. Stereochemistry of BCH formation. The photolysis of CHDN-d₄ at 185 nm produces substantial amounts of BCH¹⁵ and the information deduced from its complicated stereochemistry is helpful to better understand the reaction mechanism. As shown in Fig. 2, BCH can be formed from two five-membered ring diradicals (5DR1 and 5DR2) and the six-

membered ring diradical (6DR) without significant energy barrier. Based upon the vinyl/allyl CI structure, the formation of BCH by reaction (7) *via* ring closure of 5DR1 is analogous to the well-known di- π -methane rearrangement.¹⁵ However, the expected BCH isomers were not observed in the condensed-phase experiments.¹⁵ Therefore, this mechanism is ruled out.

A probable mechanism for BCH formation is proposed in Scheme 6. Ring closure of the linear diradical LDR1 could yield two cyclic diradical intermediates, 6DR' and 5DR2 (Fig. 2). 6DR' provides the dynamical picture to quantitatively explain the different deuterated product branching ratios and the related stereochemistry of BCH. The bending motion of 6DR' along either CD₂ or CHD leads to different deuterated BCH isomers, shown on the left and right side of 6DR' in Scheme 6, respectively. The branching ratio preference is given according to the geometrical effect which shows a 1 : 3 ratio for the top over bottom isomers (6DR' has both CD₂ and CHD groups facing downward). This “6DR' mechanism” accounts for 80% of the BCH formation. Another 20% of the BCH isomers can be accounted for by ring-closure of 5DR2, as shown on the right of Scheme 6; note the *cis* position of the two H atoms in the CH=CHD group of LDR1. Therefore, it is reasonable to prefer the bottom isomer (14%) over the top one (6%). Note that the nonplanar-featured vinyl/allyl CI structure, which is proposed to lead to a “bent” six-membered ring diradical intermediate (6DR') from reaction (6a) or a five-membered ring diradical species from reaction (10a), can be successful to quantitatively interpret the observed CHDN-d₄ stereochemistry. The planar-featured D/allyl CI, which may lead to only a planar 6DR intermediate [reaction (2a)], eventually would yield no or little preference for the deuterated isomers discussed above.

4. Isotope effects. The reported isotope effect at 185 nm (Scheme 2: CHDN yields more benzene than BCH, but CHDN-d₄ gives the opposite trend) can also be explained in terms of the proposed dynamics involving the vinyl/allyl CI. In the primary isotope effect for hydrogen elimination it is expected that the consecutive release of two D atoms to form benzene will be slower when compared with that involving H



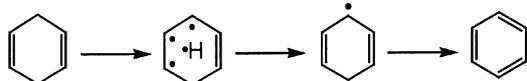
Scheme 6 BCH formation: dynamics and structures.

atoms, due to the mass effect. However, if the bending motion is the determining factor in the dynamics it is expected that very similar results will be obtained for both CHDN-h₄ and CHDN-d₄ in the BCH formation through the ring-closure process. Both the consecutive benzene and BCH formation involve the 6DR' intermediate (Schemes 5 and 6). The competition between both processes leads to a prominent isotope effect.¹⁵

IV. Conclusions

(1) On the femtosecond time scale we observed the 79 u species corresponding to the parent 1,4-cyclohexadiene minus one hydrogen atom, elucidating the non-concerted pathway of the elimination reaction to form benzene.

(2) The temporal behavior of H elimination shows the decay in 110 fs suggesting the probing of the transient hot species from the hydrogen-atom/allyl structure (CI) to the radical (79 u). Thus the mechanism for the formation of benzene must include the radical channel:



The concerted hydrogen molecule elimination may be the dominant channel if the ground-state molecule is activated by, e.g., IR multiphoton excitation.

(3) Our density functional theory calculations provide the ground-state energetics. In the excited state, there are two CIs predicted²¹ by the CASSCF method, one involves the H-atom bridging (C–H motion) and the other involves the C–C bond breakage (out-of-plane bending)—Scheme 1.

(4) From the experimental and theoretical studies, we are able to provide a unifying picture of the stereochemistry (the selective formation of deuterated benzene) and the branching ratio (benzene to bi-cyclic compounds) in the condensed phase, and the ratios of product yields at different wavelengths. The involvement of the two CIs and the energetics in the ground state provide a systematic trend for the dynamics.

(5) The spectral characteristics of the intermediate radical reported by Kumar *et al.*²⁰ following excitation at 193 nm is consistent with our observation of the 79 u species. However, the decay of the radical in their experiments is on the μ s time scale, suggesting a distribution of hot and cold molecules, caused by the bulk medium (argon at different pressures).

Acknowledgements

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