Ultrafast Dynamics of Cyclohexene and Cyclohexene-d_{10} Excited at 200 nm

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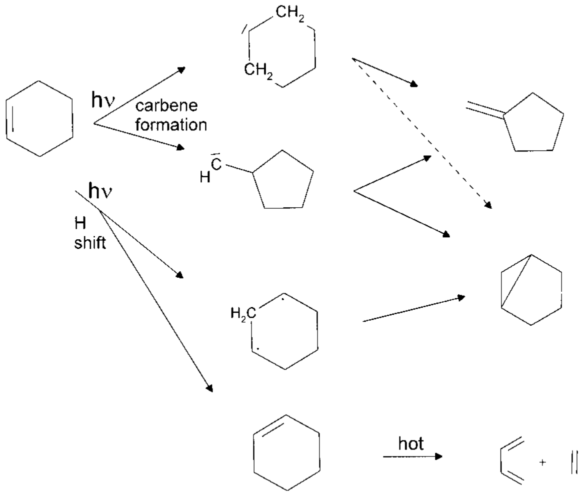
Abstract: By exciting cyclohexene in the gas phase at 200 nm and probing it by nonresonant multiphoton ionization with mass-selective detection of the ion yields, we found four time constants τ_i (20, 47, 43, 350 fs). Whereas deuteration lengthens τ_2 by a factor of 1.4, the other constants do not change. $\tau_1-\tau_3$ represent traveling times through observation windows on excited surfaces, whereas τ_4 reflects a process in the hot ground state. We assign τ_1 (20 fs) to departure from the Franck−Condon regions of the Rydberg and $\pi\pi^*$ states, which are both populated at 200 nm, and τ_2 (47 fs) to traveling along the $\pi\pi^*$ surface and suggest that a [1,3]-sigmatropic H shift begins in this state. This rationalizes the deuterium effect on τ_2. To explain why this window is followed by a process not subject to a D effect, we postulate that the $\pi\pi^*$ surface is crossed late (i.e., at low energy) by the zwitterionic state Z and that formation of a carbene (the known photochemical product, cyclopentylcarbene) begins there. The corresponding 1,2-shift of a CC bond is then (within $\tau_4 = 350$ fs) largely reversed on the ground-state surface, while a smaller part of the carbene forms products such as methylenecyclopentane within the same time. Carbene formation is probably accompanied by some cis−trans isomerization. The wavelength dependence of carbene formation is attributed to a memory for the initially excited state, based on momentum conservation. The processes are most likely typical of simple olefins. The fragmentation pattern showed that butadiene is not formed until at least 500 ps. The retro-Diels−Alder reaction, known to take place in the ground state, thus only occurs later.

1. Introduction

The photochemistry of monoalkenes has been reviewed.[1−3] The purely photochemical reactions comprise cis−trans isomerization, pericyclic reactions, formation of carbenes (which form consecutive products in ground-state reactions), and possibly dissociation (e.g., elimination of an H atom). In addition, in the gas phase, one observes reactions in the hot ground state of the reactant (formed by internal conversion accompanying the above reactions) or of products; such reactions can be suppressed by collisions, particularly in solution.

The only photochemical products observed in irradiation of cyclohexene are methylenecyclopentane and bicyclo[3,1,0]-hexane, two species believed to be formed from two carbenes (Scheme 1).[4−6] Formation of a short-lived, highly strained trans isomer was discussed in ref 4. Scavenging with methanol indicated that with 1-phenylcyclohexene it forms in 8.2% quantum yield.[7] Since in other olefins a photochemical [1,3]-sigmatropic hydrogen shift is very important,[1−3,8] it can also be assumed for cyclohexene (Scheme 1); the product in this case is identical to the reactant, unless isotopically labeled. It has been observed in 1-methylcyclohexene.[8] Also, from the detection of a partially deuterated ethylene as a photolysis product (from the hot ground state) of 3,3,6,6-tetradeuteriocyclohexene,[5] we can infer that a D shift has preceded the ground-state fragmentation. Further products observed only in the gas phase, such as those resulting from a retro-Diels−Alder reaction (butadiene and ethylene, Scheme 1) and other fragmentations, were assigned to reactions in the hot ground state;

Scheme 1. Photoreactions of Cyclohexene[a]



[a]Cis−trans isomerization is not indicated.

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the evidence was deduced from the collisional effects, from which a lifetime of 12 ns was estimated for hot cyclohexene,[4] and from photofragment spectroscopy, which suggested a lifetime around 1 ns.[9] On the other hand, on the basis of femtosecond spectroscopy of cyclohexene, norbornene, and other molecules and quantum chemical calculations, it was recently claimed that two competing retro-Diels−Alder reactions, one concerted and one stepwise, take place (mainly on the ground-state surface) in subpicosecond times.[10−12] The present work supports the nanosecond times for this reaction.

The UV spectrum of cyclohexene[13,14] is typical of alkyl-substituted olefins:[15,16] The first strong absorption corresponds to $\pi \rightarrow \pi^*$ excitation; it has a maximum near 180 nm and a wing extending beyond 200 nm. A weak precursor band (structured, maximum 203.2 nm) on top of this wing is assigned to excitation to a state with both $\pi \rightarrow \sigma^*$ and Rydberg $\pi \rightarrow 3s$ character.[15] Excitation at 200 nm will populate both states with comparable probability. The accepted view in the literature is that these two states differ in their photochemistry, the Rydberg state favoring carbene formation.[1−3] We suggest in section 4 that the choice of the different photochemical channels is only made later but that a memory effect for the initial state affects this branching. Far from the Franck−Condon region, another state plays a role, a two-electron excited zwitterionic state; in acyclic olefins its minimum is below that of the $\pi\pi^*$ state, which involves a 90° twist of the double bond (see, for example, ref 17).

Wilsey et al. presented very instructive CASSCF calculations on the ground and $\pi\pi^*$ surfaces of the related molecule norbornene and, among other things, localized two conical intersections (CIs) corresponding to [1,3]-sigmatropic shifts.[12] Wilsey and Houk emphasized the ubiquity and general structure of such CIs.[18] Soep et al. recently determined the lifetime in the Franck−Condon region of a number of olefins, including cyclohexene, by femtosecond spectroscopy;[19] for probing they used single-photon ionization, which allows a valuable comparison with our results.

In this work, we study the femtosecond dynamics of cyclohexene and its fully deuterated isotopomer after excitation at 200 nm in the gas phase at room temperature. Probing was done by nonresonant (800 nm) photoionization at high laser intensity and mass-selective detection of the ion yields as functions of the pump−probe delay time. The many signals (parent and fragment ions) in this technique, yielding correspondingly much information, allow the path of the molecule to be monitored its entire way along the potential energy surfaces from the Franck−Condon region of the reactant down to the ground state of the product(s) (see, for example, ref 20). In the cyclohexene system, we find four subpicosecond time constants, only the second one exhibiting a D isotope effect. (Three different constants were found in the previous work,[11] which used excitation to a higher state.) We suggest an assignment based on known photochemical reactions and qualitatively known electronic states. A relatively detailed picture of motion results particularly on several excited-state surfaces.

2. Experimental Section

The molecules were pumped in the gas phase by a frequency-quadrupled pulse of a Ti−sapphire laser system (200 nm, 140 fs, 10^9 W cm^{-2}) and then probed by nonresonant multiphoton dissociative ionization at the fundamental wavelength (800 nm, 110 fs, 10^{13} W cm^{-2}). The two beams were linearly polarized with an angle of 55° ("magic angle") between each other in order to avoid time dependences induced by molecular rotation. As with transient absorption, this method is based on probing of electronic transitions; both can give information (mainly lifetimes) on specific locations on the potential energy surface (PES). However, transient dissociative ionization reveals more details and can yield an effective time resolution below the pulse lengths. Both advantages result from the fact that quite a number of time-dependent ion signals (parent and fragments) are found which are linearly independent.[20,21]

For evaluation, we assume that the molecule sequentially reaches several locations i (observation windows) on the PES with lifetime τ_i. Since these times turn out to be very short (<100 fs), the transit time through the window makes a significant contribution to τ_i. Therefore, we use the terms "lifetime" (time constant) and "traveling (transit) time" interchangeably. The signals are then expressed as a sum of exponentials (with time constants τ_i) convoluted with the (Gaussian) pump and probe pulses. The exponential part of each signal is proportional to a linear combination of the time-dependent populations of each window, the coefficient being the cross section ${}^m\sigma_i$ for production of an ion of mass m from window i. The time constants τ_i were determined in two steps: (1) two longer ones ($\tau_2 = 47$ fs, $\tau_4 = 350$ fs) from a singly exponential fit to the decay of a signal; (2) the other two from simulating the signals by means of a multiexponential fit with convolution, with τ_2 and τ_4 kept fixed. This fit also confirms τ_2 and τ_4. The ${}^m\sigma_i$ are also obtained from the fit procedure.

All time constants were independent of the *probe intensity*, which was varied by a factor of 3. The effective order for generating the parent ion by the probe was 1.1. Since two probe photons are required for ionization from the excited state (pumped by a photon of 6.2 eV; probe photon 1.55 eV; ionization energy 8.94−9.11 eV[22,23]), we can infer that the probe meets a resonance with a state near 7.75 eV, which is partially saturated, in particular in window 2; i.e., the resonant level is at an energy slightly lower than 7.75 eV. The shape of the signals including the ratio of peak to pedestal also did not depend on the *pump intensity* (varied by a factor of ∼3).

Special features of transient dissociative ionization and the method of assignment are discussed in ref 20. Brief discussions have also appeared elsewhere.[21,24,25] It should be pointed out that fragmentation typically (also in the example of cyclohexene, see end of next section) takes place only after ionization within the many nanoseconds before acceleration in the ion source; it is caused by excess vibrational energy of the ion. When the neutral molecule relaxes down the potential energy surfaces, it releases kinetic (vibrational) energy, which is largely taken over to the ion on ionization.[20] Hence, fragmentation can give an indication of the vibrational—and hence also electronic (since the sum is constant)—energy in the pertinent observation window. Besides

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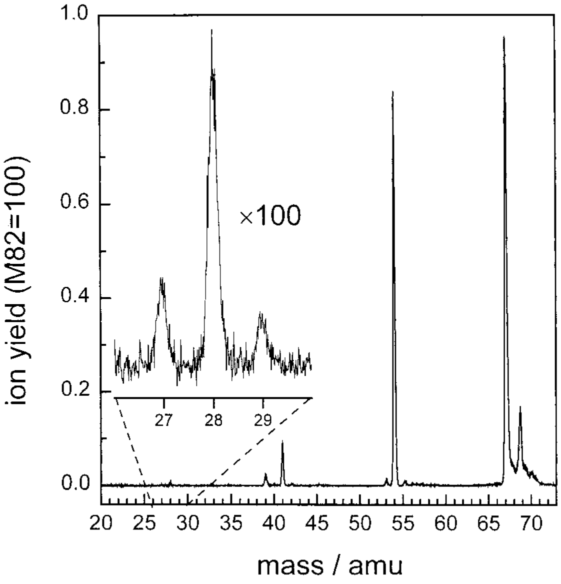

Figure 1. Transient mass spectrum of cyclohexene recorded by photoionization by 800 nm at 100 fs after pumping by 200 nm. At this delay time, fragmentation reaches its maximum. The ion yields are normalized to the parent ion (82 amu) = 100.

this source of ionic excess energy, a second one is also important in our context (for a third one, see ref 20): The ions can absorb additional probe photons and thus photodissociate. This is already the case without any pump pulse and is the reason every neutral species or precursor gives rise to a mass spectrum with typically more than one ion signal; this ionic fragmentation pattern cannot be expected to remain unaffected by pumping and the internal state of the neutral. It can thus happen that, for instance, a first location gives rise not only to the parent ion but also to a fragment signal, whereas only the latter may be observed from a second location which is populated by depletion of the first one. In this situation, the fragment signal would appear before the parent signal disappears, although the locations on the potential surface are consecutively populated. This possibility was not recognized in refs10 and 11, where the early appearance of a fragment signal was believed to be evidence against consecutive processes.

Cyclohexene (Merck) and cyclohexene-d_{10} (ABCR) were used after degassing. No impurity above 0.1% was gas chromatographically detected from the vapor phase.

3. Results

Figure 1 shows the fragmentation pattern observed 100 fs after the pump pulse. It gives the relative strengths of signals (parent = 100), which cannot be taken from Figures 2 and 3 due to normalization. Around this delay time, fragmentation is maximal. Figure 2 shows the transient signals for Xe^+ (which gives the time zero and an indication of the instrumental function), parent ion (mass 82), and typical fragment ions for cyclohexene on a linear and a logarithmic scale. Figure 3 presents analogous results for cyclohexene-d_{10}. Several neutral precursors (locations on the potential energy surfaces) must be assumed, since the signals are obviously not proportional to each other. This is demonstrated by, for instance, noncoincidence of the signal maximums, which are at 30, 68, and 80 fs for masses 82, 54, and 41, respectively (48, 86, and 108 fs for the deuterated molecule). The time dependences (in all parts including rising edges, position of maximums and decays) of $C_5H_7^+$ and $C_4H_6^+$ (masses 67 and 54, the former not shown) are practically identical. The same applies to the signals with masses 41 (shown), 39, 29, and 28. The latter four signals also show a weak (<1% of the maximum; see Figure 2), long-lived (>500 ps) pedestal, which is obviously due to an end product. The

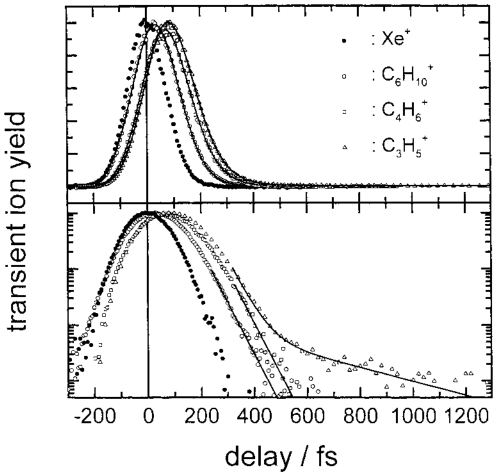

Figure 2. Typical time-resolved signals for cyclohexene on linear (top) and logarithmic (bottom) scales. The Xe^+ signal gives the time zero and approximately the instrumental function. Two time constants (τ_2, τ_4) can immediately be extracted from exponential tails (solid lines in the lower panel). Two more (τ_1, τ_3) are required to simulate (solid lines in the upper panel) the different delays of the rising edges. (The simulation used four consecutive processes and convolution with the Gaussian instrumental function; see text). The signal at mass 67 (not shown) coincides with that of mass 54, and those of masses 39, 29, 28, and 27 (not shown) with that of mass 41.

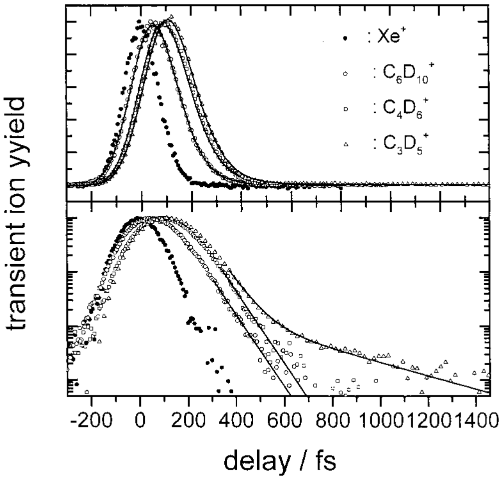

Figure 3. Typical time-resolved signals for cyclohexene-d_{10} on linear (top) and logarithmic (bottom) scales. See also explanation to Figure 2.

heavier fragments (masses 67 and 54) and the parent ion only show a short spike decaying to 0.

As mentioned, the signals can be simulated by a sum of exponential time functions convoluted with the (Gaussian) instrumental function (solid lines in Figure 2 top). Altogether we obtain four time constants $\tau_1-\tau_4$ (Table 1) by which all signals can be well reproduced. To derive them, we first determined a value of 47 fs from the singly exponential tail of the fragment signals with masses 54 (Figure 2 bottom) and 67 (not shown), and then, keeping this value fixed, another constant of 350 fs from the doubly exponential tail of the light fragments (mass ≤41). These are called τ_2 and τ_4 in Table 1. With τ_2 again kept fixed, it turned out that an additional time constant (τ_1) was necessary to reproduce the early appearance and shape of the parent ion signal (doubly exponential fit with convolution). Similarly, τ_3 had to be introduced to account for the delay and compact shape of the light fragments; this simulation also imposes the constraint $\tau_1 + \tau_3 = 63$ fs on both isotopomers.

Table 1. Lifetimes τ_i of the Locations *i* on the Potential Energy Surface and Cross Sections ${}^{m}\sigma_i$ for Generating Some Selected Ions (Mass *m*, Indicated by the Formula) for Cyclohexene and Cyclohexene-d_{10}[a]

	locations *i*				
	1	2	3	4	5
cyclohexene:					
τ_i/fs	20 ± 5	47 ± 5	43 ± 5	350 ± 100	$>500 \times 10^3$
$C_6H_{10}^+$	1	0.29	0	0	0
$C_4H_6^+$	0	1	0.52	0	0
$C_3H_5^+$	0	0.434	1	0.0037	0.0005
cyclohexene-d_{10};					
τ_i/fs	20 ± 5	65 ± 5	43 ± 5	350 ± 100	$>500 \times 10^3$
$C_6D_{10}^+$	1	0.70	0	0	0
$C_4D_6^+$	0	0.50	1	0	0
$C_3D_5^+$	0	0	1	0.0016	0.0005

[a] The error limits of τ_2 and τ_4 are the standard deviations of the values determined in 10 runs from the singly (doubly) exponential fits to the tails of signals. The full fit also gives the constraint of $\tau_1 + \tau_3 = 63 \pm 5$ fs and $\tau_3 \leq \tau_2$, which implies the error limits of τ_1 and τ_3.

The absence of a D isotope effect for the sum implies that there is no such effect for each term since a negative D effect for one term would not be reasonable.

Sums of exponentials with up to four terms are the solutions of rate equations for populations in five observation windows or locations on the potential energy surfaces (the last one with infinite lifetime) connected by four *consecutive* processes. However, such a sum also results from kinetic description of a system with *branching*, i.e., of a set of consecutive and parallel reactions; only the interpretation of the coefficients is then different. That is, purely mathematically, the two cases cannot be distinguished. But one detail is noteworthy: τ_3 was determined from the fragment ion signals with mass ≤67. The delay of these signals is isotope-sensitive; this delay contains τ_2 in the analysis with purely consecutive processes. If we assumed early branching with windows 2 and 3 in different branches, we had to introduce an additional window 2′ (before window 3) with isotope-sensitive time constant τ_2' to simulate the signal shift. But the next section shows a satisfactory assignment without introducing such additional parameters, with only consecutive processes being used. Hence, we prefer this simpler model, also because the quantum chemical calculations[12,18] showed no indication of any additional branching in the excited state. In the purely sequential case, the fit procedure also provides the sequence (τ_2 after τ_1, etc.) of the processes.

From the signals, we can also learn something of the energy of the locations: From the third window, the probe no longer produces parent ions, but only fragments. This means that the electronic energy of this window is already considerably reduced (by more than an estimated 2 eV) compared with the initially excited state (window 1) and the kinetic or vibrational energy is correspondingly higher. This excess energy is largely[20] taken over by the ion, where it induces fragmentation (estimated energy required, >2 eV) during the long time (>100 ns) of acceleration in the ion source. A similar estimate is obtained from comparison with the one-photon probing data of Soep et al.:[19] Since these authors observed windows 1 and 2 (see section 4.3), but not window 3, the latter must be below the ionization energy (8.94 [22] or 9.11 eV[23]) by >4.65 eV (Soep's probe photon), that is, below an energy of 4.29−4.46 eV; this is just 1.7−1.9 eV below the energy of the Franck−Condon region (pump photon 6.2 eV). On the other hand, this level cannot be much lower than this estimate because its ionization is still highly efficient.

The ion signals from window 4 (i.e. the signal tails decaying with τ_4) are already 100 times weaker. Thus, whereas the first three windows are on excited surfaces, window 4 probably represents the ground state of a primary product with lifetime τ_4. The fifth observation window with "infinite" (>500 ps) lifetime gives rise to signals that are even 5 times weaker; it must correspond to the ground state of an end product (itself formed by a ground-state process within τ_4) with at least such a lifetime.

The results for perdeuterated cyclohexene are very similar to those of cyclohexene itself: All time constants are identical except τ_2, which is a factor of 1.4 larger (65 fs). This factor indicates that in window 2 there is barrierless hydrogen migration, whereas in the other windows it is (mainly) other atoms or groups that move.

Since a subpicosecond retro-Diels−Alder reaction was claimed[11] (see Introduction), we checked for the presence of butadiene in the fragmentation pattern of cyclohexene after a delay of 1−500 ps; it was determined from the time-dependent signals. In this pattern, the ion of mass 41 is dominant, whereas in cold and hot butadiene it is absent. (The spectra of butadiene were measured by 800-nm ionization either without preexcitation or picoseconds after 200-nm excitation.[26] In the electron impact mass spectrum of butadiene, mass 39 is most prominent, whereas masses 41 and 29 are absent.[27]) That is, this mass does not belong to butadiene. Moreover, the time-dependent signals at masses 39, 29, 28, and 27 practically coincide with that of mass 41, indicating that they have a neutral precursor in common. That is, all the light fragments and hence all those observed at long times do not have butadiene as precursor. The authors of ref 11 only monitored one fragment, $C_4H_6^+$ (i.e., the butadiene cation, mass 54), besides the parent ion. In our experiment, the larger fragment $C_5H_7^+$ exhibits the same dependence as $C_4H_6^+$. That is, it has the same neutral precursor; it obviously has a larger mass than butadiene. The fragment with mass 54, observed here and in ref 11 at subpicosecond times only, thus does not belong to the retro-Diels−Alder product either.

This interpretation implies that all fragment signals observed are generated from locations on the potential surfaces of the *intact* molecules (cyclohexene and isomers). This is common not only in static mass spectroscopy but also in its time-resolved version; for instance, we also observed fragment ion signals after UV excitation of cycloheptatriene,[25] a molecule known not to show any photofragmentation. Fragmentation only occurs after ionization and is caused by excess energy. While there are several sources of such energy[20] (see also end of section 2), only one is emphasized here: On ionization, a hot neutral molecule will give a hot ion which can subsequently disintegrate. (Note: The ion has many nanoseconds of time for fragmentation—the time before acceleration in the ion source; the neutral has only femto- to picoseconds—the time before probing.) It is natural therefore that the smallest fragment ions (masses ≤41 in the cyclohexene case) are always observed from the ground state of the end product, including that of the reactant after internal conversion, the latter having 6.2 eV of vibrational excess energy. (Signals from end products are easily recognized: They have a pedestal, i.e., a nondecaying part.)

4. Discussion

4.1. Assignment. The assignment attempted in the following is summarized in the potential energy diagrams of Figure 4 below.

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First window. Pumping at 200 nm populates both a $\pi\pi^*$ state and a Rydberg state which also has some $\pi\sigma^*$ character.[15] The initial relaxation can be expected to follow Franck−Condon active coordinates. For the former state, this involves C═C stretch and twist; that is, no H motion is involved. There will be no pronounced deuterium effect for the other state either since the orbital with mixed Rydberg and σ^* character is delocalized; that is, it will affect not only a CH bond, and the reduced mass of the moving groups will be larger than 1. So the assignment of τ_1 to the initially populated Franck−Condon regions is consistent with the lack of an isotope effect.

The two states are not distinguished by the detection technique and only give rise to the parent ion. That is, this signal represents the sum of the two populations. They must be depleted at a similar rate (or one of them could be below the time resolution) since otherwise we would observe two time constants instead of τ_1. For the $\pi\pi^*$ surface, a steep slope and rapid acceleration along the C═C stretch and twist are expected and a time constant of 20 fs seems reasonable. (Compare the even shorter times for leaving the Franck−Condon region in 1,3-cyclohexadiene[20] and cycloheptatriene.[25]) For the Rydberg population, we suggest that it is depleted via an intersection with the $\pi\pi^*$ surface, so that the two relaxation paths merge. In fact, intersection of the two surfaces is symmetry-allowed along the C═C twist coordinate and is, as always in polyatomic molecules, conical; whereas the $\pi\pi^*$ state is strongly repulsive in this direction, the Rydberg (R) state will be less repulsive or even slightly bound. Since the wave packet can go around the lower cone of this intersection, any barrier can only be minor, so that departure from this state can also be ultrafast. It is worth noting that 20 fs corresponds to a homogeneous width of 250 cm^{-1}. This seems consistent with the widths observed in the spectrum around 50 000 cm^{-1}; the line width of the 0−0 transition at 47 710 cm^{-1} seems a little smaller (estimated 100−200 cm^{-1} [13,14]), corresponding to a somewhat longer lifetime as expected in view of the barrier. It should already be noted here that this fast R → $\pi\pi^*$ relaxation and merging of paths seem to be in contrast to the current view that the two states differ in their photochemistry. We will discuss this point in the next section.

In the *second window*, which is an excited-state not very much lower than the Franck−Condon region (because both give rise to the unfragmented parent ion), a hydrogen atom moves in a barrierless process, to judge by the D effect. An H shift is involved in formation of the carbene cyclohexylidene (Scheme 1). However, this channel seems to be much less important than formation of cyclopentylcarbene,[28] which involves a shift of a CC bond instead. Therefore, we postulate a [1,3]-sigmatropic H shift (which cannot be detected in unlabeled cyclohexene). It is photochemically allowed and occurs in 1-methylcyclohexene[8] and in many other olefins[1,2] with good yield. It probably begins in the $\pi\pi^*$ state (and can be expected to terminate in the ground state after passing through a conical intersection). This not only is consistent with experimental evidence[8] (see also Introduction) but is also generally predicted by quantum chemistry;[18] a similar reaction, the [1,3]-sigmatropic CC shifts in 1-butene[29] and norbornene,[12] was already previously predicted, in agreement with experiments. So we suggest that the second window is a region on the $\pi\pi^*$ surface contiguous to the Franck−Condon region and that the pathway changes direction on relaxing from windows 1 to 2 (from C═C stretch and twist to H shift). Previous experience with cyclohexadiene[20] and cycloheptatriene[25] indicates that our detection method is indeed sensitive to changes of direction, even if the electronic surface stays the same; this observation was interpreted by the different parts of the ionic surface reached after such a change.

In the *third window*, which is on a lower excited surface (to conclude from the absence of the parent ion and increased fragmentation; see section 3), no deuterium effect was observed. Other groups of atoms seem to move. Since the [1,3]-sigmatropic H shift does not involve such motion, we should consider the other main photoreaction, formation of cyclopentylcarbene, which involves a [1,2]-shift of a CC bond. If this reaction begins in window 3, it is at first glance difficult to understand why it should be preceded by any H motion (window 2). An explanation can, however, be provided by the zwitterionic state Z. This is a two-electron excited ($(\pi\pi^*)^2$) state, which in acyclic olefins is much higher than the normal $\pi\pi^*$ state in the Franck−Condon region, but slightly lower than it at a twist angle of 90°.[17] So, if the CC rearrangement begins in the Z state, the reason it is preceded by any motion on the $\pi\pi^*$ surface is energetic: The two surfaces just intersect very late, i.e., at low energy.

In small cyclic olefins such as cyclohexene, a C═C twist by 90° induces considerable ring strain. The $\pi\pi^*$ minimum (along this coordinate) will therefore be higher than in acyclic olefins. From the experiments, we indeed concluded that window 2 is not very much lower than the Franck−Condon region. On the other hand, the Z state prefers, in addition to the C═C twist, pyramidalization at one of the sp^2 carbons (the negative end of the zwitterion),[30−32] which is readily possible in the six-membered ring. In cyclohexene, the Z minimum will thus be substantially below the $\pi\pi^*$ minimum. In fact, the change of the fragmentation pattern showed that window 3 is energetically clearly below window 2.

More carbene is found to form with excitation of the Rydberg (R) than of the $\pi\pi^*$ state,[1,2] as evidenced by the wavelength dependence of the yields and by substituent effects: Carbene formation is suppressed by substituents that lower the $\pi\pi^*$ state to below the R state. Our result that departure from the Rydberg state is ultrafast (20 fs) requires an easily accessible conical intersection with a lower surface. This lower surface cannot be S_0, since R states are not much shifted from equilibrium geometry. (This shift is equal to that of the ion, which can be determined from photoelectron spectra. In contrast, an intersection between S_0 and the strongly displaced and lower-lying Z surface can readily be imagined.) The Rydberg population will instead relax via an easily accessible intersection (see above under “first window”) to the $\pi\pi^*$ state lying close by. The question then is whether after leaving the R state there is a memory for any property that can drive the molecule to the Z state. We suggest that this can be a momentum conserved during a short time (or traveling distance) such as on the $\pi\pi^*$ surface: If the R surface is displaced in a direction similar to that of the Z surface (namely, toward carbene formation), the wave packet will obtain on the R surface a momentum pushing it to the Z surface at the $\pi\pi^*$/Z conical intersection. Without this momentum, more molecules will stay on the $\pi\pi^*$ surface. Furthermore, circumvention of the R/$\pi\pi^*$ intersection, i.e., by going around the lower part of the double cone (lower initial path in Figure 4), for symmetry reasons requires nonplanar distortion, probably

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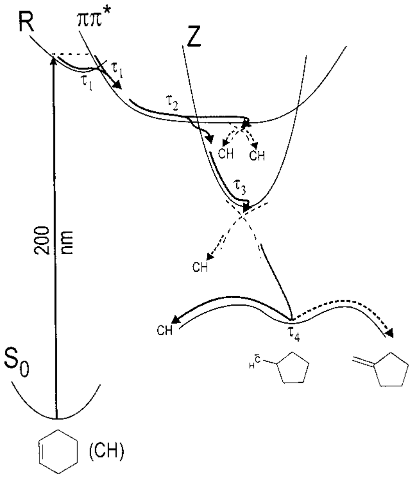

Figure 4. Suggested paths and potential energy surfaces. Initial excitation at 200 nm populates the Franck−Condon regions of a Rydberg and a $\pi\pi^*$ state (connected by horizontal broken line). τ_i near the solid arrows represent the traveling times to which we assign the time constants extracted from the signals; τ_4 is the lifetime of the carbene. Broken arrows represent probable processes not giving rise to an observable signal. CH, cyclohexene. The potential energy curves should be understood topologically; i.e., they are only intended to give qualitatively the energetic location of intersections. Coordinates of minimum energy paths on them will be different between the $\pi\pi^*$ and Z states, for instance (see also text). Another change of coordinates is hinted at by the curved arrows pointing to the conical intersections (crossing broken lines).

pyramidalization, which will act in the same way. The wavelength dependence of product formation is thus ascribed to a memory for momentum, i.e., a dynamic effect.

The *fourth window* was assigned in the previous section to a reaction in the hot S_0 state. This state could belong either to cyclohexene formed by internal conversion accompanying the photochemical reactions (branching at the CIs), as a product of the [1,3]-H shift, or to the carbene(s). The lowest-barrier reaction of the former is the retro-Diels−Alder reaction forming butadiene and ethylene. But since the fragmentation pattern after the fourth window showed that butadiene was absent (section 3), we can conclude that the process in window 4 is a rearrangement of a carbene in its hot S_0 state. Cyclopentylcarbene stabilizes either by H migration to methylenecyclopentane or by CC bond rearrangement back to cyclohexene. We suggest that the latter process dominates since no deuterium effect was observed. That is, cyclohexene recovery from the carbene is much more probable than the H shift. This implies that a substantial fraction of the molecules must have chosen the pathway via the Z surface with its CC shift. This explains why the signal from window 3 is strong, being comparable to that from window 2. This strength thus does not contradict the small quantum yield of carbene products (few percent[8,28]), since most of the carbene returns to cyclohexene.

4.2. Summary of the Pathway. In Figure 4, we try to summarize the above ideas. Solid arrows with labels τ_i indicate the windows *i*. With one exception, all locations or windows on the ground-state surface (i.e., everything below the CIs with S_0) were assumed not to be observed (broken arrows) because multiphoton ionization from the ground state gives rise to only very weak signals. The exception is process 4, the (weak) signal from which is observed at a time when all (more intense) signals from excited states have decayed. The signal from the carbene is stronger than from its product (formed within τ_4) because ionization of the nonbonding carbene electrons probably requires fewer probe photons than that of the product's bonding electrons.

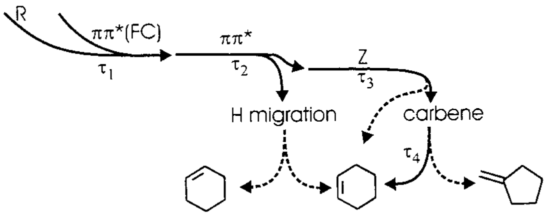

Figure 5. Kinetic scheme summarizing the sequence of processes (solid arrows with time constants τ_i) assigned to the signals. Broken arrows again denote probable processes that do not give rise to a signal. Energetics (for instance, that the Z state is below the $\pi\pi^*$ state) is also qualitatively indicated.

There are two branchings after which consecutive processes are still observed: that at the $\pi\pi^*$/Z intersection and that in the carbene S_0. It is worth noting that two processes starting from a single precursor (the branching point) imply one single time constant that describes the decay of the common precursor and the formation of each product; the ratio of the rates can in principle be determined from the ratio of product yields.

Unfortunately, calculated surfaces of excited states are not available. Therefore, we give in Figure 5 a kinetic flow diagram with only very rough energetic suggestions. This seems what can be directly deduced from the experiment without knowing details of the surfaces. The labels with names of states only serve to correlate the diagram with Figure 4. Unobserved windows are again indicated by broken arrows. It is generally conceivable that more excited states take part than are mentioned in Figure 4. Thus, Wilsey et al. mentioned that a $\sigma\pi^*$ state crosses the $\pi\pi^*$ surface at large excursion along the [1,3]-sigmatropic reaction coordinate.[12] Furthermore, when four electrons and four active orbitals in such a pericyclic reaction are considered, correlation diagrams suggest that a two-electron excited dark state also crosses the $\pi\pi^*$ surface.[33]

As usual, a photochemical reaction through a CI is only half terminated when arriving at the CI. The H migration may serve as an example. Calculations for this CI[18] and that for the analogous CC migrations are available.[12,29] At the CI, the migrating atom or group is on top of the center of an allylic− system, i.e., just halfway between positions 1 and 3. Immediately after passing the CI, the group may decide to continue toward position 3 to terminate the [1,3]-shift, or it can return to position 1 to recover the reactant. (The two directions correspond to $\pm x_1$, i.e., one of the coordinates of the branching space.) The latter process is an internal conversion occurring with the same time constant as product formation. According to both calculations, however, the migrating group may also form a bond with position 2 (motion along x_2, the second branching vector), and thereafter, the atoms 1 and 3 will be interconnected; this process is not synchronous, but the second step is (practically) barrierless and certainly too fast to allow any loss of stereoselectivity.[29] Taking as a criterion the reaction time as compared with a vibrational period, as Zewail et al. did (see, e.g., ref 11), the reaction can be called concerted. Thus, [1,3]-sigmatropic H migration is accompanied by [1,2]-migration; it leads to bicyclo[3.1.0]hexane, as indicated in the reaction scheme. Previously it was believed that the stereospecificity requires that this product be formed from a carbene, not from a diradical.[28] But the singlet diradical is short-lived enough to preserve stereospecificity.

4.3. Comparison with Other Femtosecond Experiments. Soep et al. recently studied a number of olefins, including cyclohexadiene, with excitation at 200 nm and probing by one-

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(33) Fuss, W.; Lochbrunner, S.; Müller, A. M.; Schikarski, T.; Schmid, W. E.; Trushin, S. A. *Chem. Phys.* **1998**, *232*, 161−174.

photon ionization at 267 nm.[19] They only observed the parent ion in cyclohexene. Their signal perfectly agrees with ours in the range shown by them. This strongly supports our method: The high intensities we used could have been suspected to cause time-dependent level shifts, thus perturbing the pump process and possibly introducing artificial time dependences. However, the agreement with Soep's low-intensity one-photon probing shows that there is no reason to worry.

Despite this agreement of data, we analyze our parent ion in terms of two time constants ($\tau_1 = 20$ fs, $\tau_2 = 47$ fs) instead of one (Soep et al.: 35 fs). It is mainly our better signal-to-noise ratio in the tail which enforces the longer time constant; the shorter one is then additionally needed to reproduce the rising edge. The fit quality is thereby also improved in the region shown in ref 19 (The single-time fit in ref 19 was not fully satisfactory with respect to the leading edge and maximum of the signal.) The fact that Soep et al. did not observe any consecutive time constant was already used in the previous section to localize window 3 to an energy more than 4.65 eV (i.e., Soep's probe photon of 267 nm) below the ionization energy. This is in agreement with the authors' interpretation of why they observed a second time constant in some olefins of smaller ionization potential.

Cyclohexene, norbornene, and other olefins have already been investigated by Zewail et al., employing two-photon excitation at 307 nm (2 × 4.05 eV) and probing by multiphoton ionization at 615 nm.[10,11] The authors interpreted their data by assuming two retro-Diels−Alder reactions, one concerted and one stepwise, which occur on the ground-state surface after internal conversion; the latter was assumed not to be time-resolved. The ultrafast internal conversion in one of the compounds investigated, norbornene, was rationalized by a calculated S_1/S_0 CI, which also leads to a [1,3]-sigmatropic photoreaction[12] (see section 4.2). Wilsey et al.[12] argued that the molecule can also go down from the CI along $-x_2$ instead of closing the bond between the CH_2 group and position 2 of the allyl system (which would be direction $+x_2$; see section 4.2). The diradical thus produced can then eliminate an ethylene, thereby completing a two-step retro-Diels−Alder reaction. The accessibility of this path very much depends on slopes and energetic details of the surface which could alternatively guide the molecule around the lower cone to the positive x_2 direction, so that the stepwise retro-Diels−Alder reaction would not be initiated: If the energy and momentum available remain concentrated in the $-x_2$ direction, this reaction is conceivably ultrafast; but if vibrational energy redistributes before, favored by anharmonicities, the reaction will take ~1 ns according to RRKM theory.[9]

On the assumption of stepwise ring cleavage, the reaction was claimed to be completed within 0.2 ps at the excitation energy of 8.1 eV [11] and in norbornene also at 6.0 eV.[10] In cyclohexene, we found that with an excitation energy of 6.2 eV butadiene is not formed until at least 500 ps. This is consistent with the times for butadiene formation of around 1 [9] to 10 ns[4] previously found with 6.4 and 6.7 eV. With an activation energy of 2.8 eV,[9] the reaction rate will hardly increase by 3−4 orders of magnitudes if the vibrational energy (temperature) is raised by 20% (from 6.7 to 8.1 eV); indeed, the results were very similar with norbornene for these two excitation energies.[10] It is also worth noting that the intermediate diradical postulated in ref 11 can be made by triplet sensitation.[5] A characteristic side product of this diradical (besides butadiene + ethylene) is vinylcyclobutane. This product was not detectable when cyclohexene was excited at 160 nm (7.75 eV).[5] Hence, the diradical is not formed at this energy.

The authors of ref 11 assumed that the main contributions to their signals came from two locations on the ground-state surface (the diradical intermediate I and the transient T in ref 11). If so, it is difficult to understand why the product should not give rise to a signal, too; since all signals in ref 11 decayed to 0, they cannot belong to a product. It is also hard to understand why the excited states (A and A′ in ref 11) should not contribute to the signals; they should even dominate in it since they are ionized with fewer probe photons than the ground state. An alternative assignment of the analogous signals from norbornene was attempted in ref 12: From the calculated CI, corresponding to a [1,3]-sigmatropic shift, the molecule was assumed to leave within near 0 fs to form a diradical and within 30 fs to form vibrationally excited cyclopentadiene (Scheme 13 in ref 12). The latter was assumed to decay within 220 fs to ground-state cyclopentadiene, the former within 160 fs to products of 1,3- and 1,2-shifts. However, a single branching point can only decay with one time constant, and vibrational energy in an unreactive molecule is very long-lived, being limited only by collisional quenching in practice.

We suggest that the time constants in refs 10 and 11 actually show the time evolution of highly excited states (~8 eV). They probably decay via lower ones, which can be shorter lived, as our results show. These lower states can also contribute to the signals, but then—as always in consecutive processes—only show the time constants of the slowest preceding step (departure from the higher states). This decay is connected with photochemical processes, not with a reaction in the hot ground state. Such an alternative assignment was already presented in ref 21 with respect to norbornene and norbornadiene.

5. Concluding Remarks

As stated in the Introduction, monoolefins show surprisingly many photoreactions, even if processes in the hot ground state are excluded. They can be classified into three types: cis−trans isomerization, pericyclic reactions, and carbene formation. It is an interesting question where the branching occurs. Since the work of, in particular, Olivucci et al., it has been clear that the most important branching points in organic photochemistry are CIs. The trajectories bifurcate there to return to the reactant (i.e., internal conversion) or proceed to one or several products. The decision is made by the way of recoupling the electrons. Some examples are compiled in the short review.[34]

For cyclohexene and other olefins, it is difficult to figure out one single conical intersection that could explain both carbene formation and the 1,3-sigmatropic shift. It is therefore interesting that our interpretation of the dynamics involves repeated branchings: Depending on whether the wave packet decides at the $\pi\pi^*$/Z CI to continue on the $\pi\pi^*$ or the Z surface, it arrives at two different CIs with S_0. Here it is also worth noting that the Z/S_0 CI can lead to both carbene formation and cis−trans isomerization (the latter being less important for cyclohexene due to ring strain, though not negligible[7]) besides internal conversion, as pointed out in refs 17 and 33.

The fact that the trans(oid) isomer forms despite strain implies that near the branching point the ring strain has not yet substantially built up. Otherwise the molecule would only choose the direction to the reactant or another product. Indeed, the CI responsible for cis−trans isomerization and carbene formation suggested in refs 17 and 33 involves a geometry (Chart 1) practically free of ring strain for cyclohexene: Whereas one of the CH groups (carbon $C_{(1)}$) is twisted by ~90°,

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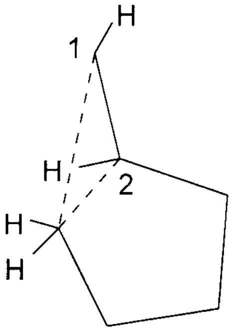
(34) Bernardi, F.; Olivucci, M.; Robb, M. A. *Chem. Soc. Rev.* **1996**, *25*, 321−328.

Chart 1. Suggested Geometry at the Z/S_0 Conical Intersection, from Where Both Cis−Trans Isomerization and Carbene Formation Can Take Place[a]



[a]Carbon atoms 2−6 are nearly within one plane. $C_{(1)}-C_{(2)}$ is the previous double bond, twisted by nearly 90°. The bridge (broken lines) is a 3-electron 3-center bond.

its CH_2 ligand forms a bridge to the other CH group ($C_{(2)}$) which itself is pyramidalized, i.e., sp^3-like. The backbone $C_{(2)}-C_{(6)}$ is then practically strain-free. If the CH_2 group keeps moving toward $C_{(2)}$, a carbene forms; if it returns to $C_{(1)}$ and the twist is reversed or, in contrast, continues, the result is recovery of the reactant or a trans isomer, respectively. The latter case is conceivable if during buildup of ring strain a barrier between the trans and cis reaction valleys comes into play that prevents traveling around the cone, so that the strained molecule is trapped. The postulate of a relatively stress-free branching region certainly applies to many photochemical reactions forming strained products.

Invoking branching to explain the various products is in contrast to the current interpretation of the wavelength effects in olefins, which states that some products are formed from the Rydberg state (namely, the carbenes) and others from the $\pi\pi^*$ state.[1,2,6] The tacit assumption is that exchange of population between the two states is very limited. However, two surfaces lying close to each other and differing in the direction of their initial slopes (which is required to explain the different photochemistry) certainly intersect in an easily accessible region. Exchange of population is then ultrafast, in agreement with the 20 fs we assigned to departure from the Rydberg to the $\pi\pi^*$ surface. (20 fs would be just one period of a 1667-cm^{-1} vibration.) In section 4.1, we instead invoked conservation of the momentum initially acquired from the initial slope. Such conservation seems generally possible within ultrashort times. The time to reach the next—and crucial—branching point (the $\pi\pi^*$/Z CI) is only 47 fs. At this CI, the wave packet will stay on the $\pi\pi^*$ surface unless it is expelled from it (from the drawing plane of Figure 4, lower arrow), that is, unless the symmetry is so perturbed as to mix the antisymmetric (B in C_2) $\pi\pi^*$ with the symmetric (A) Z state.

The short lifetimes found here have more implications: They are too short to allow any bimolecular reactions since collision times are longer even in the liquid phase. A polar reaction such as addition of methanol will thus not take place in the Rydberg or zwitterionic states, although their partial charge would support it. In fact, this reaction has been shown to proceed via protonation of ground-state *trans*-cyclohexene (see the reviews refs 35 and 36). Also photodimerization seems to involve a reaction of one trans with the cis isomer;[37] in other olefins it is believed to take place via an excimer state populated by excitation of a preformed van der Waals dimer.[17] The short times thus support these assignments. The short time constant (350 fs) assigned to the rearrangement of the intermediate carbene with the given excess energy also rationalizes why intersystem crossing to its triplet ground state cannot compete.

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