Ultrafast photochemistry of cyclopentadiene: Competing hydrogen migration and electrocyclic ring closure

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Abstract

Probing by dissociative intense-laser field ionization, we found that cyclopentadiene relaxes from the initial 1B2 state, excited at 240 nm, within 37 fs to the dark 2A1 state; a doubly exponential decay (71 and 333 fs) leads from there to S0. To explain the short times, we invoke conical intersections which we associate with photochemical pericyclic reactions: electrocyclization and a hydrogen shift. The latter reaction is dominant, as concluded from the deuterium isotope effect. A reaction (19 ps) found after departure from 2A1 is ascribed to thermal back reaction of the initially formed electrocyclization product bicyclo[2,1,0]pentene in the hot ground state, recovering cyclopentadiene. Comparing this molecule with two others, benzene and cycloheptatriene, we point out that ultrafast internal conversion is not governed by densities of states and matrix elements, but by the pathway on potential surfaces; the matrix-element approach tacitly assumes vertical transitions. But probably ultrafast radiationless transitions are always accompanied by large displacements of atoms or groups similar to that in chemical reactions, so that photophysics is a consequence of photochemistry in such cases. Both have the initial path in common, typically till the last conical intersection.

Keywords: Ultrafast dynamics; Photochemical pericyclic reactions; Branching; Dark states; Internal conversion; Fermi’s Golden rule

1. Introduction

Ultrafast nonadiabatic processes normally proceed through easily accessible conical intersections (CIs) of potential energy surfaces (PES) (see, for example [1]). The lowest excited PES and the ground-state surface will intersect not far from the S1 minimum (so that this CI will be easily accessible) only if the two surfaces are strongly shifted against each other. A large S1 shift corresponds to a displacement of atoms or groups, such as in a chemical reaction. Hence, an ultrashort lifetime (picoseconds or shorter) of a molecule points to a photochemical activity. The reverse conclusion would not be right: there are also slower photochemical reactions; some can hardly compete with fluorescence. One could suppose that reactions leading to strained products belong to the slower category, if a certain strain is already developed at the geometry of the CI, so that it would only be reached with activation energy.

The only known photochemical products of cyclopentadiene (Cp), bicyclo[2,1,0]pentene (Bp) and tricyclo[2,1,0,02,5]pentane (Tp, Scheme 1) [2–4], are highly strained. These products of electrocyclic ring closure seem to be formed only in small quantum yield: hours of illumination with a high-power lamp are required to attain good conversion [2–5]. To check whether strain slows the reaction down, we investigated the dynamics of cyclopentadiene after excitation by a femtosecond pulse in the first π → π* transition at 240 nm, probing it by ionization at 810 nm. We found several steps below 100 fs, much faster than expected. These fast processes might be connected with an unhindered photochemical
reaction, whose product is indistinguishable from the reactant, so that it was not noticed before: a photochemically allowed 1,3-sigmatropic hydrogen shift (Scheme 1). Therefore, we also investigated cyclopentadiene-d$_6$ and found indeed a deuterium isotope effect, confirming H migration. However, we find that the formation of the strained products is competitive; it proceeds at a not much slower rate. Also elimination of a hydrogen atom has been observed after UV excitation [6,7]. It is, however, a reaction taking place on a much longer time scale only after return to the ground state [7]. This assignment is consistent with our results (Scheme 2).

The method we employ (see, e.g., [8]) excites the molecules by a femtosecond UV laser pulse. For probing, they are then ionized at 810 nm at high intensity and the ion yields are measured mass-selectively. When the molecule slides down the potential energy surfaces, one observes a decrease of ionization probability, a rise of the order of ionization (since more photons may be needed for ionizing lower states) and an increase of fragmentation. (Release of electronic energy produces nuclear kinetic energy. Ionization of these hot molecules gives rise to hot ions which then can dissociate in the long time – $>$100 ns – before acceleration and detection. For the neutral molecules, the short time until probing is not sufficient for fragmentation; see also Section 4.4.) All three features help to estimate the electronic energy of the individual “observation windows”, that is, of the location on the PES from where ionization starts.

A short lifetime of excited cyclopentadiene could already be concluded from the lack of fluorescence (Section 4.4 in [9]). The first UV absorption with maximum near 233 nm (5.3 eV) is composed of two transitions: the dominant one with a vibrational structure at long wavelengths is a $\pi \rightarrow \pi^*$ transition (HOMO $\rightarrow$ LUMO, symmetry species 1B$_2$) which is excited in the present work. Superimposed on it at shorter wavelengths there is a $\pi \rightarrow$ Rydberg(3s) transition (species 1A$_2$). Spectra are presented in [10–12]. Quantum-chemical calculations helped to assign the electronic states [13–15] and vibrational structure [14,16–18]. These calculations also found a state of 2A$_1$ symmetry, containing some contribution by excitation of two $\pi$ electrons. It corresponds to the so-called dark state (because it carries only little oscillator strength) of other polyenes (see e.g. [19]). Its energy is near 6.2 eV (200 nm) at ground-state geometry [13,16–18], whereas its minimum is below that of the 1B$_2$ “spectroscopic” state [18]. Indication for a low-lying 2A$_1$ state was indeed found from resonance Raman spectroscopy [20]. Therefore, we can expect near the minimum of the spectroscopic state an intersection of the 1B$_2$ and 2A$_1$ PES, which can provide a doorway for relaxation.

From the 2A$_1$ minimum one will have to look for CIs with the ground state surface, corresponding to H migration and to electrocyclic ring closure. For the former, there is a calculation in propene [21] predicting a geometry with an H atom above C (2) of a planar allyl radical. Cyclopentadiene with its stiff backbone can serve as a test case for this predicted geometry. Analogous CIs were also calculated for 1,3-sigmatropic alkyl shifts [22–24]. The CI geometry for the electrocyclic reactions was calculated for s-cis butadiene and found to be highly twisted [25,26]. It will be interesting to see whether cyclopentadiene is still flexible enough for these required distortions or will strongly hinder this path and slow it down.

2. Experimental

Cyclopentadiene was prepared by cracking the dimer at 160–180 °C. It was deuterated three times by a 10-fold excess of D$_2$O in diethylene glycol dimethylether with base catalysis (adding $\approx$1% weight of Na). Deuteration was checked by gas-chromatography mass-spectroscopy: after the third step, the C$_5$D$_4$H/C$_5$D$_6$ ratio was below 0.5%, so that C$_5$D$_4$H$_2$/C$_5$D$_6$ should be $<10^{-5}$. (C$_3$D$_4$H$_2$ would have the same mass as C$_3$D$_5$, which is investigated in this work.)
The two species were investigated at 20 °C in the gas phase. They were introduced through a precision needle valve to the ionization region of a time-of-flight mass spectrometer at a pressure of \(10^{-7} - 10^{-5}\) mbar (the higher pressure for the weaker signals), where they were first excited at 240 nm (pulse duration 70 fs, intensity \(10^9\) W cm\(^{-2}\)) and then ionized with the delayed probe laser at 810 nm (45 fs, \(10^{13}\) W cm\(^{-2}\)). The pump radiation was generated from a Ti-sapphire laser system (Spectra Physics Tsunami + Spitfire, 2 mJ, 45 fs, 1 kHz) and a parametric generator (‘‘deep-UV Topas’’, Light Conversion); the latter comprises several nonlinear steps for frequency conversion. It was tuned to 240 nm. Varying the pump–probe delay time, ion yields were measured mass-selectively by a time-of-flight mass spectrometer. Pump and probe polarizations formed an angle of 55° (‘‘magic angle’’) to avoid effects induced by molecular rotation. In each pulse, two ion signals were simultaneously measured by two boxcar integrators: besides an ion from cyclopentadiene also Cr(CO)\(_6\) which is generated by (1+3)-multiphoton ionization of added Cr(CO)\(_6\). Subtracting a small delay (17 fs, corresponding to the lifetime of Cr(CO)\(_6\) in the initially excited state \([27]\)) versus the time zero, found from the Xe\(^+\) signal in separate experiments, the Cr(CO)\(_6\) data directly yield the instrumental function, i.e., the correlation function of the pump with the third power of the probe. This function was used to calculate the length of the pump pulse. It also served for synchronization of different scans. Details of the setup are given elsewhere \([8,28,29]\).

### 3. Results

Cyclopentadiene (C\(_5\)H\(_6\)) shows little fragmentation after ionization at 810 nm, both with or without pumping at 240 nm: the most prominent fragment ions with masses 65, 40 and 26 u have an intensity around 1% of the parent (66 u). For the time-resolved work, it was sufficient to investigate the parent signal and the fragment C\(_5\)H\(_4\)\(^+\) (40 u); the other fragments were very similar in their time behavior and did not yield additional time constants. Fig. 1a shows the time-dependent parent ion signals for C\(_5\)H\(_6\) and C\(_5\)D\(_6\) (66 and 72 u). Different time ranges of the fragments C\(_5\)H\(_5\)\(^+\) and C\(_3\)D\(_3\)\(^+\) (40 and 44 u) are given in Fig. 1b and (d). Fig. 1c illustrates, how a (fragment) signal is decomposed into contributions from different observation windows L\(_i\) with time constants \(\tau_i\) (see below). Fig. 1c shows a decomposition into two parallel paths; it will be discussed in Section 4.2.

The shape of the signals including the ratio of peak to pedestal did not depend on the pump intensity (varied by a factor of about 3). This is especially important for the pedestal (nonvanishing long-time signal) in the fragment signals and proves that it is produced by a single pump photon. Varying the probe intensity by a similar factor did not change the time constants, although the shape of the fragment signals was influenced, because some observation windows have different orders of ionization.

For the analysis of the time-resolved data, we assume that population flows over several locations L\(_i\) on the potential energy surfaces (PES) and that this flow can be described by rate equations. (Such a kinetic approximation seems suitable to describe the flow of population \([8]\), if one takes occasional additional phenomena into account such as periodic oscillations.) Their solution for the L\(_i\) populations results in sums of exponentials with time constants \(\tau_i\), no matter whether the L\(_i\) are reached consecutively or whether there is a branching of the path. Each location L\(_i\) is associated with a mass spectrum \(m\sigma_i\) representing the relative yields of ions with mass \(m\); the signals, therefore, consist of a linear combination (coefficients: \(m\sigma_i\)) of the time-dependent L\(_i\) populations convoluted with the instrumental function. (Convolution is necessary for the times shorter than about 100 fs.) For the latter, we used a Gaussian (full width at half maximum 75 fs) and a parametric generator (‘‘deep-UV Topas’’, Light Conversion) with 1 kHz) and a parametric generator (‘‘deep-UV Topas’’, Light Conversion); the latter comprises several nonlinear steps for frequency conversion. It was tuned to 240 nm. Varying the pump–probe delay time, ion yields were measured mass-selectively by a time-of-flight mass spectrometer. Pump and probe polarizations formed an angle of 55° (‘‘magic angle’’) to avoid effects induced by molecular rotation. In each pulse, two ion signals were simultaneously measured by two boxcar integrators: besides an ion from cyclopentadiene also Cr(CO)\(_6\) which is generated by (1+3)-multiphoton ionization of added Cr(CO)\(_6\). Subtracting a small delay (17 fs, corresponding to the lifetime of Cr(CO)\(_6\) in the initially excited state \([27]\)) versus the time zero, found from the Xe\(^+\) signal in separate experiments, the Cr(CO)\(_6\) data directly yield the instrumental function, i.e., the correlation function of the pump with the third power of the probe. This function was used to calculate the length of the pump pulse. It also served for synchronization of different scans. Details of the setup are given elsewhere \([8,28,29]\).

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The parent C\(_5\)H\(_4\)\(^+\) decays to 0 in a very short time (Fig. 1a)): trying to fit its wing in the range 70–170 fs (during which the signal drops by a factor of >100) with a singly exponential function would result in a time constant \(\leq\)27 fs (\(\leq\) 30 fs for C\(_3\)D\(_3\)\(^+\)). However, a simulation of the full signal (using convolution with the instrumental function) with this value is unsatisfactory; for example, it would predict a maximum at 20 fs, which is actually observed at 24 fs. The discrepancy with C\(_3\)D\(_6\) (21.4 fs versus 32 fs) is even more pronounced. Therefore, we simulated the parent signal by a doubly exponential decay (Fig. 1a inset) with the time constants \(\tau_1\) and \(\tau_2\) (Table 1). As long as the sum \(\tau_1 + \tau_2 = 37.4\) fs (52 fs for C\(_3\)D\(_6\)) is kept constant and both time constants are below the upper bound
Fig. 1. Transient ion yields (masses indicated) from cyclopentadiene (Cp) and cyclopentadiene-d$_6$. The solid lines result from the simulation. (a) The two parent ions. Also shown is Cr(CO)$_6^+$ (mass 220), which after subtracting a delay of 17 fs yield the instrumental function (Section 2). The inset shows how the signal is decomposed into two contributions, each a singly exponential decay ($\tau_3, \tau_4$) convoluted with the instrumental function. (b) The 40-u fragment signal from Cp, compared to the parent (66 u). The apparent pedestal also contains a slow decay ($\tau_5 = 19$ ps) that is shown in a longer time scale in (d). Subtracting this decay and the constant pedestal from the data reveals the preceding $\tau_3$- and $\tau_4$-decays, as shown in the inset for Cp and Cp-d$_6$. (c) Decomposition of the 40-u fragment signal into contributions from L$_1$ to L$_6$. (d) The slow decays (solid lines: singly exponential fits) of the fragments from Cp and Cp-d$_6$. These signals are normalized to 1 at long delay, whereas those of a–c are normalized to the maximum. (e) Decomposition of the 40-u fragment signal into contributions from the H-migration and electrocyclic paths, assuming a branching ratio of 0.8:0.2.
Table 1

Time constants $\tau_i$ of the locations $L_i$ on the potential energy surface of cyclopentadiene and cyclopentadiene-$d_6$ and cross-sections $^{40}\sigma_i$ to generate the ions of mass $m^+$

<table>
<thead>
<tr>
<th>$i$</th>
<th>$1$</th>
<th>$2$</th>
<th>$3$</th>
<th>$4$</th>
<th>$5$</th>
<th>$6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1(H)$</td>
<td>$22.4$ fs$^b$</td>
<td>$15$ fs$^b$</td>
<td>$71 \pm 5$ fs</td>
<td>$333 \pm 12$ fs</td>
<td>$19 \pm 2$ ps</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$\tau_1(D)$</td>
<td>$29$ fs$^b$</td>
<td>$23$ fs$^b$</td>
<td>$114 \pm 5$ fs</td>
<td>$440 \pm 13$ fs</td>
<td>$24 \pm 2$ ps</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$\tau_2(D)/\tau_1(H)$</td>
<td>$1.29$</td>
<td>$1.53$</td>
<td>$1.61 \pm 0.2$</td>
<td>$1.32 \pm 0.1$</td>
<td>$1.26 \pm 0.24$</td>
<td></td>
</tr>
</tbody>
</table>

$^{40}\sigma_1$(H) = $0.68$ |
$^{40}\sigma_2$(H) = $0.29$ |
$^{40}\sigma_3$(H) = $0.29$ |

$^{40}\sigma_1$(D)/$^{40}\sigma_1$(H) = $0.08$ |
$^{40}\sigma_2$(D)/$^{40}\sigma_2$(H) = $0.047$ |
$^{40}\sigma_3$(D)/$^{40}\sigma_3$(H) = $0.036$ |
$^{40}\sigma_4$(D)/$^{40}\sigma_4$(H) = $0.026$ |

$^{40}\sigma_5$ = $37.4 \pm 3$ fs and $^{40}\sigma_6$ = $52 \pm 3$ fs; D/H effect $1.39 \pm 0.19$. $\tau_1/\tau_2$ is arbitrarily chosen so that the H/D effect is within reasonable limits and that $\tau_1, \tau_2 \leq 27$ fs for C$_5$H$_6$ and 30 fs for C$_5$D$_6$.

(27 and 30 fs, respectively), the ratio $\tau_1/\tau_2$ is not critical for the fit. In the table, we chose this ratio so that the isotope effect is smaller for $\tau_1$ than for $\tau_2$ (see Section 4).

From the fragment signals(s), additional time constants are derived: the tail at long times yields $\tau_3$ in a singly exponential fit (Fig. 1(d)). Fixing $\tau_1, \tau_2$ and $\tau_3$ in the full simulation of these signals, we get $\tau_4$ in addition (Table 1). The full simulation using these three time constants reveals, however, small deviations from the fragment signals around 150–400 fs; by introducing another time constant ($\tau_4$), the fit becomes excellent also in this region. (To make these processes visible, in the inset of Fig. 1(b) we subtracted the L$_5$ and L$_6$ contributions from the data; a doubly exponential fit to this tail from 150 to 2500 fs gives good start values for $\tau_4$ and $\tau_3$ in the full fit.) $\tau_4/\tau_5$ reflect lifetimes of the three observation windows L$_1$–L$_4$. L$_4$ with its infinite lifetime (indicated by the pedestal of the fragment signal in Fig. 1(b)–(d)) obviously corresponds to the ground state of a product and/or the (hot) recovered reactant. To find out whether L$_4$ or L$_5$ also belong to the ground state, we measured the signal dependence on the probe intensity (Table 1). Obviously, the locations L$_4$–L$_3$ have the same order of ionization; that is, their ionization energy is not different by more than one probe quantum ($1.53$ eV). (According to the photoelectron spectrum [30], the first ionization energy is $8.58$ eV, so that ionization from the Franck–Condon region requires three (nominally $>2.2$) probe photons.)

Hence, all three represent locations on excited PES. Note, however, that the increased fragmentation from L$_3$ (no parent anymore from this observation window! See Table 1) indicates that L$_3$ is lower than L$_1$ and L$_2$. The intensity dependences show that L$_4$ requires one more photon for ionization, because $^{40}\sigma_4/^{40}\sigma_3$ increases by a factor of 2 on raising the intensity by the same factor. Such a difference of ionization energies is small enough to assign also L$_4$ to an excited surface.

Two more photons are required, however, for ionization of L$_5$ and L$_6$, as to conclude from the fourfold increase of $^{40}\sigma_5$ and $^{40}\sigma_6$ (relative to $^{3}S_{\alpha}$, for instance) on raising the intensity by a factor of 2 (Table 1). This means that not only L$_5$ but also L$_6$ is on the S$_0$ PES. Hence, $\tau_5$ corresponds to a ground-state process, whereas the preceding steps take place on excited-state surfaces.

All time constants are longer for C$_5$D$_6$ than for C$_5$H$_6$ by factors 1.3–1.6. A ratio of 1.41 would be expected for barrierless motion of an H atom. The $^{40}\sigma_i$ were imposed to be the same for C$_5$D$_6$ and C$_5$H$_6$, as mentioned; this constraint significantly reduces the error limits of the $\tau_i$.

4. Discussion

4.1. The time constants $\tau_1$ and $\tau_2$: motion on the spectroscopic surface $1B_2$

From the order of ionization and fragmentation patterns we concluded in Section 3 that the locations L$_1$–L$_4$ with their time constants $\tau_1$–$\tau_4$ belong to excited PES, L$_3$ and L$_4$ being slightly lower in energy than the other two. As mentioned in Section 1, the 2A$_1$ surface is expected to cross the initially excited ("spectroscopic") 1B$_2$ surface near its minimum. It is therefore suggestive to assign $\tau_1$ and $\tau_2$ to processes on the 1B$_2$ PES, whereas $\tau_3$ and $\tau_4$ will belong to the 2A$_1$ state. In many previous investigations, we have detected two relaxation steps on the spectroscopic surface, for example in ring opening of 1,3-cyclohexadiene [8,31,32] or hydrogen migration in cycloheptatriene [33]; the first step ($\tau_1$) was there attributed to relaxation along Franck–Condon (FC) active coordinates; this assignment was supported by the fluorescence lifetime and spectrum. The following step ($\tau_2$) involved a change of direction of motion [8,32,33], bringing the wave packet around the lower cone of the
1B/2A CI to the lower (‘‘dark’’) 2A surface; support came from the deuterium isotope effect [33] and substituent effects [32]. For the cyclopentadiene τ₁ and τ₂ a difference of H/D effect was only assumed (see below and Section 3), so that a change of direction cannot be deduced from it. However, the very nature of FC coordinates dictates that they point the way for the first motion after excitation. These coordinates are totally symmetric (a₁). Then for symmetry reasons a temporary excursion along a b₂ coordinate is necessary to allow crossing over from 1B₂ to 2A₁; that is just the path around the CI. The path thus changes direction from initial a₁ to subsequent b₂ coordinates.

The dominant FC active coordinates are two CC stretches, one of them coupled to a planar CCH bend, and a planar ring deformation induced by them [16–18]. The contribution by the H vibration will induce a b₂ symmetry. Vibrations of this kind in 1B₂ are planar CCH bends and have a maximum H/D isotope shift by a factor of 1.37 [17,18]. This is probably an acceptable agreement with the ratio τ₂(D)/τ₂(H) = 1.53 in view of the fact that 1B₂ → 2A₁ relaxation implies large-amplitude motion over a very anharmonic region, namely at the base of the CI, where there is even a negative curvature on the PES near the transition state.

The short τ₂ means that the CI (i.e., the outlet of the 1B₂ well) is on the way of the wave packet, which initially follows the FC coordinates. Hence, it is probably not far from the minimum of this surface, as indicated in Fig. 2. The CI should distort this surface in its surrounding, possibly even creating a double minimum in b₂ direction (perpendicular to the drawing plane in Fig. 2), and ab initio calculations should detect such phenomena. We note that a b₂ distortion can also be composed by a superposition of deformations with symmetries b₁ and a₂. It is therefore remarkable that an ab initio CIS (configuration interaction singles) calculation predicted that the 1B₂ state is unstable in a b₁ direction and will develop a double minimum slightly displaced towards a b₁ out-of-plane deformation of the H₃C-CH₂-H group [17]. In [14], this displacement is ascribed to vibronic interaction with a higher A₂ state.

The short τ₁ + τ₂ (37 fs for C₅H₆; 52 fs for C₅D₆) also implies some broadening of the UV spectrum. The measured room-temperature spectrum was successfully simulated by the calculated vibrational structure and an assumed width of 175 cm⁻¹ [17]. At low temperature, the width of the origin band of C₅D₆ is 152 cm⁻¹, which would correspond to a 1B₂ lifetime of 37 fs [11]. But the measured width contains some rotational broadening. Either the purely homogeneous width is only about 100 cm⁻¹, consistent with the 52-fs lifetime, or one assumes that there is a dephasing time that is shorter than the 1B₂ lifetime. The latter effect was found in butadiene [34].

4.2. The time constants τ₃ and τ₄: early branching and two separate paths from 2A₁ to S₀

The increase of the degree of fragmentation on arriving to L₃ and L₄, for example the complete absence of the parent ion, is just the same as in many previous cases after completion of the first two relaxation steps; these signals were assigned to the dark 2A state that is below the spectroscopic (1B) state. We therefore attribute also τ₃ and τ₄ in cyclopentadiene to processes on the 2A₁ surface. However, in a number of previous cases (e.g., cyclohexadiene [8,31,32]; cycloheptatriene [33]; butadiene [34] and others) only one time constant (τ₃) was found on the 2A surface. But in two molecules,
1,3-cycloheptadiene and 1,3-cyclooctadiene, we found two processes (τ_3 and τ_4) on the 2A surface; the comparison of the two molecules allowed to assign them to separate paths eventually leading to two different photochemical products [35]. Since cyclopentadiene also gives different photochemical products (resulting from H shift and from electrocyclization), it is likely that τ_3 and τ_4 correspond to two parallel processes. (More support for the parallel scheme is presented in the following; the data alone would not allow to exclude purely consecutive processes of the type L_2 → L_3 → L_4 → ...). The parallel processes must be preceded by a branching, which must be in L_2.

For explanation, it should be noted that a branching from a reactant R to two products P_a and P_b, produced with rate constants k_a and k_b, gives rise to only one observable time constant \( \tau = (k_a + k_b)^{-1} \); both products appear within the same time as the reactant disappears. However, if the branched process is followed by subsequent reactions from P_a and P_b, these reactions give rise to two independent additional time constants. Hence, in the given case an early branching (e.g., in L_2) may be recognized from later steps. To be specific, we suggest that branching takes place during \( \tau_2 \) (during leaving from the 1B_2 surface), the paths leading to two minima of the 2A_1 PES, and that departure from them towards separate CIs takes place within \( \tau_3 \) and \( \tau_4 \). Therefore, we reevaluated the data, using the branched scheme, assuming as an example a branching ratio of 0.8:0.2 in favor of the H migration. (This ratio would on the one hand be consistent with the dominant deuterium effect and on the other hand still allow detection of the minor process. It would imply \( \tau_{3H} = 19 \) fs and \( \tau_{2H} = 75 \) fs, which together give rise to the observed \( \tau_2 = 15 \) fs.) Compared with the purely consecutive scheme (constants listed in Table 1), the changes of time constants are negligible, whereas \( m_2 \sigma_3 = m_3 \sigma_3 \) increase (values given in footnote^a of Table 1). Fig. 1(e) shows how the 40-u signal is then decomposed into contributions from these two paths: the height ratio of the final pedestals (at times much longer than shown) has been chosen such that it would reflect the branching ratio, if the ionization probability were the same. The early time constants \( \tau_1 \) and \( \tau_2 \), that are still in common for both paths, are hidden by the convolution with pump and probe pulses. (The two curves coincide in this part, because the paths separate only later.) The other \( \tau \) are assigned to the two paths.

Since an activation energy seems plausible for electrocyclization (that leads to highly strained products), one will associate it with the longer time constant (\( \tau_4 \)), whereas the shorter one will correspond to hydrogen shift. The longer-lived minimum (M_4) will already involve some of the nonplanar distortion necessary for electrocyclization; because the ion has a planar ground state, the ionization energy from M_4 will be higher than from M_3. This explains the higher order of ionization and lower ionization probability. (In part, the lower signal from M_4 will also be caused by an unfavorable branching ratio; branching in favor of hydrogen migration is indicated by the deuterium effect on \( \tau_2 \).)

The existence of at least two 2A_1 minima, postulated above, is indeed supported by an ab initio (MCSCF) calculation [18]: this calculation optimized the 2A_1 state in planar geometry (which resulted in a change of CC bond lengths) and determined vibrational frequencies; imaginary frequencies were found for an a_2 and a b_1 CH bending and a b_1 ring torsion. This means that actual minima will be displaced into these directions. It is remarkable that the H-migration coordinate is a superposition of a_2 and b_1 CH bending and that electrocyclization requires out-of-plane distortion, a component of which can be the b_1 ring torsion. But whereas the calculation said that the 2A_1 surface is relatively flat, we must postulate that the minima are separated by a barrier (such as in Fig. 2) that is large enough that population exchange between them is slower than departure from the 2A_1 state; otherwise one could not observe separate time constants \( \tau_3 \) and \( \tau_4 \).

As already mentioned, another ab initio calculation found an instability of the 1B_2 state near its minimum (that is, in our L_2 window) towards a nonplanar b_1 distortion [17]; branching might be initiated there or at the 1B_2/2A_1 CI. The two regions are near by each other.

4.3. Departure from S_1 via conical intersections

Both time constants \( \tau_3 \) and \( \tau_4 \) for leaving the 2A_1 state are short enough that one must assume paths via easily accessible S_1/S_0 conical intersections, although the \( \tau_4 \) process (ascribed above to electrocyclization) seems to be slowed down by a minor barrier. For leaving a minimum towards the CI, the direction of motion must again be changed. In the case of \( \tau_4 \), this is reflected by the changed isotope effect, which has decreased to 1.32. The new coordinate hence involves less hydrogen motion, but more skeletal deformation.

This is expected for the electrocyclic CI: for example, in the CI for electrocyclic ring closure of butadiene the C_1=C_2H group is rotated out of plane (by \( \approx 60^\circ \)) around an axis connecting C_2 with C_4 [36] (indicated in Fig. 2 for cyclopentadiene); this motion is accompanied by decoupling of all four \( \pi \) electrons, which then can recouple to form the bicyclic and tricyclic products besides the reactant [25,26]. For a moving CH group an even smaller deuterium effect would be expected (1.04 from the mass ratio), if the process were barrierless. However, the long \( \tau_4 \) indicates an activation energy. Activated processes have larger isotope effects, if vibrations involving the isotopes have lower frequencies in the activated state.

The isotope effect for the other path (\( \tau_3 \)), assigned to 1,3-sigmatropic H shift, is large (1.61), as expected if the
hydrogen motion dominates. A corresponding CI was predicted by CASSCF calculations for H migration in propene [21]. In the CI, the migrating H of propene is just above C(2) (distance 1.8 Å) of a planar allyl system; except minor changes of CC bond lengths, no additional distortions of the molecules are predicted. Such a CI is obviously accessible without any strain in cyclopentadiene. The large isotope effect for τ₃ indicates that in fact not much skeletal deformation is involved on this path. Our results hence seem to support the calculation. On the other hand, a pure hydrogen motion on a barrierless path should take place in much less than τ₃ = 71 fs. (Compare, for instance, τ₂ = 15 fs, which is dominated by H displacement.) We therefore suggest that there is a minor barrier, probably caused by a small backbone distortion. (The participation of heavier masses will tend to decrease the D effect; but as explained in the preceding paragraph, the barrier can raise it again to even above 1.41, as observed.) A calculation on a higher level than CASSCF seems hence desirable, although the CI geometry will probably not change substantially.

The calculations [22] predicted that from the H-migration CI, the hydrogen can either continue its migration to complete the 1,3-shift (“Cp3” in Fig. 2), or return to C(11) to recover the reactant (“Cp” in Fig. 2). But as pointed out in [22], it can also close a bond with C(2), and thus give rise to a ground-state singlet diradical; in the calculated small model systems, the two unpaired electrons can then form a new bond in ultrashort time, giving a cyclopropane derivative. The question is whether also in the present case bicyclo[2,1,0]pentene is formed from the diradical, and possibly even the tricyclic compound. Then, the electrocyclic CI would not be needed at all to explain the observed products. However, such diradical cyclizations can certainly not compete with a simpler and much faster relaxation possible in the given case: the diradical is simply a point on the ground-state surface with three of the CC bond lengths changed; from there, the molecule could move to the S₀ minimum in a quarter of a vibrational period (wavenumber ≈1650 cm⁻¹), that is in ≈5 fs. Therefore to explain the much longer τ₃, a separate (electroyclic) CI is needed for the path leading to bicyclo pentene and tricyclo pentane.

Coming back to this electrocyclic CI and the barrier before it: the barrier implies that the nonplanar distortions calculated for this CI [25,26] present in fact a certain obstacle for reaching it in cyclopentadiene, because they are hindered by the stiff σ backbone of the five-membered ring. Nevertheless, they seem to present not too big problems. Perhaps this can be rationalized by the four π electrons uncoupled in the CI: the decoupling involves some π-antibonding, that may drive an out-of-plane torsion sufficiently strong to overcome the stiffness. The distortion seems also not so serious if one realizes that the twist of the three CC bonds simply lifts a single CH group out of plane, a motion corresponding to the beginning of a Hula twist [36]. Our observations thus support the calculated geometry, the idea with the decoupled π electrons in the CI and the description as an attempted Hula twist. As explained in [36], the lower surface on leaving the CI involves some bonding 2–4 interaction (which actually drives the out-of-plane deformation). Formation of a 2–4 bond is the first step to produce the tricyclopentane. An attractive 2–5 interaction can also develop on leaving the CI, a path that explains formation of bicyclo pente nene.

4.4. Ground-state processes (τ₅)

The fifth time constant τ₅ = 19 ps was assigned in Section 3 to a reaction in the hot ground state of either cyclopentadiene or a photochemical product. The lowest-energy thermal decomposition of cyclopentadiene is elimination of an H atom [7,37,38] (bond energy 342 kJ/mol = 3.55 eV [39,40]). The dissociation rate was calculated by RRKM theory in [7]. With our excess energy of 5.17 eV (=energy of a pump photon) it would be about 10⁷ s⁻¹, more than three orders of magnitude slower than τ₅⁻¹. (The predicted rate would be too slow to be detected in the investigated time range of 600 ps.) Therefore, τ₅ must correspond to decomposition of a product. In fact the rate of the exothermic (reaction enthalpy 2.08 eV [41]) thermal back reaction bicyclo pentene → cyclopentadiene has been determined [42] to be 10¹⁴.⁵ s⁻¹ exp(−13590 K/T). If we consider our excess energy (=5.17–2.08 eV) as an average (thermal) energy and convert it to a temperature (2208 K, using vibrational frequencies similar as in cyclopentadiene), we receive a reaction time of 3 ps. In view of the thermal approximation, the agreement with τ₅ is good enough to assign τ₅ to ground-state ring opening of bicyclo pentene (“Bp → Cp” in Fig. 2).

The relatively small amplitude of this signal is also consistent with the modest bicyclo pentene quantum yield (see Section 1). Formation of tricyclo pentane is even less efficient by a factor of 7 [4], and the activation energy for its decomposition would be much higher (2.1 eV [43] versus 1.17 eV [42]), so that this reaction is not likely to be observed in our experiment. As already explained (Section 4.3), isotope effects in activated processes can be much larger than in the absence of a barrier, even if the motion of the substituted atoms is not the dominant one. The observed D effect of 1.26 seems reasonable for the reaction, where some CH bending vibrational frequencies will be lowered in the radicalic [43] transition state. The observation of this ground-state process strongly supports the assignment that one of the S₁/S₀ CIs is associated with electrocyclic ring closure to bicyclo pentene.
5. Conclusion

An ultrashort lifetime of excited cyclopentadiene was previously inferred from the lack of fluorescence [9] and the width of the vibrational structure in the UV absorption band [11]. It was ascribed to internal conversion. Our detailed investigation of the dynamics confirms the expectation (see Section 1) that ultrafast internal conversion is associated with photochemical reactions. We identified two types of them, electrocyclic ring closure to a bicyclic and a tricyclic product and 1,3-sigmatropic H-shift. The latter was inferred from the deuterium effect. Although it dominates, it was not noticed before, because the product is identical to the reactant. The method to distinguish parallel from consecutive reactions is novel: it relies on comparing fragmentation patterns and orders of ionization, that indicate that the locations L3 and L4 have similar energetics, so that the difference in signal strengths must originate from branching (Fig. 2). The electrocyclic ring closure channel was identified by the consecutive ring opening in the ground state, whose rate was known before. This method has also been applied to branching between cis-trans isomerization and ring closure of two dienes [35].

The suggested relaxation scheme (Fig. 2) is in many respects very similar to that of other pericyclic reactions (see, e.g. [1]): after excitation to the spectroscopic (1B2) surface, motion begins along Franck–Condon active coordinates. Then the wave packet turns to a new direction, crossing over to the dark 2A1 surface. It avoids the real crossing, passing around the lower cone of the CI. The path branches from there. It reaches two different S1 minima, from where the molecule passes over small barriers via two separate CIs to the ground state of the products. The postulated branching is an extension of the previous scheme [1], but is similar to a branching for two other dienes [35].

An activation energy for reaching the electrocyclic CI was expected, because its geometry involves lifting of one CH group out of the plane of the stiff ring [36]. From the fact that τ3 is too long for a barrierless hydrogen motion, we concluded that there is also a (minor) activation energy to reach the H-migration CI and that this CI involves some nonplanar distortion, too, in contrast to a calculation [21]. Also in [1,7]-sigmatropic hydrogen migration in cycloheptatriene (which involves an H-shift to the adjacent carbon), a small barrier was calculated for reaching the last conical intersection [44,45]. It was found consistent with the lifetime of the dark state (70 fs), and also substituent effects were explained on this basis [33,44,45].

It is interesting that indene (benzocyclopentadiene) has a much longer excited-state lifetime (274 ps [46]). Obviously the CIs discussed here are not accessible anymore, perhaps because the S1 energy is lower. In fact a calculation for indene only found CIs of the benzene type, accessible via a barrier that is due to nonplanar distortion of the benzene ring [47].

Finally, we would like to present a comparison of the S1 lifetimes of cyclopentadiene, benzene and cycloheptatriene (Table 2). This is interesting in the context of the traditional approach to describe internal conversion. (For a recent work applying this method to femtosecond chemistry, see [48].) This approach tacitly assumes that the adiabatic processes are vertical and then uses Fermi's Golden rule for the internal-conversion rate k:

\[ k = \frac{4\pi^2}{\hbar} V_{el}^2 FC \rho \]  

which involves an electronic matrix element \( V_{el} \) and a Franck–Condon factor FC between the involved states and the density of states \( \rho \) in the lower electronic state. These parameters are not very different for the three molecules. (For FC, this may be inferred from the widths of the UV spectra. \( \rho \) depends on the size of the molecule and the initial excitation energy. \( V_{el} \) will be similar in view of the similarity of the excited states.) But the lifetimes differ by six orders of magnitude and depend nonmonotonically on the size of the molecule. This is obviously due to the fact that sigmatropic H migrations in cyclopentadiene and cycloheptatriene cause strong shifts of potentials, thus giving rise to easily accessible CIs; on the other hand, a CI in benzene can only be reached via a barrier, associated with nonplanar distortion of the ring towards prefulvene [49]. In other words, one must consider transient distortions of the molecules (“pathway approach” [1]). The comparison in Table 2 clearly demonstrates the failure of the traditional assumption of vertical processes. This assumption was probably motivated by the idea that electronic relaxation may be much faster than nuclear motions. It is therefore very remarkable that just the fastest internal conversions (cyclopentadiene and cycloheptatriene) follow a path with large nuclear displacements; they are caused by the H migrations. (It is worth noting that the time constant for internal conversion would be the same, if the reaction were distinguished from it by isotopic labeling; the two processes have the initial path in common and branch only at the last conical intersection.) Probably all ultrafast internal conversions are connected with an – at least attempted [36,50] – chemical reaction. And,

<table>
<thead>
<tr>
<th></th>
<th>UV maximum (eV)</th>
<th>UV spectral width (eV)</th>
<th>S1 lifetime</th>
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<tbody>
<tr>
<td>Cyclopentadiene</td>
<td>5.2</td>
<td>0.9</td>
<td>71 fs</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.8</td>
<td>0.62</td>
<td>( \leq 100) ns\textsuperscript{a}</td>
</tr>
<tr>
<td>Cycloheptatriene</td>
<td>4.8</td>
<td>0.7</td>
<td>70 fs</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Decreases with excess energy.
of course, chemistry is not a matter of matrix elements, Franck–Condon factors and densities of states that are calculated in a static way, ignoring molecular distortions (see p. 458 of the discussion in [51]).

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References