Femtosecond dynamics of diradicals: transition states, entropic configurations and stereochemistry

Steven De Feyter, Eric W.-G. Diau, Alfred A. Scala, Ahmed H. Zewail *

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, USA

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Abstract

With femtosecond-resolved mass spectrometry, we report real-time studies of the dynamics of reactive diradicals: trimethylene, tetramethylene and structurally-constrained (by a bridge) tetramethylene. These comparative studies elucidate the role of transition states, entropic configurations and IVR on the global potential energy surface. The critical time scale for rotational clocks in stereochemistry is illustrated in the reaction mechanism for cyclization and fragmentation products. © 1999 Elsevier Science B.V. All rights reserved.
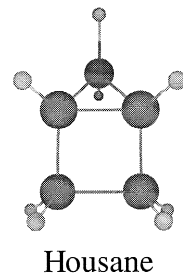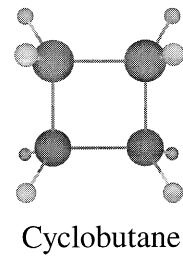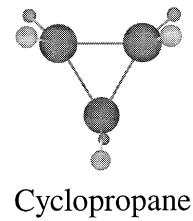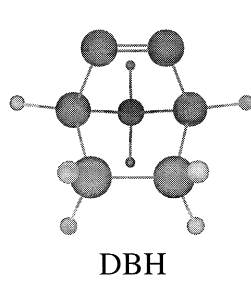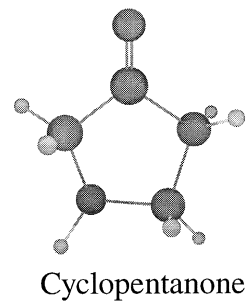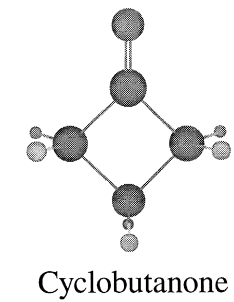
1. Introduction

Diradicals play a major role as intermediates in numerous thermally-activated and photochemical reactions. Their study has been at the forefront of research in physical organic chemistry as they are central to the understanding of bonding, reaction mechanisms and stereochemistry [1]. Typically, one infers the mechanism for the involvement, or lack thereof, of diradicals from stereochemistry, kinetics, and the effect of different precursors. The time 'clock' for rates is internal, the rotation of a single bond, and from the retention or inversion of stereochemistry the mechanism is deduced [2,3]. The theoretical approaches involve thermodynamical analysis of the energetics and semiemperical or ab initio calculations of the potential energy surfaces (PESs), and the molecular dynamics.

With femtosecond (fs) time resolution it is possible to study the dynamics of these intermediates. Using fs-resolved mass spectrometry in a molecular beam, trimethylene (1,3-diradical) and tetramethylene (1,4-diradical), produced by the fs-initiated decarbonylation of the corresponding cyclic ketones, were observed to have very different lifetimes and the studies elucidated the existence of reactive intermediates in the transition-state region [4]. Theoretical studies [5–8] of both the PESs and the dynamics (vide infra) were made by Doubleday and others to directly compare with the experimental results. With high-level theoretical calculations the importance of the dynamics to the nature of transition states (TSs), energy barriers and entropy effects can be addressed, as shown in the recent study of tetramethylene by Moriarty et al. [9]; see also Refs. [5–8].

Cyclobutanone

Cyclopropane   Cyclization ←   Trimethylene   1,2 H-shift →   Propene

Cyclopentanone

Cyclobutane   Cyclization ←   Tetramethylene   Fragmentation →   Ethylene (2)

DBH

Housane   Cyclization ←   1,3-cyclopentanediyl   1,2 H-shift →   Cyclopentene
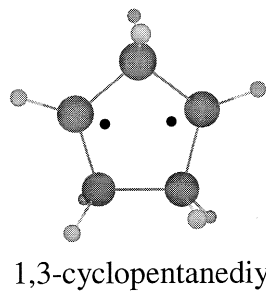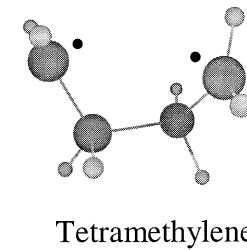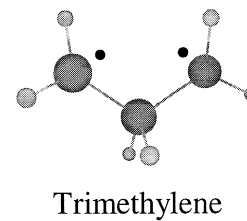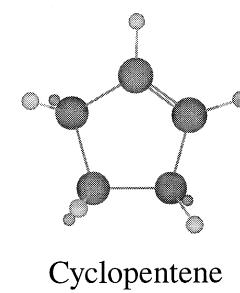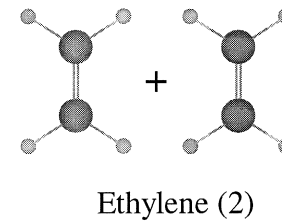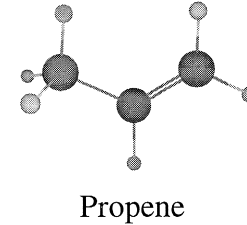
Scheme 1. Molecular structures of precursors, diradical intermediates, and products.

Another class of diradicals are those constrained trimethylenes and tetramethylenes (see Scheme 1). They are formed by the thermal- or photochemical activation of bridged diazenes, e.g., 2,3-diazo-bicyclo[2.2.1]hept-2-ene (DBH), the subject of numerous reports [10] gives, after nitrogen extrusion, 1,3-cyclopentanediyl diradical (constrained diradical). These diradicals are unique in that the additional CH_2 bridge to tetramethylene restricts the many degrees-of-freedom involved in the reaction dynamics.

In this Letter, we report direct fs studies of the constrained diradical formed by the nitrogen extrusion of DBH. We compare the dynamics of the constrained diradical with those of unbridged trimethylene and tetramethylene. The focus is on (1) the dynamical time scales, (2) the stereochemistry, (3) the entropic and energetic effects, and (4) the conformational constraints. We address the issues of concertedness and stereochemistry and explore critical features of the PESs through ab initio and density functional theory (DFT) calculations.

2. Experimental

The fs laser and molecular beam apparatus have been described in detail elsewhere [11]. 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 pair, was a 80 fs width (Gaussian) pulse with an intensity of ~ 150 μJ/pulse at 615 nm. The pulse was split to provide the pump and probe beams. For the pump, the 615 nm output was frequency doubled. The probe beam was passed to a computer-controlled translation stage for the time delay. The time zero was measured in situ [11,12]. The two beams were spatially combined and were focussed onto the supersonic molecular beam containing the time-of-flight mass spectrometer. Both pump and probe beams were appropriately attenuated to minimize background signals. By gating the signal due to a particular ion, the temporal evolution of each species was measured. DBH was synthesized following the procedure described in Ref. [13].

3. Theoretical: PESs and reaction paths

Fig. 1 depicts reaction paths of tetramethylene obtained by using the spin-unrestricted DFT method at the B3LYP/6-31G(d) level (see Ref. [14] and refs. therein). The results are similar to those of Houk et al. [15], although there is inconsistency in the results of figs. 5 and 6 in Ref. [15], and we suspect a drawing error. The PES is rather 'flat', and this feature was shown by recent high-level ab initio calculations [6,9]. Depending on the level of theory, the energy difference between the stationary points varies but did not exceed a few kcal/mol (vide infra).

Calculations of the PESs (Fig. 2) of the ground-state reaction paths of the constrained diradical and the nitrogen extrusion of DBH were also performed at the B3LYP/6-31G(d) level. As discussed elsewhere [14,17], the restricted method was used for all closed-shell species, whereas the unrestricted one was employed for open-shell species. Vibrational frequencies were calculated at the same level of theory in order to characterize the nature of the stationary points and to determine the zero-point energy correction. To confirm that the TS is the correct saddle point connecting two local minima, intrinsic reaction coordinate calculations were further performed. All calculations were carried out using the G94 package [18].

The reaction paths for the constrained diradical (Fig. 2A) are shown for three product channels. The barrier for ring closure is very small (~ 3 kcal/mol), while for cyclopentene formation, via a 1,2 hydrogen shift, it is ~ 28 kcal/mol. The barrier for 1,4-pentadiene formation, via a β-cleavage of the σ-bond and formation of two π-bonds, is ~ 27 kcal/mol. Fig. 2B presents the results obtained for the nitrogen-extrusion reaction path. For comparison, the ab initio results of Yamamoto et al. [16] at the CASSCF level (with MP2 correction) are also given, when available, in parentheses. Our DFT calculations suggest that the PES of the diazenyl diradical (33 kcal/mol) is characterized by a shallow minimum with a very low barrier (~ 1 kcal/mol) for both the formation of DBH and the loss of N_2 to yield the constrained diradical. All the rotamers of the diazenyl diradical are similar in energy and, therefore, only one rotamer is shown. The PES indicates that the concerted
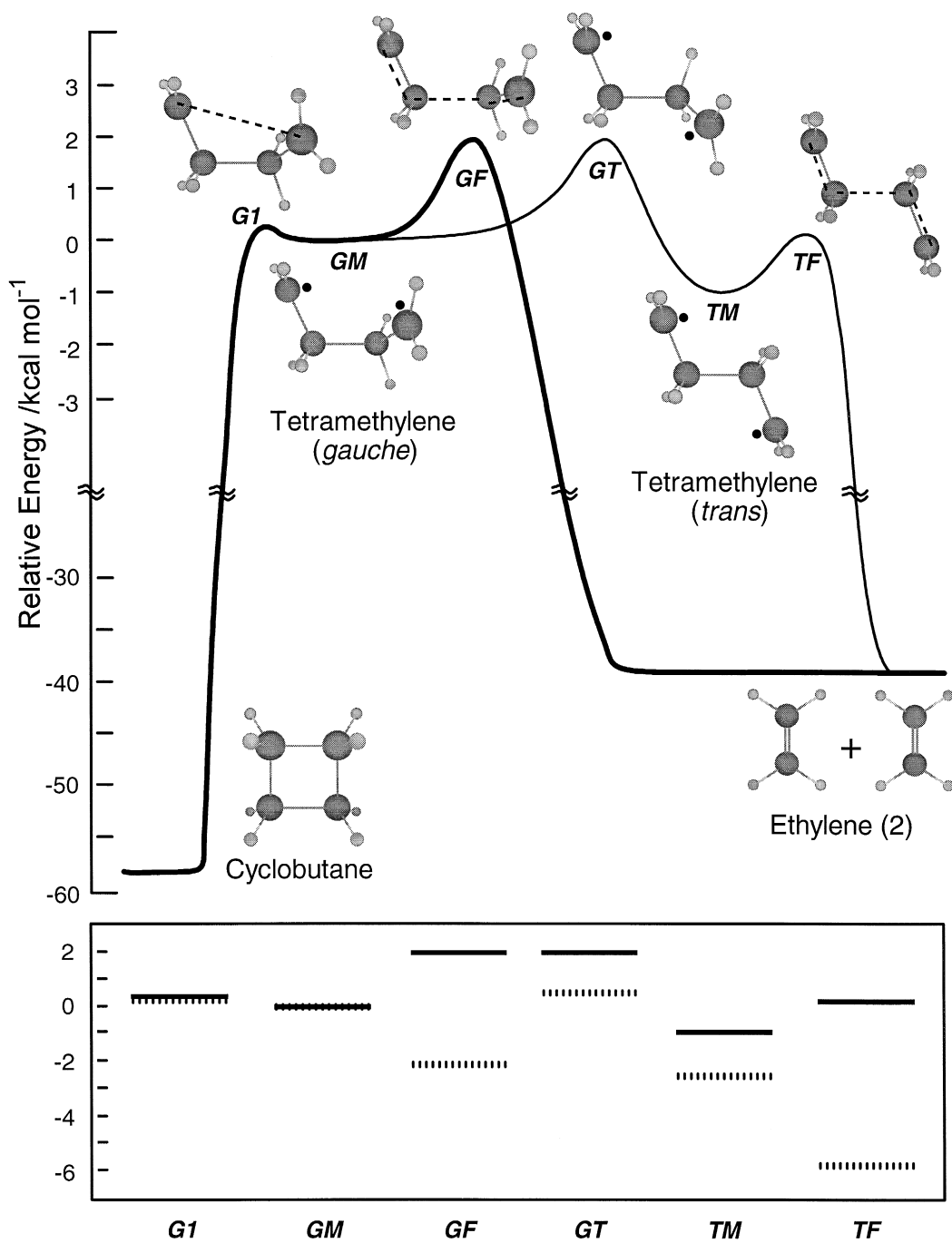
and the stepwise elimination of N_2 are energetically very similar.

4. Results and discussion

4.1. Tetramethylene: dynamical time scales and stereochemistry

The mass spectrum and the transients are presented in Fig. 3A and Fig. 4A, respectively. The 84 amu species decays in 120 ± 20 fs, while that of the 56 amu, the tetramethylene diradical, builds up in 150 ± 30 fs and decays with a lifetime of 700 ± 60 fs. The total decay rate of the diradical is the sum of the two rates for cyclization and fragmentation (Fig. 1); the *gauche* to *trans* isomerization channel is not included because the decay is that of the total population. Dervan and his group have provided evidence for the existence of common 1,4-diradicals from careful studies of the stereochemistry [2,3]. They give the relative rates of rotation (terminal), cleavage and closure at 712 K for tetramethylene-d_2 (generated from a diazene precursor) to be $k_{rot}:k_{frag}:k_{cyc} = 12 \pm 3:2.2 \pm 0.2:1.0$.

At our total energy, if these ratios are similar, then we can obtain the individual rates: $k_{cyc} = 0.45$ ps^{-1} (2.2 ps), $k_{frag} = 0.99$ ps^{-1} (1 ps), and $k_{rot} = 5.4$ ps^{-1} (185 fs) (see Fig. 5). From our DFT calculations of all vibrational modes, the average internal energy $\langle E \rangle$ of tetramethylene at 712 K is 12.6 kcal/mol (note that it is significantly less than the classical limit: number of modes (30) times $kT = 42.4$ kcal/mol). At the experimental available energy, the tetramethylene internal energy is estimated to be 39 kcal/mol, using an impulsive model (see Ref. [19]) for the breakage of the C–C bond, or 82 kcal/mol, using a simple statistical model [20].

The rotational time τ_{rot} of ~ 200 fs is significant for two reasons: (1) its fs duration makes it a clev-erly-used clock for obtaining the ratios of rate constants, as discussed below; and (2) it allows for a comparison with the Arrhenius-type estimate, widely used in stereochemical studies. From ESR experiments [21], the activation energy for rotation of primary radicals was reported to be 0.4 or 3.1 kcal/mol; comparison with results of other alkyl radicals favors the lower value [22]. Moreover, ab initio calculations suggest that the barrier is even < 0.4 kcal/mol [23]. Using our DFT calculation of the average vibrational frequencies of the two internal rotations of the terminal C–C bonds (150 cm^{-1}), for the preexponential factor, and a barrier of 0.4 kcal/mol we obtain k_{rot} of 4.6 ps^{-1} or $\tau_{rot} = 220$ fs; the effect of substitution at the radical centers will be discussed in Section 4.3. The values of the lifetime for ring closure, fragmentation and rotation indicate that the terminal CH_2 groups, on the average, rotate during the fragmentation and closure processes. Such time scales are crucial in determining the stereochemistry of the two processes.
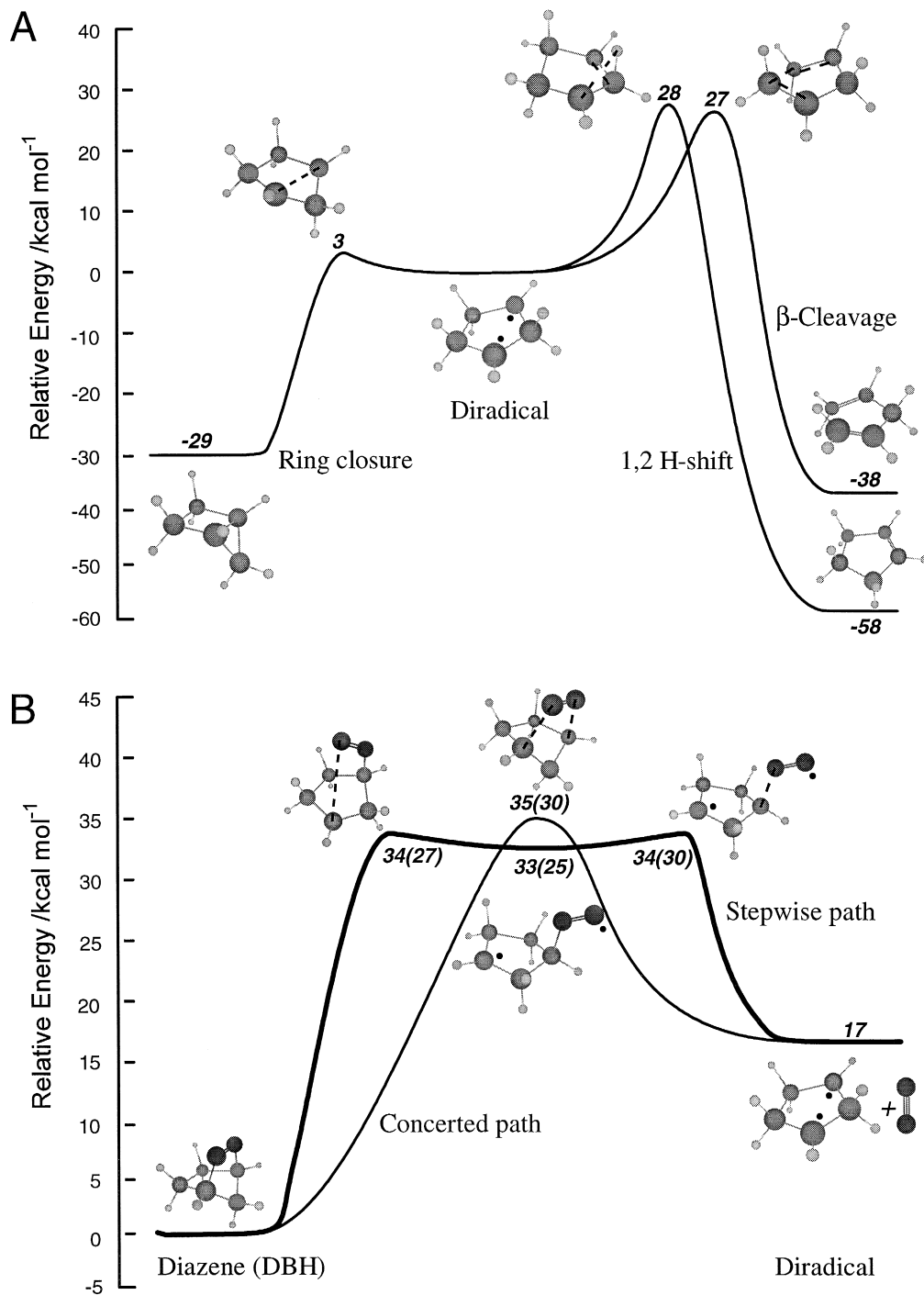
4.2. The constrained diradicals

Fig. 3B shows the mass spectrum obtained for DBH which is dominated by the 68 amu, 1,3-cyclopentanediyl (constrained) diradical. Housane (its cyclization product), cyclopentene and 1,4-pentadiene all have this mass but they represent final products. The very small peak at 96 amu fits the signal of the parent and/or the diazenyl diradical. Fig. 4B displays the 68 amu transient which can be fitted to a rise (30 ± 10 fs) and a decay (190 ± 10 fs). The signal at 96 amu was too weak to measure. The very small absorption coefficient [24,25] of DBH at the excitation wavelength (307 nm) suggests that the pump process involves the absorption of two photons, 186 kcal/mol (153 nm), and this was confirmed by the dependence of the ion current on the

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Fig. 1. Ground-state reaction paths of tetramethylene. The theoretical calculations were performed using DFT at the B3LYP/6-31G(d) level. The following stationary points were calculated: (GM) the *gauche* minimum; (TM) the *trans* minimum; (G1) the transition state from GM to cyclobutane; (GF) the transition state from GM to fragmentation; (TF) the transition state from TM to fragmentation; and (GT) the transition state for *gauche* to *trans* interconversion. The reaction pathway involving the *gauche* minimum is shown as a heavy bold curve. The lower panel compares the energy of the stationary points relative to the *gauche* minimum: the solid bars represent our DFT values, while the dotted bars correspond to the high-level ab initio calculations of Moriarty et al. [9]: the geometry was optimized at the CASSCF(4, 4)/6-31G(d) level and the energy was calculated at CASPT2(8, 8)/ANO-2 level.

intensity of the pump pulse. The mass spectrum of trimethylene is presented in Fig. 3C and the tran-

sients are shown in Fig. 4C. The 70 amu signal of cyclobutanone gives a decay time of 105 ± 10 fs.
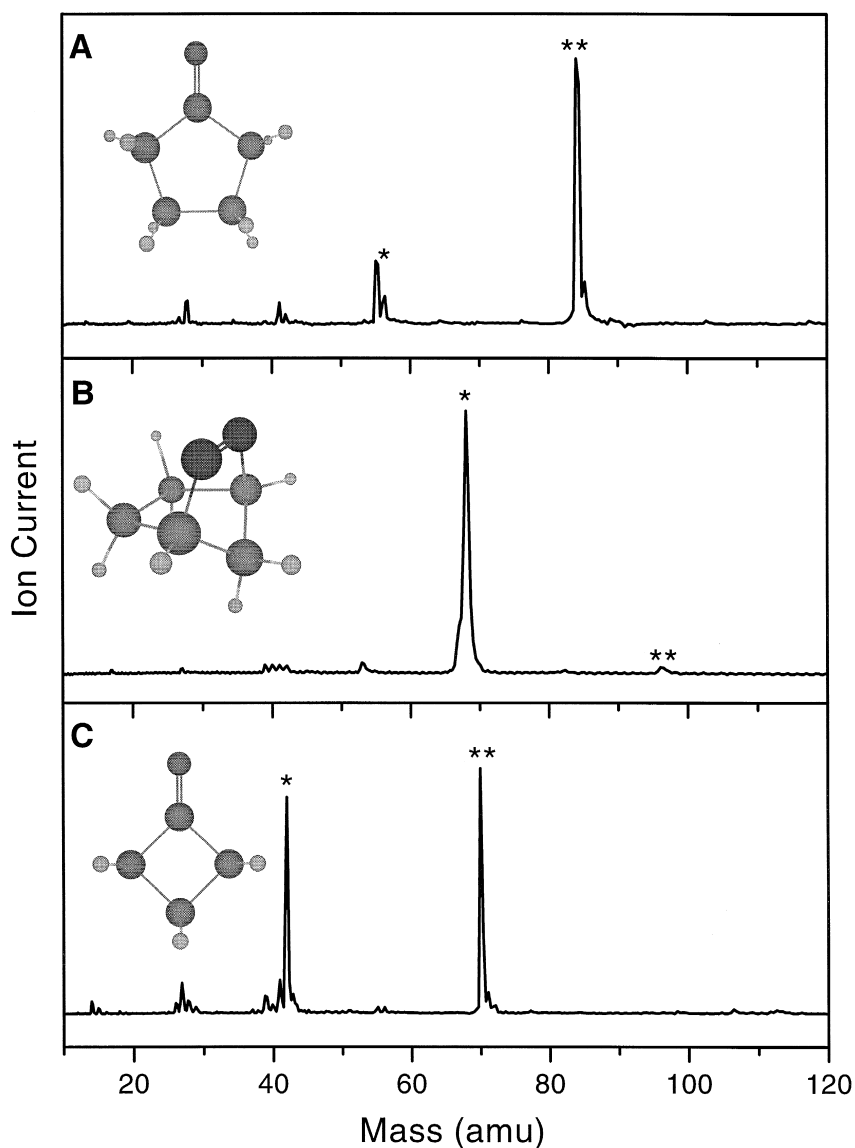
Fig. 3. The mass spectra obtained with fs pulses (the parent peak (∗∗) and the diradical peak (∗) are marked): (A) cyclopentanone (tetramethylene); (B) 2,3-diazobicyclo[2.2.1]hept-2-ene (DBH) (constrained diradical); and (C) cyclobutanone (trimethylene). The molecular structures are displayed on the left for the precursors.

Trimethylene (42 amu) shows a transient behavior with a similar rise and decay time of 120 ± 20 fs [4].

Direct comparison of the cyclization dynamics, the common reaction path, is only justified when the

Fig. 2. (A) Ground-state PES of the constrained diradical (1,3-cyclopentanediyl diradical) performed at the B3LYP/6-31G(d) level of theory. Three reaction paths are characterized: ring closure (housane formation), 1,2 H-shift (cyclopentene formation) and β-cleavage (1,4-pentadiene formation). (B) Ground-state PES of DBH (2,3-diazobicyclo[2.2.1]hept-2-ene). Both concerted and stepwise (heavy bold) reaction pathways of nitrogen extrusion are shown. The values in parentheses are according to the data of Yamamoto et al. [16] at the CASSCF level (with MP2 correction).
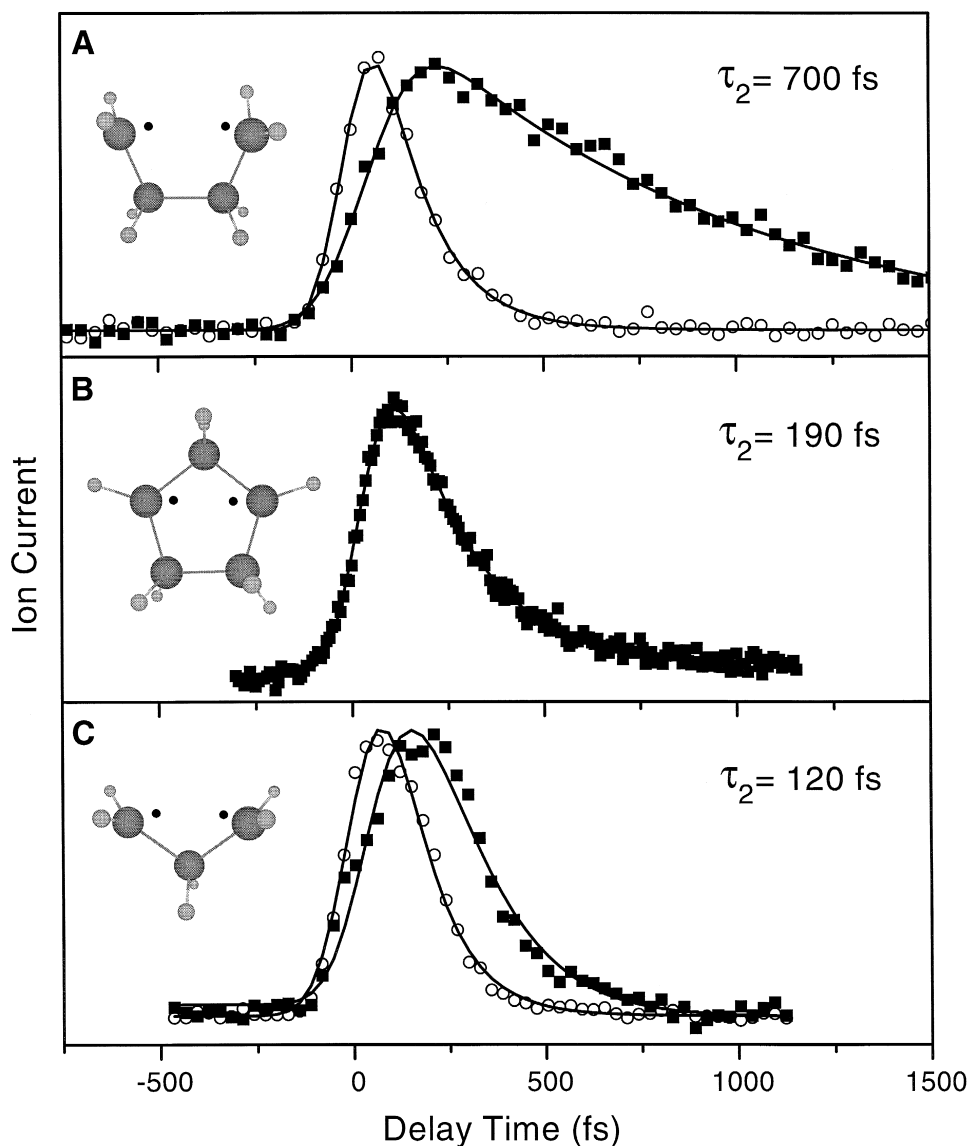
Fig. 4. Femtosecond transients of the parent (○) and the diradicals (■): (A) tetramethylene; (B) constrained diradical; and (C) trimethylene. τ_2 is the decay time of the diradical. The radical molecular structures are shown on the left.

lifetimes are determined by the process, i.e., cyclization is the only or major reaction channel of the diradicals. However, for all radicals under investigation other reaction products compete with cyclization (see Scheme 1). For trimethylene, classical trajectory calculations suggest (at 99 kcal/mol) the branching ratio of 1:1 for cyclopropane:propylene [8]. For te-

tramethylene, the pyrolysis experiments [3] at 712 K give the cyclobutane:ethylene ratio to be ∼ 1:2.2, as mentioned before. There are no trajectory calculations for tetramethylene; RRKM values [5] give a ratio of 1:19. For the constrained diradical, the photolysis at 185 nm in apolar solvents [26] yields for housane:cyclopentene the ratio 1:0.73. From our de-
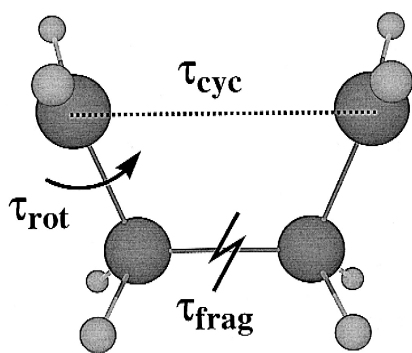
Fig. 5. Snapshot of tetramethylene structure in the process of cyclization (τ_{cyc}), fragmentation (τ_{frag}) and rotation of the terminal carbon (τ_{rot}). The time constants discussed in the text are $\tau_{cyc} = 2.2$ ps, $\tau_{frag} = 1$ ps, and $\tau_{rot} = 185$ fs.

cay rates and the reported branching ratios, we obtained the specific rate constants for cyclization: $1/240$ fs^{-1} for trimethylene, $1/2.2$ ps^{-1} for tetramethylene and $1/330$ fs^{-1} for the constrained diradical; longer times will be obtained for tetramethylene if the RRKM branching ratios are used instead. Cyclization in trimethylene and the constrained diradical has higher rates than in tetramethylene.

4.3. PES, IVR and entropy effects

For both DBH and cyclic ketones, two identical bonds (C–N or C–C, respectively) must be broken to form the diradical and eject N_2 or CO. The C–N bond energy is ~73 kcal/mol and the C–C bond energy is ~83 kcal/mol; on the other hand, the net energies of formation of N≡N (from N=N) and C≡O (from C=O) are ~117 and ~80 kcal/mol, respectively. Because the total energy deposited is 186 kcal/mol, the available energy to be partitioned among the constrained diradical and N_2 is 169 kcal/mol (Fig. 2B), 116 kcal/mol for trimethylene and CO, and 99 kcal/mol for tetramethylene and CO [4]. The PES of tetramethylene in Fig. 1 indicates the flatness within few kcal/mol: the ring closure as well as the fragmentation products can be reached by paths of monotonically decreasing energy. The PESs of the constrained diradical (Fig. 2A) and trimethylene [8] are similarly flat, as far as the cyclization reaction is concerned; the 1,2-hydrogen migration, which is a common reaction path for

trimethylene and the constrained diradical, involves a barrier of ~7 and ~28 kcal/mol, respectively. Accordingly, the internal energy should not a priori be the dominant force in the reaction (barrierless) dynamics and IVR and entropy effects become very significant (vide infra). Even for barrier reactions, the statistical RRKM calculations show that the rates reach a plateau and the effect of internal energy at high energies is less significant [27].

Entropy and IVR effects are governed by the nature of the reaction trajectories on the (nuclear) multidimensional PESs. Consider first the case of tetramethylene adopting a whole range of conformations without an energy minimum on the PES, the so-called 'twixtyl' state [28]. This situation is expected to force the molecule to spend a 'long' time exploring the surface. Although this reaction-path picture is helpful, it was shown that the lengthening of time is still on the fs time scale [4]. It is mandatory to consider the full landscape of the PESs. This is amply demonstrated in the study of Møller and Zewail [29], who considered the case of a transition state ABA‡ on its way to form products in two channels, A + BA and A + B + A. Besides the stable configurations at A–B–A‡, A + B–A, and A + B + A, there exist a whole set of transient configurations A · · B · · · A‡ which form a family of trajectories to produce A + B + A (or A + BA). As shown experimentally [30] and theoretically [29], this family of trajectories results in much longer reaction times.

The transient configurations represent an entropic trapping of the system since in these configurations the energy in, for example, A · · B · · · A‡ could be trapped in the 'A · · B part' (very long time) but exceeds dissociation in the 'B · · · A part'. At such coordinates there are no stable vibrational modes as the system only increases the number of possible new configurations (increased entropy) for trajectories to visit. In other words, such dynamical motion is distinct from IVR between well-defined vibrational states. Experimentally, such behavior was evident in the temporal and kinetic-energy distributions [29,30].Moriarty et al. [9] have shown that with a high-level ab initio calculation the PES is indeed flat to within 0.5 kcal/mol, contrary to previous theoretical calculations of 3–5 kcal/mol (see citations in Ref. [4]). They proposed the entropy effect on a microcanonical level; in Ref. [31] 'entropic locking'

was considered on a canonical level and using the MCSCF/CI PES. From studies of lifetime change with energy [4], and using statistical theories, the well was estimated to be a few kcal/mol. However, in view of the nonstatistical behavior reported recently [27] and the recent MD study of elementary systems [29,30], the important role of entropic trapping, or what we will call the existence of 'transient configurations', must be part of the description. For a barrierless PES, the dependence of rates on energy is not significant unless one considers such effects.

The phase space involving cyclization is more limited than that of fragmentation; fragmentation may occur at any dihedral angle while ring closure is only successful at certain angles. The *probability* that the intermediate has a favorable conformation for ring closure is likely to be smaller than for fragmentation, resulting in a longer lifetime for ring closure. Although the nuclear rearrangement (bent) upon cyclization of the constrained diradical is substantial – constrained diradical is almost planar while housane exists in a highly bent conformation – the geometry for cyclization is much more favorable in the constrained diradical and hence the shorter lifetime (~ 330 fs) than tetramethylene (~ 2.2 ps), which nearly rotates freely.

Both trimethylene and tetramethylene have nearly a terminal free rotation and this would predict a similar time scale for cyclization. However, trimethylene terminal motion is the only critical rotation for cyclization, while in tetramethylene there are many more motions, including the central C–C rotation. Thus the order-of-magnitude difference in the cyclization time for trimethylene (240 fs) and tetramethylene (2.2 ps) and the close value of trimethylene and the constrained (330 fs) diradical. Of course, upon cyclization of the constrained diradical the p-orbitals containing the unpaired electrons need to rotate a considerable angle in order to form the σ bond and bend motions are involved. For fragmentation, IVR is important. Upon preparation of tetramethylene energy has to flow into the reaction coordinate for fragmentation which occurs in tetramethylene on the 1 ps time scale. Thus, IVR to the central bond must occur in less than 1 ps and this is consistent with the results in Ref. [27].

Substitution of the terminal hydrogen atoms with methyl groups substantially increases the total lifetime: 1.8 ps for 1,1,4,4-tetramethyl-tetramethylene vs. 700 fs for tetramethylene. The presence of methyl groups normally increases the lifetime, or decreases the rate, a well-known observation in the literature. Three effects contribute, but all are in the same direction: (1) the rotation rate slows down by the mass effect (the *probability* to find the intermediate in a favorable conformation for reaction becomes smaller); (2) the energy barrier for ring closure may increase due to steric hindrance, and (3) IVR for fragmentation may slow down due to the increased number of 'bath modes'. These effects are more pronounced for methyl-substituted tetramethylene than for the deuterated species (total lifetime 1.15 ps), in agreement with the observed trend in the decay times.

4.4. Concertedness

The issue of concertedness is basic in mechanistic organic chemistry. Usually it is defined with an operational criterion. For example, the reaction is said to be concerted if it takes place in a single kinetic step. A stepwise reaction involves two kinetically distinguishable steps via a stable intermediate. Only the direct detection of the intermediate can answer the question if a reaction follows a concerted or stepwise path. As pointed out elsewhere [32,33], the correct criterion must address the nuclear motions in relation to the time scale of the reaction coordinate. For instance, in the case of acetone, fs experiments have revealed that the release of the methyl groups occurs in a stepwise process, as both the dynamics of the parent acetone and the CH_3CO radical were observed: the first methyl group is released in ~ 50 fs, the second one in ~ 500 fs [32].

Earlier the rotational motion of the entire molecule was invoked as a clock, and this rotation, which is few ps, makes the reaction appear 'concerted'. In stereochemical studies, physical organic chemists use internal rotations of a single bond. As discussed above, this is reasonable given the fs time scale which can calibrate the retention or inversion of stereochemistry. In the case reported here, the time scales of the reactions are all much different and are longer than the time scale of the reaction coordinate (30–100s fs), indicating non-concertedness.

Acknowledgements

Appendix A. Nitrogen extrusion

The majority of the experimental work (see citations in Ref. [16]) in conventional photolysis ($S_1 \leftarrow S_0$ at 339 nm; 84.5 kcal/mol) favors the formation of N_2 and the constrained diradical by a stepwise C–N cleavage of DBH. At our excitation energy (186 kcal/mol) the concerted elimination of N_2 could also become important, as suggested by the study at 185 nm (155 kcal/mol) [26]. Recent theoretical investigations [16] have revealed the stepwise elimination of N_2 upon S_1 excitation (n, π^*). The system evolves via a transition state for α C–N ring-opening in the excited state, yielding an acyclic structure, which decays to the ground state via a conical intersection. On the ground state, this diazenyl diradical (Fig. 2B) finally loses molecular nitrogen, to produce the constrained diradical. Taking into account the fs dynamics [12,33,34] of conical intersections, the short rise time (30 fs) for the constrained diradical formation can be understood in terms of extremely fast elimination of N_2, similar to the stepwise elimination in azomethane [33].

The picture we have for the extrusion is the following. The initial fs wave packet, after absorption, directly forms the diazenyl diradical (by the typical σ^* orbital excitation of azoalkanes [35]) or first converts to the S_1 surface and then forms the diazenyl diradical. The S_1/S_0 conical intersection is critical for the subsequent dynamics as shown by Yamamoto et al. [16]. In the case of azomethane, the reaction coordinate (RC) involves a CNNC twist motion. DBH, with a rigid structure, involves a NNC bend vibration (stretch of one CN). This bend motion facilitates the NN π bond breakage which leads to a diradicaloid structure on the downhill side of the S_1 surface. Along the bend RC, the energy of S_0 increases, because of the breakage of both π and σ

bonds, ultimately reaching the S_0/S_1 CI. Upon the formation of the ground-state diazenyl diradical (by reforming the π bond), the strong interaction between the unpaired electron in the p-orbital of the N atom and the weak CN bond gives rise to the ultrafast N_2 extrusion, similar to the mechanism described for azomethane.

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