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Mechanism of Thermal Deazetization of 2,3-Diazabicyclo[2.2.1]hept-2-ene and Its Reaction Dynamics in Supercritical Fluids

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Abstract: The mechanism of thermal deazetization of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) is examined both theoretically and experimentally in this paper. The theoretical work involves CASPT2 ab initio MO calculations using the 6-31G(d) basis set. These calculations are shown to give relative enthalpies for the stationary points on the potential energy surface that are within ±3 kcal/mol of the experimental values. Surprisingly, the transition structure for the rate-limiting step is found to correspond to synchronous C−N cleavage, leading to the formation of the cyclopentane-1,3-diyl biradical. The alternative mechanism, involving stepwise C−N bond scission, is found to have an activation enthalpy that is at least 7 kcal/mol higher. The synchronous mechanism is in apparent conflict with earlier calculations and experiments, all of which seemed to favor the stepwise pathway. A resolution of this disagreement is proposed. The well-known preference for inversion of stereochemistry in the deazetization of 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-d_2 (DBH-d_2) is proposed to involve nonstatistical dynamical effects. This mechanism is similar to, but not identical with, one first proposed by Allred and Smith over 30 years ago. The deazetization of DBH-d_2 in supercritical propane is studied experimentally. The pressure dependence of the reaction stereochemistry is shown to be qualitatively and quantitatively consistent with the dynamic model, but not to be consistent with any mechanisms that would require separate reaction paths across the potential energy surface. In supercritical carbon dioxide, the pressure dependence is found not to be fit by any simple model. Calculations suggest that this may be because CO_2 forms weak complexes (binding energies of approximately 2 kcal/mol for each CO_2) with the cyclopentane-1,3-diyl intermediate. The calculations also suggest that similar complexes can be expected between CO_2 and simple monoradicals.

Introduction

It has recently been reported that the pressure dependence of the branching ratio for reaction of cyclopentane-1,3-diyl-*cis*-4,5-d_2, thermally generated from 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-d_2 in supercritical propane, is consistent with expectations for a reaction exhibiting nonstatistical dynamics.[1] In this paper the first CASPT2 calculations on the reaction are described, and an extension of the experimental study to supercritical carbon dioxide is reported. The calculations suggest that a revision of the previously proposed potential energy surface may be in order, although the reaction dynamics appear to be qualitatively similar to those previously suggested. The new experiments suggest that in supercritical carbon dioxide a more complex model of the interaction between the cyclopentane-1,3-diyl and the fluid medium is necessary. Calculations indicate that this may be due to a weak attractive interaction between the biradical and CO_2.

The Reaction and Its Proposed Mechanisms. The reaction studied in this work was the thermal fragmentation of labeled azo compound 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-d_2 (DBH-d_2, **1x**), giving stereoisomeric bicyclo[2.1.0]pentanes **6x** and **6n**. The principal point of interest in this reaction, since its first recognition more than 30 years ago, has been the reason for the preferential formation of stereoisomer **6x**, given that the equilibrium constant between **6x** and **6n** is 1 within experimental error.[2]

Roth and Martin offered two mechanistic explanations for the preferred inversion of configuration. The first (Scheme 1) postulated a synchronous cleavage of the two C−N bonds of **1x**, with simultaneous backside overlap of the C−N σ orbitals, leading to formation of the new C−C bond.[3] They later revised the mechanism to one involving sequential scission of the C−N bonds, with generation of diazenyl biradical **3x** as an intermediate (Scheme 2).[4] In this latter mechanism, the product **6x** was postulated to arise primarily by concerted C−C bond formation and C−N bond scission in the diazenyl biradical **3x**. If the concerted bond formation and cleavage occurred with inversion of configuration at carbon, the preference for formation of **6x** might be rationalized.

Although no explicit pathway for the direct formation of **6n** was suggested by these authors in either of their mechanisms, a plausible choice would be the generation of the cyclopentane-1,3-diyl intermediate **4c**, either directly from **1x** or from **3x**. These pathways are shown as dashed arrows in Schemes 1 and 2. In the context of standard kinetic models, biradical **4c** could reasonably be expected to give **6x** and **6n** in a ratio very close

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[1] Reyes, M. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1998**, *120*, 1641−2.

[2] Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.* **1981**, *46*, 2116−9.

[3] Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1−7.

[4] Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695−8.

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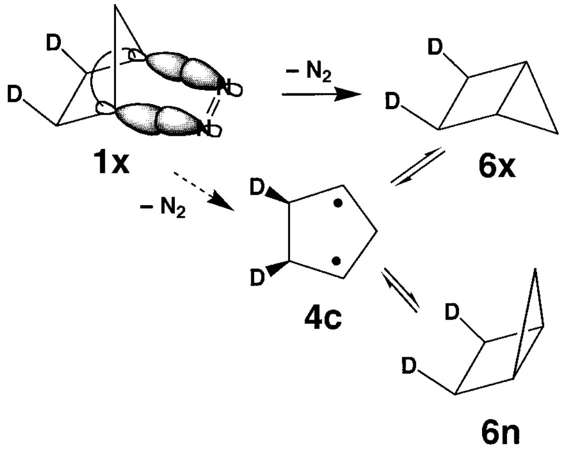
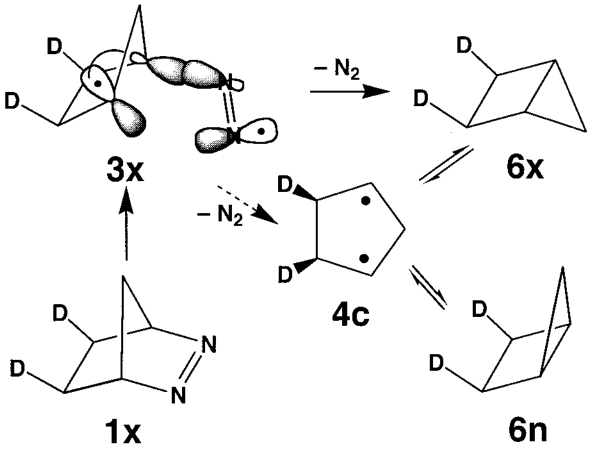
Scheme 1. First Roth and Martin Mechanism, with Intermediate **4c** Added as a Possible Source of Observed Product **6n**



Scheme 2. Second Roth and Martin Mechanism, with Intermediate **4c** Added as a Possible Source of Observed Product **6n**

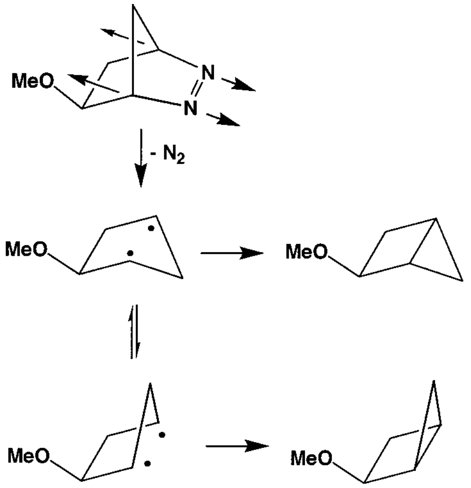


to 1:1 and would presumably also be involved in the known interconversion of **6x** and **6n**.[2]

At about the same time as the Roth and Martin studies, Allred and Smith investigated the thermal fragmentation of *exo*- and *endo*-5-methoxy derivatives of DBH.[5] They too found a preference for inversion during the deazetization but suggested a different explanation. They proposed a synchronous cleavage of the two C−N bonds to generate two stereoisomeric methoxy-substituted cyclopentane-1,3-diyl intermediates (Scheme 3). These stereoisomers were built on an envelope-conformation of the five-membered ring, which would have C_s symmetry in the absence of the methoxy substituent. They postulated[5] that the preference for inversion was "...a consequence of recoil from energy released by C−N bond breaking." In part because of the novelty of this suggestion, in part because subsequent experiments (vide infra) led people to favor a sequential mechanism for the C−N scissions in the deazetization of DBH, and in part because ab initio calculations favored a C_2 rather than a C_s equilibrium geometry for cyclopentane-1,3-diyl, the Allred and Smith proposal has received relatively little recent attention. However, as described below, there may now be reason to revive interest in it.

Work from this laboratory has led to the proposal of a fourth mechanism. It bears some similarity to Allred and Smith's mechanism but proposes that the preference for formation of the doubly inverted bicyclopentane arises not from the dynamic selection of a particular cyclopentane-1,3-diyl conformation in the nitrogen extrusion step but rather from the dynamic selection of exit channels by that intermediate in the final ring-closure step.[6] The distinction between the two mechanisms is described in more detail below.

Scheme 3. Allred and Smith's Mechanism



Synchronous or Asynchronous C−N Bond Cleavage in DBH. The question of concert in the C−N cleavage of azo compounds, which is seen to be relevant to the mechanisms that have been proposed for the present reaction, has been long debated. In the case of compound **1**, the experiments of Adams et al. on the direct photolysis[7]and Simpson et al. on the thermal reaction[8] each seemed to show strong support for the stepwise pathway. The basis for interpretation of these experiments was a paper by Bauer,[9]who suggested that the synchronous C−N cleavage should generate vibrationally hot N_2 since (a) the N=N distance in DBH is much longer than that in N_2, and (b) the N=N stretching vibration would be orthogonal to the reaction coordinate in the synchronous mechanism. In both of the experiments—the direct photolysis and the shock-tube pyrolysis—the N_2 derived from DBH was found to carry very little excess vibrational energy.[7,8] This result, given the Bauer hypothesis, seemed to indicate that C−N bond scission must be sequential and that there must be a diazenyl biradical intermediate. One curious feature of the results should be noted however. In the experiments of Adams et al. it was possible to deduce the rotational energy of the N_2 as well its vibrational energy. Had the N_2 been formed from a ground-state diazenyl biradical, the N_2 would have been expected to be rotationally hot, since the geometry of the biradical would ensure that a torque was applied to the diatomic fragment as it departed. However, the experiments showed that the N_2 was *both* vibrationally and rotationally "cool". To rationalize this apparent discrepancy, Adams et al. hypothesized[7b] that the reaction occurred via an electronic excited state of the biradical in which the C−N=N angle was 180°. Departure of the N_2 along the C−N axis would then produce the observed result.

These experimental results, seeming to favor the stepwise C−N bond cleavage in DBH, in combination with similar

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(5) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 7133−4.

(6) Lyons, B. A.; Pfeifer, J.; Peterson, T. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 2427−37.

(7) (a) Adams, J. S.; Burton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 7935−8. (b) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115−21.

(8) Simpson, C. J. S. M.; Wilson, G. J.; Adam, W. *J. Am. Chem. Soc.* **1991**, *113*, 4728−32.

(9) Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 3688−9.

conclusions from AM1-CI[6] and MP2/6-31G(d)[10] calculations, have formed the basis for all subsequent mechanistic and dynamic analyses. However, recent MRCI calculations on trans-azomethane, carried out by Liu et al., have suggested that the symmetric cleavage of the C−N bonds is enthalpically favored on the ground electronic surface (although entropy effects make the stepwise process favored at higher temperatures).[11] The authors of this paper specifically pointed out that any calculations omitting nondynamic electron correlation for the electrons in the two C−N σ bonds and the N═N π bond may artificially favor the stepwise mechanism.[11] They also found that inclusion of dynamic electron correlation was necessary in order to obtain activation barriers and reaction enthalpies in reasonable accord with experimental values.[11]

The most recent ab initio calculations on the DBH reaction have included the features that Liu et al. suggested.[12] A thorough investigation of the ground, first excited singlet, and triplet potential energy surfaces was carried out by Yamamoto et al. using CASSCF/6-31G(d) calculations to provide nondynamic electron correlation and then a multireference MP2 correction to provide dynamic electron correlation at the stationary points. The active spaces for the various calculations varied between (6,5)—involving one C−N σ/σ^* pair, one lone-pair orbital, and the N═N π/π^* pair—and (10,8)—involving addition of the second lone pair orbital and the second C−N σ/σ^* pair to the (6,5) space. On the ground-state potential energy surface, Yamamoto et al. found a preference of 17.4 kcal/mol for the synchronous over the asynchronous N_2 extrusion at the CASSCF level. In the latter pathway, the cleavage of the first C−N bond was found to be rate-limiting. The diazenyl biradical was found to be essentially unbound.[13] However, inclusion of the MP2 correction had a dramatic effect. The synchronous and asynchronous pathways became essentially isoenergetic (the former being favored by just 0.1 kcal/mol), and the diazenyl biradical became sufficiently strongly bound (6.3 kcal/mol) that cleavage of the second C−N bond now became rate-limiting.[12] No transition state for the direct conversion of the diazenyl biradical to bicyclo[2.1.0]pentane + N_2, of the kind postulated in the second Roth and Martin mechanism, was located. The computed activation enthalpies of 29.8 kcal/mol for the synchronous extrusion and 29.9 kcal/mol for the asynchronous extrusion were judged to be in reasonable accord with the experimental value of 36 kcal/mol.

Two features of the calculations of Yamamoto et al. seemed worth reinvestigating to us. First, because the primary interest of Yamamoto et al. was not the issue of synchronous vs asynchronous bond scission in DBH, they used for most of their calculations an active space (the (6,5) space described above) that could be biased in favor of the asynchronous mechanism, since it would afford unbalanced nondynamic electron correlation for the two C−N bonds. Second, it seemed useful to investigate whether the dramatic effects of the MP2 correction seen by Yamamoto et al. were a consequence of the particular computational model employed, or whether other methods that use a multireference second-order perturbation theory correction to a CASSCF wave function would show similar behavior. In particular, the CASPT2 method[14] seemed worth exploring, since it has been shown to give very good agreement with experiment in a number of reactions involving singlet biradicals.[15]

Results and Discussion

CASPT2 Calculations on the Reaction. Calculations on **1**−**6** were carried out at the CASPT2/6-31G(d)//CASSCF/6-31G(d) level. Two transition structures were also located, as described below. For the nitrogen-containing species, the CASSCF and CASPT2 calculations used a six-electron, six-orbital active space, correlating the electrons that originally formed the two C−N σ bonds and the N═N π bond of **1** in an active space consisting of the corresponding bonding and antibonding molecular orbitals. Unlike the calculations of Yamamoto et al., the lone pair electrons were not included in the active space. The justification for this choice was that a simple GVB diagram, of the kind recommended by Schmidt and Gordon for selection of active spaces,[16] revealed that the lone pairs on the nitrogens of DBH are weakly involved in the bonding changes during either synchronous or asynchronous nitrogen extrusion on the ground-state potential energy surface. The sp^2 lone pairs of the reactant transform smoothly into the sp lone pairs of N_2 in the synchronous mechanism, while in the asynchronous mechanism they become the sp^2 and sp lone pairs of the diazenyl biradical. That the present choice of active space was reasonable is suggested by the fact that the total energies of all of the stationary points turned out to be equal to or lower than those for the corresponding structures in the calculations of Yamamoto et al. using the same basis set.

For geometry optimization of cyclopentane-1,3-diyl, **4**, and its ring-closure transition structure, **5**, only the two unpaired electrons were included in the active space. In bicyclo[2.1.0]-pentane, the CASSCF calculations included only two electrons in the σ and σ^* molecular orbitals of the strained C1−C4 bond. During geometry optimization of N_2, the active space consisted of four electrons in the two π and two π^* orbitals. To preserve size consistency with the results for DBH, **1**, transition structure **2**, and the diazenyl biradical, **3**, CASPT2 calculations on cyclopentane-1,3-diyl were carried out with a N_2 molecule 10 Å removed from the hydrocarbon fragment and orthogonal to the C_2 symmetry axis. In this complex a (6,6) active space was used, with two electrons in two orbitals on the hydrocarbon and four electrons in four orbitals on the nitrogen. Relative energies of the ring-closure transition structure, **5**, and bicyclo-[2.1.0]pentane, **6**, were then determined with respect to cyclopentane-1,3-diyl by CASPT2(2,2) calculations on just the hydrocarbon fragments. No attempt was made to correct for basis-set superposition error in any of the calculations.

The first significant result of the calculations was that geometry optimization of the diazenyl biradical, **3**, in its first-formed *endo* conformation, could not be accomplished at the CASSCF(6,6)/6-31G(d) level because the N_2 dissociated from the hydrocarbon fragment with no apparent activation barrier.

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[10] Sorescu, D. C.; Thompson, D. L.; Raff, L. M. *J. Chem. Phys.* **1995**, *102*, 7910−24.

[11] Liu, R.; Cui, Q.; Dunn, K. M.; Morokuma, K. *J. Chem. Phys.* **1996**, *105*, 2333−45.

[12] Yamomoto, N.; Olivucci, M.; Celani, P.; Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 2391−407.

[13] A minimum corresponding to an *exo* conformation of the diazenyl biradical can be found at the CASSCF(10,8) level, in accord with the results of Yamamoto et al. However, the difference in potential energy between the transition structure for N_2 loss and the biradical is only 0.056 kcal/mol. When ZPE (scaled by 0.89) is included, the difference becomes negative (−0.49 kcal/mol). In other words, at this level the diazenyl biradical is unbound. Details are given in the Supporting Information.

[14] Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218−26.

[15] See for example: (a) Duncan, J. A.; Azar, J. K.; Beathe, J. C.; Kennedy, S. R.; Wulf, C. M. *J. Am. Chem. Soc.* **1999**, *121*, 12029−34. (b) Lewis, S. B.; Hrovat, D. A.; Getty, S. J.; Borden, W. T. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2339−47. (c) Haberhauer, G.; Gleiter, R. *J. Am. Chem. Soc.* **1999**, *121*, 4664−8.

[16] Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233−66.

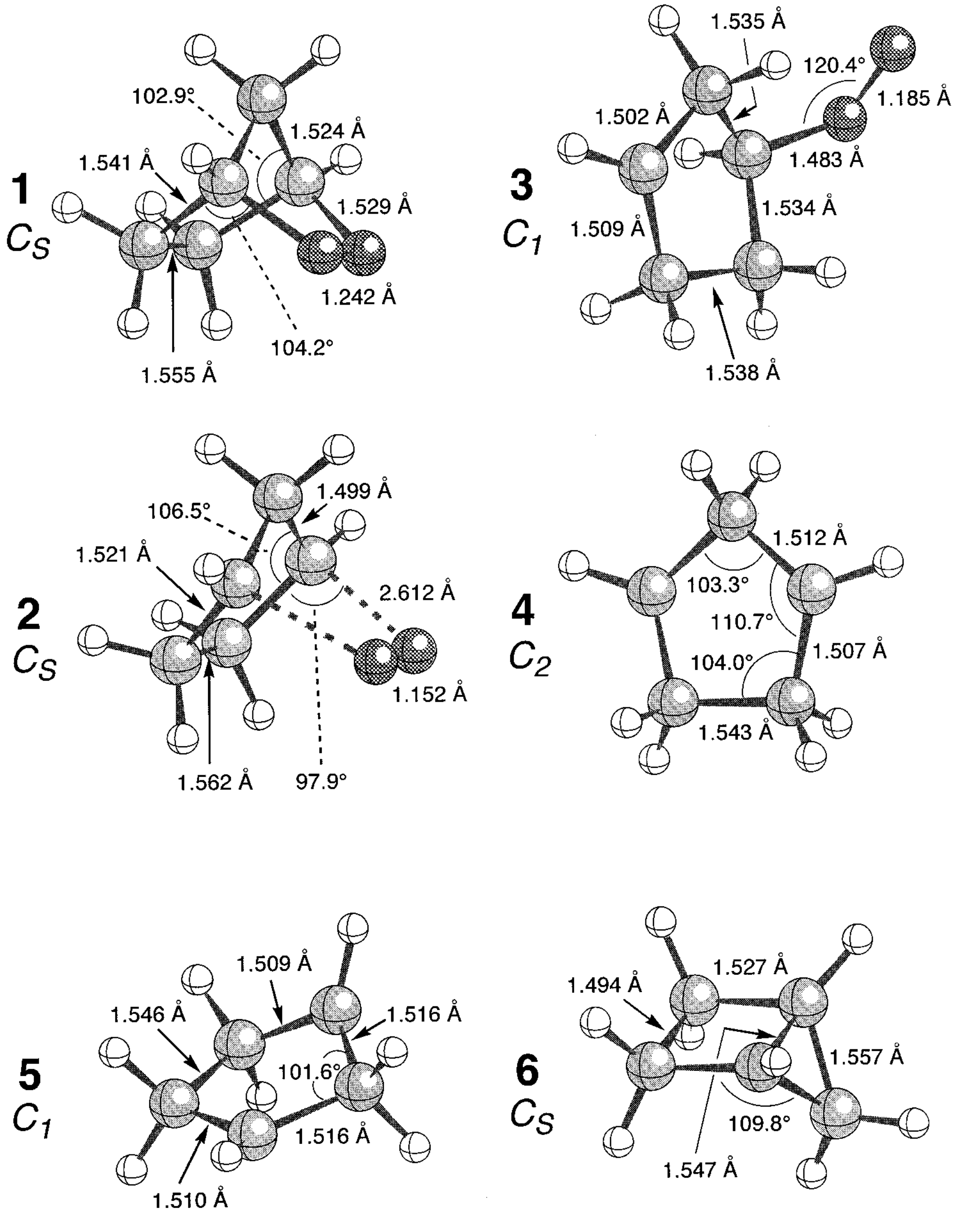

Figure 1. Geometries of the key stationary points for DBH deazetization. Structures 1 and **2** were determined at the CASSCF(6,6)/6-31G(d) level, and structure **3** was determined at the CASSCF(4,4)/6-31G(d) level. The others were optimized at the CASSCF(2,2)/6-31G(d) level.

Even a calculation in which the C−N distance was fixed and all other geometrical parameters were optimized showed the same result once the C−N distance constraint was relaxed. A local minimum for the *endo* conformation of **3** could be found at the CASSCF(4,4)/6-31G(d) level, in which the C−N σ and σ^* orbitals were excluded, so the energy of the diazenyl biradical was estimated from a CASPT2(6,6)/6-31G(d)//CASSCF(4,4)/6-31G(d) calculation.[13] The important contribution from the nondynamic correlation for the electrons in the C−N σ bond of **3** was revealed by the fact that the CASSCF(6,6)/6-31G(d)//CASSCF(4,4)/6-31G(d) energy was found to be 15.1 mhartrees (9.5 kcal/mol) lower than the value found by Yamamoto at the CASSCF(6,5)/6-31G(d) level for the corresponding structure (geometry optimized in the (6,5) space). It is perhaps worth emphasizing that the diazenyl biradical in this calculation has artificial kinetic stability because it is denied the electron correlation that would permit homolysis of the C−N bond.

When the transition structure for the first reaction of DBH was located, it was found to have C_s symmetry. A vibrational frequency analysis (using numerical methods for calculation of the Hessian) confirmed that this was a true transition structure with a single imaginary frequency (699.1i cm^{-1}) and a reaction coordinate eigenvector corresponding to the nitrogen departure. This transition structure is clearly the same as the one located by Yamamoto et al. (their structure XXIII), also found with the (6,6) active space. However, an asynchronous transition structure could not be located when the search was conducted in the (6,6) space. Reinvestigation of the putative asynchronous TS labeled IX by Yamamoto et al., using the (6,5) active space, suggested that it was actually a transition structure for C−N internal rotation of the diazenyl biradical rather than for C−N cleavage of DBH, since an intrinsic reaction coordinate (IRC) calculation failed to connect it to DBH. A series of 20 points along the asynchronous C−N stretching coordinate using the (6,5) active space, and with complete optimization of all geometrical parameters except the stepped C−N distance, revealed a Morse-like potential energy profile with no maximum attributable to a true transition structure.

For cyclopentane-1,3-diyl a C_2 local minimum was found, confirming the results of Sherrill et al. which had been obtained

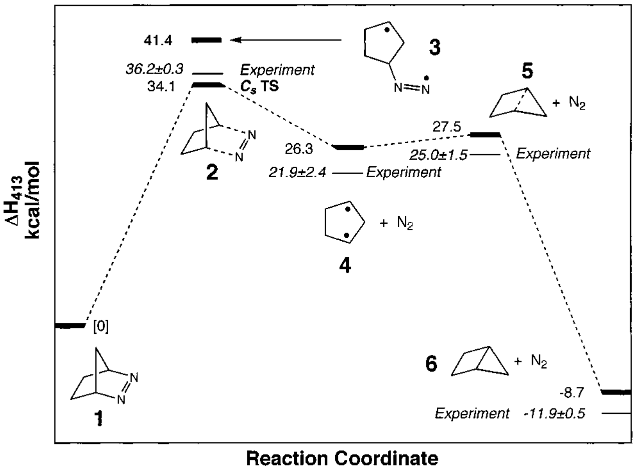

Figure 2. Computed (bold lines) and experimental relative enthalpies of key stationary points for the thermal nitrogen elimination from DBH.

Table 1. Summary of Computational Results on DBH Deazetization

structure	E_{CASPT2}, hartree	ΔE, kcal/mol	ΔH_0, kcal/mol	ΔH_{413}, kcal/mol	ΔS_{413},[a] cal/(mol K)	ΔG_{413},[a] kcal/mol
1	−303.838 720 616	[0]	[0]	[0]	[0]	[0]
2	−303.778 178 271	38.0	32.4	34.1	6.6	31.4
3	−303.771 800 983	42.0	39.0	41.4	12.8	36.1
4 + N_2	−303.790 860 033[b] −194.540 811 628[c]	30.0	22.7	26.3	78.5	−6.1
5 + N_2	−194.537 698 417[c]	32.0	24.6	27.5	76.8	−4.2
6 + N_2	−194.598 319 594[c]	−6.1	−10.8	−8.7	72.7	−38.8

[a] With respect to a standard state of 1 bar. [b] CASPT2(6,6) energy including N_2. [c] CASPT2(2,2) energy of hydrocarbon fragment only.

using a TCSCF/DPZ (Dunning−Huzinaga) model.[17] However, unlike Sherrill et al., we found the transition structure for ring closure of cyclopentane-1,3-diyl to bicyclo[2.1.0]pentane to have C_1 rather than C_s symmetry. We believe that this discrepancy is due not to the relatively small difference in basis sets employed but rather to the fact that the search for a transition structure was carried out with a C_s symmetry constraint in the earlier study.[17] An IRC calculation confirmed that the C_1 transition structure found in the present work did link C_2 cyclopentane-1,3-diyl and C_s bicyclo[2.1.0]pentane.

The geometries of the key stationary points for the reaction are shown in Figure 1. Full Cartesian coordinates and vibrational frequencies are listed in the Supporting Information.

Figure 2 summarizes the computed enthalpy profile for the reaction at 140 °C—a typical temperature used in the experimental studies—and compares the results with experimental values. Zero-point energies and thermodynamic functions were derived from the harmonic frequencies scaled by a factor of 0.892. This factor was found to give the best fit of the calculated frequencies to the observed ones for DBH.[18] The computational results are presented in more detail in Table 1.

It is clear that this level of theory shows an enthalpic preference for the synchronous C−N cleavage mechanism. Significantly, CASPT2 *does not* cause the dramatic changes in the potential energy surface upon inclusion of dynamic electron correlation that Yamamoto et al. found at the CASMP2 level.

The agreement of the CASPT2 stationary-point relative enthalpies with the experimental ones[19] suggests an average error of about ±3 kcal/mol in the calculations. The largest deviation (4.4 kcal/mol) occurs for cyclopentane-1,3-diyl, which is also the species having the largest experimental uncertainty (±2.4 kcal/mol) in its relative heat of formation.[18a,c] The computed difference in enthalpy between the synchronous TS and the diazenyl biradical (7.3 kcal/mol) would appear to be outside of the range of likely error in the calculations.

Table 2. Total Energies (hartrees) of Three Key Stationary Points at the CASSCF Level (from Yamamoto et al. (A) and from the Present Work (B)), and from Three Methods of Multireference Second-Order Perturbation Theory[a]

structure	CASSCF A	CASSCF B	CASMP2	MCQDPT	CASPT2
1	−302.9245	−302.9245	−303.7680	−303.8064	−303.8387
2	−302.8750	−302.8750	−303.7125	−303.7605	−303.7782
3	−302.8503	−302.8654	−303.7212	−303.7463	−303.7718

[a] Structures **1** and **2** were geometry optimized at the CASSCF(6,6) level, and the reported energies are also for the (6,6) active space. Structure **3** was geometry optimized at the CASSCF(6,5) level for the CASMP2 calculations, and the CASMP2 energy is also for the (6,5) space. For the MCQDPT and CASPT2 calculations, geometry optimization was at the CASSCF(4,4) level, but single point energies were in the (6,6) active space.

In trying to assess the reason for the difference between CASPT2 and CASMP2 results, it is perhaps worth noting that the MP2 correction implemented in the GAMESS program (the MCQDPT method of Nakano[20]), while not giving results in as good agreement with experiment as those from CASPT2, does concur that no qualitative changes in the potential energy surface are to be expected when dynamic electron correlation is included. Why such changes occur with the CASMP2 method is unclear.[21] The results of the three methods are compared in Table 2.

Entropy Effects on the Synchronous and Asynchronous Pathways. A lower activation enthalpy for the synchronous mechanism was found for the deazetization of azomethane in the calculations of Liu et al.[11] However, they suggested that there would be a preference for the stepwise mechanism once the activation entropies were taken into account.[11] In the present case, the activation entropy for the stepwise mechanism cannot be calculated because no such pathway exists at the CASSCF(6,6) level. At the CASSCF(4,4) level it does, but the transition state for C−N bond cleavage of diazenyl biradical **3** cannot be reliably found with only four electrons included in the active space, so there is no way to know whether the transition structure for formation of **3** or for its fragmentation ought to be considered rate limiting. However, a reasonable estimate of the activation entropy for the stepwise mechanism can be made by using the entropy of **3** itself, calculated at the CASSCF(4,4) level for the *endo* conformation, which would be the one closest in structure to the asynchronous C−N scission TS for DBH. This value (95.3 cal/(mol K) at 140 °C, using a hindered-rotor partition function with a 3 kcal/mol barrier for the torsion about the C−N bond) when compared to the

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(18) Gernet, D.; Kiefer, W. *Fresenius J. Anal. Chem.* **1998**, *362*, 84−90.

(19) Experimental enthalpies of formation of stationary points came from the following sources. (a) DBH (**1**): Engel, P. S.; Melaugh, R. A.; Mansson, M.; Timberlake, J. W.; Garner, A. W.; Rossini, F. D. *J. Chem. Thermodyn.* **1976**, *8*, 607−21. (b) Deazetization TS: Cohen, S. G.; Zand, R.; Steel, C. *J. Am. Chem. Soc.* **1961**, *83*, 2895−900. An independent determination is reported in ref 3. (c) Cyclopentane-1,3-diyl (**4**): Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 2681−3. (d) Cyclopentane-1,3-diyl ring-closure TS (**5**): See ref 2. (e) Bicyclo[2.1.0]pentane (**6**): Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R., *Chem. Ber.* **1991**, *124*, 2499−521.

(20) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983−92.

(21) Other cases have been noted where CASMP2 seems to give results different from those of alternative multireference perturbation theory methods. See footnote on p 36 of: Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1−97.

calculated value for DBH (82.5 cal/(mol K) at 140 °C, at the CASSCF(6,6) level), gives an estimate of 12.8 cal/(mol K) for $\Delta S^{\ddagger}$ of the stepwise pathway. The synchronous mechanism is calculated to have a $\Delta S^{\ddagger}$ of 6.6 cal/(mol K), so the difference in entropy between the two pathways is not enough to compensate for the enthalpic advantage enjoyed by the synchronous mechanism. At 140 °C, the activation free energies are calculated to be 31.4 kcal/mol for the C_s-symmetry pathway and 36.1 kcal/mol for formation of the diazenyl biradical, corresponding to a rate-constant ratio of 300:1 in favor of the synchronous pathway. If a true transition structure for the asynchronous mechanism could be found, its energy would presumably be higher than that of **3**, making the preference for the synchronous pathway even larger. The calculated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the synchronous reaction (34.1 kcal/mol and 6.6 cal/(mol K), respectively) appear to be in good agreement with the experimental values[19b] ($\Delta H^{\ddagger} = 36.4 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = 6.5 \pm 0.5$ cal/(mol K) in one study and $\Delta H^{\ddagger} = 36.0 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = 5.6 \pm 0.6$ cal/(mol K) in another).

It is perhaps worth noting that the small difference (6.2 cal/(mol K)) in activation entropy for the two pathways calculated for the deazetization of DBH stands in marked contrast to the very large difference (28.4 cal/(mol K)) proposed by Liu et al. for the corresponding reaction of azomethane.[11] At first sight, this may seem to be explained by the fact that the first C−N cleavage of the stepwise mechanism creates two particles in the azomethane reaction, whereas it represents only a rearrangement for DBH. However, closer inspection reveals that the $\Delta\Delta S^{\ddagger}$ value of Liu et al. is almost certainly too large. Although no value for $\Delta S^{\ddagger}$ of either mechanism is reported in their paper, Liu et al. do report computed standard entropies of the symmetrical transition structure (83.9 cal/(mol K)) and the rate-determining transition structure for the stepwise pathway (112.3 cal/(mol K)).[11] We have computed the standard entropy of azomethane from scaled (0.93) MP2/6-311G(2d,p) frequencies (the same procedure used by Liu et al.) and find a value of 69.1 cal/(mol K). This gives a $\Delta S^{\ddagger}$ value of 14.8 cal/(mol K) for the synchronous mechanism and 43.2 cal/(mol K) for the stepwise pathway. Not only does the latter value seem unreasonably large, it is also in very poor agreement with the experimental estimates of 11−18 cal/(mol K).[22] We believe that the problem arises in the calculation of the entropy of the stepwise TS. Liu et al. find a small barrier (0.2 kcal/mol) for N_2 loss from methyldiazenyl radical but none for the endothermic scission of the first C−N bond of the reactant, and so assign the second C−N cleavage as the rate-determining step.[11] However, in so doing they have implicitly ignored the centrifugal barrier[23] that should be present for the first bond scission, and would almost certainly be larger than 0.2 kcal/mol. This means that the real rate-determining step for the sequential mechanism is very probably the first one. The entropy of this transition structure would be much lower than that of the second, since now the additional translational entropy of the methyl radical would be absent. While the activation entropy for the stepwise cleavage of azomethane thus remains unknown, this analysis suggests that the apparently large difference between our results on DBH and Liu et al.'s on azomethane is probably not real.[24]

Mechanistic Implications of the Calculations. The CASPT2 calculations support neither of the mechanisms proposed by Roth and Martin. Their first mechanism[3] involved synchronous C−N cleavage and C−C bond formation, but the C_s transition structure, **2**, found at the CASSCF(6,6)/6-31G(d) level shows no evidence of incipient C−C bond formation. The distance between the bridgehead carbons is calculated to be 2.309 Å, compared to 2.188 Å in DBH (**1**) itself. The second Roth and Martin mechanism[4] is also not supported, since it involved a diazenyl biradical, **3**, which is found to be a local minimum on the PES at the CASSCF(4,4)/6-31G(d) level, but not at the CASSCF(6,6)/6-31G(d) level. Furthermore, CASPT2(6,6) calculations on the CASSCF(4,4) structure place it 7.3 kcal/mol higher in enthalpy than the synchronous TS, **2**.

The failure of the calculations to support the mechanisms of Roth and Martin is consistent with a key experimental observation, which also strongly suggests that neither mechanism is correct. The observation is that the branching ratio shows no temperature dependence.[6] In neither of their mechanistic proposals did Roth and Martin suggest how the minor product stereoisomer **6n** might have been formed. Whatever path one thinks of, it seems unavoidable that its transition structure would be very different from that for a concerted reaction with inversion of configuration (which, in different variants, is the proposal for formation of **6x** in both of the Roth and Martin mechanisms). Differences in geometry of isomeric structures generally translate to differences in heats of formation, and that should lead to a temperature dependence of the branching ratio. However, the rate constant ratio k_i/k_r (see below for definition) experimentally shows no detectable temperature dependence in the range $129.8 \leq T \leq 180.5$ °C.[6]

The Allred and Smith mechanism,[5] at least in its full detail, is also not supported by the calculations since it relied on the existence of a C_s double-minimum equilibrium structure for cyclopentane-1,3-diyl (**4**), whereas the calculations favor a C_2 structure. The putative C_s biradical would have distinct *exo* and *endo* faces to which substituents could be attached, whereas in the C_2 structure the faces are related by the 2-fold rotation. Nevertheless, the mechanism that we do favor clearly has some resemblance to the Allred and Smith proposal, as detailed below.

To the extent that the more recent dynamic mechanisms for the reaction have assumed a stepwise C−N cleavage from DBH,[6,10] they too are disfavored by the present ab initio results. However, as we discuss below, there is reason to think that the nonstatistical dynamic phenomena that had been invoked for the stepwise mechanism would be retained, and perhaps even enhanced in the synchronous one. Thus, while it now appears that the detailed simulations were probably based on an incorrect PES, the qualitative description of the reaction dynamics is largely unaffected.

In the previous work on the reaction from this laboratory, a mechanism involving the diazenyl biradical, **3**, was invoked. The loss of nitrogen from **3** was postulated to create **4** with a dynamic preference for formation of one bicyclopentane stereoisomer over the other.[6] The large-scale dynamic simulations of Raff et al. supported this picture.[10] We suggested that this preference was derived from the detailed dynamics of the C−N bond cleaving step in **3**, which was accompanied by an inversion motion at the carbon to which the nitrogen was attached.[6] Now that the involvement of **3** no longer seems plausible, a modification of the mechanism is obviously necessary. However, examination of the reaction-coordinate eigenvector for the symmetrical nitrogen loss from **1** shows that a similar inversion motion is imparted to *both* of the erstwhile bridgehead carbons.

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(22) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99−149.

(23) See, for example: Rynefors, K. *Chem. Phys.* **1983**, *81*, 349−56.

(24) A reviewer has suggested that the anomalously large activation entropy found by Liu et al. may also derive from the use of harmonic partition functions for the low frequencies in the calculation of $\Delta S^{\ddagger}$.

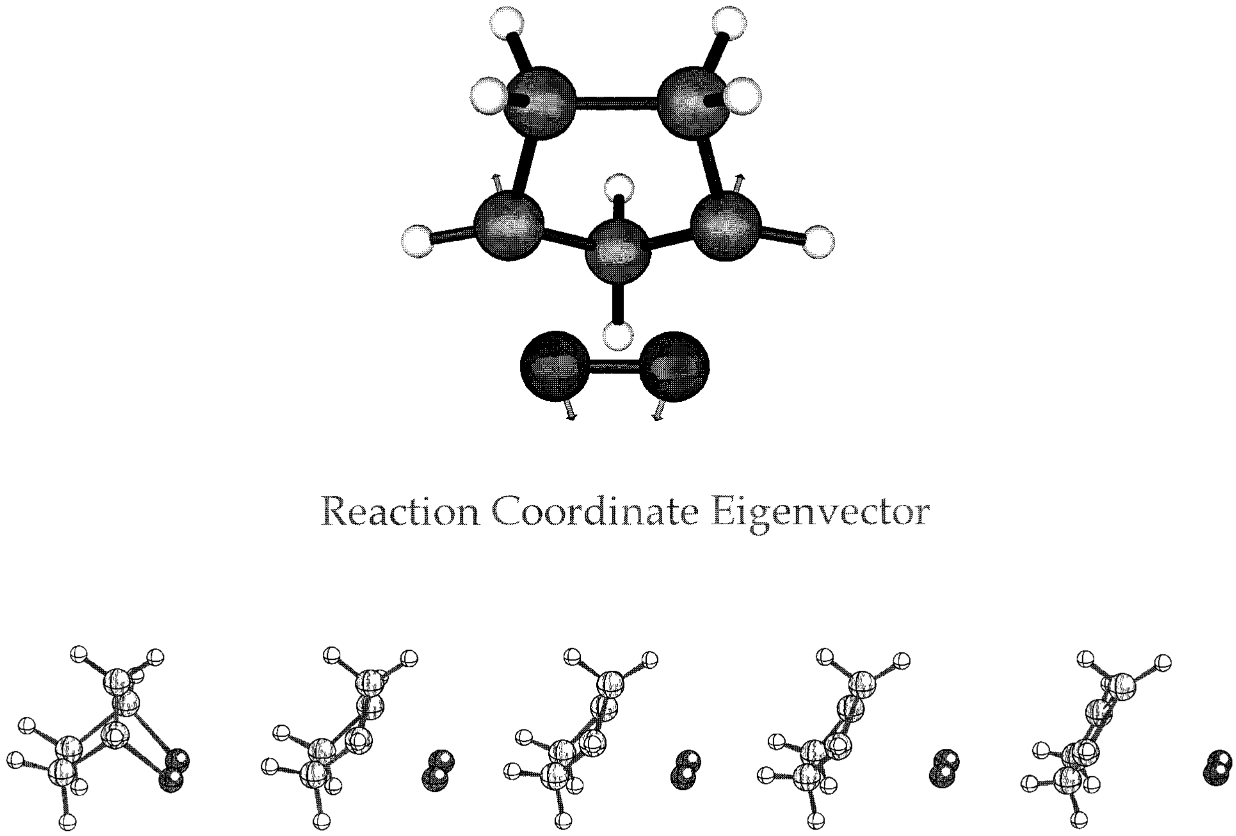

Figure 3. CASSCF(6,6)/6-31G(d) reaction coordinate eigenvector for synchronous nitrogen extrusion from DBH. The upper diagram shows the principle components of atomic motion from the normal-mode analysis, while the lower one shows a series of snapshots along the direction of the reaction coordinate. Both representations indicate that nitrogen loss is accompanied by an inversion of configuration at the erstwhile bridgehead carbons.

This may provide an even stronger dynamic preference for formation of the inverted bicyclopentane product (see Figure 3).

Such a mechanism is obviously closely related to that originally proposed by Allred and Smith.[5] However there are some important differences. Apparently, there are not two envelope conformations of the cyclopentane-1,3-diyl, each connected to one bicyclopentane on the PES, as Allred and Smith had proposed. Rather, there are two enantiomeric conformations of C_2 symmetry (in the absence of the deuterium labels), each connected to both bicyclopentanes by C_1-symmetry transition structures. In the Allred and Smith proposal, the formation of a particular bicyclopentane conformation was dynamically determined, but its subsequent closure was dictated by the topology of the PES.[5] In the present proposal, the ring closure of the cyclopentane-1,3-diyl must be dynamically determined, since it occurs with unequal probability via two transition structures that would be enantiomeric in the absence of labels. The distinction is illustrated in Figure 4.

The "... energy released by C−N bond breaking ...", which Allred and Smith had proposed to be the source of an impulsive kick to the hydrocarbon fragment,[5] is not in evidence in the present calculations. In general, breaking bonds does not release energy—it costs energy. Such is the case in the present reaction; the conversion of DBH to cyclopentane-1,3-diyl + N_2 is calculated to be endothermic by 26.3 kcal/mol. The origin of the inversion is related to the need for momentum conservation during the nitrogen expulsion.

Kinetic Model for the Reaction in the Gas Phase. The gross observations on the thermal deazetization of labeled DBH **1x** are captured by the simple kinetic model shown in Scheme 4. The phenomenological rate constants for formation of the products **6x** and **6n** are called respectively k_i and k_r, since these products arise from double inversion or complete retention of configuration at the bridgehead carbons. The stereoisomeric labeled bicyclo[2.1.0]pentanes are known to interconvert slowly under the reaction conditions, reaching an equilibrium ratio that has previously been shown to be experimentally indistinguishable from unity.[2] The rate constant for this interconversion is called k_f.

The differential rate equations for this system can be integrated analytically, giving the expressions for the mole fractions of the two products as a function of time in eqs 1 and 2.[25]

$$[\mathbf{6x}] = \frac{1}{2}\left(1 + \frac{(k_i - k_r)e^{-2k_f t} + 2(k_f - k_i)e^{-(k_i+k_r)t}}{k_i + k_r - 2k_f}\right) \quad (1)$$

$$[\mathbf{6n}] = \frac{1}{2}\left(1 - \frac{(k_i - k_r)e^{-2k_f t} + 2(k_f - k_i)e^{-(k_i+k_r)t}}{k_i + k_r - 2k_f}\right) \quad (2)$$

From the time of the first experiments on this system by Roth and Martin, it has been known that $k_i > k_r$. Early estimates[3] were that the ratio was about 3, but later work that included a correction for the interconversion of products has shown the value of k_i/k_r to be 4.7 ± 0.9 in the gas phase in the temperature range 130−180 °C.[6]

Recent molecular dynamics simulations on reactions involving transient intermediates such as singlet biradicals have

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(25) Equations 1 and 2 were derived with initial conditions $\chi_{\mathbf{1x}} = 1$, $\chi_{\mathbf{6x}} = \chi_{\mathbf{6n}} = 0$, where c_i is the mole fraction of species i.

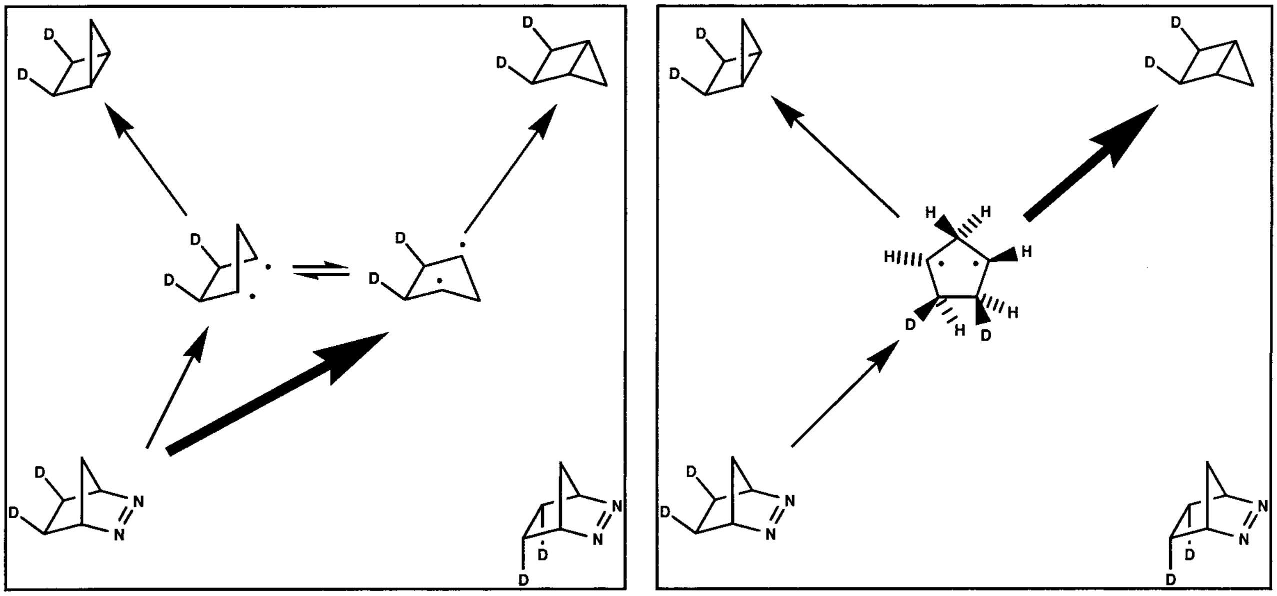
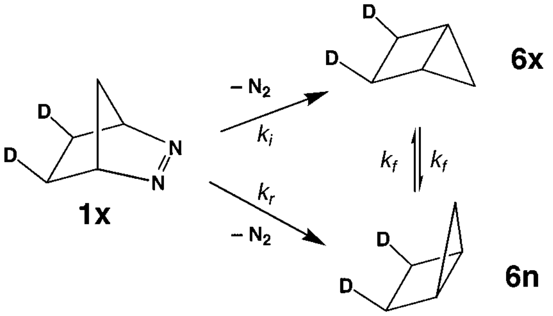
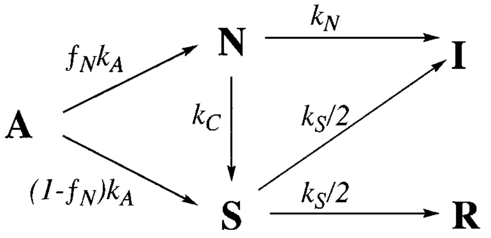


Figure 4. Contrast between the Allred and Smith mechanism (left) and the present proposal (right). In the former, the dynamic preference (bold arrow) is expressed in the formation of a particular biradical conformation. In the latter the dynamic preference is expressed in the ring-closure step.

Scheme 4. Mechanism-Independent Kinetic Model for the Deazetization of DBH



Scheme 5. Kinetic Representation of the Proposed Mechanism for the Deazetization of DBH[a]



suggested that these intermediates can show bimodal lifetime distributions when nonstatistical dynamics of the kind invoked here are involved. Some of the intermediates are formed on direct, reactive trajectories to one of the products, whereas others have incorrect initial energy distributions for such behavior, and so become temporarily trapped in the PES local minimum, before exiting to the products with probabilities that could presumably be assessed quite reliably by statistical kinetic models. The nonstatistical population (**N** in Scheme 5) typically has a much smaller mean lifetime than that of the statistical (S) population.

The key to one experimental test of this mechanism is the arrow labeled k_C in Scheme 5. This represents a collision event, and as the kinetic model indicates, we hypothesize that it can serve to convert the nonstatistical population of biradicals to the statistical population. The basis for this expectation is that the biradicals formed on direct trajectories to the inversion product (N) necessarily have their excess internal energy distributed among a limited subset of the available vibrational modes. Since a collision is likely to promote intramolecular vibrational energy redistribution (IVR), it can also be expected to deenergize this critical set of modes and energize nonreactive ones, thereby converting the biradical suffering the collision from a member of the **N** population to a member of the **S** population. Application of the steady-state approximation to the two biradical populations allows the phenomenological rate constants k_i and k_r of Scheme 4 to be expressed in terms of the mechanistic rate constants of Scheme 5. Since reversible interconversion of the products is not included in Scheme 5, there is no corresponding relationship for the phenomenological rate constant k_f. The results are summarized in eqs 3−5.

$$k_i = \frac{(k_C + (1 + f_N)k_N)k_A}{2(k_C + k_N)} \tag{3}$$

$$k_r = \frac{(k_C + (1 - f_N)k_N)k_A}{2(k_C + k_N)} \tag{4}$$

$$\frac{k_i}{k_r} = \frac{k_C + (1 + f_N)k_N}{k_C + (1 + f_N)k_N} \tag{5}$$

Qualitatively, eq 5 predicts that the ratio of phenomenological rate constants k_i/k_r should decrease with increasing collision frequency. This prediction forms the basis for the experiments described below.

Reaction in Supercritical Propane. Experimental testing of the prediction embodied in eq 5 requires that the collision frequency be both controllable and high enough (ca. 10^{13} s^{-1}) to intercept the putative direct trajectories. Supercritical fluids have properties that satisfy both of these criteria,[26] with the collision frequency being modulated by change of pressure at constant temperature above the critical temperature.[27] The first

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[26] Randolph, T. W.; O'Brien, J. A.; Ganapathy, S. *J. Phys. Chem.* **1994**, *98*, 4173−9, and references cited therein.

[27] For an early experiment in which the influence of a similar phenomenon on the overall magnitude of a phenomenological rate constant was investigated see: Dutton, M. L.; Bunker, D. L.; Harris, H. H. *J. Phys. Chem.* **1972**, *76*, 2614−7.

supercritical fluid studied was propane, which was selected because it has a convenient critical temperature (369.85 K) and is presumably chemically inert toward the various species involved in the reaction under study.

Each point in the pressure-dependence study required a separate run in the high-pressure apparatus, a fact that undoubtedly contributed to the scatter in the data. Products were analyzed by ^{2}H NMR in order to determine the ratio of products **6x**:**6n** and of both to the starting material, **1x**. From these data, the k_i/k_r ratio could be determined from eqs 1 and 2 by nonlinear least-squares fitting.

Qualitatively, the dynamic model predicts that the k_i/k_r ratio should decrease with increasing pressure. By contrast, one might expect the rate-constant ratio to *increase* with increasing pressure from a competitive-mechanisms model, such as either of those in Scheme 1 or 2, since the only influence of pressure that one might expect in this model would arise from differences in activation volume for the two mechanistic pathways. It is well-known that activation volumes for uncharged systems are related to numbers of bonds being made and broken in the rate-limiting transition structure.[28,29] By this criterion, the activation volume for the putative concerted pathway should be smaller than that for the stepwise one, so the former should be favored at higher pressure, leading to an increase of k_i/k_r. However, it should be noted that the range of pressures explored in the actual experiment is smaller than that used in studies where such effects have been detected,[28] so the magnitude of the change in k_i/k_r could be below the detection limit. Thus, the competitive-mechanisms model should really be considered to predict either an increase in k_i/k_r with increasing pressure or an effectively constant ratio, depending on the magnitude of the difference in $\Delta V^{\ddagger}$ and the range of pressures explored.

This difference in expected outcomes from the two models is not specific to the reaction studied here. It will generally be true that the dynamic model will lead to predictions of a lower branching ratio with increasing pressure, whereas the competitive-mechanisms model will predict an increasing or effectively constant ratio (at least for the common situation in which the mechanisms in competition are stepwise and concerted versions of the same transformation).

Aside from the qualitative prediction of a decreasing k_i/k_r ratio made by eq 5, it should be possible to fit the data on the pressure dependence of this ratio quantitatively, provided a suitable model can be found that relates the collision frequency to the pressure of the supercritical fluid. Two such models were considered—an isolated-binary-collision (IBC) model,[30] which would treat the fluid as a dense, nonideal gas, and a diffusive model of the kind proposed by Troe.[31] Both models require knowledge of the density of the supercritical fluid at the selected temperature and pressure, and the Troe model additionally requires knowledge of the viscosity of the medium. These two parameters were obtained from the Benedict−Webb−Rubin empirical equation of state for propane, as implemented in the NIST12 database.[32]

The IBC model allowed the collision rate constant to be calculated from eq 6

$$K_C = \frac{1}{\boldsymbol{\rho}^{-1/3} - \sigma_{12}} \left(\frac{8k_B T}{\pi M}\right)^{1/2} \tag{6}$$

where ρ is the number density, σ_{12} is the collision diameter for propane and cyclopentane-1,3-diyl, k_B is Boltzmann's constant, and M is the reduced mass.

In the Troe model, the viscosity of propane was used to compute the self-diffusion coefficient by interpolation (using eq 9) between the gas−kinetic (eq 7) and Stokes−Einstein limits (eq 8).

$$D_0 = \frac{3}{8} \frac{\sqrt{RT/2\pi M}}{N_A s_{11}{}^2 W^{(1,1)*}} \frac{1}{\rho} \tag{7}$$

$$D_\infty = \frac{k_B T}{3\pi \sigma_{11} h} \tag{8}$$

$$\frac{\boldsymbol{\kappa}_{\mathbf{B}}\mathbf{T}}{\boldsymbol{\eta} D} \approx \left(\frac{\mathrm{k}_B T}{\eta D}\right)_\infty \left\{1 - \exp\left[-\left(\frac{k_B T}{\eta D}\right)_0 \Big/ \left(\frac{k_B T}{\eta D}\right)_\infty\right]\right\} \tag{9}$$

In these equations, N_A is Avogadro's number, σ_{11} is the self-collision diameter for propane, $\Omega^{(1,1)*}$ is a reduced collision integral,[33] and η is the viscosity. The collision frequency was then computed[31] from eq 10, where $k_C{}^0$ is the gas−kinetic collision frequency at low pressure (we used 10^{-5} bar).

$$K_C = \frac{C_c{}^0 D}{D_0} \tag{10}$$

Both the IBC and Troe models were fit to the observed k_i/k_r ratio as a function of pressure, using τ_N ($=k_N{}^{-1}$), f_N, and the appropriate collision diameter (σ_{12} in eq 6 or σ_{11} in eqs 7 and 8) as adjustable parameters. The fitting was carried out by nonlinear least-squares optimization, using the Levenberg−Marquardt algorithm.

The results are shown in Figure 5. The lines through the data points correspond to best fits of the IBC model and the Troe model. It is clear that the ratio of phenomenological rate constants decreases with increasing pressure, as expected for the dynamic model. The data smoothly interpolate between previously determined gas-phase and solution-phase values of k_i/k_r.[6] Furthermore the best-fit values of the adjustable parameters for the IBC and Troe models seemed physically reasonable. The best-fit collision diameters were found to be respectively 4.9 ± 1.3 and 5.9 ± 0.9 Å for the IBC and Troe models. Of special interest were the fraction (f_N) of deazetization events occurring via direct, nonstatistical trajectories, which turned out to be 0.67 ± 0.08 for both models, and the lifetime ($\tau_N = k_N{}^{-1}$) of the nonstatistical population which was found to be 130 ± 22 fs by the IBC model and 103 ± 13 fs by the Troe model. These lifetimes are consistent with that (about 140 fs) for the structurally related singlet trimethylene biradical, determined experimentally by femtosecond spectroscopy[34] and theoretically by molecular-dynamics simulation.[35]

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(28) Klärner, F.-G.; Krawczyk, B.; Ruster, V.; Deiters, U. K. *J. Am. Chem. Soc.* **1994**, *116*, 7646−57.

(29) For lucid general descriptions of the physical basis for pressure effects on elementary reactions, including some cautionary notes on interpretation of activation volumes, see: (a) Montgomery, J. A., Jr.; Chandler, D.; Berne, B. J. *J. Chem. Phys.* **1979**, *70*, 4056−66. (b) Troe, J. *J. Phys. Chem.* **1986**, *90*, 357−65. (c) Hase, W. L. *J. Phys. Chem.* **1986**, *90*, 365−74.

(30) Schultz, K. E.; Russell, D. J.; Harris, C. B. *J. Chem. Phys.* **1992**, *97*, 5431−8.

(31) (a) Otto, B.; Schroeder, J.; Troe, J. *J. Chem. Phys.* **1984**, *81*, 202−13. (b) Hippler, H.; Schubert, V.; Troe, J. *J. Chem. Phys.* **1984**, *81*, 3931−41. (c) Maneke, G.; Schroeder, J.; Troe, J.; Voss, F. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 896−906.

(32) *NIST12*, version 3.0; Fluid Mixtures Data Center, Thermophysics Division, National Institute of Standards and Technology: Gaithersburg, MD.

(33) *Molecular Theory of Gases and Liquids*; Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., Eds.; Wiley; New York, 1954.

(34) Pedersen, S.; Herek, J. L.; Zewail, A. H. *Science* **1994**, *266*, 1359−64.

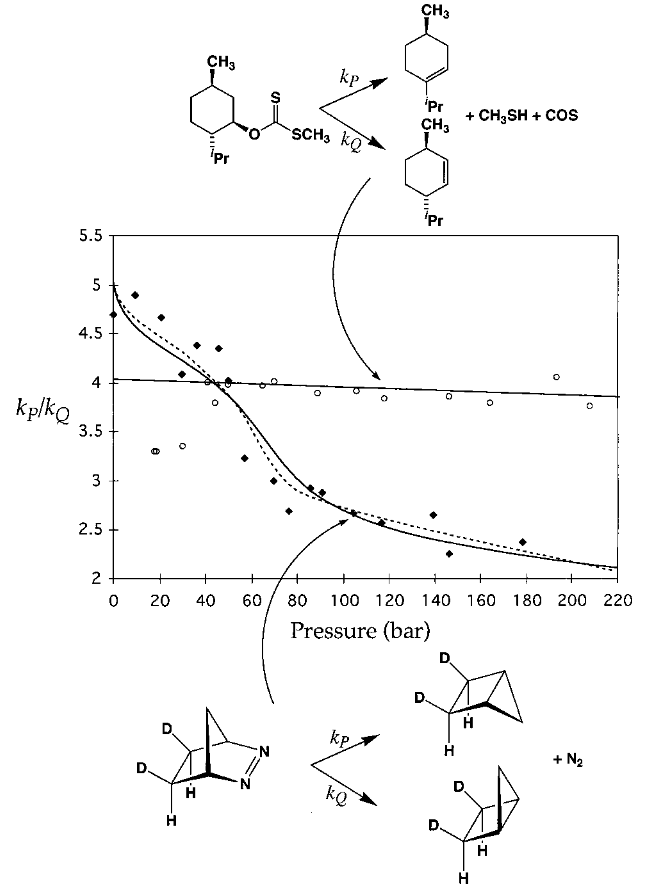

Figure 5. Pressure dependence of the branching ratio for DBH deazetization and for a control reaction. The DBH data are fit by two models: an IBC model (solid curve) and a diffusive model proposed by Troe (dashed curve). See text for further description.

Also shown in Figure 5 are results for a control reaction in which the products really do come from two competitive mechanisms. The competitive pathways for the control are both believed to be concerted reactions,[36] and in accord with that, one sees little dependence of product ratio on pressure in the region where the reactant is miscible with the supercritical fluid (above about 40 bar). That the labeled DBH, **1x**, was miscible with the supercritical propane throughout the pressure range was demonstrated by determining the temperature dependence of the vapor pressure of DBH. It is given by eq 11. Assuming ideal-gas behavior, this equation suggests that up to 1.8 mmol of azo compound **1** could be completely vaporized in the 19 mL pressure cell at 140 °C. In practice, no more than 0.3 mmol was used in any experiment.[37]

$$\log (P/\text{Torr}) = -1796.6/T + 7.746 \qquad (11)$$

Reaction in Supercritical Carbon Dioxide. Reinvestigation of the pressure dependence of the branching ratio was carried out in supercritical CO_2 at 140 °C in order to determine whether the nature of the supercritical fluid had a significant influence on the outcome. In particular, one might imagine that CO_2, being a rigid triatomic molecule with a lower density of vibrational states than propane at any given energy, might be a less efficient collision partner for the nonstatistical component of the cyclopentane-1,3-diyl biradical.

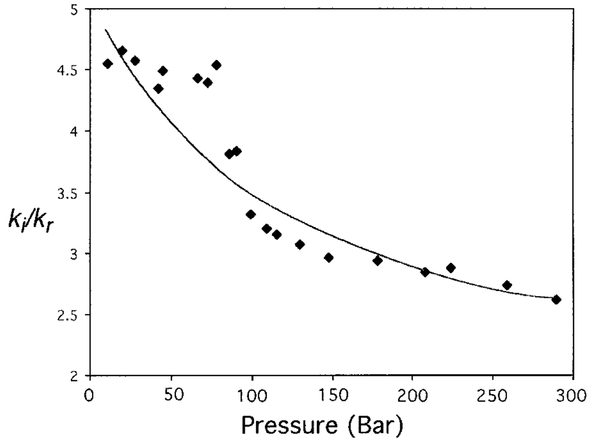

Figure 6. Data and best-fit of the Troe model (see text) for DBH deazetization in supercritcal CO2 at 140 °C.

In the event, as shown in Figure 6, the data obtained in supercritical CO_2 were quite surprising. The best fit of either model (the Troe model is shown in Figure 6) failed to reproduce the rather sharply sigmoidal nature of the experimental data. We explored several modifications of the original kinetic scheme in order to improve the fit, but none did so satisfactorily.

To investigate whether some sort of attractive interaction between the biradical and CO_2 could explain the data,[38] we carried out a number of ab initio calculations. In fact, 1:1 and 2:1 complexes with CO_2 were found for the singlet state and a 2:1 complex was found for the triplet state of cyclopentane-1,3-diyl. Their structures are summarized in Figure 7. Presumably the 1:1 complex exists also for the triplet, but this was not investigated since the singlet state is the mechanistically relevant one. The singlet calculations were carried out at the GVB/6-311+G(2d) level and the triplet calculations at the UB3LYP/6-311+G(2d) level.

Weak interactions of the kind postulated here are extremely difficult to capture accurately in ab initio electronic structure calculations. In particular, large basis sets are necessary in order to minimize basis-set superposition error (BSSE) and high levels of dynamic electron correlation are necessary in order to detect dispersion interactions.[39] The combination of these two requirements makes the calculations typically very large. Since a basis set larger than 6-311+G(2d) could not be combined with calculations above the MP2 level for the system of interest, we sought to determine how sensitive the results were to basis set size and level of electron correlation in a smaller model system: $CH_3{}^\bullet + CO_2$. This complex was geometry optimized at the UB3LYP/6-311+G(2d) level. A C_1-symmetry structure resulted, although there was essentially no barrier to rotation

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(35) (a) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 5251−2. (b) Hrovat, D. L.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1997**, *119*, 5253−4. (c) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Phys. Chem. A* **1998**, 102, 3648−58.

(36) Nace, H. R. *Org. React.* **1962**, *12*, 57−100.

(37) Equation 11 defines an enthalpy of vaporization for DBH, which turns out to be 8.2 kcal/mol. This value is smaller than those in the literature (10.49 kcal/mol: Engel, P. S.; Wood, J. L.; Sweet, J. A.; Margrave, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 2381−7. 13.21 kcal/mol: Engel, P. S.; Melaugh, R. A.; Mansson, M.; Timberlake, J. W.; Garner, A. W.; Rossini, F. D. *J. Chem. Thermodyn.* **1976**, *8*, 607−21). However, the literature values come from experiments conducted at temperatures well below the 98 °C melting point of DBH, and so include the enthalpy of fusion, whose magnitude is unknown. The present value constitutes the enthalpy of vaporization from hydrocarbon solution at temperatures above the melting point and would not be expected to be equal to either of the literature values.

(38) We thank Professor Michael Fayer (Stanford University) for suggesting this possibility. The Fayer group has recently reported anomalous influences of supercritical CO_2 on vibrational lifetimes and has hypothesized that this might be due to specific solute−solvent interactions of the kind postulated here (Myers, D. J.; Shigeiwa, M.; Fayer, M. D.; Cherayil, B. J. *J. Phys. Chem. B* **2000**, *104*, 2402−14).

(39) Rappé, A. K.; Bernstein, E. R. *J. Phys. Chem. A* **2000**, *104*, 6117−28.

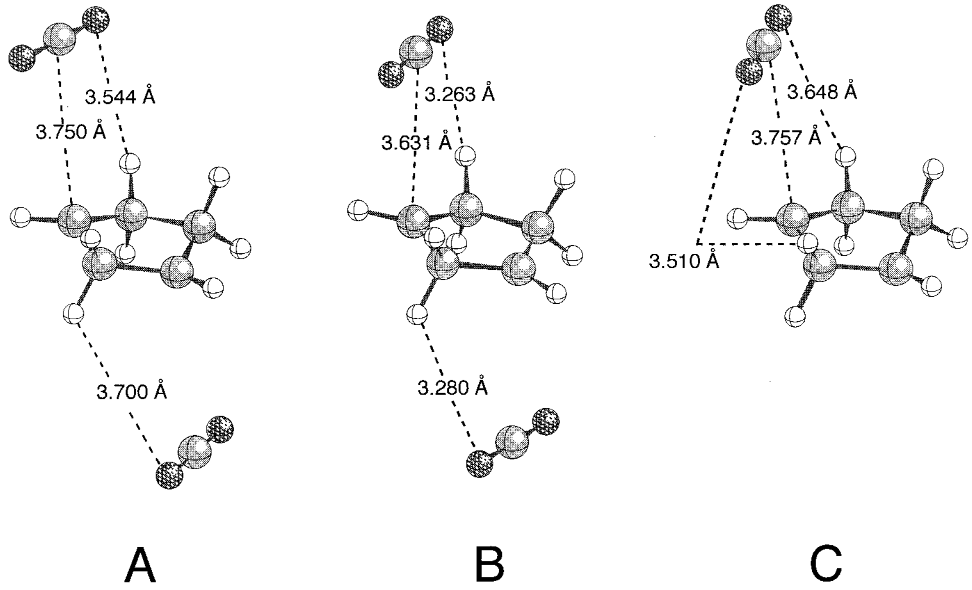

Figure 7. Calculated geometries of CO_2 complexes with cyclopentane-1,3-diyl. A is the C_2-symmetry 2:1 complex with the singlet state, **B** is the C_2-symmetry 2:1 complex with the triplet state, and **C** is the C_1-symmetry 1:1 complex with the singlet state. Full Cartesian coordinates are given in the Supporting Information.

Table 3. Summary of Single-Point Calculations on the $CH_3{\cdot}/CO_2$ Complex at the UB3LYP/6-311+G(2d) Geometry (Absolute Energies, hartrees; Energy Differences and Zero-Point Energies, kcal/mol)

theoretical model	$E(CH_3)$	$E(CO_2)$	$E(CH_3{\cdot}CO_2)$	ΔE
HF/6-311+G(2d)	−39.567 5672	−187.694 6540	−227.262 6154	−0.25
B3LYP/6-311+G(2d)	−39.849 9263	−188.650 6402	−228.501 0768	−0.32
MP2/6-311+G(2d)	−39.693 2880	−188.245 4849	−227.940 2388	−0.92
MP3/6-311+G(2d)	−39.709 9916	−188.225 0999	−227.936 4865	−0.88
MP4(SDQ)/6-311+G(2d)	−39.713 1007	−188.239 3448	−227.953 8363	−0.87
MP4(SDTQ)/6-311+G(2d)	−39.715 8266	−188.271 8719	−227.989 2615	−0.98
CCSD(T)/6-311+G(2d)	−39.717 4276	−188.261 2360	−227.980 2005	−0.96
HF/aug-cc-pVTZ	−39.577 9929	−187.709 4306	−227.287 6762	−0.16
MP2/aug-cc-pVTZ	−39.738 3001	−188.321 2618	−228.061 1344	−0.99
MP3/aug-cc-pVTZ	−39.756 2531	−188.303 3325	−228.061 0676	−0.93
MP4(SDQ)/aug-cc-pVTZ	−39.758 1701	−188.314 6954	−228.074 3310	−0.92
ZPE (B3LYP/6-311+G(2d))	18.578 80	7.313 81	26.290 60	0.40

of the $CH_3{\cdot}$ with respect to the CO_2 about the axis between the carbons, so the geometry optimization terminated when the forces became negligibly small, even though significant components of relative motion of the two fragments remained. A number of higher-level single-point calculations were then carried out on the complex and on the separate fragments. The results are summarized in Table 3. One sees from these results that the HF calculations underestimate the binding energy between $CH_3{\cdot}$ and CO_2, as apparently the B3LYP calculations do.[40] However all of the other theoretical models show results that are rather insensitive to the level of electron-correlation treatment and to the size of the basis set. They indicate a binding energy of roughly 0.6 kcal/mol when zero-point energy differences are included. No attempt was made to correct for BSSE, since the commonly employed counterpoise method has been shown to be subject to errors that may be as large as the problem that it is trying to correct.[41] Other techniques for correcting for BSSE are limited to closed-shell systems.[42] The small difference between results with the 6-311+G(2d) and aug-cc-pVTZ basis sets leads us to believe that the former is adequate for the purposes.

For cyclopentane-1,3-diyl, GVB/6-311+G(2d) calculations on the singlet state indicate essentially additive binding energies of 0.26 kcal/mol for the first CO_2 and 0.24 kcal/mol for the second (including ZPE from harmonic frequencies scaled by 0.89). However, these calculations include nondynamic electron correlation only for the "unpaired" electrons. All other electrons are treated only at the HF level. On the basis of the $CH_3{\cdot} + CO_2$ results, one might expect that the CO_2 binding energy would therefore be underestimated. In principle this question could be addressed with a CASPT2(2,2) calculation, which would provide MP2-quality dynamic electron correlation. However, the calculations could not be performed with the available computer systems because CASPT2 cannot be conducted in direct mode, and with the 6-311+G(2d) basis set, the two-electron integrals over atomic orbitals required storage (>20 GB) that exceeded the available disk space. Consequently, we turned our attention to the triplet-state complex. UB3LYP/6-311+G(2d) calculations gave a geometry for the C_2-symmetry complex that was very similar to the one found with the GVB calculations on the singlet. The binding energy per CO_2 was calculated to be only 0.17 kcal/mol at this level (including ZPE differences from B3LYP frequencies scaled by 0.97). A UMP2/

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(40) The inability of current functionals to reproduce dispersion interactions has been noted previously: (a) Diep, P.; Jordan, K. D.; Johnson, J. K.; Beckman, E. J. *J. Phys. Chem. A* **1998**, *102*, 2231−6. (b) Lein, M.; Dobson, J. F.; Gross, E. K. U. *J. Comput. Chem.* **1999**, *20*, 12−22.

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6-311+G(2d)//B3LYP/6-311+G(2d) calculation, run in the fully direct mode, significantly increased the estimate of the binding energy to 1.9 kcal/mol per CO_2. Thus, as with the $CH_3^{\bullet} + CO_2$ calculations, MP2 suggests a much stronger interaction than do HF-level or B3LYP calculations. On the basis of those model calculations, we estimate that higher-level Møller−Plesset or coupled-cluster calculations would reveal a binding energy similar to that calculated from MP2. We hypothesize that the binding energy between cyclopentane-1,3-diyl and CO_2 is larger than that between methyl radical and CO_2 in part because of an attractive interaction of the CO_2 quadrupole with the syn hydrogens on C2 and C5 (or C2 and C4) of the biradical.

The weak bonding interaction between cyclopentane-1,3-diyl and CO_2 suggested by these calculations substantially complicates the picture for the reaction dynamics of DBH in supercritical carbon dioxide—to the point where fitting of a kinetic model to the data no longer seems feasible. Even the simplest model would have so many adjustable parameters that the fitting exercise would seem to have little point. Thus, the labeled biradical **4c** would form two 1:1 complexes (one with the labels syn to the CO_2 and one with them anti). Given the proposed asymmetry in the dynamics of formation of **4c** from **1x**, it is unlikely that these stereoisomeric complexes would be formed in equal amount, and also unlikely that they would have the same branching ratios to the stereoisomeric bicyclopentane products. The role, if any, played by the 2:1 complex in the overall reaction dynamics is also unknown. At this stage, the only way we can imagine determining whether the formation of complexes can quantitatively explain the pressure-dependence data would be to run full-scale molecular-dynamics simulations including explicit CO_2 molecules. We hope to be able to do that in the future. We do note that the apparent bonding interaction between radicals and CO_2 sounds a cautionary note for the interpretation of other kinetic data on free-radical reactions in supercritical carbon dioxide.[43]

Mechanistic Analysis of Combined Theory and Experiment. A key conclusion from the calculations reported in this paper appears, at first sight, to be incompatible with prior experimental results. It is the proposal that the preferred mechanism for thermal nitrogen extrusion from DBH involves synchronous cleavage of the two C−N bonds. The apparent contradiction comes from experiments showing that in both the thermal[8] and direct photolytic[7] reaction the nitrogen is extruded with little or no excess vibrational energy. Given the argument of Bauer,[9] this would appear to constitute a clear disagreement. His proposal was that the N═N compression and C−N stretching coordinates would be orthogonal for the synchronous extrusion mechanism, causing the N_2 to be formed with an abnormally long N≡N bond, corresponding to vibrational excitation. However, we believe that this argument bears reexamination. The N═N compression and C−N stretching vibrations both belong to the *A'* irreducible representation of the C_S point group and so are permitted to mix. That the motions do indeed mix can be seen in two ways. First, the reaction-coordinate motion summarized by the vectors in the upper part of Figure 3 shows that the two nitrogen atoms are simultaneously moving away from the bridgehead carbons and toward each other. Second, the N═N distance has been reduced from 1.242 Å in DBH to 1.152 Å in the transition structure, according to the CASSCF(6,6) calculations. Thus there appears to be no requirement that the N_2 depart with excess vibrational energy.

According to experiment, the energy available for combined vibrational, rotational, and translational excitation of the fragments (beyond whatever excess energy there may be in the transition structure) is 14.3 ± 2.4 kcal/mol. Given that the density of vibrational states in the cyclopentane-1,3-diyl fragment vastly exceeds that of the N_2 at all energies, it seems implausible that the N_2 would carry off 47% of this excess energy, as would be required for it to reach the $v = 1$ state. Thus, the failure to detect vibrational excitation of the N_2 is, we believe, entirely consistent with the synchronous mechanism.

It is also interesting to note that the synchronous mechanism predicts no rotational excitation of the N_2, consistent with the observed outcome for the direct photolysis of DBH. As noted by Adams et al.,[7b] the lack of rotational excitation in the extruded N_2 is *not* consistent with reaction via a diazenyl biradical, unless some electronic excited state of the biradical with a linear C−N═N$^{\bullet}$ unit is invoked. However, the calculations of Yamamoto et al.[12] suggest that such a structure corresponds to a superimposed S_0/S_1 and T_1/T_2 conical intersection and that there is no direct N_2 dissociation from this geometry. Thus, while the present work has not directly addressed the photochemical mechanism, since the calculations were carried out only on the S_0 electronic state of DBH and its products, the experimental observation of a lack of N_2 rotational excitation suggests that this reaction may also occur without involvement of a diazenyl biradical.

Recent results on the temperature dependence of product ratios by Adam et al.[44] have been interpreted as supporting the S_H2 (Roth and Martin mechanism 2) reaction of a singlet diazenyl biradical generated by direct photolysis of a tricyclic analogue of DBH. However, the data are equally consistent with a mechanism in which the $^1(n,\pi^*)$ state of the azo compound proceeds directly to a ground-state, nitrogen-free singlet biradical whose ring closure is subject to dynamic control similar to that proposed in the present work. To our knowledge, there are no experimental data in the literature that require the intermediacy of a diazenyl biradical generated thermally or photochemically from any DBH analogue.

If one accepts that the deazetization mechanism most consistent with the experiments on N_2 vibrational and rotational energy distributions and with the present calculations is one that occurs by synchronous C−N cleavage, then the second Roth and Martin mechanism (Scheme 2) is ruled out as an explanation for the preferred stereochemistry of the reaction. The calculations also offer no support for their first mechanism (Scheme 1), since there is no sign of incipient C−C bond formation in the transition structure for N_2 loss. Both Roth and Martin mechanisms are also disfavored by the lack of temperature dependence of the k_i/k_r ratio, a result that could be explained only as a coincidental equality of activation enthalpy for two different pathways if either of these mechanisms were correct.

For the reasons described earlier, the Allred and Smith mechanism is also not fully consistent with the calculations reported here. Nevertheless, their revolutionary proposal of a dynamic origin for the reaction stereochemistry is very definitely in line with the mechanism that we favor. The results obtained in supercritical propane seem to be both qualitatively and quantitatively consistent with expectations based on a reaction involving significant intervention from nonstatistical dynamics. They are not obviously consistent with a mechanism involving two different pathways for the formation of the product stereoisomers.

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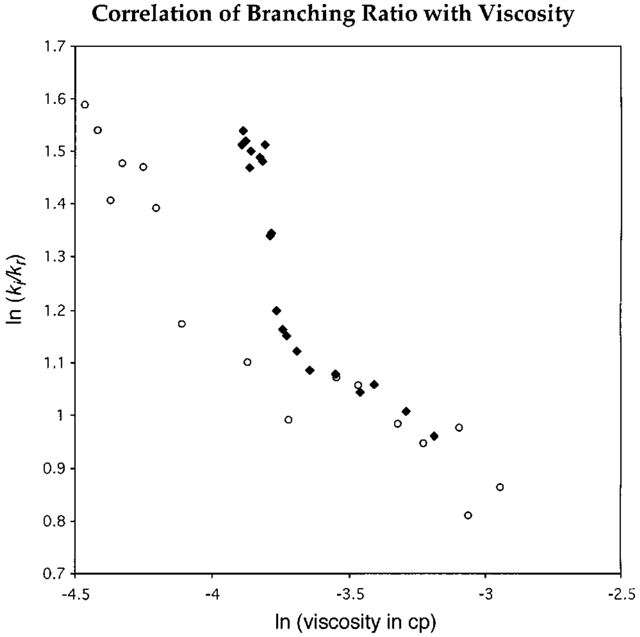

Figure 8. Viscosity correlation of k_i/k_r for thermal deazetization of 1x (see ref 45). Open circles are data for supercritical propane; filled diamonds are data for supercritical CO_2.

It should be noted, however, that Adam et al.[45] have very recently demonstrated that the ratio of product stereoisomers can be correlated with the solvent viscosity for photochemical deazetization of a trialkyl derivative of DBH (*endo*-1-ethyl-4,7-dimethylbicyclo[2.2.1]hept-2-ene). That raises the question of whether the present results could be equally well-explained by a simple viscosity argument. We think that they cannot, for two reasons. First, Adam et al. showed that there is a linear correlation between the logarithm of the product ratio and the logarithm of the solvent viscosity. Since we know the viscosity of our supercritical fluids at all of the pressures studied, we can check for such a relationship. The results are shown for propane and CO_2 together in Figure 8. Not only is the relationship highly nonlinear, the slope of the best-fit straight line ($R^2 = 0.68$) is a factor of 2 larger than that found by Adam et al.[45]

The second reason for doubting that changes in viscosity are sufficient to explain the data is that we have previously shown[6] that the k_i/k_r ratio is insensitive to temperature over a 50 °C range, in three different liquids. Since the viscosities of organic liquids typically change by a factor of 2−3 over this temperature range,[46] the lack of temperature dependence to the rate-constant ratio does not seem compatible with a significant viscosity dependence.

It is not obvious why the product ratio for deazetization of a substituted DBH analogue should be sensitive to the medium viscosity whereas that for the parent molecule is not. One possibility is that the volume swept out during stereochemical change is larger for the substituted molecule. The interconversion of bicyclopentane stereoisomers may look like a reaction that also involves significant atomic motion, even for the parent molecule, if one focuses on the cyclopropane ring moving with respect to a fixed cyclobutane moiety. However, the actual motion of the atoms about the center of mass of the molecule involves primarily the bridgehead carbons and their attached hydrogens. These atoms move quite small distances, and the reaction could very probably be accomplished with little disturbance of surrounding solvent molecules.

The attractive interaction between CO_2 and cyclopentane-1,3-diyl that we have suggested as a possible explanation of the unusual pressure dependence of k_i/k_r in that medium, results in a detailed mechanism that is too complex to be susceptible to quantitative fitting. However, it seems qualitatively plausible that the formation of various CO_2/biradical complexes could explain the results. Presumably the rate of formation of such complexes would increase with pressure. It also seems likely that the efficiency of IVR between the components of a relatively long-lived cluster would be greater than in a transient encounter complex. If both of these postulates were correct, the result would be a higher-order dependence of the IVR rate on pressure than predicted by the simple collision model of Scheme 5. That appears to be what we observe experimentally.

Experimental Section

Computational Details. CASSCF calculations were mostly carried out with GAMESS[4747] although some analytical frequency calculations were carried out with Gaussian 98.[48] CASPT2 calculations were carried out with MOLCAS.[49] All other calculations were carried out with Gaussian 98. All calculations with the 6-31G(d) basis set used six Cartesian d functions. Those using larger basis sets employed the numbers and types of d and f functions that are the defaults for Gaussian 98.

Calculations were carried out on a 500 MHz dual-processor Compaq Alpha DS-20E workstation, a 195 MHz SGI Impact-10000 workstation, and a 466 MHz G3 Power Macintosh computer.

Synthesis of 2,3-Diazabicyclo[2.2.1]hept-2-ene-*exo,exo*-5,6-d_2 (1x). The synthesis of DBH-d_2 (**1x**) was carried out as described previously.[6]

Synthesis of Menthol Methylxanthate. To a suspension of sodium hydride (0.28 g, 11.52 mmol) in tetrahydrofuran (THF, 40 mL) at 0 °C under a N_2 atmosphere was added (−)-menthol (1.5 g, 9.60 mmol) in THF. The reaction was stirred for 30 min, warmed to room temperature, and then stirred for another 30 min. Carbon disulfide (0.877 g, 11.52 mmol) was then added and the reaction mixture stirred for another 1 h. After this period, iodomethane (1.635 g, 11.52 mmol) was added and the reaction mixture stirred for an additional 1 h. The mixture was partitioned between water (30 mL) and diethyl ether (50 mL). The organic layer was separated and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residual crude product subjected to column chromatography on silica gel, with the products being eluted with hexanes. Menthol methylxanthate (1.66 g, 70% yield) was obtained as a foul-smelling yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.81 (d, $J = 7.0$ Hz, 3H), 0.92 (d, $J = 7.1$ Hz, 3H), 0.94 (d, $J = 7.7$ Hz, 3H), 1.01−1.87 (m, 8H), 2.19−2.28 (m, 1H), 5.53 (td, $J = 4.4$, 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.97, 18.79, 20.56, 21.96, 23.77, 26.61, 31.33, 34.14, 39.61, 47.24, 84.49, 215.41.

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Reactions in Supercritical Fluids. Reactions in supercritical propane and carbon dioxide were carried out in a 19 mL stainless steel cylindrical reactor rated up to 15 000 psi. This reactor was immersed in an oil bath, which was maintained at 140.0 ± 0.2 °C by a Haake temperature controller. The fluids were pressurized with a piston screw pump from High-Pressure Equipment, Inc., and the pressure was determined with a Heise digital gauge. Pressure variation during a run was $\leq$ 1 psi. Sample introduction was achieved through a Rheodyne HPLC injector.

Analysis of products was carried out by NMR. For DBH deazetization, ^{2}H NMR was used. Peaks at δ 1.38, 1.56, and 2.14 corresponded respectively to compounds **6n**, **1x**, and **6x**. Integration of these peaks gave the ratio of the three compounds. For the elimination of menthol methylxanthate, ^{1}H NMR was used. Resonances at δ 5.59 (1H) and 5.44 (2H) corresponded respectively to the 4-methyl-1-isopropylcyclohexene and 3-methyl-6-isopropylcyclohexene products.

Conclusion

There are four principal conclusions from the combined computational and experimental study reported here.

(1) The mechanism for deazetization of DBH that appears most consistent with the present CASPT2 calculations and with earlier experiments on the energy distribution between the fragments is one involving synchronous cleavage of the two C−N bonds.

(2) Neither of the two mechanisms proposed by Roth and Martin is consistent with the CASPT2 calculations. Nor does either of them seem consistent with the experimental studies showing a lack of temperature dependence to the k_i/k_r ratio. The pressure dependence of this rate-constant ratio in supercritical propane is also inconsistent with expectations from either of their mechanisms. No calculation on the deazetization of DBH ever reported[6,10,12] has found a transition structure for concerted C−N cleavage and C−C formation as Roth and Martin proposed in both of their mechanisms.

(3) The results in supercritical propane are consistent with a mechanism involving nonstatistical dynamics that is similar to, but not identical with, one first proposed by Allred and Smith. Earlier proposals for a dynamically controlled mechanism from this laboratory[6] and others[10] now seem incorrect to the extent that they were based on an erroneous potential energy surface. However the qualitative features of the dynamics are largely unchanged.

(4) Calculations suggest that in supercritical carbon dioxide, the cyclopentane-1,3-diyl produced by deazetization of DBH may form 1:1 and 2:1 complexes with the CO_2. The formation of such complexes may contribute to the unusual pressure dependence of k_i/k_r observed in that medium. The results suggest that studies[43] of monoradical kinetics in supercritical CO_2 may also need to consider such complexes.

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Supporting Information Available: Cartesian coordinates, energies, and harmonic vibrational frequencies for all stationary points in the calculations (15 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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