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Calculations on Tunneling in the Reactions of Noradamantyl Carbenes

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Supporting Information

ABSTRACT: Noradamantylchlorocarbene has been found experimentally to undergo ring expansion to 2-chloroadamantene at cryogenic temperatures. The rate constant, calculated with inclusion of small-curvature tunneling, is within a factor of 2 of the rate constant measured at 9 K in a nitrogen matrix. Our calculations predict that noradamantylfluorocarbene will not be found to rearrange under these conditions. The rate constant for carbon tunneling in the ring expansion of noradamantylmethylcarbene (**1d**) to 2-methyladamantene at $T \lesssim 10$ K is calculated to be lower by more than 8 orders of magnitude than the rate constant for formation of 3-vinylnoradamantane from **1d** by hydrogen migration.

Although tunneling by carbon is much less common than tunneling by hydrogen, tunneling by carbon can occur when the barrier to reaction is both low and, even more important, narrow.[1] The first reaction in which evidence for tunneling by carbon was obtained was the shift of the double bonds in cyclobutadiene-d_2 (eq 1 in Figure 1), a reaction that was studied experimentally by Whitman and Carpenter.[2] Calculations by Carpenter[3] and subsequently by others[4] showed that the anomalously low A factor, found in the rate constant for this reaction around 0 °C, was due to a large contribution to the rate of reaction from tunneling by carbon.[5]

Calculations have found that the ring expansion of singlet methylcyclobutylfluorocarbene (eq 2) at 8 K proceeds from the zeroth vibrational level of the reactant, by quantum mechanical tunneling by carbon.[6] The calculated rate constant for tunneling was within a factor of 5 of the rate constant that was measured.[6]

Calculations have also predicted the importance of tunneling by carbon in two more reactions—the degenerate rearrangement of semibullvalene (eq 3)[7] and the ring-opening of cyclopropylcarbinyl radical (eq 4).[8] The prediction of the importance of tunneling in the latter reaction at low temperatures has been confirmed by measurements of the intramolecular ^{13}C kinetic isotope effects on the regiochemistry of the product formed.[9]

Given the central role that calculations have played in understanding and/or predicting the tunneling reactions in eqs 1−4,[10] we decided to perform calculations on another reaction that almost certainly involves tunneling by carbon—the ring expansion of singlet noradamantylchlorocarbene (**1c**) to 2-chloroadamantene (**2c**) at very low temperatures.[11] Moss, Sheridan, and co-workers found that, at 9 K, this reaction proceeds with a rate constant of $k = 2.3 \times 10^{-7}$ s^{-1}. This observed rate constant is 10^{111} faster than the rate constant that these authors computed for passage over the reaction barrier at this temperature,[11] so they concluded that rearrangement of **1c** to **2c** at 9 K proceeds by tunneling through the barrier.

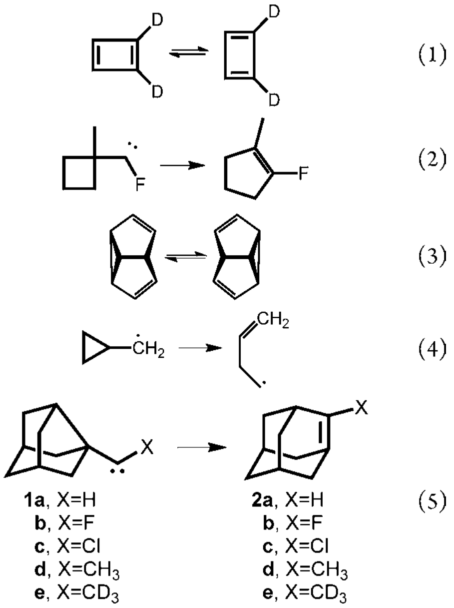

Figure 1. Some reactions in which tunneling by carbon has been calculated and/or found to play an important role.

Our computational studies of this reaction had several goals. In addition to testing how well our tunneling calculations would reproduce the experimental rate constant for ring expansion of **1c**, we also wanted to predict the tunneling rate constants for two as-yet unstudied reactions, the ring expansion reactions of noradamantylfluorocarbene (**1b**) and noradamantylmethylcarbene (**1d**).

In the case of **1d**, there is another reaction that might compete with ring expansion: a 1,2-hydrogen shift to give 3-vinylnoradamantane (**3d**, eq 6). Even if the ring expansion reaction in eq 5 were faster than the 1,2-hydrogen shift in eq 6 at room temperature, the much smaller mass of hydrogen than of carbon might tend to selectively favor the formation of **3d**, rather than **2d**, by tunneling at cryogenic temperatures.[12] If

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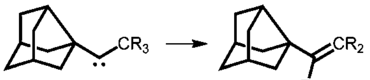

1d, R=H
e, R=D

3d, R=H
e, R=D

(6)

observed, this change in the reaction product with temperature would constitute another example of "tunneling" control in product formation.[1b]

Tunneling calculations were performed with the B3LYP functional,[13] using the 6-31G(d) basis set[14] for the ring expansion reactions in eq 5. For the H-migration reaction in eq 6, the 6-31G(d,p) basis set was used, in order to provide polarization functions on the reacting hydrogen.[14] For comparative purposes, calculations on the ring expansion of **1d** were carried out with both basis sets.[15]

Rate constants were calculated using canonical variational transition-state theory (CVT),[16] and the contributions of multidimensional tunneling to the rate constants computed for ring expansion were incorporated using the small curvature tunneling (SCT) approximation.[17,18] The tunneling calculations were carried out with Polyrate,[19] using Gaussrate[20] as the interface between Polyrate and Gaussian09.[21]

Below 20 K the calculated rate constants for the ring expansion reactions of **1b**−**e** are computed to be nearly independent of temperature because, below 20 K, all four reactions are predicted to occur by tunneling from the lowest vibrational level of the reactants. At all temperatures, ring expansion of noradamantylmethylcarbene (**1d**) is calculated to be the fastest reaction and that of noradamantylfluorocarbene (**1b**) the slowest.

At 300 K, where passage over the reaction barrier dominates all three reactions, the activation energies ($\Delta H^{\ddagger} + RT$) are computed to be E_a = 9.4, 5.6, and 5.5 kcal/mol for the ring expansion reactions of, respectively, **1b**, **1c**, and **1d**. The relative heights of the barriers decrease with decreasing stabilization of the reactant by electron donation from the substituent X into the unoccupied 2p atomic orbital on the carbene carbon.[22] Thus, for X = H, where the carbene substituent has no lone pairs of electrons or C−H bonds, the E_a for rearrangement of **1a** is calculated to be only 0.4 kcal/mol.[23]

As already noted, in the ring expansion reactions of **1b**−**e**, the calculated rate constants at 20 K and below are the rate constants for tunneling from the lowest vibrational level of each of the reactants. These rate constants are $k = 7.3 \times 10^{-16}$, 3.7×10^{-7}, and 8.9×10^{-4} s^{-1}, for the ring expansion reactions of, respectively, **1b**, **1c**, and **1d** below 20 K.

The calculated rate constant for rearrangement of chlorocarbene **1c** to adamantene **2c** is within a factor of 2 of the experimental value of $k = 2.3 \times 10^{-7}$ s^{-1} at 9 K.[11] This agreement provides an indication that the computed rate constants for the ring expansion reactions of **1b** and **1d** below 20 K are also likely to be reasonably accurate.

Below 20 K, the calculated half-time for ring expansion of fluorocarbene **1b**→**2b** is 3×10^7 years. Therefore, it seems safe to predict that, in experiments carried out at cryogenic temperatures, rearrangement of **1b**→**2b** is highly unlikely to be observed within the lifetime of any experimentalist.[24]

The B3LYP/6-31G(d) rate constant for ring expansion of methylcarbene **1d** to **2d**, by tunneling from the lowest vibrational energy level, is calculated to be $k = 8.9 \times 10^{-4}$ s^{-1} [1.6×10^{-3} s^{-1} with the 6-31G(d,p) basis set], which is ca. 10^3 faster than the rate constant for chlorocarbene **1c**→**2c**.[25] Whether or not this prediction can be tested experimentally depends on the relative rate of the competing 1,2-hydrogen shift in **1d** to form **3d**.

As shown in Figure 2, there are actually two low-energy conformations of carbene **1d**, with conformation **1d$_A$** calculated to be lower in energy than conformation **1d$_B$** by 0.2 kcal/mol. From conformation **1d$_A$**, both ring expansion to form 2-methyladamantene (**2d**) and hydrogen shift to form 1-vinyladamantane (**3d**) can occur easily, because the unoccupied 2p atomic orbital on the carbene carbon is properly aligned with both the strained noradamantyl C−C bond and one C−H bond of the methyl group.

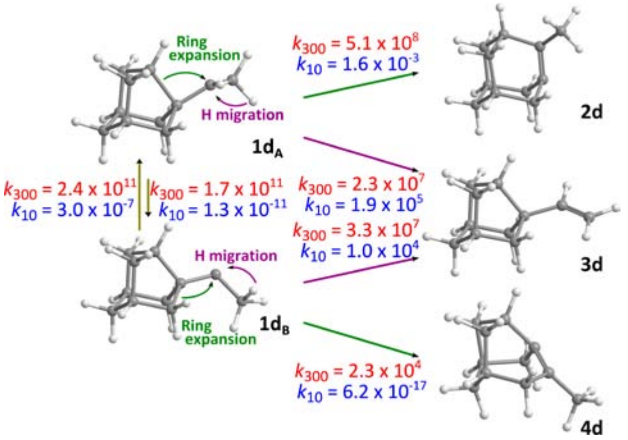

Figure 2. Calculated rate constants (in s^{-1}) for the reactions of the two conformers, **1d$_A$** and **1d$_B$**, at T = 300 K and T = 10 K.

Although 1,2-hydrogen shifts in carbenes are usually faster than 1,2-alkyl migrations, the 1,2-alkyl migration that leads to ring expansion of **1d$_A$** to **2d** results in significant amounts of strain relief. Consequently, without inclusion of the effects of tunneling, at 300 K the CVT value of E_a = 5.4 kcal/mol that is calculated for ring expansion of **1d** to **2d** with the 6-31G(d,p) basis set is actually lower than the CVT value of E_a = 8.6 kcal/mol that is calculated for the 1,2-hydrogen migration that converts **1d** to **3d**.

However, the rate of rearrangement of carbene **1d$_A$** by tunneling should be very sensitive to the mass of the migrating group,[12] which is carbon in the case of the ring expansion to **2d** and hydrogen in the case of the 1,2-shift that leads to formation of **3d**. In fact, despite the higher CVT barrier height for the rearrangement of **1d$_A$** to **3d**, at $T \leq 20$ K, tunneling is predicted to result in a rate constant for rearrangement of **1d$_A$** to **3d** of $k = 1.9 \times 10^5$ s^{-1},[18] which is ca. 10^8 faster than the calculated rate constant of $k = 1.6 \times 10^{-3}$ s^{-1} for ring expansion of **1d$_A$** to **2d** at $T \leq 20$ K.

Even at room temperature, the 1,2-hydrogen shift that forms **3d** from **1d$_A$** is calculated to proceed mostly by (vibrationally activated) tunneling. However, with inclusion of tunneling, the calculated rate constant of $k = 2.3 \times 10^7$ s^{-1} at 300 K is only about 5 times faster than the CVT rate constant for 1,2-hydrogen shift by passage over the reaction barrier. Consequently, the 3.2 kcal/mol lower CVT barrier height for ring expansion of **1d$_A$** than for 1,2-hydrogen shift makes the CVT + SCT rate constant of $k = 5.1 \times 10^8$ s^{-1} for ring expansion of **1d$_A$** to **2d** at 300 K about a factor of 20 faster than the rate constant for 1,2-hydrogen shift to form **3d**.

In the higher energy conformation of **1d** (**1d**$_{\text{B}}$), the empty 2p atomic orbital on the carbene carbon is aligned with a C−H bond and with one of the less strained C−C bonds of the noradamantyl skeleton. Therefore, like **1d**$_{\text{A}}$, **1d**$_{\text{B}}$ can undergo hydrogen shift to form **3d**, but ring expansion from **1d**$_{\text{B}}$ leads to 4-methyltricyclo[4.3.1.0^{3,8}]dec-3(4)-ene (**4d**), rather than to 2-methylnoradamantene (**2d**).

B3LYP/6-31G(d,p) calculations find **4d** to be lower in energy than **2d** by 13.3 kcal/mol. However, these calculations also find that the CVT transition structure (TS) leading to **4d** is 6.5 kcal/mol higher in energy than the TS leading to **2d**.[26] That is why, as shown in Figure 2, the rate constants calculated for ring expansion of **1d**$_{\text{B}}$ to **4d** are much smaller than those for ring expansion of **1d**$_{\text{A}}$ to **2d** at both 300 and 10 K.

Figure 2 also gives the rate constants computed for the interconversion of conformations **1d**$_{\text{A}}$ and **1d**$_{\text{B}}$. B3LYP/6-31g(d,p) calculations predict that conformation **1d**$_{\text{A}}$ is 0.2 kcal/mol lower in energy than conformation **1d**$_{\text{B}}$ and that they are separated by a barrier of only 1.5 kcal/mol on going from **1d**$_{\text{B}}$ to **1d**$_{\text{A}}$. Therefore, the rate constant for forming **1d**$_{\text{A}}$ from **1d**$_{\text{B}}$, by rotating about the C−C bond connecting the noradamantyl group to the carbene carbon, is computed to be fast at 300 K, $k = 2.4 \times 10^{11}\ \text{s}^{-1}$. Since the equilibrium constant at 300 K is calculated to be $K = 1.4$, the rate of the reverse reaction is also computed to be very fast, with a calculated rate constant of $k = 1.7 \times 10^{11}\ \text{s}^{-1}$.

However, the situation is predicted to be very different at cryogenic temperatures. Although the height of the barrier separating **1d**$_{\text{A}}$ from **1d**$_{\text{B}}$ is calculated to be only 1.5 kcal/mol, at cryogenic temperatures **1d**$_{\text{B}}$ must tunnel through this barrier, rather than pass over it, in order to reach **1d**$_{\text{A}}$. The required rotation about the C−C bond connecting the noradamantyl group to the carbene carbon involves movement of the methyl group through an angle of 64°. Consequently, the barrier is wide, and the wide barrier, combined with the large mass of the methyl group that must tunnel through it,[12] leads to a very small computed rate constant of $k = 3.0 \times 10^{-7}\ \text{s}^{-1}$ for **1d**$_{\text{B}}$→**1d**$_{\text{A}}$ at $T \leq 10$ K.[27]

As shown in Figure 2, the 1,2-hydrogen shift to form 3-vinylnoradamantane (**3d**) is calculated to be fast at 10 K from both conformations **1d**$_{\text{A}}$ and **1d**$_{\text{B}}$. Therefore, the slow interconversion of these two conformations at 10 K should have no effect on the composition of the product formed from **1d**. However, the slow rate of interconversion, predicted for these two conformers of **1d**, suggests that in other reactions run at cryogenic temperatures, rotation from an unreactive to a reactive conformation could be the rate-determining step in a rearrangement.

We believe that the most interesting of the results summarized in Figure 2 is the prediction that tunneling control will result in a dramatic change in the preferred pathway for rearrangement of carbene **1d**, from ring expansion at 300 K to 1,2-hydrogen shift at 10 K.[28] The difference between the masses of the migrating groups in these two competing reactions of **1d** is predicted to result in an increase of ca. 10^9 in the ratio of the rate constants for formation of **3d** and **2d**, when **1d** rearranges by tunneling through each of these reaction barriers at $T \leq 20$ K. This huge, predicted change in the ratio of rate constants for formation of **3d** and **2d** is apparent in the Arrhenius plots for these two reactions of **1d** in Figure 3.

Substituting the three deuteriums in **1e** for the three hydrogens in **1d** is computed to reduce the rate constant for 1,2-shift at $T \leq 20$ K by a factor of about 10^3 for both of the low-energy conformations of **1d**. In contrast, the rate of ring expansion of **1e** is actually calculated to be faster than in **1d** giving a calculated inverse H/D kinetic isotope effect (KIE) of 0.92. Nevertheless, the rate constant for the formation by tunneling of **3e** is still predicted to be higher than that of formation of **2e** by a factor of ca. 10^5. Therefore, tunneling control should be found in the products formed by rearrangement of both **1d** and **1e** at cryogenic temperatures.

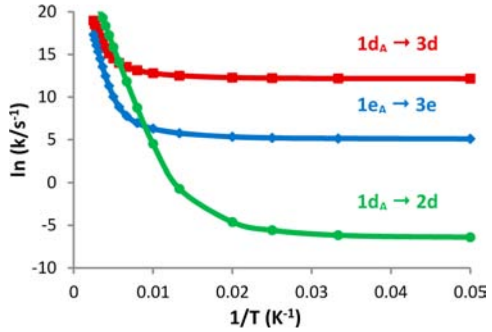

Figure 3. Arrhenius plot down to 20 K for ring expansion (**1d**$_{\text{A}}$ to **2d**, eq 5) and H or D migration (**1d**$_{\text{A}}$ to **3d** and **1e**$_{\text{A}}$ to **3e**, eq 6) reactions of methylnoradamantyl carbene.

In summary, our calculations make the following experimentally testable predictions: (a) Fluorocarbene **1b** should be kinetically stable to ring expansion to 2-fluoroadamantene (**2b**) at cryogenic temperatures, where chlorocarbene **1c** undergoes ring expansion to 2-chloroadamantene (**2c**). (b) At room temperature, the ring expansion of methylcarbene **1d** to **2d** should be about a factor of 10−20 faster than the 1,2-hydrogen shift that forms **3d**. (c) In contrast, at cryogenic temperatures, where both reactions proceed by tunneling, the lighter mass of hydrogen, compared to carbon, should make formation of **3d** much faster than that of **2d**. (d) At cryogenic temperatures, substitution of the deuteriums in the methyl group of **1e** for the hydrogens in the methyl group of **1d** should make the rate of formation of **3e** by tunneling a factor of ca. 10^3 slower than the rate of formation of **3d**. (e) However, despite the large KIE predicted for formation of **3e** by tunneling, the preferred product formed from **1e** under cryogenic conditions should still be **3e**, rather than **2e**.

We very much hope that some or all of these predictions will be tested by experiments.[29,30]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Geometries, energies, rate constants at different temperatures for all of the molecules herein, comparisons of the results of calculations on **1b−d** with different functionals against CCSD(T)-F12b results, description of the methodology used to calculate the tunneling rate constant for **1d**$_{\text{A}}$→**3d**, and complete refs 19−21. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(18) See the Supporting Information for a description of the methodology used to compute the rate constants for tunneling from **1d**$_A$ and **1d**$_B$ to **3d**. The most favorable pathway for each multidimensional tunneling reaction, determined from the principle of least action. Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1983**, *79*, 4931 is found not to pass through either of the two TSs that connect **1d**$_A$ and **1d**$_B$→**3d**. These TSs lie on the lowest energy pathways for passage over the energy barrier that separates **1d**$_A$ and **1d**$_B$ from **3d**, but the TSs do not lie on the pathways that provide the fastest rate constants for *tunneling* from **1d**$_A$ and **1d**$_B$ to **3d**.

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(24) The barrier for the ring expansion reaction in eq 2 is calculated to be lower than that for the analogous ring expansion reaction of **1b** in eq 5.[6] Therefore, it is the rearrangement of the fluorocarbene in eq 2 whose rate can be measured, while 1-methylcyclobutylchlorocarbene is calculated to rearrange too quickly to be observed.[6]

(25) Since the barrier heights for these two reactions are computed to be nearly the same, the ca. 10^3 difference in rates of ring expansion by tunneling can be attributed to the difference in mass between the carbene substituents, Cl in **1c** and CH_3 in **1d**.

(26) Previous calculations on the two possible modes of ring expansion of **1a** have found similar energy differences between the two products, **2a** and **4a**, formed and between the two TSs leading to them: Tae, E. L.; Ventre, C.; Zhu, Z.; Likhotvorik, I.; Ford, F.; Tippmann, E.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 10146. As discussed in detail in the Supporting Information, the energy difference between the two products reflects the fact that the bridgehead π bond in adamantene (**2a**) is more strained than the bridgehead π bond in tricyclo[4.3.1.0^{3,8}]dec-3(4)-ene (**4a**), whereas the energy difference between the two TSs reflects the fact that the σ skeleton of adamantane is less strained than that of tricyclo[4.3.1.0^{3,8}]-decane.

(27) When the methyl group in **1d** is replaced by a hydrogen atom in **1a**, despite the barrier to rotation about the noradamantylcarbene C−C bond increasing from 1.5 to 2.4 kcal/mol, the much lower mass of hydrogen, compared to methyl, results in the calculated rate constant for tunneling from the high-energy to the low-energy conformer at $T \leq 10$ K speeding up by a factor of 6.7×10^{11}.

(28) Schreiner and co-workers reported the results of calculations on the ring expansion of cyclopropylcarbene and on the 1,2-hydrogen shift in cyclopropylmethylcarbene. Unfortunately, they did not report the results of calculations on the ring expansion of cyclopropylmethylcarbene: Gerbig, D.; Ley, D.; Schreiner, P. *Org. Lett.* **2011**, *13*, 3526. The stabilizing effect of the methyl group on the carbene center in cyclopropylmethylcarbene should make the rate of its ring expansion much slower than that of unsubstituted cyclopropylcarbene.

(29) An insurmountable problem in the experimental test of our predictions about the reactions of singlet noradamantylmethylcarbene (**1d**) at cryogenic temperatures would occur if **1d** turned out to have a triplet ground state. Then ISC of singlet **1d** to triplet **1d** might occur much faster than rearrangement of the singlet carbene to **2d** and possibly to **3d**. However, CCSD(T)-F12b/cc-pVTZ calculations of the singlet−triplet energy difference in **1d** predict a singlet ground state, with the triplet higher by 2.0 kcal/mol. Calculations at this level of theory *overestimate* the energy of the lowest singlet state of CH_2, relative to the triplet, by 1.0 kcal/mol; so our CCSD(T)-F12b calculations on **1d** leave very little doubt that the singlet is the ground state of **1d**.

(30) Experiments that are intended to test our prediction about tunneling control of the preferred product formed from rearrangement of **1d** at cryogenic temperatures would have to be careful to distinguish between product formation from **1d** and from a photochemically generated excited state of a diazirine precursor of **1d**.