2-Norbornyl Ion-Pair Leakage in Electrophilic Addition of HCl to Nortricyclene and Norbornene

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Received August 26, 2009

ABSTRACT

Ion pair “leakage” pathways, located computationally by means of multidimensional potential energy surface scans, rationalize the unsymmetrical D-label scrambling observed experimentally in the DCl addition products of nortricyclene and norbornene. “Classical” addition transition structures can interconvert (“leak”) to symmetrical nonclassical 2-norbornyl ion pair species, either TS’s or a minimum, before products form.

Controversies concerning the mechanistic interpretations of carbocationic 2-norbornyl reactions were among the most contentious disputes in chemistry during the last half-century.¹,² But they were never resolved.³ Rather than free ions,²ᵃᵇ ion pair intermediates, first postulated by Wilson⁴ in Wagner–Meerwein rearrangements and then established by Winston and Trifan⁵ in 2-norbornyl sulfonate solvolyses, provide the key insights needed to fully understand the details of the reaction mechanisms.

Electrophilic DCl additions to nortricyclene⁶,⁷ (eq 1) and to norbornene⁷,⁸ (eq 3) to give 2-exo-norbornyl chloride in nonpolar solvents like CH₂Cl₂ illustrate the interpretive problems. In both cases, the distribution of the D label


deviated significantly from expectations based on symmetrical nonclassical (bridged) 2-norbornyl cation intermediates. Brown proposed a rapidly interconverting pair of classical 2-norbornyl cations, trapped before full equilibrium was complete, to explain the results.\(^{1c}\) In contrast, nonclassical carboxylation advocates suggested that “leakage” from classical addition mechanisms to pathways involving bridged ion intermediates was incomplete.\(^{1d}\) Neither of these two contrasting ad hoc hypotheses has been proven.

Our initial computational explorations of these two HCl additions gave startling results. Direct HCl−norbornylene addition gave the “wrong” product, 2-endo- instead of 2-exo-norbornyl chloride, and there was no d-scrambling (eq 2)! Likewise, the computed direct cis-exo HCl-norbornene addition proceeded via a 4-center ion-pair transition structure. Although the product was 2-exo-norbornyl chloride, d-scrambling was absent as well (eq 4)!

We now elucidate the mechanisms of these reactions by locating the nonclassical 2-norbornyl ion “leakage” pathways, which account for the discrepancies between eqs 1 and 2 as well as between eqs 3 and 4.

Computational Methods. The computations used the Gaussian 03 program\(^{9}\) at the B3LYP/6-311+G(d,p) density functional level.\(^{10}\) All computed harmonic frequencies of fully optimized minima were real, whereas transition structures had a single imaginary frequency. Intrinsic reaction coordinate analyses of the minimum energy pathways (MEPs) confirmed the connection of transition structures to the reactants and products, as described in the text. We used the polarized continuum model (PCM)\(^{11}\) implemented in the Gaussian 03 program to evaluate the stabilizing effect of simulated CH2Cl2 bulk solvation, which was substantial on the ion pairs.\(^{12,13}\) PCM-based single-point energy computations were carried out on the intermediate geometries of the “leakage” pathways (Figures 2 and 4). However, continuum-based SCI-PCM simulations\(^{13,14}\) with full geometry optimizations were applied to all stationary points 1−10. The united atom topological model (UAKS) was used to specify the molecular cavity. The small energy differences between PCM and SCI-PCM in Figure 3 justify our use of PCM for the scans in Figures 2 and 4.

Addition of HCl to Nortricyclene (NT). Brown et al.\(^{7}\) observed that DCl addition to nortricyclene gave 2-exo-norbornyl chloride exclusively and that the D label was scrambled about equally to the 6-endo and 6-exo positions (eq 1). In contrast, our initial computational exploration of the addition of “DC1” to nortricyclene gave quite different results (eq 2). (The actual use of an isotope label is obviated by following the reaction course.) The optimized geometries (1−8) involved are depicted in Figure 1. The direct addition pathway involves an initial weakly bound C−symmetrical H-bonded cyclopropane−HCl complex\(^{15}\) (1). The computed reaction barrier via the unsymmetrical ion-pair transition structure 2 is 21.2 kcal/mol in “CH2Cl2” medium (35.2 kcal/mol in isolation). Although 2 has some nonclassical character (note the 1.7 Å C−C distance), it collapses to the “wrong” product, 6-endo-D-2-endo-(not 2-exo)-norbornyl chloride (3 instead of 8), and there is no d scrambling (eq 2). The IRC of 2 confirms its connection with 1 and 3.

How can these computational discrepancies with the experimental results (eq 1) be reconciled? Although 8 is ∼1 kcal/mol less stable than the endo-3 (in isolation and “CH2Cl2” medium), simple endo → exo epimerization via TS 6 is precluded by a large 3 → 6 barrier (51.0 kcal/mol in isolation; 35.4 kcal/mol in CH2Cl2 medium). Furthermore, the exo products from this “classical” pathway (1 → 2 → 3 → 6 → 8) would still have unscrambled d labels.

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(9) Frisch, M. J. Gaussian 03, Revision C. 02, 2004.
(10) Numerous exploratory computations at various theoretical levels: B3LYP/6-311+G(d,p), M052X/6-311+G(d,p), and MP2/6-31G(d) were generally consistent with the B3LYP/6-311+G(d,p) data reported in this paper. See the Supporting Information for further details.
classical 2-norbornyl ion pairs. This competing, but unexpectedly complex “nonclassical” mechanism, explains the formation of D-scrambled exo-8. The remarkable reaction pathway (1 → 4 → 5 → 7 → 8, Figure 1) involves HCl attack on NT via TS 4, which is distinctly different from TS 2 but has nearly the same energy (see Figure 1). However, TS 4 does not lead to covalent product directly. Instead, its IRC connects with 5, a Cs-symmetrical ion pair minimum! This “nonclassical” intermediate also has nearly the same energy as both 4 and 2, but its Cl– counterion is located over the center of the C-1,2,6 face of the bridged 2-norbornyl cation. Notably, intermediate 5 is related to TS 4 and to its enantiomeric TS but is not involved directly in the racemization of 2-exo-norbornyl chloride (8). Instead, this enantioomerization involves TS 7, which, like 5, also has Cs symmetry and a bridged 2-norbornyl cation moiety; however, the Cl– ion position in 5, equidistant to C-1 and C-2, but far from C-6, is very different from that in 7.

Consequently, an unconventional “leakage” pathway, connecting the two nonclassical 2-norbornyl ion pairs, i.e., 5, a minimum, and 7, a TS, must be involved; it was located straightforwardly by two-dimensional potential energy surface (PES) scan, which moves the Cl– anion from the position in 5 to the position in 7. Figure 2 shows that the interconversion barrier is about 6 kcal/mol in isolation, but only 3 kcal/mol barrier in simulated CH2Cl2. After Cs 7 is reached, the bifurcating Wagner–Meerwein rearrangement leads to the enantiomeric exo products (8) but with the D label scrambled to the 6-endo and 6-exo positions.

In summary, the NT-HCl addition PES is quite flat. The energies of TS 2, TS 4, intermediate 5, TS 6, and TS 7 are all quite close to one another, both in isolation and in simulated CH2Cl2 (Figure 1). A nonclassical 2-norbornyl ion pair “leakage pathway” leads to 2-exo-norbornyl chloride products with 6-endo- and 6-exo-D-scrambling, in general accord with Brown’s NT-DCI experimental observations.

Addition of HCl to Norbornene (NB). Experimentally, DCI addition to norbornene1 resulted exclusively in 2-exo-norbornyl chloride, but the D-label was distributed 55 ± 3% to exo-C3 and 45 ± 3% to syn-C7 (eq 3). Computationally, direct NB–HCl addition proceeds via a Cs weakly H-bonded

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Figure 1. Geometries 1–8 involved in the NT-HCl addition. \( \Delta E \) is the relative \( E + ZPE \) (unscaled) at B3LYP/6-311+G**. Bond lengths are in Å and \( \Delta E \) are in kcal/mol, both in isolation and in SCI-PCM-simulated CH2Cl2 solvation (in parentheses).
π-complex\(^{15}\) (9) and passes through a \(C_1\) four-center ion-pair transition state (10) to give 2-exo-norbornyl chloride (8) (Figure 3, left side). No D-label scrambling with DCI would occur by this mechanism (eq 4), contrary to experiment (eq 3).

A “leakage” mechanism from TS 10 to TS 7 (see Figures 3 and 4) rationalizes this discrepancy. The subsequent bifurcation from the nonclassical ion-pair TS 7 leads to the 3-exo, 7-syn D scrambling shown on the right side of Figure 3.

Figure 3. PES profiles for the cis-exo HCl addition to NB (left side) and for degenerate Wagner—Meerwein rearrangement (right side). The “leakage” pathways in dash lines join these processes (see Figure 4). \(E\) (in kcal/mol) are in isolation, PCM CH\(_2\)Cl\(_2\), and SCI-PCM simulated CH\(_2\)Cl\(_2\) respectively. D-label isotope calculations show negligible energy difference between 3-exo and 7-syn-D-2-exo-norbornyl chloride (8).

A “leakage” pathway for the conversion of 10 to 7 is shown in Figure 4; the geometries of the intermediate points (in the Supporting Information) map the course of bridging from the rather classical 2-norbornyl ion-pair geometry 10 (Figure 3) to the nonclassical (bridged) ion pair 7 (Figure 1): the \(C_1-C_6\) distance lengthens, and the \(C_2-C_6\) and the \(C_1-C_2\) distances shorten. These changes are accompanied by delocalization of the \(C_1-C_6\) electron density as well as alteration in ring strain. While the energy of 7 is almost 7 kcal/mol greater than 10 in isolation (Figure 4, black curve), this leakage pathway is facilitated by bulk CH\(_2\)Cl\(_2\) simulation; the difference is only \(~2\) kcal/mol in simulated CH\(_2\)Cl\(_2\) (Figure 4, red curve).

Simulated SCI-PCM CH\(_2\)Cl\(_2\) solvation generally increases the cation—anion separations in the ion-pair TS’s and intermediates from the distances in isolation (compare the data in Figures 1 and 3). The considerable energetic bulk medium stabilization of ion pairs by simulated CH\(_2\)Cl\(_2\) solvation facilitates the “leakage” between different mechanistic pathways by decreasing the interconversion energies (Figures 2 and 4).

Ion pair “leakage” pathways rationalize the experimental results of DCI additions to nortricyclene and to norbornene and reconcile discordant computational findings. The computed “classical” HCl addition pathways involving classical 2-norbornyl ion pair geometries can interconvert “leak” to pathways involving nonclassical (bridged) 2-norbornyl ion pair structures.

Acknowledgment. We thank Dr. Basem Kanawati (University of Munich) for preliminary calculations, the National Science Foundation (Grant No. CHE-0716718) for support, and the China Scholarship Council (CSC) for a graduate study grant (to J.K.).

Supporting Information Available: Full citation of ref 9. Optimized structures 1–10 and intermediates in leakage pathways as well as energetic data both in isolation and simulated CH\(_2\)Cl\(_2\) medium. This material is available free of charge via the Internet at http://pubs.acs.org.

OL901984X