Effect of Olefin Pyramidalization on the Proton Affinity of Tricyclo[3.3.3.0³,⁷]undec-3(7)-ene as Determined by ab Initio Calculations and Kinetic Method Measurements

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Abstract: The effects of alkene pyramidalization on proton affinity (PA) were investigated, using the pyramidalized olefin tricyclo[3.3.3.0³,⁷]undec-3(7)-ene (**1**), with bicyclo[3.3.0]oct-1(5)-ene (**2**) as a reference compound. The expectation that the relief of olefin strain energy associated with protonation of **1** will result in a substantially greater proton affinity for **1** compared with **2** was confirmed by *ab initio* calculations. This was also evident from measurements made by the kinetic method in which competitive dissociations of proton-bound cluster ions of the olefin of interest and a reference base were examined in an ion trap mass spectrometer. However, the ab initio calculations show a smaller PA difference (11.7 kcal/mol) between **1** and **2** than the experiments which yield a difference of 23 ± 2 kcal/mol. This discrepancy is reconciled by proposing that, in the experiments involving **1**, protonation leads not to carbocation **1**-H⁺ but to a rearranged carbocation. This type of isomerization was demonstrated experimentally by measurements of the PAs of 3,3-dimethyl-1-butene (**7**) and 2,3-dimethyl-2-butene (**10**), and *ab initio* calculations indicate that the tertiary cyclopropylcarbinyl carbocation, **5**, is considerably lower in energy than **1**-H⁺. Cation **5** could be formed either directly from **1**-H⁺ or by protonation of vinylcyclopropane **4**, an isomer of **1** which could be formed under the conditions of the experiment. The most stable alkene that can be formed by deprotonation of **5** is the diene **6**, which is calculated to have PA = 219.6 kcal/mol at the MP4SDQ/6-31G* level of theory. The difference of 20.7 kcal/mol between the calculated PAs of **2** and **6** is in good agreement with the measured difference ΔPA = 23 ± 2 kcal/mol and thus supports the hypothesis that the experiments involving **1** have measured the PA corresponding to formation of carbocation **5**.

Introduction

Gas-phase ion chemistry shows great promise for obtaining thermodynamic information about molecules that are far too reactive to study using traditional calorimetric methods. For example, gas-phase ion chemistry has been used to measure the heats of hydrogenation of two highly strained, pyramidalized[1] alkenes, bicyclo[1.1.0]but-1(3)-ene[2] and cubene.[3,4] The differences between these heats of hydrogenation and that of an unstrained, tetrasubstituted alkene were found to be in good agreement with the olefin strain energies (OSEs)[5] predicted by ab initio calculations.[6]

Tricyclo[3.3.3.0³,⁷]undec-3(7)-ene (**1**)[7] is a member (*n* = 3)[8] of a homologous series of highly pyramidalized alkenes that we have prepared. Unlike bicyclo[1.1.0]but-1(3)-ene, cubene, and the lower members of the series to which **1** belongs, **1** is isolable. Hence, its heat of hydrogenation is measurable by calorimetry, at least in principle. The difference between the

heats of hydrogenation measured for **1** and for bicyclo[3.3.0]-oct-1(5)-ene (**2**)[9] would provide an experimental value for the OSE of **1**. This value could be compared with the value that has been predicted computationally.[6,10]

1   **2**
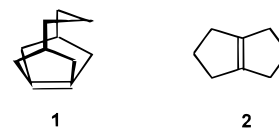
In practice, the calorimetric measurement of the heat of hydrogenation of **1** would be made difficult by the need for sizable quantities of the olefin, coupled with the length of the synthesis by which **1** has been prepared.[7] Since the 17 steps that are required afford **1** in an overall yield of only 2−3%,

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(4) Gas-phase ion chemistry has also yielded heats of formation for *ortho-*, *meta-*, and *para*-didehydrobenzenes (Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994,** *116,* 6401 and references cited therein), which, when subtracted from the heat of formation of benzene, yield the heats of hydrogenation of these highly reactive molecules.

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(6) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988,** *110,* 4710.

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(8) For *n* = 1, see: (a) Renzoni, G. E.; Yin, T.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986,** *108,* 7121. (b) Radziszewski, J. G.; Yin, T.-K.; Renzoni, G. E.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1993,** *115,* 1454. For *n* = 2, see: (c) Renzoni, G. E.; Yin, T.-K.; Miyake, F.; Borden, W. T. *Tetrahedron* **1986,** *42,* 1581. (d) Radziszewski, J. G.; Yin, T.-K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1986,** *108,* 3544. (e) Yin, T.-K.; Radziszewski, J. G.; Renzoni, G. E.; Downing, J. W.; Michl, J.; Borden, W. T. *J. Am. Chem. Soc.* **1987,** *109,* 820. A bis-ethano derivative of *n* = 0 has been prepared: (f) Branan, B. M.; Paquette, L. A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992,** *114,* 774. Generation of a dimethyl derivative has also been reported: (g) Camps, P.; Font- Bardi, M.; Pérez, F.; Solans, X.; Vázquez, S. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 912.

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(10) RHF/6-31G* predicts 19 kcal/mol, without correction for zero-point energy differences.[6] When two-configuration (TC)SCF/6-31G* calculations were performed for **1** and **2**, the OSE calculated for **1** decreased by 2.3 kcal/mol, which is slightly larger than the decrease expected on the basis of RHF and TCSCF calculations on model compounds.[6]

considerable time and effort would have to be expended in order to prepare the olefin in sufficient amounts for a precise calorimetric measurement of its heat of hydrogenation. In addition, although **1** is stable toward dimerization, on exposure to air, it reacts very rapidly with oxygen.[7] Consequently, samples of **1** could easily become contaminated with the products of this oxidation reaction, thus making an accurate determination of the heat of hydrogenation of **1** very difficult, even with samples large enough for high-precision calorimetry.

Both of these difficulties with a calorimetric determination of the heat of hydrogenation of **1** would be absent from a gas-phase measurement of its proton affinity (PA). The sensitivity with which ions, such as the carbocation formed by protonation of **1**, can be detected would obviate the need for large sample sizes; and selection of ions by mass would make the determination of the PA of **1** transparent to the presence of oxidation products in the samples.
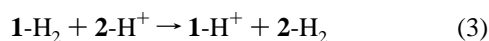
Of course, the difference between the PAs of **1** and **2**, which is given by the energy of the reaction in eq 1,

$$\mathbf{1}\text{-}H^+ + \mathbf{2} \rightarrow \mathbf{1} + \mathbf{2}\text{-}H^+ \tag{1}$$
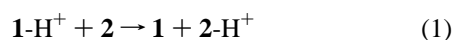
is not the same as the difference between the heats of hydrogenation, which is given by the energy of the reaction in eq 2:
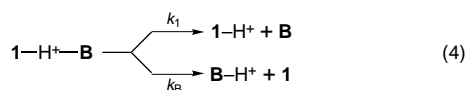
$$\mathbf{1}\text{-}H_2 + \mathbf{2} \rightarrow \mathbf{1} + \mathbf{2}\text{-}H_2 \tag{2}$$
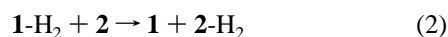
Subtracting eq 1 from eq 2 gives eq 3:

$$\mathbf{1}\text{-}H_2 + \mathbf{2}\text{-}H^+ \rightarrow \mathbf{1}\text{-}H^+ + \mathbf{2}\text{-}H_2 \tag{3}$$

The energy of the reaction in eq 3 yields the difference between the hydride affinities of the carbocations formed by protonating **1** and **2**. Calculations at the RHF/6-31G* level find the energy of the reaction in eq 3 to be only 1.5 kcal/mol, which is less than 10% of the RHF/6-31G* energy of 17.4 kcal/mol of the reaction in eq 1. Thus, the measurement of the difference between the PAs of **1** and **2** is expected to provide a good approximation to the difference between the heats of hydrogenation and, hence, to the OSE of **1**.

The kinetic method, a mass spectrometric method based on the ratios of the ions formed when a cluster ion fragments, was used in this study to measure the PAs of **1** and **2**. The kinetic method has been used previously to obtain thermochemical information on many chemical systems.[11] The method relies on the formation and isolation of cluster ions bound by protons (or other anions or cations). The proton-bound dimers are activated and dissociate competitively to yield the individual protonated monomers, whose relative yields are quantitatively related to the differences in proton affinities between the two monomers. In the case of interest here, where one monomer is the pyramidalized olefin, **1** (or the unstrained olefin, **2**), and the other is a reference base, **B**, the following equations can be written:

$$\mathbf{1}\text{--}H^+\text{--}\mathbf{B} \overset{k_1}{\underset{k_B}{\rightarrow}} \begin{array}{l} \mathbf{1}\text{--}H^+ + \mathbf{B} \\ \mathbf{B}\text{--}H^+ + \mathbf{1} \end{array} \tag{4}$$

$$\ln \frac{k_1}{k_B} = \frac{PA(\mathbf{1}) - PA(\mathbf{B})}{RT_{eff}} \tag{5}$$

where the effective temperature, T_{eff}, is a measure of the internal energy of the activated cluster ion.

Although the kinetic method has been used for determining the proton affinities of various organic molecules,[12−14] and for estimating other ion affinities, including ammonium ion,[15] metal ion,[16,17] chlorine cation,[18] electron,[19,20] free radical,[21,22] cyanide cation,[23] and carbonyl isocyanate cation[24] affinities, it has not been applied to olefins. One reason is that it is more difficult, in conventional mass spectrometer ion sources, to form proton-bound dimers when the bases are alkenes than when bases contain nitrogen and other heteroatoms. In this study, an ion trap mass spectrometer was used so that the reaction time scales could be on the order of 100 ms, allowing formation of larger abundances of the dimers. In addition, the ion trap mass spectrometer may be better for these experiments than other instruments with shorter time scales because it minimizes the energy needed for dissociation, so that only the most favored products are studied.

It will be evident from the results which follow that a strained system can isomerize, either in the course of forming the proton-bound dimer or in the course of its dissociation. Hence, for a strained olefin, **1** for which a lower enthalpy isomer, **3**, is accessible by rearrangement (perhaps by acid catalysis via formation of a carbocation intermediate), the following behavior is possible:

$$\tag{6}$$
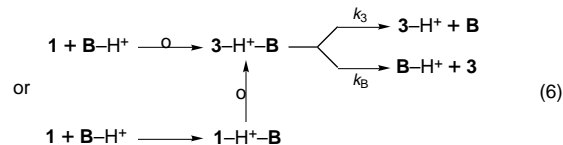
If isomerization does occur, it will influence the observed PA measurements since the experiment will yield PA(**3**) instead of PA(**1**).

Experimental Section

Experiments were performed using a Finnigan ITS-40 ion trap mass spectrometer. A modified version of the commercial software was used to implement the cluster ion isolation and the product ions scan stages of the experiment. Activation in MS/MS was achieved through the use of a supplemental frequency synthesizer.[25] The frequency of this supplemental ac signal was adjusted so as to match the oscillation frequency of the cluster ion.[26] The cluster ion acquired enough internal energy from this resonant process to dissociate into the respective protonated monomers. The timing of the activation period was determined by a software trigger, which was used to activate an analog switch, allowing the signal from the frequency synthesizer to be applied to the endcap electrodes via a balun box.

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The principal samples used in these experiments, bicyclo[3.3.0]oct-1(5)-ene (**2**) and tricyclo[3.3.3.0³,⁷]undec-3(7)-ene (**1**), were synthesized at the University of Washington. Tricyclo[3.3.3.0³,⁷]undec-3(7)-ene was prepared by the published 17-step synthesis.[7] As in the last two steps in the synthesis of **1**, **2**[9] was prepared from bicyclo[3.3.0]octane-1,5-diol[9c] by formation of the dimesylate and its reduction with a sodium amalgam in ether. The samples of **1** and **2** were stored in degassed pentane in sealed ampules for shipment from the University of Washington to Purdue University. The alkenes were separated from the pentane by slow evaporation (distillation in the case of **1**) of the pentane under vacuum over a period of several days. The resulting samples were then stored under nitrogen or in vacuum to avoid exposure to air. Compound **2** was introduced into the ion trap by evaporation at room temperature, while the sample vial containing **1** was heated to 60 °C. The manifold and the inlet lines were maintained at a temperature of 60 °C in both cases. The sample, reference, and helium buffer gas were introduced simultaneously into the ion trap via three separate leak valves to allow optimization of the partial pressure of each.

For these experiments, electron impact was used to ionize the reference compound, **B**, and a subsequent reaction with the neutral gas (over a period of 50 ms) produced the protonated reference compound, **B**-H⁺. The protonated reference compound was then isolated from other ions by the rf/dc isolation procedure.[27] After isolation, it was allowed to react with neutral **1** or **2** for approximately 100 ms. This procedure led to the formation of the proton-bound dimer of the reference (**B**) and sample (**M**), viz. to the cluster ion (**M**−H⁺−**B**). The proton-bound dimer was in turn isolated by the rf/dc method and then dissociated by collision-induced dissociation (CID), achieved by applying a dipolar AC field across the endcap electrodes at a frequency which was in resonance with the secular frequency of the trapped cluster ion.[26,28] The activation period was about 8 ms, and the amplitude of the supplementary voltage was varied from 200 to 500 mV$_{pp}$ to control the degree of fragmentation. The rf frequency applied to the ring electrode was 1.1 MHz, and the amplitude of the rf voltage was adjusted so as to place each of the proton-bound dimers at a q_z value of 0.30 during its dissociation. This value for the Mathieu parameter, q_z, was chosen to optimize and standardize the conditions for forming and trapping fragment ions.[29] The products of dissociation were detected by performing a product ion MS/MS scan[27,30] using a standard mass-selective instability scan of the rf amplitude.[31]

Results and Discussion

General Considerations. By observing the abundance of the CID product(s) formed from the proton-bound dimer, it can be determined (eq 5) if the proton affinity of the sample is greater than or less than that of the reference compound. In this manner, by examining a number of reference compounds, the kinetic method can be used to estimate proton affinities quite accurately, often within 1 kcal/mol. It is preferred that the reference compounds be similar in size and functional group to the sample compound for highest accuracy, although this has not been the case in a number of recent studies.[21,22,32] As reported previously,[29] the long times used in the ion trap allow for dissociation under gentle activation conditions. Cluster ions, in particular, will dissociate when they have low excess internal energies, i.e. near threshold. Under these circumstances, the ratio of the two products of eq 1 may be so large that only the energetically favored product is observed. In fact, it has been previously found for ion traps that generally only one product ion will be seen from fragmentation of proton-bound dimers if

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Table 1. Experimental Results of the Kinetic Method Experiments to Determine the Proton Affinity of Bicyclo[3.3.0]oct-1(5)-ene (**2**)

proton affinity (kcal/mol)[33]	ref compd	[Ref+H]⁺:[2+H]⁺
192.5	acetone	covalent adduct
193.6	methyl acetate	covalent adduct
194.6	cyclopentanone	covalent adduct
194.6	tetrahydrofuran	0.25:1
195.6	2-butanone	0.44:1
196.0	diethyl ether	covalent adduct
196.1	methyl vinyl ketone	covalent adduct
196.5	ethyl acetate	1:0.75
197.2	3-pentanone	1:0.00

the difference in PAs is more than 0.4 kcal/mol.[29] In cases where only one product ion is seen, it is useful to bracket the unknown PA value by employing a series of reference compounds.

One of the difficulties in using the dissociation of dimers to make thermochemical determinations is that the loosely-bound dimer may not be formed or may isomerize into a *covalent* adduct with only a small activation energy. In these instances, the product ion spectrum typically consists of many characteristic, low abundance, fragment peaks rather than just the abundant, protonated monomers that are characteristic of the fragmentation of proton-bound dimers. Higher collision energies (greater ac excitation voltages) are also required to cause fragmentation of such covalent complexes. In cases where a covalent adduct is formed, PA comparisons cannot be made. For tricycloundecene, **1**, covalent adduct formation occurred in all cases except for the complexes involving the inert fluoropyridine reference compounds. This type of adduct also formed with about one-half of the reference compounds for bicyclooctene, **2**. The solution to this problem was to add to the reaction mixture a buffer gas (*n*-hexane) with a large number of degrees of freedom. It is believed that hexane undergoes collisions with the nascent complex and cools it more rapidly than it can isomerize to a covalent adduct. In many cases (but not all), the presence of *n*-hexane appears to inhibit the covalent adduct from forming, allowing the proton-bound dimer to be formed and subsequently isolated. Although a covalent structure may contribute to the parent ion population in some experiments, it is believed, from the ease of dissociation of the parent ion and from the observed fragmentation products (only **M**-H⁺ and **B**-H⁺), that a loosely bound ion-centered cluster structure must be the principal dissociating species.

Proton Affinity of Bicyclo[3.3.0]oct-1(5)-ene (2). The proton affinity of bicyclooctene was investigated by the kinetic method using various reference compounds, chosen to cover a range of PA values. In each case, a proton-bound dimer was formed between the protonated reference compound and **2**. The dimer was isolated and then collisionally dissociated. Formation of either one or both of two protonated monomers with the expected *m/z* values was observed. Table 1 shows the relative abundances of the product ions and the range of PA values[33] represented by the reference compounds. The product ion spectrum of the dimer generated with tetrahydrofuran (PA 194.6 kcal/mol)[33] shows a very small peak, corresponding to the protonated reference compound, and a much larger peak corresponding to protonated **2**. The dominant presence of only protonated **2** indicates that its proton affinity is much greater than that of tetrahydrofuran. Conversely, protonated 3-pentanone (PA 197.2 kcal/mol)[33] is the only CID product in the spectrum of the dimer formed from it and **2**, indicating that the

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Table 2. Experimental Results of the Proton Transfer Method to Determine the Proton Affinity of Bicyclo[3.3.0]oct-1(5)-ene (**2**)

proton affinity[33] (kcal/mol)	ref compd	isolate [Ref+H]⁺ then react [Ref+H]⁺:[2+H]⁺	isolate [2+H]⁺ then react [Ref+H]⁺:[2+H]⁺
192.5	acetone	1:0.05	0.00:1
194.6	tetrahydrofuran	1:0.08	0.00:1
196.5	ethyl acetate	1:0.08	0.01:1
197.2	3-pentanone	1:0.00	0.03:1
198.1	dipropyl ether	1:0.00	0.11:1
201.0	dipentyl ether	1:0.00	0.15:1

Table 3. Experimental Results of the Kinetic Method Experiments to Determine the Proton Affinity of Tricyclo[3.3.0$^{(3,7)}$]undec-3(7)-ene (**1**)

proton affinity (kcal/mol)[33]	ref compd	[Ref+H]⁺:[1+H]⁺
210.6	2-fluoropyridine	0.0:1
214.3	3-fluoropyridine	0.0:1
214.4	2-chloropyridine	0.0:1
215.7	pyridazine	0.0:1
218.2	2,5-dimethylpyrrole	0.0:1
219.0	6-chloro-2-picoline	0.5:1
219.4	morpholine	1:0.0
220.8	pyridine	1:0.0

proton affinity of **2** is significantly lower than 197.2 kcal/mol. Consistent with these two results, peaks for both the protonated reference and protonated **2** were observed when 2-butanone (PA 195.6 kcal/mol)[33] or ethyl acetate (PA 196.5 kcal/mol)[33] was used as the reference. The relative magnitudes of these signals indicate that the proton affinity for **2** lies between 195.6 and 196.5 kcal/mol. However, the estimated errors in the PAs of these two reference bases are ±1.5[34] and ±2 kcal/mol,[35] respectively, so the estimated proton affinity of **2** is 196.3 ± 2 kcal/mol.

The proton affinity of **2** was also measured by a different method, the proton transfer method (viz. ion/molecule bracketing[34]). Rather than forming the proton-bound dimers, the ease of proton transfer between the protonated reference compound and **2** was monitored (eq 7).

$$\mathbf{B}\text{-}H^+ + \mathbf{2} \rightarrow \mathbf{B} + \mathbf{2}\text{-}H^+ \qquad (7)$$
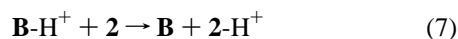
By using reference compounds of different proton affinities, the proton affinity of **2** could be determined within a narrow range by this technique (Table 2). Proton transfer from the protonated reference base occurred for ethyl acetate (PA 196.5 kcal/mol)[33] and bases of lower PA, but not for 3-pentanone (PA 197.2 kcal/mol)[33] and bases of greater PA. Similarly, when the reverse proton transfer was attempted, it occurred (just barely) for ethyl acetate (PA 196.5 kcal/mol) but not for compounds of lower proton affinity. The results of these experiments give a value of 196.5 ± 2 kcal/mol for the proton affinity of **2**, in excellent agreement with the value obtained by the kinetic method. This good agreement provides evidence that the kinetic method should give an accurate value for the PA of alkenes such as **1**, which is a bridged derivative of **2**.

Proton Affinity of Tricyclo[3.3.0³,⁷]undec-3(7)-ene (1). The proton affinity of tricycloundecene **1** was also determined by the kinetic method. Table 3 shows the relative abundances of the product ions and the range of PA values represented by the reference compounds. These data show that, for all reference compounds with a PA ≤ 218.2 kcal/mol, only the

ion corresponding to protonated **1** is observed upon fragmentation of the proton-bound dimer. The spectra for morpholine and pyridine show that the protonated reference compound is the favored product of dissociation of the proton-bound dimer, indicating that the apparent proton affinity of **1** is lower than 219.4 kcal/mol. The product ion spectrum of the dimer formed with 6-chloro-2-picoline (PA 219.0 kcal/mol) shows a peak corresponding to *m/z* 127 (the mass of protonated ³⁵Cl isotope of the reference) and a slightly more intense peak corresponding to *m/z* 149 (the mass of protonated **1**). As previously noted, the presence of peaks in the product ion spectrum corresponding to both the protonated reference and protonated **1** indicates that the two proton affinities are quite close to each other. The presence and magnitudes of these peaks indicate that the proton affinity of **1**, assuming that it maintains its structural integrity in the dimer, must be slightly greater than 219.0 kcal/mol. This lower limit is well-established since loosely-bound dimers were formed with many reference compounds with proton affinities less than 219 kcal/mol, but only protonated **1** was observed in the product ion spectrum. The uncertainty in the experimental procedure is probably better than ±1 kcal/mol. However, there is significant error in the PA values of the reference compounds. The literature[34] indicates that the uncertainty in the proton affinity is ±2 kcal/mol for both 6-chloro-2-picoline and morpholine. Therefore, a conservative estimate for the apparent proton affinity of **1** is 219 ± 2 kcal/mol.

Error Analysis. One consideration in applying any relative method is that the accuracy of the bracketed value is dependent on the accuracy of the values for the reference compounds. The uncertainty in the PA values for the reference compounds in this study is typically ±2 kcal/mol. For this reason, the error in the bracketed PA value is on the order of ±2 kcal/mol, although the error in the experimental procedure alone is probably less than ±1 kcal/mol. Newer and more accurate values of the PAs of some of the reference compounds used in this study have become available since publication of the NIST compilation.[33] The most reliable of these values, from experimental work by Szulijko and McMahon[36] and calculations by Smith and Radom,[37] are 1−2 kcal/mol larger than those in the compilation. However, these data do not suggest that the differences between the proton affinities of the reference compounds used to determine the PAs of **1** and **2** should change.

A systematic error may also be introduced by errors in the values for reference bases in the PA scale. Isobutylene provides the reference PA for all the bases used in the experiments involving **2** while ammonia and *n*-propylamine provide the reference PAs for the bases used in the experiments involving **1**. The PA values for the bases are based on a PA of 191.7 kcal/mol for isobutylene, a PA of 204.2 kcal/mol for ammonia, and a PA of 217.9 kcal/mol for propylamine.[33] Any errors in these absolute values would affect the relative proton affinity scale, resulting in a systematic change in the experimentally determined PA values of **1** and **2**.

When considering the accuracy of these PAs, the applicability of the kinetic method must also be considered. There are several possible sources of error in this method. The entropy effects should ideally be kept small by choosing reference compounds which are similar in size and type of functional group to the sample.[11] In this study of the PAs of **1** and **2**, there were significant structural dissimilarities between the reference bases and these two alkenes. However, the good agreement between

(34) Aue, D. H.; Bowers, M. T. in *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(35) Vajda, J. H.; Harrison, A. G. *Int. J. Mass Spectrom. Ion Processes* **1979**, *30*, 293.

(36) Szulejko, J. E.; McMahon, T. B.; *J. Am. Chem. Soc.* **1993**, *115*, 7839.

(37) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 6468.

Table 4. Experimental Results of the Kinetic Method Experiments to Determine the Proton Affinity of Isobutylene (C_4H_8)

proton affinity (kcal/mol)[33]	ref compd	[Ref+H]$^+$:[C_4H_8+H]$^+$
189.8	valeronitrile	0.1:1
190.1	butyronitrile	0.0:1
191.5	trimethylacetonitrile	0.8:1
191.7	benzonitrile	1:0.1
192.5	acetone	1:0.1

the PAs for **2**, obtained from both the kinetic method and bracketing experiments, indicates that these structural dissimilarities did not result in a significant error in the PA obtained by the kinetic method.

Nevertheless, an additional study was performed to validate the use of the kinetic method for alkenes. Table 4 shows the results for kinetic method experiments that were used to determine the proton affinity of isobutylene. The measured proton affinity was 191.6 ± 2 kcal/mol, placing the PA of isobutylene between the proton affinities of trimethylacetonitrile and benzonitrile. This result is in good agreement with the literature values of 191.7[33] and 191.6 kcal/mol[38] for the PA of isobutylene. Hence, the structural dissimilarities between the reference bases and isobutylene do not appear to introduce significant error in the determination of the PA of isobutylene by the kinetic method. Thus, there is no reason to believe that these structural dissimilarities will affect the experimental results for the determination of **1** or **2**.[39]

Ab Initio Calculations. Calculations of the relative PAs of **1** and **2** were performed by computing the energy of the proton-exchange reaction in eq 1. The geometries of **1**, **2**, and the protonated alkenes were optimized at the RHF/6-31G* level of theory.[40] (Optimized geometries are available as Supporting Information.[41]) The zero-point energies (ZPEs) and heat capacities (C_v 298), which were needed to obtain ΔPA^{298} from ΔE for eq 1, were obtained from vibrational analyses at the RHF/6-31G* level of theory, using unscaled frequencies. At the RHF/6-31G* optimized geometries, single-point calculations were performed at the MP2,[42,43] MP3,[42,43] and MP4SDQ[44] levels of theory, using the 6-31G*,[45] 6-31G**,[45] and 6-311G*[46] basis sets. The results are given in Table 5. All calculations were performed with the Gaussian 92[47] or 94[48] series of *ab initio* programs.

(38) Traeger, J. C. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 119.

(39) Larger errors than normal may arise for particular systems if steric hindrance in the dimer distorts the product ratios. For example, when comparing the bicyclooctene and tricycloundecene samples, tricycloundecene might present more steric hindrance in the dimer since it is a bridged structure. If this were the case, steric hindrance is expected to weaken bonding to the proton leading to an underestimation of the PA value of the olefin.

(40) RHF and Möller−Plesset calculations at the TCSCF-optimized geometries for **1** and **2** gave energies for the reaction in eq 1 that were 0.2−0.3 kcal/mol larger than those performed at the RHF-optimized geometries.

(41) See paragraph at end of article regarding Supporting Information.

(42) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(43) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

(44) Krishnan, R.; Pople, J. A., *Int. J. Quantum Chem.* **1978**, *14*, 91.

(45) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

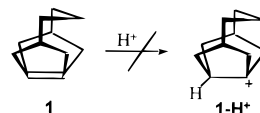(46) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A., *J. Chem. Phys.* **1980**, *72*, 650.

(47) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, D.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Steward, J. J. P.; and Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.;

As shown in Table 5, the RHF calculations all give values of ΔPA between **1** and **2** that are slightly greater than 16 kcal/mol. Not only is this value considerably smaller than the experimental value of $\Delta PA = 23 ± 2$ kcal/mol, but calculations that include electron correlation give even lower values for ΔPA; and these calculated values decrease further upon expansion of the size of the basis set. Comparison of the MP2 results with the 6-31G* and 6-311G* basis sets suggests that the MP4SDQ/6-31G* value of $\Delta PA = 12.4$ kcal/mol would decrease by 0.7 kcal/mol with the 6-311G* basis set, so the best computational estimate of ΔPA is 11.7 kcal/mol. This value is only about one-half the size of the value of $\Delta PA = 23 ± 2$ kcal/mol, determined experimentally.

It seems highly unlikely that the calculations of the relative PAs of **1** and **2** are grossly in error. In fact, it appears that even the absolute PAs are calculated with reasonable accuracy at the MP4SDQ/6-31G* level of theory. For example, the data in Table 5 give a $PA^{298} = 198.9$ kcal/mol for **2**, which is 3 kcal/mol higher than the experimental value of $196 ± 2$ kcal/mol. For isobutylene, the MP4SDQ/6-31G* value of $PA^{298} = 193.7$ kcal/mol is higher by 2.0 kcal/mol than the experimental value of 191.7 kcal/mol. Since both of these calculated PAs are slightly higher than the experimental values, the calculated value of $\Delta PA^{298} = 5.2$ kcal/mol for **2** versus isobutylene is only 0.9 kcal/mol higher than the experimental value of $\Delta PA = 4.3$ kcal/mol and well within the probable error in this value.

The most likely explanation of the very large discrepancy between the calculated and experimental values of ΔPA between **1** and **2** is that, upon protonation of **1**, the carbocation actually formed is significantly lower in energy than **1**-H$^+$, the carboca-

tion on which the calculated value for the PA of **1** is based. An attempt was made to try to find geometries of **1**-H$^+$ where hydrogen bridging, either by a hydrogen adjacent to the carbocationic center or by the *endo* hydrogen at C-10 of the three-carbon bridge, would lower the calculated energy. However, MP2 calculations gave energies for such nonclassical cations that were substantially higher than the MP2 energy calculated at the RHF/6-31G*-optimized geometry for **1**-H$^+$.[49]

An alternate possibility is that protonation leads not to carbocation **1**-H$^+$ but to a rearranged carbocation. This carbocation could be formed either directly from **1**-H$^+$ or by protonation of a rearrangement product of **1**, generated within the proton bound dimer. Further calculations were conducted in an attempt to determine the most probable structure and origin of this carbocation.

Carbocation 5. Many possible rearrangement products of **1**-H$^+$ would have lower energies than this bridgehead carbocation, but almost all of them would be deprotonated to form

Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(49) Electron correlation must be included, in order to compute the energies of classical and nonclassical cations accurately. See, for example: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 379−396. Raghavachari, K.; Haddon, R. C.; Schleyer; P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1983**, *105*, 5915. Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 3227.

Table 5. Relative Proton Affinities at 298 K of Tricyclo[3.3.0$^{(3,7)}$]undec-3(7)-ene (**1**) and Bicyclo[3.3.0]oct-1(5)-ene (**2**) Calculated at RHF/6-31G*-Optimized Geometries

	1-H$^+$	2	1	2-H$^+$	ΔE	ΔPA^{298}
ZPE^a	174.1	122.1	166.6	128.7	−0.9	
$C_v^{298} \times 298^a$	10.5	7.6	10.0	8.0	−0.1	
RHF/6-31G* ^{b}	−426.1801	−309.9185	−425.8126	−310.2582	17.4	16.4
MP2/6-31G*	−427.5882	−310.9483	−427.2487	−311.2685	12.1	11.1
MP3/6-31G*	−427.6709	−311.0076	−427.3224	−311.3344	13.6	12.6
MP4SDQ/6-31G*	−427.6899	−311.0201	−427.3404	−311.3482	13.4	12.4
RHF/6-31G**	−426.2069	−309.9370	−425.8370	−310.2795	17.2	16.2
MP2/6-31G**	−427.7228	−311.0454	−427.3792	−311.3703	11.7	10.7
RHF/6-311G*	−426.2498	−309.9713	−425.8842	−310.3093	17.3	16.3
MP2/6-311G*	−427.7359	−311.0584	−427.4021	−311.3741	11.4	10.4

^{a} In kcal/mol. ^{b} Electronic energies are in hartrees.

Scheme 1^a
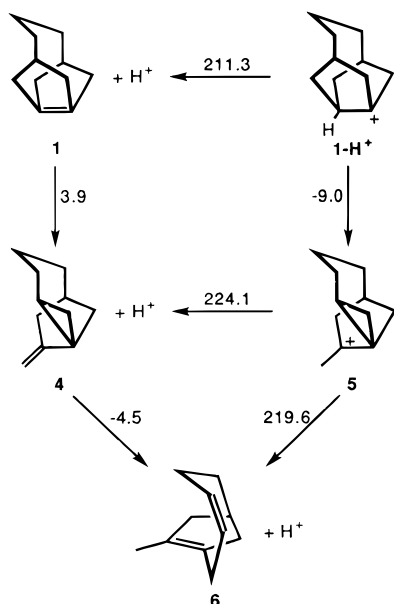
^{a} Proton affinities and relative energies, calculated at the MP4SDQ/6-31G* level of theory, in kcal/mol.

olefins that have much lower OSEs than **1**. In order for a rearrangement product of **1** to have a higher PA than **1**, the energy difference between **1**-H$^+$ and the rearranged cation would have to be larger than the energy difference between **1** and the isomer of **1**, formed by deprotonation of the rearranged carbocation. Of all of the rearranged cations that were considered, this was only computed to be the case for the cyclopropylcarbinyl cation **5** (Scheme 1).

The stabilization of the cationic carbon in **5** that is provided by the adjacent cyclopropyl ring would be expected to provide a substantial thermodynamic driving force for rearrangement of the bridgehead carbocation **1**-H$^+$ to **5**. As shown in Scheme 1, **5** could be formed by protonation of vinylcyclopropane **4**. Lower members of the homologous series of pyramidalized olefins to which **1** belongs have been found to undergo the retrograde vinylcyclopropane rearrangement that would transform **1** into **4**.[8e] Thus, there is excellent precedent for the occurrence of this rearrangement in molecules closely related to **1**, and the activation energy for this rearrangement of **1** might come from the energy released by formation of the proton-bound dimer of **1**.

In the lower, more highly pyramidalized, members of the series of olefins to which **1** belongs, the retrograde vinylcyclopropane rearrangement is exothermic.[8e] However, this is not computed to be the case for the rearrangement of **1** to **4**. Using the data in Tables 5 and 6, the rearrangement of **1** to **4** is calculated to be thermoneutral at the RHF/6-31G* level and

somewhat endothermic at the MP2 and MP4SDQ levels of theory. However, the rearrangement of cation **1**-H$^+$ to **5** is, as expected, computed to be quite exothermic at all levels of theory. Scheme 1 gives the relative energies of alkenes **1** and **4** and carbocations **1**-H$^+$ and **5**, calculated at the MP4SDQ/6-31G* level of theory.

As shown in Scheme 1, computations at the MP4SDQ/6-31G* level indicate that these energy changes make the PA for **4**, 12.8 kcal/mol greater than that for **1** and 25.2 kcal/mol greater than that for **2**. This calculated value of ΔPA = 25.2 kcal/mol between **4** and **2** is much closer to the experimental value of ΔPA = 23 ± 2 kcal/mol than is the MP4SDQ/6-31G* value of ΔPA = 12.4 kcal/mol between **1** and **2**. However, as will be discussed subsequently, it is more likely that the deprotonation of **5** would lead to diene **6**, rather than vinylcyclopropane **4**.

Possible Rearrangements of 1-H$^+$. Protonation of a small amount of **4** that is in equilibrium with **1** in the collision complex provides an attractive mechanism for the formation of carbocation **5** from **1**. Vinylcyclopropane **4** could be formed directly from **1** or by rearrangement of **1**-H$^+$ to a primary carbocation intermediate, followed by deprotonation of this intermediate. However, it is also possible to write a mechanism, involving the same primary carbocation intermediate, for rearrangement of **1**-H$^+$ directly to **5**, without the intermediacy of **4**.

We have obtained evidence for the occurence of carbocation rearrangements under our experimental conditions, and this evidence is now described. The kinetic method was used to determine the proton affinities of 3,3-dimethyl-1-butene (**7**) and 2,3-dimethyl-2-butene (**10**). The secondary carbocation (**8**),
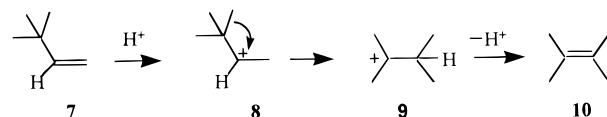
formed by protonation of **7**, would be expected to rearrange to tertiary cation **9**. Since **10** also forms **9** upon protonation, the same proton-bridged complex should be generated from each alkene. Hence, the complexes formed from both alkenes should yield the same ratio of fragments in the kinetic method measurements. Tables 7 and 8 show that the measured fragment ion abundance ratios for 3,3-dimethyl-1-butene and 2,3-dimethyl-2-butene are the same within experimental error. Both compounds have an apparent proton affinity of about 197.2 kcal/mol. The results in Tables 7 and 8 clearly indicate that 3,3-dimethyl-1-butene (**7**) rearranges upon formation of a proton-bound complex. This provides permissive evidence that at least one carbocation rearrangement may be involved in the rearrangement of **1**-H$^+$ to **5**.

Deprotonation of Carbocation 5. Vinylcyclopropane **4** may not be an intermediate in the formation of carbocation **5**, and it is also not the most stable alkene that can be formed directly

Table 6. Energies[a] Computed for **4**−**6** at RHF/6-31G*-Optimized Geometries and Proton Affinities[b] of **4** and **6** Relative to **2** at 298 K

	4	5	6	ΔPA_4^{298}	ΔPA_6^{298}
ZPE[a]	165.0	173.0	164.5		
$C_v^{298} \times 298$[a]	10.7	11.3	11.1		
RHF/6-31G*	−425.8112	−426.1894	−425.8191	22.5	17.5
MP2/6-31G*	−427.2392	−427.6099	−427.2438	30.1	27.1
MP3/6-31G*	−427.3140	−427.6855	−427.3214	26.4	21.7
MP4SDQ/6-31G*	−427.3329	−427.7038	−427.3399	25.2	20.7

[a] Electronic energies are in hartrees. [b] In kcal/mol.

Table 7. Experimental Results of the Kinetic Method Experiments to Determine the Proton Affinity of 3,3-Dimethyl-1-butene (**7**)

proton affinity (kcal/mol)[33]	ref compd	[Ref+H]$^+$:[**7**+H]$^+$
195.6	2-butanone	0.05:1
196.9	3-methyl-2-butanone	0.38:1
197.2	3-pentanone	0.61:1
197.2	cyclohexanone	covalent adduct
198.1	*tert*-butyl methyl ketone	1:0.00
198.6	*tert*-butyl acetate	1:0.00

Table 8. Experimental Results of the Kinetic Method Experiments to Determine the Proton Affinity of 2,3-Dimethyl-2-butene (**10**)

proton affinity (kcal/mol)[33]	ref compd	[Ref+H]$^+$:[**10**+H]$^+$
195.6	2-butanone	0.00:1
196.9	3-methyl-2-butanone	0.34:1
197.2	3-pentanone	0.57:1
197.2	cyclohexanone	1:0.22
198.1	*tert*-butyl methyl ketone	1:0.05
198.6	*tert*-butyl acetate	1:0.00

by deprotonation of **5**. Of the possible deprotonation products whose geometries were optimized, diene **6** proved to have the lowest RHF/6-31G* energy.[50] As summarized in Scheme 1, the data in Table 6 show that diene **6** is more stable than **4** by 4.5 kcal/mol at the MP4SDQ/6-31G* level of theory. Thus, if deprotonation of **5** under these experimental conditions leads to the most stable alkene that can be formed directly from **5**,[51,52] then the PA that the experiments measure is that for formation of **5** from **6**, not from **4**.

At the MP4SDQ/6-31G* level, after correction for differences in ZPEs and heat capacities, Table 6 shows that the difference between the PAs of **6** and **2** is calculated to be 20.7 kcal/mol. This calculated value is within the error limits of the experimental value of $\Delta PA = 23 \pm 2$ kcal/mol. This good agreement provides evidence that it is, indeed, the enthalpy corresponding

to formation of cation **5**, not **1**-H$^+$, that is measured in the experiments starting with **1**.

Conclusions

The results reported here for isobutylene and bicyclo[3.3.0]-oct-1(5)-ene (**2**) demonstrate the applicability of the kinetic method to the measurement of proton affinities of olefins. Our results increase confidence in this method by extending its application to a previously unstudied class of compounds. Our gas-phase measurements appear to confirm the expected increase in PA associated with relief of olefin strain. The apparent proton affinity of tricyclo[3.3.3.0^{3,7}]undec-3(7)-ene (**1**) was found to be much higher than that of **2**. Theory and experiment agree that the strained olefin has a much higher PA than **2**; however, the ΔPA between **1** and **2**, obtained by *ab initio* calculations, is only one-half of the experimentally measured value.

The most likely explanation for this apparent disagreement is that, in the experiments involving **1**, protonation leads not to carbocation **1**-H$^+$ but to rearranged carbocation **5**. This tertiary cyclopropylcarbinyl carbocation is calculated to be considerably lower in energy than **1**-H$^+$. Cation **5** could be formed either directly from **1**-H$^+$ or by protonation of vinylcyclopropane **4**, which might be in equilibrium with **1** under the conditions of our experiment. The most stable alkene that can be formed by deprotonation of **5** is **6**, which is calculated to have PA = 219.6 kcal/mol at the MP4SDQ/6-31G* level of theory. The difference of 20.7 kcal/mol between the calculated PAs of **6** and **2** is in agreement with the measured difference of $\Delta PA = 23 \pm 2$ kcal/mol and thus supports our hypothesis that it is the PA corresponding to formation of carbocation **5** that the experiments involving **1** have measured.

An experimental test of this hypothesis would be provided by the synthesis of alkenes **4** and **6** and measurement of their PAs by the kinetic method. The finding that both of these alkenes have PA = 219 kcal/mol, the apparent PA that is measured for **1**, would provide confirmatory evidence that the same carbocation (**5**) is formed from all three of these alkenes under our experimental conditions.

Supporting Information Available: Listings of optimized geometries for **1**, **1**-H$^+$, **2**, **2**-H$^+$, and **5**−**7** (8 pages). See any current masthead page for ordering and Internet access instructions.

JA960776T

(50) The RHF/6-31G* energy of the isomer of **4** with an endocyclic double bond was 1.6 kcal/mol higher than that of **4**, and the RHF/6-31G* energy of the diene, formed by deprotonating the CH$_2$ group in the cyclopropane ring of **5**, was 2.8 kcal/mol higher than that of **6**.

(51) Smith, J. M.; Hrovat, D. A.; Borden, W. T. *Tetrahedron Lett.* **1993**, *38*, 5991.

(52) Alkene **1** has almost exactly the same MP4SDQ/6-31G* energy as **6**, but in contrast to **6**, **1** is unlikely to be formed by deprotonation of **5**. In fact, direct deprotonation of **5** would not lead to **6** but to an isomer that is considerably higher in energy, because it contains a *trans* double bond. The lowest energy pathway from **5** to **6** would involve flipping of the propano bridge in **5**,[51] deprotonation of the resulting conformational isomer of **5** to give a conformational isomer of **6**, followed by a second propano bridge flip to form **6**. The RHF/6-31G* energies of the conformational isomers of **5** and **6** are respectively 8.0 and 5.9 kcal/mol higher than those of **5** and **6**.