

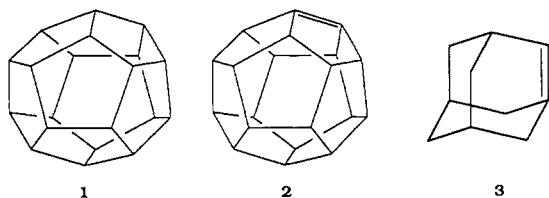
Measurement of the Double-Bond Strain Energy in Dodecahedrene by Thermochemical Bracketing of Gas-Phase Ion-Molecule Reactions

Jeffrey P. Kiplinger,[†] Fernando R. Tollens,[†] Alan G. Marshall,^{*,†,§} Tomoshige Kobayashi,[†] Dean R. Lagerwall,[†] Leo A. Paquette,^{*,†} and John E. Bartmess[‡]

Contribution from the Departments of Chemistry and Biochemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210, and the Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996. Received February 7, 1989

Abstract: The synthesis of dodecahedrene ($C_{20}H_{20}$) in 1982 generated a great deal of interest in highly symmetric and highly strained hydrocarbons, just as the synthesis of adamantane did more than 20 years ago. Both dodecahedrene and adamantane have proved difficult to synthesize, however, since the rigidly locked skeletons of the saturated systems would enforce a high degree of distortion at the olefinic carbons. A great deal of interest thus centers on the amount of additional energy necessary to incorporate a strained double bond into these systems, relative to an unstrained hydrocarbon. We have successfully measured this "double-bond strain energy" by thermochemically bracketing the gas-phase 1,2-elimination reaction of trifluoroacetyldodecahedrene. From this thermodynamic measurement, we obtain the *relative* gas-phase heats of formation of dodecahedrene and dodecahedrene. Attempts to induce the same reaction in trifluoroacetyladamantane gave a more ambiguous result, but nevertheless yielded useful thermochemical information. For dodecahedrene, our measurement yields the heat of hydrogenation, which may be compared to that for unstrained systems as a measure of the strain involved in the pyramidalized double bond. Thermodynamic and geometric data from AM1 semiempirical calculations are in good agreement with the experimental results. The present method should be extendable to the thermochemistry of other strained systems.

In 1982, Paquette and co-workers reported the first synthesis of dodecahedrene¹ (**1**), the most complex of the regular "Platonic solids". This $C_{20}H_{20}$ hydrocarbon has generated major interest in a variety of areas, e.g., as an example of an exceptionally symmetric (I_h) and stable system,² as a potential cage for small ions or molecules,³ and as a potential carrier for functional groups of pharmaceutical interest.⁴ More recently, Paquette et al. have reported the synthesis of a variety of substituted dodecahedrenes⁵ and have been pursuing the synthesis of dodecahedrene (**2**),⁶ which holds a great deal of interest as a highly strained olefin.⁷ Dodecahedrene should, when eventually examined crystallographically, exhibit a high degree of pyramidalization of the olefinic carbon atoms,⁸ probably with near-tetrahedral geometry at these centers.



Adamantane (**3**) has been recently prepared, matrix-isolated, and examined spectroscopically.⁹ Previously reported force-field calculations¹⁰ suggest that this system is also pyramidalized and twisted at the olefinic carbons, although it is not pyramidalized to as high a degree as would be required in the dodecahedrene system. Calculations¹⁰ indicate that adamantane should have a lower absolute heat of hydrogenation than dodecahedrene.

In this paper, we report the preparation of dodecahedrene as the inferred neutral product of gas-phase ion-molecule reactions carried out in the trapped-ion cell of a Nicolet FTMS-2000 mass spectrometer.¹¹ Although we cannot observe this compound directly, our evidence for its production is very strong and our results provide direct experimental measurement of the energy necessary to incorporate a double bond into this highly strained system. Experimental thermochemical data are not readily available for the majority of such unusual olefins, primarily because the compounds are not usually synthesized in sufficient

quantity for calorimetric analysis.

Evaluation of the results of parallel experiments designed to produce adamantane indicates that a different neutral product may result in that case. Nevertheless, thermochemical calculations, combined with the experimental results, verify predictions of the relative amounts of double-bond strain in the adamantane and dodecahedrene systems. The relative bond strains are interpretable in terms of the calculated geometries and energies of the two systems.

Experimental Section

Ions were observed by Fourier transform ion cyclotron resonance mass spectroscopy,¹² with a Nicolet FTMS-2000 instrument operating at 3.0

(1) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *Ibid.* **1983**, *105*, 5446.

(2) (a) Gallucci, J. C.; Doecke, C. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 1343. (b) Allinger, N. L.; Geise, H. J.; Pyckhout, W.; Paquette, L. A.; Gallucci, J. C. *Ibid.* **1989**, *111*, 1106. (c) Gallucci, J. C.; Taylor, R. T.; Kobayashi, T.; Water, J. C.; Krause, J.; Paquette, L. A. *Acta Crystallogr.*, in press.

(3) (a) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 5677. (b) Dixon, D. A.; Deerfield, D.; Graham, G. D. *Chem. Phys. Lett.* **1981**, *78*, 161.

(4) Weber, J. C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 5183.

(5) (a) Paquette, L. A.; Weber, J. C.; Kobayashi, T. *J. Am. Chem. Soc.* **1988**, *110*, 1303. (b) Olah, G. A.; Prakash, G. K. S.; Kobayashi, T.; Paquette, L. A. *Ibid.* **1988**, *110*, 1304. (c) Paquette, L. A.; Kobayashi, T.; Gallucci, J. C. *Ibid.* **1988**, *110*, 1305.

(6) Kobayashi, T.; Lagerwall, D., unpublished results.

(7) (a) Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, pp 299-366. (b) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189. (c) Borden, W. T. *Chem. Rev.*, in press.

(8) (a) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *Ibid.* **1980**, *102*, 7218. (c) Volland, W. V.; Davidson, E. R.; Borden, W. T. *Ibid.* **1979**, *101*, 533. (d) Radziszewski, J. G.; Yin, T.-K.; Miyake, F.; Ranzoni, G. E.; Borden, W. T.; Michl, J. *Ibid.* **1986**, *108*, 3544. (e) Ranzoni, G. E.; Yin, T.-K.; Borden, W. T. *Ibid.* **1986**, *108*, 7121. (f) Paquette, L. A.; Shen, C.-C.; Krause, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2351.

(9) (a) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637. (b) Michl, J.; Radziszewski, G. J.; Downing, J. W. *Pure Appl. Chem.* **1983**, *55*, 315.

(10) (a) Ermer, O. *Aspekte von Kraftfeldrechnungen*; Wolfgang Baur Verlag: Munich, W. Germany, 1981. (b) Matella, D. J.; Jones, M.; Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 7634. (c) Allinger, N. L.; Sprague, J. T. *Ibid.* **1972**, *94*, 5734.

(11) Nicolet Instrument Corp., 5225-1 Verona Rd., Madison, WI 53711-0508.

[†] Department of Chemistry, The Ohio State University.

[§] Department of Biochemistry, The Ohio State University.

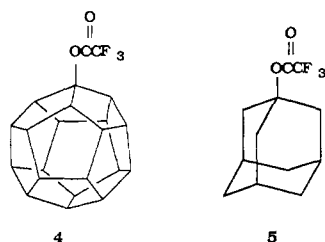
[‡] Department of Chemistry, The University of Tennessee.

T with a dual trapped-ion cell.¹¹ Our instrument has been modified to operate with two CTI-Cryogenics CRYO-TORR 8 cryopumps (1250 L s⁻¹ pumping speed for N₂) rather than diffusion pumps, and both sides of the dual vacuum chamber are backed by a single 50 L s⁻¹ Leybold-Heraeus TMP-50 model turbopump.

Experiments were conducted only on the "source" (sample) side of the dual cell, in order that ion-molecule reactions might more easily be observed in its higher pressure environment. Volatile samples (alkyl nitrites, water, and trifluoroacetoxyadamantane) were introduced via molecular leaks from sample reservoirs after purification by several freeze-pump-thaw cycles on the foreline vacuum chamber of the instrument. Nonvolatile samples (dodecahedrane derivatives) were introduced via a heated solids probe to a steady-state pressure of 1.5×10^{-8} Torr. For samples introduced directly to the cell from the probe, ion-molecule *absolute* reaction rate constants are not measurable. The ion gauge on the "source" side of the instrument must be located on the far side (with respect to the sample) of the cryopump, about 3 ft away from the cell in order to avoid the fringe field of the superconducting solenoidal magnet. Thus, the steady-state pressure measured at the ion gauge can differ substantially (by a factor of up to 100) from the actual pressure in the cell (as reflected by the ICR spectral peak width). Moreover, our confidence in estimating ion gauge sensitivities¹³ for these compounds is low. However, we can determine ion-molecule reaction *relative* rate constants with confidence, by introducing a sample to the same ion gauge pressure reading in different experiments.

Typical conditions for ion formation, trapping, excitation, detection, and processing were: 10-ms electron beam (0.5 eV to generate alkoxide ions from the corresponding alkyl nitrites, 5.3 eV to generate hydroxide ion from water) at a collector-measured emission current of 12 μ A; -2 V applied across a 2-in. end-to-end cell dimension to trap negative ions; and 32K time-domain data padded with another 32K zeroes and Blackman-Harris apodized before Fourier transformation.

Dodecahedrane derivatives were prepared as previously described⁵ and were used as obtained after one recrystallization. In the FT/ICR mass spectra of dodecahedrane and its derivatives, the primary interferences resulting from near-thermal electron impact were halide ions. In particular, bromide ions were present in negative ion spectra of trifluoroacetoxydodecahedrane (**4**), presumably because bromododecahedrane is its synthetic precursor. Since ion cyclotron resonant prior ejection of any of the anionic bases did not affect the abundance of subsequently detected bromide ions, we conclude that bromide is not produced via an ion-molecule reaction and thus does not present an interference. Because bromine has such a high electron affinity (3.3 eV),²³ even tiny amounts of Br-containing compounds in the ICR ion trap often capture electrons and dissociate to give high yields of bromide ion. Therefore, we believe that our crystalline sample of **4** is essentially pure. Likewise, the FT/ICR

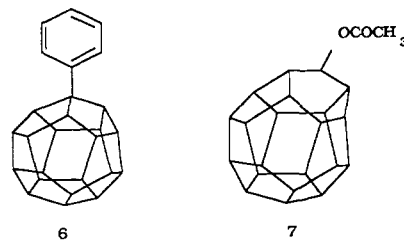


mass spectrum of **4** also shows an m/z 166 anion, whose chemical formula was established as C₃F₆O⁻ by high-resolution accurate mass measurement. Selective ejection of possible precursor ions confirmed that C₃F₆O⁻ was not the product of an ion-molecule reaction; presumably it is the result of a pyrolytic process, either on the heated probe or on the ion gauge filament.^{14,15} The trifluoroacetate ester of 1-adamantanol (**5**) was prepared according to literature methods¹⁶ and was used without further purification.

Results and Discussion

A previously published study from our laboratories examined some aspects of the positive ion-molecule chemistry of dodeca-

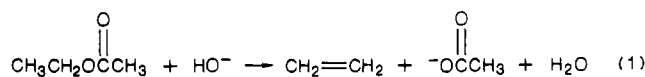
hedrane, methyl dodecahedrane, and 1,16-dimethyldodecahedrane.¹⁷ Electron ionization of various dodecahedrane derivatives produces a positive ion at m/z 258, corresponding to C₂₀H₁₈^{•+}, a species isobaric with the radical cation of dodecahedrene. In particular, compound **4** and phenyldodecahedrane (**6**) show m/z 258 as the dominant peak in their positive ion mass



spectra under high-energy electron impact. However, C₂₀H₁₈^{•+} may represent a ring-opened structure because of the high degree of strain in the system. Therefore, the production of C₂₀H₁₈^{•+} does not necessarily represent the introduction of a strained π -system into the molecule. Similarly, trifluoroacetoxyadamantane produces only a low-abundance (<1%) molecular cation under electron impact conditions, and the principal positive ions in the spectrum are C₁₀H₁₄^{•+} and C₁₀H₁₅^{•+} at m/z 134 and 135.

Our indirect evidence for the gas-phase production of dodecahedrene is based on the observation of a β -elimination reaction when strong gas-phase anionic bases react with trifluoroacetoxydodecahedrane (**4**). Ejection of the reactant primary bases confirms that this ion is the product of an ion-molecule reaction and is not produced on electron capture by **4**. The ionic product of this reaction is trifluoroacetate ion at m/z 113. In order to infer the structure of a neutral molecule that cannot be directly observed, however, the appearance of an expected ionic product is not a sufficiently strong argument. Consideration of the thermochemistry of this process together with alternative pathways is necessary to support this postulated reaction mechanism.

Gas-phase synthesis of the olefins as neutral molecules may be accomplished by a β -elimination reaction. However, since only exothermic processes are generally observable in ion cyclotron resonance owing to the near-thermal conditions and limited ion-trapping period, incorporation of a strained double bond into a molecule requires a very strong gas-phase base and a very weakly basic anionic leaving group. For example, the homododecahedryl acetate **7**¹⁸ cannot be induced to undergo elimination in the ICR spectrometer even on reaction with the strong base HO⁻. Reaction of ethyl acetate (taken as an example of an analogous system without enforced strain) with hydroxide (eq 1) in the gas phase



can be computed as 108 kJ/mol exothermic.¹⁹ If the extra amount of enthalpy required to introduce a double bond into a strained system is greater than 108 kJ/mol, the corresponding β -elimination reaction will be endothermic (and almost certainly endoergic at room temperature, since the corresponding entropy change, although favorable, is small), and therefore not observed under the ion trapping conditions in the FT/ICR mass spectrometer.

Compound **7** undergoes a reaction with hydroxide to produce C₂₁H₂₁O⁻, an alkoxide ion. No acetate ion is observed. The observed product ion may be the result of a B_{AC}2 hydrolysis reaction, or it may be produced by an elimination reaction in which the base abstracts an α -proton from the ester and produces the

(12) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282. (b) Comisarow, M. B.; Marshall, A. G. *Ibid.* **1974**, *26*, 489. (c) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.

(13) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

(14) Caldwell, G.; Bartmess, J. E. *Int. J. Mass Spectrom. Ion Proc.* **1981**, *40*, 269.

(15) Caldwell, G.; Bartmess, J. E. *Int. J. Mass Spectrom. Ion Proc.* **1983**, *50*, 235.

(16) Raber, D. J.; Propeck, G. J. *J. Org. Chem.* **1982**, *47*, 3324.

(17) Santos, I.; Balogh, D. W.; Doeke, C. W.; Marshall, A. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 8183.

(18) Paquette, L. A.; Kobayashi, T.; Kesselmayr, M. A., to be submitted.

(19) Neutral molecule gas-phase heats of formation are available from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986, or may be calculated (trifluoroacetate esters) from group additivity rules. See Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. Anion gas-phase heats of formation are available from ref 23.

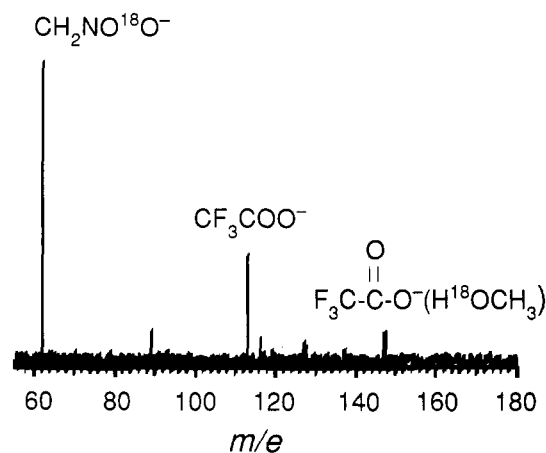


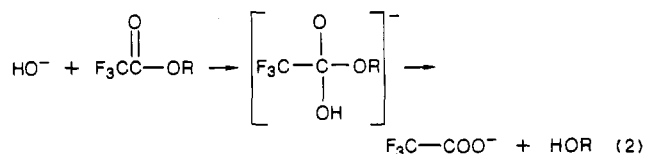
Figure 1. FT/ICR mass spectrum of the ionic products of the reaction of trifluoroacetoxydodecahedrene and ^{18}O -labeled methoxide. The lack of ^{18}O label in trifluoroacetate ($\text{C}_2\text{F}_3^{16}\text{O}_2^-$ at m/z 113, but no $\text{C}_2\text{F}_3^{16}\text{O}^{18}\text{O}^-$ at m/z 115) and the presence of the proton-bound dimer, $\text{CF}_3\text{CO}_2\text{-(H}^{18}\text{OCH}_3\text{)}$ ($\text{C}_3\text{H}_4^{16}\text{O}_2^{18}\text{O}^-$ at m/z 147), support a 1,2-elimination mechanism to produce (unobserved) neutral dodecahedrene product (see text).

alkoxide and neutral ketene.²⁰ The latter process has been observed to be the dominant pathway in reactions between bases and acetate esters in the gas phase.²¹ The β -elimination pathway is apparently precluded in this system either by the thermodynamic limitation or by a kinetic barrier on the reaction surface. Thus, the strain inherent in the double bond in the homo alkene is apparently greater than 108 kJ/mol relative to ethene.

The use of a better leaving group should reduce the endothermicity of the elimination. The reaction corresponding to eq 1 but with trifluoroacetate as the leaving group is 216 kJ/mol exothermic. Thus, trifluoroacetoxydodecahedrene (**4**) reacts with hydroxide and methoxide in the ICR spectrometer to produce a single ionic product, the trifluoroacetate ion at m/z 113. Ethoxide ion, which is 13 kJ/mol less basic than methoxide in the gas phase (based on known differences in the gas phase $\Delta H^\circ_{\text{acid}}$ for methanol and ethanol²³), does not yield the trifluoroacetate product ion. Trifluoroacetoxyadamantane (**5**) reacts with $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$ and stronger gas-phase bases to produce only trifluoroacetate, but will not react with $(t\text{-C}_4\text{H}_9)_2\text{CHO}^-$, which is 12 kJ/mol less basic than $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$ in the gas phase.

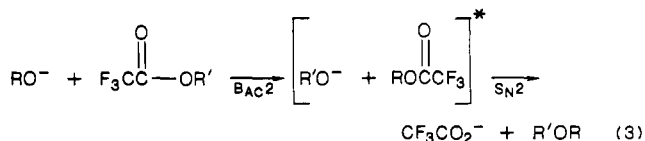
We now consider alternate pathways which might produce the CF_3CO_2^- ion. Trifluoroacetate ion may be produced from a trifluoroacetate ester with β -hydrogen atoms by elimination, substitution, or a $\text{B}_{\text{AC}2}$ reaction. In gas-phase ion-molecule reactions, substitution is generally not observable in cases where elimination can also occur. In fact, even when a substitution pathway is more exothermic than a competitive elimination process, elimination appears to be preferred.^{22,24-26} In the dodecahedrene system, we are fortunate that substitution is a sterically unreasonable pathway, since backside attack is prohibited, and frontside substitution at carbon has never been documented in a gas-phase ion-molecule reaction. However, trifluoroacetate

may also be produced by reaction of **4** with hydroxide in a $\text{B}_{\text{AC}2}$ process, as shown in eq 2. The activated tetrahedral intermediate



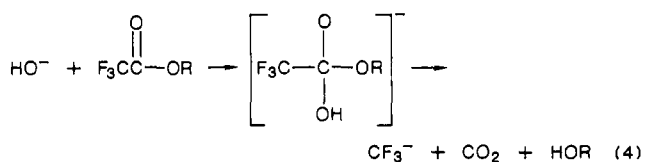
should break up preferentially to trifluoroacetate rather than to the dodecahedrene alkoxide owing to the greater gas-phase acidity of trifluoroacetic acid.²³ Reaction of **4** with $^{18}\text{OH}^-$ (produced by impact of 5.3-eV electrons on H_2^{18}O , Aldrich Chemical Co., 98.5% isotopic purity confirmed by FT/ICR) by this $\text{B}_{\text{AC}2}$ mechanism should produce $\text{CF}_3\text{CO}^{18}\text{O}^-$ at m/z 115 as the ionic product, thereby allowing us to differentiate between the two possible mechanisms. The ratio of m/z 113 to 115 produced in this experiment was approximately 2.5:1, a direct measurement of the branching ratio for the elimination versus $\text{B}_{\text{AC}2}$ pathways. Thus, the $\text{B}_{\text{AC}2}$ pathway is active, but as long as m/z 113 is observed, the elimination reaction must also be occurring.

For alkoxide bases, a similar process could be proposed to produce the activated intermediate complex shown in eq 3. This



complex might then exist long enough to react further by an E2 [only if RO^- is ethoxide (not observed)] or $\text{S}_{\text{N}2}$ process to produce the trifluoroacetate ion. However, reaction of both **4** and **5** with $\text{CH}_3^{18}\text{O}^-$ produces an ion at m/z 113 (unlabeled trifluoroacetate) but not 115. If eq 3 were the operative mechanism, then the ^{18}O label would have been incorporated into the product ion. Thus, eq 3 can be rejected as the sole source of CF_3CO_2^- . Additional direct evidence for an elimination mechanism is provided by our observation of a proton-bound dimer, $\text{F}_3\text{CCO}_2\text{-(H}^{18}\text{OCH}_3\text{)}$ at m/z 147 (see Figure 1). Observation of a similar proton-bound dimer has previously been taken as strong evidence for gas-phase elimination.²⁴

McDonald and Chowdhury²⁵ have observed that trifluoroacetate esters will also react with anionic bases through a tetrahedral intermediate to produce CF_3^- (eq 4). CF_3^- was not observed when



either **4** or **5** reacted with any of these bases, even though the above results indicate that a tetrahedral intermediate is formed.

Thermochemical considerations prohibit the production of trifluoroacetate by dissociation of the radical anion of **4**, which might be produced after electron transfer from a primary anionic base. The overall transfer of an electron from methoxide to CF_3CO_2^* is exothermic by 2.4 eV (240 kJ/mol),²³ but that amount of energy is insufficient to overcome the barrier for breaking a C-D bond in **4**.

We can thus be confident that the production of trifluoroacetate ion from both neutral reactants is by an elimination mechanism. If we assume the simplest possible case, a 1,2-elimination, the neutral products must at least initially be the desired olefins. ESR spectra of matrix-isolated adamantene^{9a} indicate that the compound definitely contains a double bond, rather than existing as a 1,2 biradical, and we see no reason to doubt that dodecahedrene, given the similar type of distortion of the double bond, also exists as a true olefin. The question that remains to be answered is whether the reactivity thresholds we observe represent true thermodynamic thresholds or rather a kinetic effect operating to slow these elimination reactions before the thermodynamic

- (20) Kleingeld, J. C.; Nibbering, N. M. M.; Grabowski, J. J.; DePuy, C. H.; Fukuda, E. K.; McIver, R. T., Jr. *Tetrahedron Lett.* **1982**, 23, 4755.
 (21) Takashima, K.; Riveros, J. M. *J. Am. Chem. Soc.* **1978**, 100, 6128.
 (22) (a) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, 109, 1715. (b) DePuy, C. H.; Bierbaum, V. M. *Ibid.* **1981**, 103, 5034. (c) Kleingeld, J. C.; Nibbering, N. M. M. *Tetrahedron Lett.* **1980**, 21, 1687. (d) Jones, M. E.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, 111, 1645. (e) Sumpter, T.; Kiplinger, J. P.; Bartmess, J. E., to be published.
 (23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. D. *Gas-Phase Ion and Neutral Thermochemistry. J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, 17.
 (24) (a) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, 98, 1160-1165. (b) Kiplinger, J. P. Ph.D. Dissertation, Indiana University, 1984.
 (25) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, 104, 902.
 (26) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972.

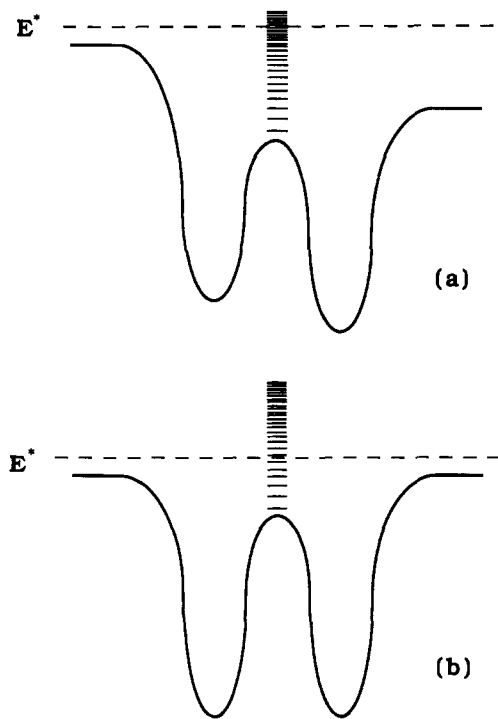


Figure 2. Model potential energy surfaces for two elimination reactions with a central barrier: (a) exothermic, (b) thermoneutral. See text for explanation.

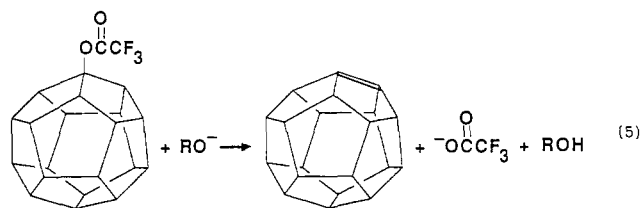
threshold is reached. If the observed thresholds are truly thermodynamic, then they should indicate the amount of energy required to incorporate a double bond into these strained systems.

Elimination reactions with strong bases are generally believed to proceed through transition states that resemble proton-transfer reactions, i.e., are relatively loose in character, have closely spaced vibrational/rotational states close to the zero-point energy in the transition state manifold, and hence are kinetically facile.²² For the most part, therefore, elimination reactions have been observed to have small potential barriers on the reaction surface, and to proceed at near-collision rate if exothermic. For trifluoroacetydodecahedrane, elimination undoubtedly follows this generalization. Measurement of the relative rate constants for the reaction of methoxide and hydroxide ions with **4** shows that there is little difference (<10%) in rate for these two processes, whereas ethoxide does not produce trifluoroacetate even at very long reaction periods. A process having a significant barrier on its potential surface is expected to show a significant decrease in rate as ΔH_{rx} becomes less negative, rather than exhibiting a sharp cutoff as ΔH_{rx} approaches zero.

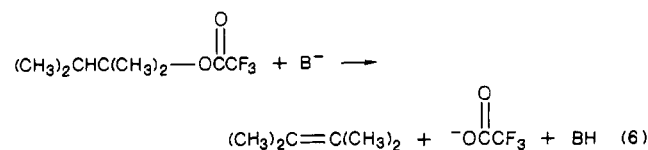
Figure 2 illustrates this principle by showing examples of ion-molecule reaction potential surfaces for two high-barrier reactions. Figure 2a shows an exothermic process and Figure 2b shows a near-thermoneutral process. Since ion-molecule reactions in ICR spectroscopy proceed at extremely low pressures where collisions are rare, reactions proceed adiabatically above the reaction surface, and the rate-limiting factor is the density of vibrational and rotational states in the transition-state manifold.²⁶ In an exothermic process, the barrier is lowered relative to the energy of the reactants E^* simply because the overall process is downhill in energy. As the reaction becomes less exothermic, the reactants must pass through the region of lower state density closer to the top of the transition state barrier, and the reaction should slow down and become unobservable on the ICR time scale before the thermochemical threshold is reached. Since we do not observe any gradual slowing for either of the observed elimination reactions as weaker bases are used, we are confident that the reactions do not proceed over a significant kinetic barrier. The reaction simply stops when ΔH_{rx} becomes positive because the reactant energy E^* is close to thermal. The observed threshold is therefore not the result of a kinetic barrier on the reaction surface and represents

a true thermodynamic threshold. Based on knowledge of the location of this threshold and by comparison with equivalent elimination reactions in unstrained systems, we can determine the amount of extra energy required for the introduction of a strained double bond.

Several further points must be considered in order to convert this thermodynamic threshold for elimination of carboxylate from **4** to the heat of hydrogenation of dodecahedrane. Since no other thermochemistry is known for dodecahedrane or its derivatives, we cannot simply use the threshold for reaction 5 to obtain a heat of formation of dodecahedrane.



We therefore begin by comparing the thermochemistry of the observed elimination of **4** to that of the open-chain analogue shown in eq 6. This reaction also produces a tetrasubstituted alkene,

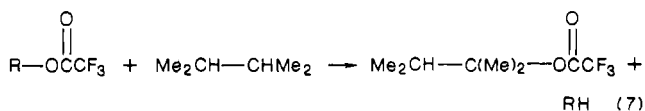


but in this case a planar unstrained one. From ionic and neutral heats of formation,¹⁷ reaction 6 is calculated to be 173 kJ/mol exothermic for $\text{RO}^- = \text{methoxide}$, and 159 kJ/mol exothermic for $\text{RO}^- = \text{ethoxide}$. Because methoxide induces elimination in trifluoroacetydodecahedrane, whereas ethoxide does not, the amount of extra energy to produce the strained olefin, dodecahedrane, compared to the unstrained case in reaction 6, must therefore lie between the two values for reaction 6, namely, at 166 ± 12 kJ/mol. The advantage of this comparative method in obtaining relative heats of reaction is that no absolute thermochemistry for dodecahedryl derivatives is needed.

A problem with the use of observed thresholds for ion/molecule reactions as thermochemical (enthalpic) criteria is that there can be "entropy driven" reactions, which are slightly endothermic, yet still proceed at near-collision rate because of the number of states available in the transition state or products is sufficiently high. To a first approximation, the free energy of reaction 6 at the experimental macroscopic temperature (here, 305 K) is an appropriate measure of reaction probability. The observed threshold should thus be taken as a *free energy* threshold, not an *enthalpic* one. For reaction 6, $T\Delta S$ is significant, since three species are being formed from two species; we calculate an *external* ΔS of $146 \text{ J mol}^{-1} \text{ K}^{-1}$ for reaction 6 for both methoxide and ethoxide as the bases.¹⁷ Although there is some question of the exact internal energy and therefore the temperature of the products, we are not using the *absolute* value of the threshold in our calculations, but rather the *relative* values for reactions 5 and 6. These two reactions have similar entropy changes, save for loss of internal rotation, so that much of any entropic shift of the threshold should cancel in judging their relative reactivities. The loss of rotation about the C-C single bond in the ester in reaction 6, on forming the alkene, costs $\sim -35 \text{ J mol}^{-1} \text{ K}^{-1}$ in *internal* entropy, in addition to the external entropy. No such loss is present in reaction 5, where the rotation is already frozen out in the dodecahedryl ester. Finally, there is a symmetry correction ($\sigma = 3$ for **4** and 2 for **2**) of $+4 \text{ J mol}^{-1} \text{ K}^{-1}$ favoring reaction 5. We thus assume that the difference in enthalpies for reaction 5 versus 6 is the same as the difference in free energies, save that reaction 5 is more likely by $31 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$ in entropy. The final relative enthalpy of elimination that we derive for reaction 5 is $166 \pm 12 \text{ kJ/mol} - 298 \text{ K} \cdot 31 \text{ J mol}^{-1} \text{ K}^{-1} = 156 \pm 15 \text{ kJ/mol}$.

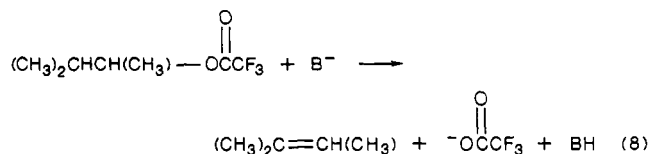
This value of 156 kJ/mol is for the relative enthalpies of elimination of trifluoroacetic acid for the two esters, not the loss

of molecular hydrogen. The two are the same only if the reaction



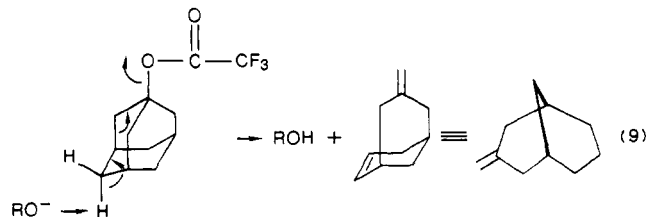
is thermoneutral. A sufficient condition for thermoneutrality is that the C-H and C-O bond strengths are the same in both the strained and unstrained compounds. That assumption underlies the group additivity arguments¹⁹ used in several places in this paper. Errors introduced by the assumption of thermoneutrality in eq 7 should be small (≤ 1 kcal/mol) and will be neglected. Finally, we add the heat of hydrogenation of 2,3-dimethyl-2-butene, 100 kJ/mol,¹⁷ to the difference in heats of hydrogenation of 156 kJ/mol, to obtain the net heat of hydrogenation of dodecahedrene of 266 ± 17 kJ/mol.

In the elimination reactions designed to produce adamantene, the leaving group is the same as for the dodecahedrene-forming reactions, but the bases necessary to promote the reaction are weaker. Equation 8 is similar to eq 6 but shows the production



of a trisubstituted unstrained olefin for comparison to the adamantene elimination. ΔH_{rx} for eq 8 is calculated¹⁹ to be -129 kJ/mol with $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$ as the base, and -118 kJ/mol with $(t\text{-C}_4\text{H}_9)_2\text{CHO}^-$. If we assume that adamantene is produced in the elimination reaction, these two bases would bracket the thermochemical threshold for the elimination reaction producing adamantene, so the amount of extra energy, relative to 2-methyl-2-butene, necessary to produce this strained olefin is 124 ± 6 kJ/mol. Again, the heat of hydrogenation of adamantene can now be obtained as the sum of this value and the heat of hydrogenation of 2-methyl-2-butene. With regard to entropy difference for **5**, an analysis similar to that given above for **4** ($35 \text{ J mol}^{-1} \text{ K}^{-1}$ for rotational loss in reaction 9 versus 8 and $-9 \text{ J mol}^{-1} \text{ K}^{-1}$ for the change in symmetry for the two) yields a final ΔH value of 116 ± 15 kJ/mol. These entropy differences should not change the ΔH difference between dodecahedrene and adamantene, only the absolute values. When combined with ΔH_{hyd} for 2-methyl-2-butene, we obtain an *apparent* ΔH_{hyd} of 228 kJ/mol for adamantene.

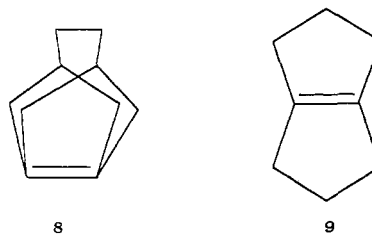
Although published calculations¹⁰ of the heats of hydrogenation of adamantene and dodecahedrene predict that adamantene should be the more strained olefin, our results imply that 40 kJ/mol *less* energy should be required to incorporate a double bond into the adamantane skeleton. This inconsistency forces consideration of a more complex mechanistic possibility, namely, a 1,4-elimination reaction (eq 9). In an unstrained system, a 1,4-elimination would



be unlikely; the energy gained from formation of a second double bond would be offset by the cost of breaking a carbon-carbon single bond. The heat of hydrogenation of two ethene molecules to produce butane is approximately -230 kJ/mol.¹⁹ In the case of the adamantane system, however, this cost may be offset by the relief of strain in the system on opening the ring. AM1 calculations³⁴ (see below) indicate that the diene produced by the 1,4-elimination should be ~ 163 kJ/mol lower in energy than adamantene. In contrast, in the case of dodecahedrene, there is no energy advantage in a 1,4-elimination. The diene produced

is calculated³⁴ to be 225 kJ/mol *higher* in energy than dodecahedrene, presumably because the rigid system prevents much relief of strain in the diene. Also, a 1,4-elimination in this system would necessarily proceed via a grossly misaligned orbital construct. *Therefore, we can state with reasonable certainty that dodecahedrene is produced in a 1,2-elimination, whereas adamantene is not.* The heat of hydrogenation of adamantene is better estimated as the sum of the threshold value (-116 kJ/mol), the heat of hydrogenation of 2-methyl-2-butene (-112 kJ/mol), and the calculated -163 kJ/mol difference between the diene and adamantene energies, for $\Delta H_{\text{hyd}} = -391$ kJ/mol.

This type of experimental thermochemical data is not readily available for highly strained systems. A few examples of calculated enthalpies for strained molecules may be found in the literature, however.^{10,28,30,31} For example, the relative heats of hydrogenation for the two olefins **8** and **9** have been calculated by the MNDO semiempirical method;²⁶ for **8**, it is 197 kJ/mol more exothermic than for **9**.^{30a} The geometry of compound **8** was optimized at



the STO-3G level,³⁰ and the olefinic carbon atoms were found to exhibit nearly tetrahedral geometries, in contrast to the planar compound **9**. More recent *ab initio* values^{30b} are somewhat less (140 to 175 kJ/mol) exothermic. The experimental result reported here indicates that the relative heat of hydrogenation of dodecahedrene is 156 kJ/mol more exothermic than for 2,3-dimethyl-2-butene. Given the uncertainties inherent in the above computational methods, the calculated values for the "zero-bridged" (double bond at two bridgeheads), pyramidalized tricyclic dodecene **8** compare favorably with our experimental result on dodecahedrene.

A recent study of bridgehead and pyramidalized olefins³¹ reported calculated heats of hydrogenation for both dodecahedrene and adamantene by force-field molecular mechanics methods (MM1).³² That study³¹ predicts that the heat of hydrogenation of dodecahedrene will be $185 - 110 = 75$ kJ/mol more negative than that of 2,3-dimethyl-2-butene,¹⁹ whereas our experimental result indicates a value of 156 ± 15 kJ/mol. Similarly, adamantene is predicted³¹ to have a heat of hydrogenation 172 kJ/mol more negative than that of 2-methyl-2-butene,¹⁹ whereas our present experimental result is 116 ± 15 kJ/mol. Although force-field calculations have been used successfully for estimating *relative* energies of conformational isomers,³² the method has never been proved reliable in providing *absolute* heats of formation or heats of reaction. Adamantene and dodecahedrene are different types of strained olefins,³³ namely, bridgehead versus nonplanar zero-bridged; thus, it is unreasonable to expect an accurate theoretical prediction from such calculations on two such different structures. We have therefore performed semiempirical molecular orbital calculations on these systems in hope of better under-

(27) Bartmess, J. E.; Melver, R. T., Jr. In *Gas Phase Ion Chemistry*; M. Bowers, M., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(28) For a recent study of the heats of hydrogenation of triquinacene and its congeners, consult: Liebman, J. F.; Paquette, L. A.; Peterson, J. R.; Rogers, D. W. *J. Am. Chem. Soc.* **1986**, *108*, 8267.

(29) (a) Dewar, M. J. S.; Theil, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Rzepa, H. S. *Ibid.* **1978**, *100*, 784.

(30) (a) Radziszewski, J. G.; Yin, T.-K.; Mayike, F.; Renzoni, G. E.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544. (b) Hrovat, D. A.; Borden, W. T. *Ibid.* **1988**, *110*, 4710.

(31) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(32) (a) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579. (b) Allinger, N. L.; Sprague, J. T. *Ibid.* **1975**, *31*, 21. (c) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(33) Fawcett, F. S. *Chem. Rev.* **1950**, *47*, 219.

Table I. Heats of Hydrogenation of Various Alkenes by Several Methods (kJ/mol)

alkene	$-\Delta H$ (AM1) ^a	$-\Delta H$ (MM1) ^b	$-\Delta H$ (expt) ^c	$-\Delta H$ (expt) ^d
CH ₂ =CH ₂ ^e	142	135	136	
(CH ₃) ₂ C=CH(CH ₃)	109	110	112	
(CH ₃) ₂ C=C(CH ₃) ₂	94.6 ^f 77.0 ^g	110 ^f	110 ^f 84 ^g	
dodecahedrene (2)	304, 529 ^h	185		266
adamantene (3)	373, 210 ^h	275		228

^a This work, calculated by the method of ref 34. ^b Force field, ref 28 and 32. ^c Reference 17. ^d Experimental, this work, ± 12 kJ/mol. See text for explanation. ^e Taken from ref 31. ^f Staggered, lowest energy configuration. ^g Eclipsed configuration of alkane (see text). ^h For double hydrogenation, as per reaction 9.

standing the significance of the experimental results.

The results of molecular orbital calculations at the AM1 level³⁴ are summarized in Table I. We report heats of hydrogenation in this table for the various alkenes rather than the calculated absolute heats of formation, since the latter are known to be somewhat unreliably predicted by AM1. For example, AM1 predicts cyclopentane to be 43.9 kJ/mol more stable than found experimentally,³⁴ and the heat of formation of dodecahedrane is not known for comparison to the calculated value. However, the heats of hydrogenation reported here are simply the *difference* in heats of formation between the alkene and alkane, and systematic errors in the absolute heats of formation should therefore cancel. The heats of hydrogenation obtained for the unstrained simple alkenes compare favorably with those obtained from ref 19.

On hydrogenation of dodecahedrene, the two added hydrogen atoms are placed in an eclipsed arrangement. This feature adds some strain to the system and hence makes the heat of hydrogenation less negative. To model this, we take the rotational barrier in 2,3-dimethylbutane, 18 ± 1 kJ/mol,³⁵ as the difference in ΔH_{hyd} for the relaxed versus eclipsed forms. This results in a "corrected" ΔH_{hyd} of Me₂C=CMe₂ of 92 kJ/mol.

(34) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Calculations performed using AMPAC version 4.0 (QCPE Program No. 455) implemented on an IBM RT computer by J. E. Bloor, M. Spotswood, and J. E. Bartmess at the University of Tennessee, Knoxville.

(35) Luna, L.; Ingold, K. H. *J. Am. Chem. Soc.* **1977**, *99*, 4573.

The heat of hydrogenation of adamantene has been estimated here as the sum of the experimental threshold, the heat of hydrogenation of 2-methyl-2-butene, and the calculated³² energy difference between the alkene and diene, as described above. Both this value and the experimental value for the heat of hydrogenation of dodecahedrene are reasonably reproduced by the AM1-calculated heats of hydrogenation, within the stated ± 21 kJ/mol average uncertainty for hydrocarbon ΔH_f .³⁴

In the adamantene system, geometry optimization by AM1 shows significant pyramidalization of the double bond at both olefinic carbons (more at the bridgehead), but a significant amount of the distortion of the system is in the twisting of the double bond necessary to accommodate a trans configuration in a six-membered ring. The torsion angle across the double bond is nearly 17° twisted, instead of completely pyramidalized. In dodecahedrene, as expected, all of the distortion is in pyramidalization, with a torsion angle between the α -carbons of 133° (versus 180° in a planar bond). The experimental results shown here indicate that although adamantene is not so rigidly locked into a pyramidalized configuration as dodecahedrene, the twisting distortion of its double bond contributes significantly to its instability.

In their evaluation of the stability of a variety of bridgehead olefins, Maier and Schleyer³¹ discuss a parameter they call "olefinic strain", which is closely related to the heat of hydrogenation of a bridgehead olefin. Rough rules of thumb may be used with this parameter to predict whether a given olefin may be isolable. Based on their results, adamantene should be difficult to isolate, even in low-temperature matrices, whereas dodecahedrene is predicted to possibly be stable at very low temperatures. Adamantene has been matrix-isolated and examined spectroscopically.⁹ Our results indicate that dodecahedrene may be synthetically accessible in bulk quantity, at least at low temperature.

After this paper was submitted for publication, the first condensed-phase synthesis of a (tetrasubstituted) dodecahedrene was reported,³⁶ further corroborating our present claim for a stable unsubstituted dodecahedrene.

Acknowledgment. The authors thank J. L. Beauchamp for helpful discussions. This work was supported by National Science Foundation Grant CHE-8617244 (AGM), National Institutes of Health Grant AI-11490 (LAP), and The Ohio State University.

(36) Melder, J.-P.; Pinkos, R.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 305-310.