

Cycloalkane and Cycloalkene C–H Bond Dissociation Energies

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Abstract: Both C–H bond dissociation energies for cyclobutene were measured in the gas phase (BDE = 91.2 ± 2.3 (allyl) and 112.5 ± 2.5 (vinyl) kcal mol⁻¹) via a thermodynamic cycle by carrying out proton affinity and electron-binding energy measurements on 1- and 3-cyclobutenyl anions. The results were compared to those for an acyclic model compound, *cis*-2-butene, and provide the needed information to experimentally establish the heat of formation of cyclobutadiene. Chemically accurate G3 and W1 calculations also were carried out on cycloalkanes, cycloalkenes, and selected reference compounds. It appears that commonly cited bond energies for cyclopropane, cyclobutane, and cyclohexane are 3 to 4 kcal mol⁻¹ too small and their π bond strengths, as given by BDE1 – BDE2, are in error by up to 8 kcal mol⁻¹.

Introduction

Carbon–hydrogen bond strengths are an indicator of free radical stabilities and play a critical role in understanding structure–reactivity relationships, reaction mechanisms, and complex kinetic modeling of combustion, atmospheric, and interstellar processes.¹ Many carbon-centered radicals are electron deficient and decrease in stability with increasing s-character at the unpaired electron site. This well-known trend was recently found to give rise to a linear relationship between C–H bond dissociation energies (BDEs) and hybridization (as given by heteronuclear ¹³C–H coupling constants) for hydrocarbons such as methane, ethylene, acetylene, cyclopropane, and bicyclo[1.1.0]butane.² It was surprising, therefore, to find that the vinyl C–H bond in 3,3-dimethylcyclopropene is 27 kcal mol⁻¹ weaker than the C–H bond in acetylene (106.7 ± 3.7 versus 133.3 ± 0.1 kcal mol⁻¹) and only 1.7 ± 3.7 kcal mol⁻¹ stronger than the bond in methane despite having the hybridization (and acidity) of an alkyne. This is due to an unanticipated orbital interaction that stabilizes the vinyl radical and can be viewed as a manifestation of angle strain. This finding makes it interesting to determine the vinyl C–H bond energies for cyclobutene, cyclopentene, and cyclohexene, which currently are unavailable.

Allylic C–H BDEs of small ring compounds also are of interest but are either poorly established or unknown. The experimental value for cyclopropene (90.6 ± 4.0 kcal mol⁻¹)³ is widely cited and is indicative of aromatic stabilization in the

radical but is inconsistent with high level calculations and is in error.⁴ The corresponding bond energy for cyclobutene has not been reported but is needed to complete an experimental determination of the heat of formation of cyclobutadiene.⁵ Cyclopentene⁶ and cyclohexene⁷ have been measured by kinetic methods, but several additional assumptions were required in the latter determination and a gas-phase value does not appear to be available.⁸ In this work, we report experimental determinations of both C–H bond strengths for cyclobutene and chemically accurate G3⁹ and W1¹⁰ computations for cycloalkenes, cycloalkanes, and selected reference compounds. To our surprise, the literature bond energies for cyclopropane, cyclobutane, and cyclohexane appear to be too small by 3 to 4 kcal mol⁻¹ and the π bond strengths in the corresponding cycloalkenes consequently would be in error by up to 8 kcal mol⁻¹.

Experimental Section

General. 3-Chlorocyclobutene was purchased from Fluka and prepared as previously described.¹¹ Diethyl ether was dried over sodium

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metal, hexamethylphosphoramide was distilled over calcium hydride under vacuum, and the reactions below were carried out under a dry argon atmosphere in flame-dried glassware. ^1H and ^{13}C NMR spectra were recorded on Varian VI-300, VXR-300, and VI-500 spectrometers and are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. High-resolution mass spectral analyses were performed on a Finnigan MAT 95 mass spectrometer. Preparative gas chromatography was carried out using a Gow-Mac series 350 gas chromatograph equipped with a thermal conductivity detector and a 4 m \times 7 mm column of 10% SE-30 on Chromosorb P. Medium-pressure liquid chromatography (25–60 psi) and flash column chromatography were carried out on J. T. Baker (230–400 mesh) silica gel. Analytical thin-layer chromatography was performed on 0.25 mm Mashery-Nagel silica gel plates, and compounds were visualized with UV light (254 nm) and vanillin/methanol/ H_2SO_4 (0.75:97.75:1.5) or phosphomolybdic acid (7% EtOH solution) stains.

3-Trimethylsilylcyclobutene. To a stirred solution of hexamethyldisilane (0.717 g, 4.90 mmol) in 6 mL of HMPA at 0–5 $^\circ\text{C}$, 3.13 mL (5.01 mmol) of a 1.6 M solution of MeLi in diethyl ether was added dropwise. After being stirred for an additional 3 min, the resulting red solution was diluted with 12 mL of diethyl ether and cooled to –60 $^\circ\text{C}$. The reaction mixture turned yellow after 5 min, at which point 0.177 g (2.00 mmol) of 3-chlorocyclobutene dissolved in 2 mL of Et_2O was added dropwise. The resulting solution was stirred for an additional 1 h at –50 to –60 $^\circ\text{C}$ and then was poured into a mixture of 100 mL of pentane and 100 mL of saturated aqueous ammonium chloride. The aqueous material was extracted with pentane (2 \times 20 mL), and the combined organic solution was washed with H_2O (4 \times 20 mL) and dried over MgSO_4 . Distillation of the pentane and ether through a Vigreux column at atmospheric pressure afforded a concentrated residue that contained 3-trimethylsilylcyclobutene in a 75% yield as determined by gas chromatography. Further purification of this material was carried out by preparative GC employing the following instrument parameters: He flow rate, 30 mL min^{-1} ; injector temperature, 60–80 $^\circ\text{C}$; oven temperature, 30 $^\circ\text{C}$; detector temperature, 70 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ –0.01 (s, 9H), 2.32 (m, 1H), 2.35 (bs, 1H), 2.68 (m, 1H), 5.99 (m, 1H), 6.06 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ –3.2, 32.4, 35.0, 134.1, 139.2. HRMS-Cl (NH_3) calcd for $\text{C}_7\text{H}_{15}\text{Si}$ ($\text{M} + \text{H}$) $^+$ 127.0943, found 127.0938; calcd for $\text{C}_7\text{H}_{18}\text{NSi}$ ($\text{M} + \text{NH}_4$) $^+$ 144.1200, found 144.1208.

3-Triphenylsilylcyclobutene. A 30% dispersion of sodium in xylene (447 mg, 19.4 mmol) was washed and decanted three times with 5 mL portions of diethyl ether, and the residual solvent was removed under vacuum. An argon atmosphere and 6 mL of diethyl ether were introduced into the flask, and then a solution of chlorotriphenylsilane (0.736 mg, 2.50 mmol), naphthalene (0.064 g, 0.50 mmol), and 5 mL of diethyl ether was quickly added to this suspension. After the reaction mixture was stirred for 1 h at room temperature, HMPA (1.04 mL, 5.98 mmol) was added, and 30 min later the deep green-black solution was quenched with 3-chlorocyclobutene (0.118 g, 1.33 mmol) in 1.5 mL of diethyl ether over a 2 min period. During this short time interval, the reaction mixture turned brownish-red and then light violet. The solution darkened over approximately the next 30 min at which point 1 mL of H_2O was carefully added dropwise to destroy the excess sodium, and then 2 mL of 10% aqueous HCl and 20 mL of CH_2Cl_2 were added. The aqueous layer was extracted twice with CH_2Cl_2 (5 mL portions), and the combined organic material was washed with H_2O (4 \times 5 mL). After being dried with MgSO_4 , the solvent was removed under reduced pressure and the product was purified by MPLC on a silica gel column using hexane as the eluent to afford 101 mg (24%) of 3-triphenylsilylcyclobutene as a colorless solid. Further purification can be carried out by recrystallization from hexane (mp 121–123 $^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ 2.67 (dm, 1H, $J = 13.5$ Hz), 3.04 (dd, 1H, $J = 13.5$ and 4.5 Hz), 3.42 (m, 1H), 6.01 (m, 1H), 6.33 (d, 1H, J

= 2.0 Hz), 7.42–7.54 (m, 9H), 7.61–7.66 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 32.2, 33.4, 128.0, 129.7, 134.8, 135.1, 135.9, 138.4. HRMS-EI calcd for $\text{C}_{22}\text{H}_{20}\text{Si}$ (M) $^+$ 312.1353, found 312.1334.

1-Trimethylsilylcyclobutene. This compound was prepared as described in the literature¹² but was purified by preparative gas chromatography using the following conditions: He flow rate, 30 mL min^{-1} ; injector temperature, 160 $^\circ\text{C}$; oven temperature, 60 $^\circ\text{C}$; detector temperature, 180 $^\circ\text{C}$.

Gas-Phase Experiments. A dual cell model 2001 Finnigan Fourier transform mass spectrometer equipped with a 3 T superconducting magnet and controlled by a Sun workstation running Odyssey version 4.2 was used for these studies. Fluoride ion was prepared by electron ionization of NF_3 at 8.7 eV and was allowed to react with a static pressure of $\sim(4-10) \times 10^{-8}$ Torr of 1- or 3-trimethylsilylcyclobutene. The product ions were transferred to the second cell where the m/z 53 ($\text{M} - \text{TMS}$) ion was isolated using a stored-waveform inverse Fourier transform (SWIFT) excitation.¹³ Neutral reagents were introduced via slow leak valves, and subsequent reactions were monitored as a function of time. For the DePuy acidity determinations,¹⁴ OH^- was prepared by electron ionization (7.5 eV) of H_2O in the source cell and then transferred to the analyzer cell. After a pulse of argon up to a pressure of $\sim 10^{-5}$ Torr and a 1000-ms delay period, the product ions were ejected using a broadband chirp excitation, and the reaction with the selected silane ($\sim 2.0 \times 10^{-8}$ Torr) was monitored over a 0.2–4 s time period during which the product ratio was found to be constant.

Amide was produced by electron ionization (7.3 eV) of a pulse of NH_3 up to a pressure of $\sim 1 \times 10^{-6}$ Torr and ethylamide was generated in the same way, but better signals were obtained by deprotonating a static pressure of EtNH_2 ($\sim 4 \times 10^{-7}$ Torr) with NH_2^- . Both bases were used to deprotonate cyclobutene, and the resulting ions were transferred to the second cell where the m/z 53 ion was isolated and its reactivity was explored. Alternatively, EtNH^- was transferred to the second cell before reacting it with a static pressure of cyclobutene ($\sim 4 \times 10^{-7}$ Torr) to obtain the proton-transfer rate constant. In this way, forward and reverse proton-transfer rate constants were measured, and the equilibrium constant ($K = k_1/k_{-1}$) for the acid–base reaction was determined.

Computations. G3⁹ and W1¹⁰ calculations were carried out as previously described in the literature using Gaussian 2003 on IBM and SGI workstations at the Minnesota Supercomputer Institute.¹⁵ All of the resulting energies are reported as enthalpies at 298 K and were obtained using scaled HF (0.8929, G3) and B3LYP (0.985, W1) vibrational frequencies. In both cases, small vibrational frequencies that contribute more than $(1/2)\text{RT}$ to the thermal energy were replaced by $(1/2)\text{RT}$. Heats of hydrogenation and C–H bond energies were computed using calculated energies for all of the species involved; the experimental values for H_2 and H^\bullet were not employed as is sometimes done.

Results and Discussion

Fluoride-induced desilylation of 3-trimethylsilylcyclobutene (**1a**) affords 3-cyclobutenyl anion (m/z 53, **2a** $^-$, eq 1). This ion



is basic and deprotonates benzonitrile ($\Delta H^\circ_{\text{acid}} = 383.2 \pm 2.5$ kcal mol^{-1}), water ($\Delta H^\circ_{\text{acid}} = 390.7 \pm 0.1$ kcal mol^{-1}), and ethylamine ($\Delta H^\circ_{\text{acid}} = 399.3 \pm 1.1$ kcal mol^{-1}), but not

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Table 1. DePuy Kinetic Acidity and Electron Affinity Measurement Data for 3-Trimethylsilylcyclobutene, 3-Triphenylsilylcyclobutene, and 1-Trimethylsilylcyclobutene

RSi(CH ₃) ₃ [RSi(C ₆ H ₅) ₃]	ratio (R) ^a	ln(3R)	ΔH ^o _{acid} (RH) ^b	EA(R) ^b
ethyl	0.16 ± 0.01	−0.73 ± 0.05	420.1 ± 2.0	−6.0 ± 2.0
methyl	1.00	0.00	416.7 ± 0.7	1.8 ± 0.7
	[0.010 ± 0.002]	[−3.51 ± 0.70]		
cyclopropyl	1.02 ± 0.03	1.12 ± 0.03	411.5 ± 2.0	8.4 ± 2.0
	[0.045 ± 0.004]	[−2.00 ± 0.18]		
vinyl	2.49 ± 0.06	2.01 ± 0.05	409.4 ± 0.6	15.4 ± 0.6
	[0.042 ± 0.004]	[−2.07 ± 0.20]		
phenyl	8.18 ± 0.50	3.20 ± 0.20	401.7 ± 0.5	25.3 ± 0.1
	[1.00]	[0.00]		
1-naphthyl			394.2 ± 1.2	31.6 ± 0.5
	[3.32 ± 0.22]	[2.30 ± 0.15]		
3-cyclobutenyl	9.04 ± 0.54	3.30 ± 0.19	402.1 ± 1.5 ^c	
	[0.29 ± 0.03]	[−0.14 ± 0.01]	[403.1 ± 1.4] ^c	
1-cyclobutenyl	5.41 ± 0.37	2.74 ± 0.20	404.6 ± 1.5 ^c	21.5 ± 2.0 ^c

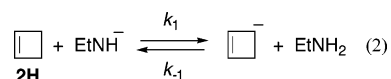
^a Ratio = (R₃SiO[−]/R'(R₂)SiO[−]) where R equals Me or Ph and is isotopically corrected. The data for the triphenylsilyl derivatives are given in brackets. ^b All values are in kcal mol^{−1} and come from refs 14 and 16. ^c This work.

ammonia (ΔH^o_{acid} = 403.6 ± 0.8 kcal mol^{−1}).¹⁶ In the last instance, signal loss is observed, but when ND₃ is used a small amount of deuterium incorporation also is seen. If long reaction times are examined, the incorporation of a second deuterium atom can be detected. These results suggest that the proton affinity of **2a**[−] is between ethylamide and amide (i.e., 401.5 ± 2.3 kcal mol^{−1}) but an acid-catalyzed isomerization to the corresponding vinyl anion cannot be ruled out. Therefore, a selective approach for measuring the acidity of cyclobutene at the allylic position is desirable, and the DePuy kinetic method was applied.¹⁴

This methodology makes use of the reaction of OH[−] with a series of trimethylsilanes (RSi(CH₃)₃) in which RH has a known acidity. By plotting ΔH^o_{acid}(RH) against the natural logarithm of the statistically and isotopically corrected (CH₃)₃SiO[−]/R(CH₃)₂SiO[−] product ratios (*R*), a calibration line is obtained that can be used to obtain the acidity of compounds with unknown values at specific locations. Five reference compounds were employed in this work (*R* = ethyl, methyl, cyclopropyl, vinyl, and phenyl), and a linear least-squares analysis of the data gave the following equation: ΔH^o_{acid}(RH) = −4.49 × ln(*R*) + 416.9 kcal mol^{−1}, *r*² = 0.984 (Table 1). 3-Trimethylsilylcyclobutene reacted with hydroxide ion to give an isotopically corrected product ratio of 9.04 ± 0.54, which leads to an acidity of 402.1 ± 1.5 kcal/mol^{−1}. In a similar way, five triphenylsilyl derivatives were used to construct a calibration line (ΔH^o_{acid}(RH) = −3.89 × ln(*R*) + 402.6 kcal/mol, *r*² = 0.987), and 3-triphenylsilylcyclobutene led to an acidity of 403.1 ± 1.4 kcal mol^{−1}. These values and the bracketing results indicate that ΔH^o_{acid} = ∼402 kcal mol^{−1} for the allylic position, and this suggests that an equilibrium determination might be possible. This turns out to be the case since 1- and 3-cyclobutenyl anions (**2v**[−] and **2a**[−], respectively) are readily differentiated (see below), and only the allylic ion is observed when cyclobutene (**2H**) is deprotonated by amide or ethylamide; NH₂[−] undoubtedly abstracts a vinyl proton some of the time to give **2v**[−], but equilibration in the presence of **2H** leads to insignificant quantities (∼1%) of this ion.

To obtain the equilibrium acidity of cyclobutene, the forward (*k*₁) and reverse (*k*_{−1}) rate constants for proton transfer with

ethylamide and ethylamine were measured (eq 2). Three



independent determinations were carried out in both directions to afford *k*₁ = (2.25 ± 0.29) × 10^{−10} and *k*_{−1} = (2.49 ± 0.09) × 10^{−11} cm³ molecule^{−1} s^{−1}, where the uncertainties are the standard deviations in the measurements. The resulting equilibrium constant is 9.04 ± 1.21, but given the inherent difficulties in measuring neutral gas pressures with an ionization gauge, a more conservative error for *K* of ±9.04 was adopted for the subsequent data analysis (i.e., a 100% uncertainty was used). This leads to ΔΔ*G*^o_{acid} = −1.3 ± 0.6 kcal mol^{−1}, which can be combined with Δ*G*^o_{acid}(EtNH₂) = 391.7 ± 0.7 kcal mol^{−1} to give Δ*G*^o_{acid}(**2H**) = 393.0 ± 0.9 kcal mol^{−1}. B3LYP/aug-cc-pVTZ geometries and vibrational frequencies were used to derive Δ*S*^o_{acid}(**2H**) = 26.2 eu, which is only 0.2 eu larger than the value for a proton and leads to ΔH^o_{acid}(**2H**) = 400.9 ± 1.1 kcal mol^{−1}.¹⁷ This result is in excellent accord with the bracketing and DePuy method determinations and is extremely well reproduced by G3 and W1 predictions of 401.2 kcal mol^{−1}. It also is our recommended value for the acidity of cyclobutene at the allylic position because equilibrium determinations are the most reliable method for measuring acidities.¹⁶

To put this quantity in perspective, we note that cyclobutene is 10.6 kcal mol^{−1} less acidic than *cis*-2-butene (ΔH^o_{acid} = 390.3 kcal mol^{−1} at the G3 level of theory). The decreased acidity is a direct result of the constrained geometry of **2a**[−], which has a C1–C2–C3 bond angle that is 34° smaller than that for allyl anion (i.e., 97.9° versus 132.1°).¹⁸ There also is an unfavorable orbital interaction between the terminal carbon atoms of the allylic system that is diminished by the pyramidalization of **2a**[−] (Figure 1).

The electron affinity of 3-cyclobutenyl radical (**2a**[•]) was determined directly from the equilibrium acidity of cyclobutene by employing a recently reported linear correlation between experimental ΔH^o_{acid}(RH) and EA(R[•]) values for delocalized carbanions (i.e., ΔH^o_{acid}(RH) = (−1.274 ± 0.058) EA(R[•]) + 405.9 ± 1.6 kcal mol^{−1}).¹⁹ This leads to EA(**2a**[•]) = 3.9 ± 2.0

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(17) An arbitrary but conservative uncertainty of ±2 eu was assigned to the computed Δ*S*^o_{acid}.

(18) The cited values are at the B3LYP/aug-cc-pVTZ level.

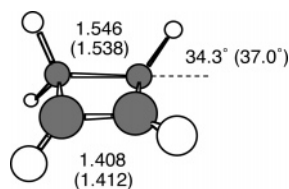


Figure 1. Computed B3LYP and MP2 structures of 3-cyclobutenyl anion ($2a^-$). Both geometries have C_2 symmetry, but the first value corresponds to a B3LYP/cc-pVTZ+d structure, whereas the parenthetical quantities are from a MP2(full)/6-31G(d) optimization.

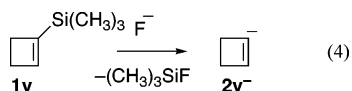
kcal mol⁻¹ (or 0.17 ± 0.09 eV), which is in excellent accord with our bracketed value of 0.24 ± 0.21 eV; the latter result is based upon the observation that $2a^-$ undergoes electron transfer with O₂ (EA = 0.448 ± 0.006 eV) but not NO (EA = 0.026 ± 0.005).¹⁶ It also is in excellent agreement with G3 and W1 theories, which predict values of 3.7 and 4.2 kcal mol⁻¹, respectively. Interestingly, the computed G3 electron affinity of *cis*-CH₃CH=CHCH₂• (0.44 eV or 10.1 kcal mol⁻¹) is 6.2 kcal mol⁻¹ larger than the experimental value for $2a^-$. This difference is a little more than half of that for the acidities, which suggests that the destabilization of the cyclic radical is a little less than half of that for the anion (i.e., 4.4 versus 10.6 kcal mol⁻¹). Given that the C1–C2–C3 bond angle in allyl radical is smaller than that in its corresponding anion (i.e., 125.1° versus 130.4°), this is not surprising.¹⁸

Bond dissociation energies are related to acidities and electron affinities via a thermodynamic cycle (eq 3), and the latter two quantities can be used to derive the former one since the ionization potential of hydrogen atom is well established (313.58 kcal mol⁻¹).

$$\text{BDE}(\text{RH}) = \Delta H^\circ_{\text{acid}}(\text{RH}) - \text{IP}(\text{H}^\bullet) + \text{EA}(\text{R}^\bullet) \quad (3)$$

For cyclobutene, an allylic C–H BDE of 91.2 ± 2.3 kcal mol⁻¹ is obtained, and this value is well reproduced by G3 and W1 computations of 90.6 and 91.7 kcal mol⁻¹, respectively. It also is 4.6 kcal mol⁻¹ larger than the G3 prediction for the C–H BDE of *cis*-2-butene. More importantly, it can be combined with our recently reported values for the proton affinity of cyclobutadiene (PA = 224.3 ± 2.7 kcal mol⁻¹) and the ionization potential of 3-cyclobutenyl radical (IP = 167.0 ± 1.4 kcal mol⁻¹) to give the heat of hydrogenation of cyclobutadiene ($\Delta H^\circ_{\text{H}_{\text{yd}}} = 64.7 \pm 3.8$ kcal mol⁻¹) and its heat of formation ($\Delta H^\circ_{\text{f}} = 102.2 \pm 3.8$ kcal mol⁻¹).⁵

The vinyl anion of cyclobutene ($2v^-$) was generated via the fluoride-induced desilylation of 1-trimethylsilylcyclobutene ($1v$, eq 4). This species readily can be distinguished from its allylic



isomer based upon their different reactivities (Table 2). For example, $2v^-$ deprotonates NH₃ to afford NH₂⁻ and reacts with COS to produce a C₄H₃O⁻ ion (*m/z* 67), neither of which are formed from $2a^-$. In contrast, $2a^-$ undergoes electron transfer with CS₂, whereas $2v^-$ does not. Consequently, we were able to show that under low-pressure CI conditions ($\sim 10^{-7}$ Torr), deprotonation of cyclobutene affords its allylic isomer rather

Table 2. Ion–Molecule Reaction Products for 1- and 3-Cyclobutenyl Anions ($2v^-$ and $2a^-$, Respectively)

reagent	reaction products	
	$2a^-$	$2v^-$
NH ₃	signal loss	NH ₂ ⁻ (<i>m/z</i> 16)
COS	HS ⁻ (<i>m/z</i> 33, ~70%),	HS ⁻ (<i>m/z</i> 33, 20%),
	C ₄ H ₃ S ⁻ (<i>m/z</i> 85, 30%)	CH ₂ =CHC≡CO ⁻ (<i>m/z</i> 67, 20%), C ₄ H ₃ S ⁻ (<i>m/z</i> 85, 60%)
CS ₂	HS ⁻ (<i>m/z</i> 33, ~15%),	HS ⁻ (<i>m/z</i> 33, ≤25%),
	CS ₂ ⁻ (<i>m/z</i> 76, 70%),	C ₄ H ₃ S ⁻ (<i>m/z</i> 85, ≥75%)
	C ₄ H ₃ S ⁻ (<i>m/z</i> 85, 15%)	

than the vinyl anion. Under the higher pressure conditions of a flowing afterglow device (~ 0.4 Torr), the allylic ion is too fragile to survive and only the vinyl species is observed, albeit in low conversions.²⁰

These results indicate that the proton affinity of $2v^-$ is similar to or larger than that of NH₂⁻ ($\Delta H^\circ_{\text{acid}}(\text{NH}_3) = 403.6 \pm 0.8$ kcal mol⁻¹), and bracketing is not a feasible method for refining this quantity because suitable reference compounds are not available in this range of the acidity scale. Therefore, the DePuy kinetic method was used and $\Delta H^\circ_{\text{acid}} = 404.6 \pm 1.5$ kcal mol⁻¹ was obtained for the vinyl position of cyclobutene (Table 1). This result is in accord with the reactivity data, G3 and W1 predictions of 403.9 and 404.0 kcal mol⁻¹, respectively, and a value of 405.8 kcal mol⁻¹ based upon the hybridization of cyclobutene and a previously reported linear correlation between $\Delta H^\circ_{\text{acid}}$ and $J(^{13}\text{C}-\text{H})$.^{21,22} Interestingly, the product ratios (*R*) for the reference silanes also were found to correlate with the electron affinity of R• (EA(R•) = $7.70 \times \ln R + 0.36$ eV, $r^2 = 0.994$). This result follows from the observation that $\Delta H^\circ_{\text{acid}}(\text{RH})$ is linearly correlated to EA(R•) for related families of compounds, including hydrocarbon acids which give localized anions.¹⁹ Consequently, the product ratio determination for the reaction of 1-trimethylsilylcyclobutene with HO⁻ not only gives the acidity of cyclobutene but also affords the electron affinity of 1-cyclobutenyl radical ($2v^\bullet$). The resulting value for the vinyl radical is 21.5 ± 2.0 kcal mol⁻¹ (0.93 ± 0.09 eV), which is in good agreement with a bracketed electron affinity of 0.96 ± 0.15 eV based upon the observation that $2v^-$ undergoes electron transfer with SO₂ (EA = 1.107 ± 0.008 eV) but not with chloropentafluorobenzene (EA = 0.82 ± 0.11 eV) and reagents with smaller electron affinities (Table 3).^{23,24} It also is well reproduced by G3 and W1 computations, which give values of 0.97 and 0.96 eV, respectively.

The vinyl C–H BDE of cyclobutene was derived using eq 3 and is 112.5 ± 2.5 kcal mol⁻¹. G3 and W1 predictions of 111.9 and 112.4 kcal mol⁻¹, respectively, are in excellent accord with this result. This bond energy also is larger than the G3 prediction for *cis*-2-butene (107.7 kcal mol⁻¹), which suggests that $2v^\bullet$ is destabilized relative to acyclic analogues (Table 4).

To put our measured bond energies in greater context, BDEs were computed for alkanes, cycloalkanes, and cycloalkenes

(20) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849–2852.

(21) The coupling constant for cyclobutene is 170 Hz, as given in ref 22, and $\Delta H^\circ_{\text{acid}} = -0.319J + 460.0$ kcal mol⁻¹, as given in ref 2.

(22) Hill, E. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2047–2049.

(23) The electron affinity also can be obtained using the linear correlation between $\Delta H^\circ_{\text{acid}}(\text{RH})$ and EA(R•) for localized carbanions ($\Delta H^\circ_{\text{acid}}(\text{RH}) = -0.613 \times \text{EA}(\text{R}^\bullet) + 414.7$ kcal mol⁻¹) reported in ref 19, but in this case this approach gives results with an average error of 4.2 kcal mol⁻¹. When we applied this to $2v^-$, we obtain EA = 16.5 kcal mol⁻¹.

(24) This approach fails for $2a^-$ because it is a delocalized ion whereas the reference compounds correspond to localized species.

(19) Fattahi, A.; Kass, S. R. *J. Org. Chem.* **2004**, *69*, 9176–9183.

Table 3. Electron Affinity Bracketing Results for 1-Cyclobutenyl Radical ($2\mathbf{v}^{\bullet}$)^a

compd	EA (eV)	electron transfer
carbon disulfide	0.58 ± 0.05	no
pentafluoropyridine	0.68 ± 0.11	no
chloropentafluorobenzene	0.82 ± 0.11	no
sulfur dioxide	1.107 ± 0.008	yes

^a All of the cited electron affinities come from ref 16.

Table 4. Summary of Experimental Quantities Determined in This Work along with G3 and W1 Predictions^a

quantity	expt	calcd	
		G3	W1
$\Delta H^{\circ}_{\text{acid}}(\mathbf{2H})$	400.9 ± 1.1 (allylic)	401.2	401.2
	404.6 ± 1.5 (vinylic)	403.9	404.0
EA($\mathbf{2a}^{\bullet}$)	3.9 ± 2.0	3.7	4.2
EA($\mathbf{2v}^{\bullet}$)	21.5 ± 2.0	22.4	22.1
BDE($\mathbf{2H}$)	91.2 ± 2.3 (allylic)	90.6	91.7
	112.5 ± 2.5 (vinylic)	111.9	112.4
$\Delta H^{\circ}_{\text{Hyd}}(\text{c-C}_4\text{H}_4)$	64.7 ± 3.8 ^b	63.5	64.8
$\Delta H^{\circ}_{\text{f}}(\text{c-C}_4\text{H}_4)$	102.2 ± 3.8 ^b	103.9	102.0

^a All values are in kcal mol⁻¹. ^b These values come from ref 5.

(Tables 5 and 6),^{25–31} some of which previously have been reported at the G3 level.^{4d,e} The alkane data serve to further benchmark the G3 and W1 results, and as expected these two computational methods are in excellent accord with each other and experiment. The largest deviation between these two procedures is 0.5 kcal mol⁻¹, and the largest disagreement with the experimental results given by Blanksby and Ellison is 0.8 kcal mol⁻¹. Therefore, it is quite surprising that the C–H bond energies for the cycloalkanes are predicted to be 3 to 4 kcal mol⁻¹ larger than the experimental values with the exception of cyclopentane, which is well reproduced by theory. Given the documented accuracy of these theoretical methods and the good accord between the G3 and W1 results, we are forced to conclude that the commonly cited C–H bond energies for cyclopropane, cyclobutane, and cyclohexane are most likely in error.

The literature value cited in Table 5 for cyclopropane comes from an equilibrium determination with Cl[•] in a very low-pressure pyrolysis reactor,³² the cyclobutyl C–H BDE was determined via iodination and competitive photobromination kinetics,³³ and the BDE for cyclohexane was derived from single-pulse shock tube measurements and a correlation between bromination activation energies and bond dissociation energies.^{33b,34} All of these methods for determining BDEs are experimentally demanding and subject to various pitfalls, but they also are capable of giving accurate thermochemical results.²⁸ Conse-

quently, there is no single reason for the discrepancy between experiment and theory, but it appears that a re-examination of some of the cycloalkyl C–H BDEs is warranted. It also is worth noting that our computations indicate that the C–H BDE for cyclopentane is 3 to 4 kcal mol⁻¹ smaller than that for cyclohexane, which can be attributed to the reduction of four eclipsing interactions upon the removal of a hydrogen atom from cyclopentane.

There is limited experimental data for cycloalkenes, but the computed vinyl C–H bond energies are in good accord with the available results. To our surprise, the bond strengths do not increase in going from larger to smaller rings as expected based upon hybridization. Instead, the opposite trend is observed (i.e., acyclic < 3 < 4 < 5), and cyclopentene is predicted to have the strongest C–H bond. The corresponding value for cyclohexene is 4.5 kcal mol⁻¹ smaller than that for cyclopentene and is the same as that for cyclopropene. The spread in energies for these compounds is only 6.2 kcal mol⁻¹, but the ordering is nonintuitive and reflects a combination of factors, including hybridization and delocalization of the unpaired electron. These two effects are counterbalancing since the latter preferentially stabilizes small ring radicals. This is qualitatively reflected by the Mulliken spin densities at the radical center that increase with ring size (e.g., 0.64 (3) < 0.84 (4) < 0.93 (5 and 6)).³⁵ Both of these effects operate in the same direction at the allylic position, and consequently these BDEs span a larger range (~17 kcal mol⁻¹) and the order is as expected (i.e., 3 > 4 > 5 ≈ 6), if one uses the computed bond energy for cyclopropene rather than the experimental value. This is reasonable because a number of very reliable computational approaches indicate that the measured BDE is too small by ~9–13 kcal mol⁻¹.⁴ It was also recognized in the original work that if cyclopropene radical cation rearranges then the reported BDE would be incorrect, and subsequently it was found that this ion does readily ring open.³⁶

Homoallylic bond energies for cyclopentene and cyclohexene also were computed, and they are the same as those for the corresponding cycloalkanes within the limits of the accuracy of these calculations. This suggests that homoconjugation is energetically unimportant in 4-cyclopentenyl and 4-cyclohexenyl radicals and, presumably, in most other homoallylic radicals.

Heats of hydrogenation and π bond strengths, which were obtained by taking the difference in the C–H BDEs of the cycloalkanes (BDE1) and their corresponding cycloalkyl radicals (BDE2), are given in Table 6. Experiment and theory are in good accord with $\Delta H^{\circ}_{\text{Hyd}}$ in that the disparity between the two ranges from 0.1 to 1.7 kcal mol⁻¹ and the average unsigned deviations are 0.6 (G3) and 1.1 (W1) kcal mol⁻¹. For the π bond energies, the values span almost a 10 kcal mol⁻¹ range and the disagreement with the predictions is almost as large (i.e., up to 8.2 kcal mol⁻¹). This is largely a reflection of the difference between the experimental and computational results for the cycloalkane C–H BDEs since BDE1 – BDE2 is equivalent to 2BDE1 – $\Delta H^{\circ}_{\text{Hyd}}$ – BDE(H–H). As for the G3

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Table 5. Alkane and Cycloalkane C–H Bond Energies^a

compd	BDE		expt			
	G3	W1	ref 25	ref 26	ref 27	ref 28
CH ₄	104.2	104.3	104.99 ± 0.03	104.9 ± 0.1	105.1 ± 0.2	105.0 ± 0.1
CH ₃ CH ₃	101.2	101.2	101.1 ± 0.4	101.1 ± 0.4	98.2 ± 1	100.5 ± 0.3
(CH ₃) ₂ CH ₂	98.9	98.4	98.6 ± 0.4	97.8 ± 0.5	95.1 ± 1	98.1 ± 0.7
CH ₃ CH ₂ CH ₂ CH ₃	98.8	98.8	98.2 ± 0.5	98.3 ± 0.5	95.5 ± 1	98.3 ± 0.5
<i>c</i> -C ₃ H ₆	109.2	109.0		106.3 ± 0.3	106.3 ± 0.3	106.3 ± 0.3
<i>c</i> -C ₄ H ₈	100.5	99.9		96.5 ± 1.0	96.5 ± 1.0	96.8 ± 1.0
<i>c</i> -C ₅ H ₁₀	96.4	96.9		96.4 ± 0.6	94.5 ± 1.0	95.6 ± 1.0
<i>c</i> -C ₆ H ₁₂	100.0			95.5 ± 1.0	95.5 ± 1.0	99.5 ± 1.2

^a All values are in kcal mol⁻¹.

Table 6. Alkene and Cycloalkene C–H Bond Energies^a

compd	BDE			$\Delta H_{\text{hyd}}^{\circ}$			π BDE		
	G3	W1	expt	G3	W1	expt ^b	G3	W1	expt ^c
<i>c</i> -C ₃ H ₄									
vinyl	109.6	109.8	106.7 ± 3.7 ^d	54.6	55.2	53.5 ± 0.6	59.2	58.6	54.9 ± 0.8
allyl	100.4	100.4	90.6 ± 4.0 ^e						
<i>c</i> -C ₄ H ₆									
vinyl	111.9	112.4	112.5 ± 2.5	32.4	32.4	30.7 ± 0.4	64.0	63.2	58.1 ± 1.5
allyl	90.6	91.7	91.2 ± 2.3						
<i>c</i> -C ₅ H ₈									
vinyl	113.9			26.5	27.2	26.4 ± 0.4	61.7	62.4	62.0 ± 0.8
allyl	84.2	85.0	82.3 ± 1.1 ^f						
hallyl ^g	96.8	96.9							
<i>c</i> -C ₆ H ₁₀									
vinyl	109.4			28.7		28.3 ± 0.3	66.6		58.4 ± 1.4
allyl	83.9		85 ± 1 ^h						
hallyl ^g	99.2								
Z-2-butene									
vinyl	107.7	108.5		28.4	29.1	28.3 ± 0.3	64.5		63.9 ± 0.7
allyl	86.0	87.0	89.7, 85.6 ± 1.5 ⁱ						

^a All values are in kcal mol⁻¹. ^b Cycloalkane and cycloalkene heats of formation come from refs 29 and 30. ^c These energies were obtained using the cycloalkane C–H BDEs given in ref 28. ^d The experimental value is for 3,3-dimethylcyclopropane. See ref 2. ^e Reference 3. ^f Reference 6. ^g hallyl = homoallyl. ^h Reference 7. ⁱ References 27 and 31, but the stereochemistry was not addressed.

ordering (i.e., 3 < 5 < 4 < 6), the π bond strength for cyclopentene seemingly is out of place. Presumably, this is related to the weak C–H BDE for cyclopentane relative to that for cyclobutane and cyclohexane.

Conclusions

Both the allyl and vinyl C–H BDEs for cyclobutene were measured in the gas phase using a thermodynamic cycle. The resulting values (91.2 ± 2.3 and 112.5 ± 2.5 kcal mol⁻¹, respectively) enable the heat of formation of cyclobutadiene to be experimentally established ($\Delta H_{\text{f}}^{\circ} = 102.2 \pm 3.8$ kcal mol⁻¹) and were compared to other cycloalkenes. High level G3 and W1 computational models indicate that the allylic C–H bond strengths decrease with increasing ring size and flexibility (i.e., 3 > 4 > 5 ≈ 6) as one would anticipate. In contrast, the vinyl C–H bond strength sequence is surprising and increases from cyclopropane to cyclopentene before falling off (i.e., 5 > 4 > 3 ≈ 6). This ordering reflects the interplay of at least two counterbalancing effects, hybridization and electron delocalization. The former preferentially stabilizes small ring radicals,

whereas the latter effect has the opposite influence. It was also found that the commonly cited C–H bond energies for cycloalkanes ((CH₂)_n, n = 3, 4, and 6) appear to be in error by 3 to 4 kcal mol⁻¹, and this discrepancy is approximately twice as large for cycloalkene π bond energies. Finally, we note that the allylic hydrogens in cyclobutene are only 3.7 ± 1.9 kcal mol⁻¹ more acidic in the gas phase than the vinyl ones. This represents a crossing point in that the vinyl position of cyclopropane is much more acidic than the allylic site, whereas for cyclopentene the order is reversed.

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Supporting Information Available: Computed structures and energies and complete ref 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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