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Carbon–Hydrogen Bond Dissociation Energies: The Curious Case of Cyclopropene

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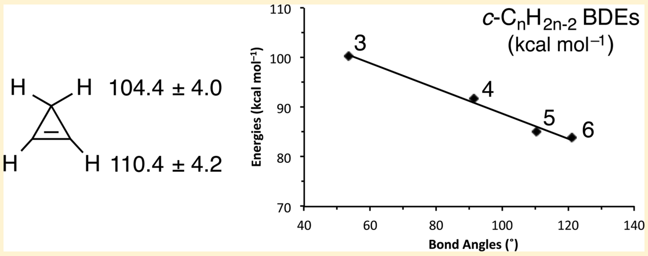
S *Supporting Information*

ABSTRACT: The ionization energy (IE) of the 3-cyclopropenyl radical (6.00 ± 0.17 eV) was measured in the gas phase by reacting 3-cyclopropenium cation (c-$C_3H_3^+$) with a series of reference reagents of known IEs. This result was combined in a thermodynamic cycle to obtain the heat of formation of c–$C_3H_3^\bullet$ (118.9 ± 4.0 kcal mol^{-1}) and the allylic C–H bond dissociation energy (BDE) of cyclopropene (104.4 ± 4.0 kcal mol^{-1}). These experimental values are well reproduced by high level G3 and W1 computations and reveal that the BDE is similar to that for cyclopropane and the vinyl position of cyclopropene. This is unprecedented and is a reflection of the unusual nature of cyclopropene.



INTRODUCTION

Carbon–hydrogen homolytic bond dissociation energies (BDEs) are the most commonly used measure for radical stability, and they play an invaluable role in probing reaction mechanisms and exploring structure–reactivity relationships.[1−4] They are also used in modeling atmospheric, combustion, and interstellar processes and are employed in numerous other applications.[5−7] As a result, bond energies have been the focus of large numbers of experimental and theoretical studies.

Small strained-ring compounds are another topic of general significance, and cyclopropene occupies a special place in this regard.[8−10] Its allylic cation, the 3-cyclopropenium ion (c-$C_3H_3^+$), is aromatic and remarkably stable, whereas the corresponding anion, 3-cyclopropenyl anion (c-$C_3H_3^-$), is the textbook example of an antiraromatic ion.[11−14] The latter view, however, is incorrect from an energetic point of view. That is, the gas-phase proton affinities of 3-cycloalkenyl anions (c-$C_nH_{2n-3}^-$, $n = 3-6$) were recently reported to increase linearly with the central C_1–C_2–C_3 bond angle, and the geometries distort from planarity when C_1–C_2–$C_3 \leq 104°$ as a result of the electrostatic repulsion.[15] There is nothing unique about c-$C_3H_3^-$ in this regard, so it is best viewed as nonaromatic. This raises a question about 3-cyclopropenyl radical (c-$C_3H_3^\bullet$): Is it a stabilized, destabilized or an ordinary allylic radical? Hückel theory indicates that it is aromatic in that c-$C_3H_3^\bullet$ is 0.17β more stable than allyl radical, whereas Glukhovtsev et al. have argued that it is not aromatic because G2 calculations indicate that the stabilization energy of 3-cyclopropenyl radical is much less than for the corresponding cation (i.e., 8.9 vs 59.1 kcal mol^{-1}).[16] To address this issue further, the allylic C–H BDE of cyclopropene is needed, and while a widely cited value of 90.6 ± 4.0 kcal mol^{-1} has been reported,[17] it is also known to be in error.[18]

In 1979, Defrees et al. generated a C_3H_4 radical cation from cyclopropene in an ion cyclotron resonance mass spectrometer and reacted it with a series of reference bases with known proton affinities.[17] As noted in the original publication, if the radical cation maintains the cyclic structure, then the measured proton affinity can be combined with the ionization energies of cyclopropene and hydrogen atom to afford the allylic C–H BDE. This was assumed to be the case, and the resulting bond energy is the only experimental source for this quantity. Chen subsequently noted, however, that c-$C_3H_4^{+\bullet}$ does not maintain its ring structure, and consequently the reported BDE is incorrect.[18] High level computations are also inconsistent with the experimental value and suggest that it is too small by ~10 kcal mol^{-1}.[16,19−21] If this is indeed the case, then the vinyl C–H bond of 3,3-dimethylcyclopropene, which was determined to be 106.7 ± 3.7 kcal mol^{-1},[22] would appear to be similar in strength to the allylic C–H bond energy of the parent compound. Such a situation is unprecedented, and in order to resolve this issue and establish the heat of formation of 3-cyclopropenyl radical, we report herein the "first" experimental determination of the allylic C–H BDE of cyclopropene. This was accomplished by making use of a gas-phase thermodynamic cycle, and the subsequent results were compared to high-level G3[23] and W1[24,25] computations.

RESULTS AND DISCUSSION

Cyclopropenium cation was generated in a FTMS by reacting CH_3^+ with acetylene, and then it was carefully isolated and vibrationally cooled with one or more pulses of argon to pressures of ~10^{-5} Torr. The resulting c-$C_3H_3^+$ ion was then

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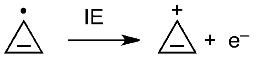
allowed to react with a series of reference compounds with known IEs,[26] and the products were monitored as a function of time. No electron transfer was observed with six different reagents with IEs ranging from 6.98 to 6.16 eV, but the 3-cyclopropenium cation does react with dimethyl tungstanocene (Me_2WCp_2) to afford $Me_2WCp_2^{+\bullet}$ (Table 1). These results indicate that the IE of 3-cyclopropenyl radical is between 5.84 and 6.16 eV, which enables us to assign IE(c-$C_3H_3^\bullet$) = 6.00 ± 0.17 eV or 138.4 ± 3.9 kcal mol^{-1}. This value is well reproduced by G3 (6.12 eV) and W1 (6.10 eV) predictions as well as G2 (6.06 eV),[16] RCCSD(T) (6.02 eV),[27] and CBSQ (6.17 eV)[28] results found in the literature. The IE of 3-cyclopropenyl radical is substantially smaller than that for allyl radical (8.13146 ± 0.00025 and 8.13088 ± 0.00024 eV)[29,30] and 3-cyclobutenyl radical (7.24 ± 0.06 eV),[31] but this is expected since c-$C_3H_3^+$ is an unusually stable aromatic ion.

Table 1. Bracketing Reaction of c-$C_3H_3^+$ with Reference Reagents with Known Ionization Energies

compd	IE[a]	ET[b]
Me_2WCp_2	5.84 ± 0.10	yes
E-p-$(NMe_2)C_6H_4CH{=}CH(p$-$C_6H_4OMe)$	6.16 ± 0.10	no
$NiCp_2$	6.24 ± 0.07	no
E-p-$(NMe_2)C_6H_4CH{=}CH(p$-$C_6H_4F)$	6.40 ± 0.10	no[c]
Et_2NNEt_2	6.50 ± 0.05	no[c]
c-C_4H_8NPh	6.80 ± 0.02	no
$PhNEt_2$	6.98 ± 0.05	no[c]

[a] Values come from ref 26. The uncertainties for the two benzenamines were not reported, so a value of ±0.10 eV was adopted since this corresponds to the accuracy of the scale. [b] ET = electron transfer. A yes in this column means that electron transfer was observed whereas a no indicates that it was not. [c] Proton transfer was observed.

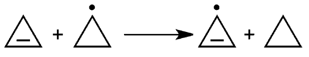
The heat of formation of 3-cyclopropenyl radical can be derived from our experimentally determined ionization energy and the previously measured heat of formation for c-$C_3H_3^+$ (257.3 ± 0.8 kcal mol^{-1})[32] as illustrated in eq 1.This leads to



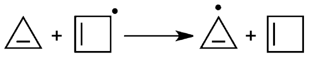
(1a)

$$\Delta H^\circ_f(c\text{-}C_3H_3^\bullet) = \Delta H^\circ_f(c\text{-}C_3H_3^+) - \mathrm{IE} \qquad (1b)$$

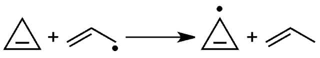
$\Delta H^\circ_f(c$-$C_3H_3^\bullet)$ = 118.9 ± 4.0 kcal mol^{-1}, which can be combined with $\Delta H^\circ_f(c$-$C_3H_4)$ = 66.2 ± 0.6 kcal mol^{-1} and $\Delta H^\circ_f(H^\bullet)$ = 52.1 kcal mol^{-1} in a similar fashion to afford BDE (c-C_3H_3−H) = 104.4 ± 4.0 kcal mol^{-1} for the allylic C−H bond.[33] High level G3 (100.4 kcal mol^{-1}) and W1 (100.4 kcal mol^{-1}) calculations are in good accord with this result, nevertheless in addition to these direct computations of this quantity, three isodesmic reactions were also examined (eqs 2−4). In this latter approach, the computed reaction enthalpies



(2)



(3)



(4)

were combined with the experimental C−H BDEs of the auxiliary compounds (i.e., cyclopropane, cyclobutene, and propene) to derive the allylic C−H BDE of cyclopropene (Table 2).[1,34,35] All of these approaches span a narrow range (1.9 (G3) and 1.3 (W1) kcal mol^{-1}) with average values of 101.3 (G3) and 100.5 (W1) kcal mol^{-1} when one excludes the predictions from eq 2. This was done because the G3 and W1 C−H BDEs for cyclopropane differ from the experimental BDE by a large enough amount (i.e., 2.9 (G3) and 2.7 (W1) kcal mol^{-1}) to question its reliability.[35] These computations, consequently are in good accord with our experimental determination and are within the uncertainty of the measurement.

Table 2. G3 and W1 Computations of the Allylic Carbon−Hydrogen Bond Dissociation Energy of Cyclopropene[a]

	ΔH°_{rxn}		BDE (c-C_3H_3−H)		
method	G3	W1	G3	W1	expt
direct determination			100.4	100.4	
eq 2[b]	−8.8	−8.6	97.5	97.7	
eq 3[c]	9.8	8.7	101.1	99.4	
eq 4[d]	13.5	12.9	102.3	101.7	
avg[e]			101.3	100.5	104.4 ± 4.0

[a] All values are in kcal mol^{-1}. [b] BDE(c-C_3H_5−H) = 106.3 ± 0.3 kcal mol^{-1}; see ref 34. [c] BDE(c-C_4H_5−H) = 91.2 ± 2.3 kcal mol^{-1}; see ref 35. [d] BDE(C_3H_5−H) = 88.8 ± 0.4 kcal mol^{-1}; see ref 1. [e] The BDE obtained from eq 2 was not used in the average; see the text for details.

3,3-Dimethylcyclopropene has a C−H BDE at the vinyl position of 106.7 ± 3.7[22] kcal mol^{-1}, and if one corrects this value for the presence of the two methyl groups using the G3 difference in bond energies between the parent compound and its 3,3-dimethyl derivative (i.e., the BDE for c-C_3H_3−H is larger by 3.3 kcal mol^{-1}, and we arbitrarily adopt an uncertainty of ±2 kcal mol^{-1} for this quantity), then one obtains 110.0 ± 4.2 kcal mol^{-1} for cyclopropene. This BDE is only 5.6 ± 5.8 kcal mol^{-1} larger than for the allylic position of cyclopropene which is well reproduced by both G3 and W1 predictions of 9.2 and 9.4 kcal mol^{-1}, respectively. It is also a remarkably small difference for these two very different types of bonds especially when one compares this difference to that for cyclobutene (i.e., 21.3 ± 3.4 (expt), 21.3 (G3) and 20.7 (W1) kcal mol^{-1}), *cis*-2-butene (i.e., 21.7 (G3) and 21.5 (W1) kcal mol^{-1}), and cyclopentene (i.e., 29.7 (G3) kcal mol^{-1}).[35] One can attribute the small ΔBDE for cyclopropene, at least in part, to the small vinyl C−H bond energy resulting from an allylic-type delocalization of the vinyl radical via its interaction with the distal carbon−carbon bond.[22] As for the allylic C−H BDE in cyclopropene, it is larger than those for cyclobutene, cyclopentene, and cyclohexene by 13.2 ± 4.6, 22.1 ± 4.1, and 19.4 ± 4.1 kcal mol^{-1}, respectively.[35] These differences presumably are a reflection of the constrained nature of the allylic radical in the three-membered ring. To assess this further, the allylic C−H BDEs for these ring compounds were plotted versus their central C−C−C bond angles and a straight line results (Figure S1, Supporting Information). In order to compare the 3-cyclopropenyl radical with its corresponding anion and cation, similar correlations for the proton affinities of 3-cycloalkenyl anions and the hydride affinities of 3-cycloalkenyl cations were plotted and all of the data were normalized relative to the six-membered ring so that it can be compared in one graph (Figure 1).[15] As can be seen for the cations, 3-cyclopropenyl cation does not lie on the correlation and is 22 kcal mol^{-1} more stable than predicted because it is an aromatic ion.

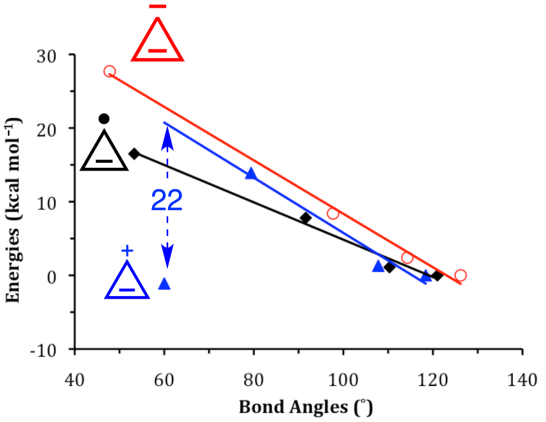


Figure 1. Cycloalkene (C_nH_{2n-2}, n = 3−6) acidities (red circles), bond dissociation energies (black diamonds), and hydride dissociation energies (blue triangles) vs B3LYP/cc-pVT(+d)Z central C−C−C bond angles; the acidities and hydride dissociation energies come from ref 15.

In contrast, neither 3-cyclopropenyl anion or 3-cyclopropenyl radical deviate from their corresponding lines, and thus both species are energetically best viewed as nonaromatic. This indicates that the allylic C−H BDE of cyclopropene is larger than for other cycloalkenes because of the constrained geometry and reduced central C−C−C bond angle (i.e., the B3LYP/cc-pVT(+d)Z C1−C2−C3 bond angles for 3-cyclopropenyl and allyl radicals are 53.3° and 125.1°, respectively). This results in decreased stabilization of the allylic radical due to enhanced electrostatic repulsion of the three π electron system since it occupies a smaller volume than an analogous unconstrained species.

As for the structure of 3-cyclopropenyl radical, it is predicted to be nonplanar and adopts a C_s geometry. Its C_2 form is only 2.9 kcal mol^{-1} less stable at the W1 level, however, even though it is computed to be a transition structure for the interconversion of the C_S species (Figure 2). This behavior is identical to that for 3-cyclopropenyl anion, but the radical geometries are much less severely distorted. A similar situation applies to the allylic radical of cyclobutene (i.e., it is planar whereas the corresponding anion is not) and is consistent with an electrostatic argument accounting for the structures of these species.[15]

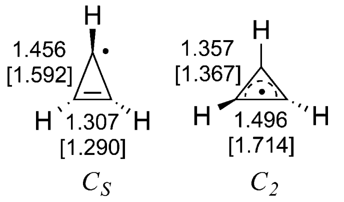


Figure 2. Computed B3LYP/cc-pVTZ(+d) structures for the C_S and C_2 3-cyclopropenyl radicals. Values for the corresponding anions are given in brackets. The C−H out-of-plane angles for the C_S species are 44.7° (C3) and 0.3° (C1 and C2) for the radical and 73.5° and 10.0°, respectively, for the anion. For the C_2 structures, the out-of-plane angles at C1 and C2 are 28.0° (radical) and 56.2° (anion).

CONCLUSIONS

The heat of formation (118.9 ± 4.0 kcal mol^{-1}) of 3-cyclopropenyl radical (i.e., c-$C_3H_3^\bullet$) and the allylic C−H BDE of cyclopropene (104.4 ± 4.0 kcal mol^{-1}) were measured by bracketing the ionization energy of c-$C_3H_3^\bullet$ in the gas phase and making use of a thermodynamic cycle. High level G3 and W1 computations are in good accord with these quantities, and thus both ΔH_f°(c-$C_3H_3^\bullet$) and BDE (c-C_3H_3−H) need to be revised upward by 13.8 kcal mol^{-1}. In addition, the view of 3-cyclopropenyl radical that emerges is also different. It is weakly stabilized in that the presence of the double bond in cyclopropene lowers the C−H bond energy by only 1.9 ± 4.1 kcal mol^{-1}; W1 theory gives a difference of 8.6 kcal mol^{-1} of which 2.7 kcal mol^{-1} is due to the discrepancy for the C−H BDE of cyclopropane. A plot of cycloalkene (C_nH_{2n-2}, n = 3−6) BDEs versus the central C_1−C_2−C_3 bond angle of these allylic radicals is linear including the point for cyclopropene. This indicates that the radical is nonaromatic based upon energetic considerations and allylic resonance is less effective when the π system has three or four electrons and occupies less space.

Cyclopropene has relatively weak vinyl and strong allylic C−H bond energies, and they are estimated to differ by only 5.6 ± 5.8 kcal mol^{-1}. This value is predicted to be 9.4 kcal mol^{-1} by W1 computations and is a consequence of the ring strain that makes cyclopropene such an unusual compound.

EXPERIMENTAL SECTION

General Methods. Nickelocene, *N*-phenylpyrolidine, and *N*,*N*-diethylbenzeamine were purchased and used as received, while *N*,*N*-dimethyl-*E*-4-(2-(4-methoxyphenyl)ethenyl)benzenamine,[36,37] *N*,*N*-dimethyl-*E*-4-(2-(4-fluorophenyl)ethenyl)benzenamine,[36,37] tetraethylhydrazine,[38] and dimethyltungstanocene[39,40] were prepared as described in the literature. The hydrazine was purified before use by preparative gas chromatography with a 4 m × 6.4 mm 10% SE30 column on chromosorb P. A He flow rate of 30 mL min^{-1} and injector, column, and detector temperatures of 160, 60, and 180 °C, respectively, were employed.

Gas-Phase Experiments. A dual cell Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and controlled by a workstation running IonSpec Omega ver. 8 software was used for this work. Cyclopropenium cation (c-$C_3H_3^+$) was generated in the source cell by reacting methyl cation (generated by 65 eV electron ionization (EI) of methane) with acetylene as previously described.[41] The resulting c-$C_3H_3^+$ ion was transferred to the analyzer cell, and after a pulse of argon up to a pressure of ~10^{-5} Torr and a subsequent 1000 ms pump out and cooling period, the ion of interest was isolated using a stored-waveform inverse Fourier transform (SWIFT) excitation[42] with a 20 amu window or via single frequency chirp excitations.[43] Electron-transfer reactions were then carried out with reference reagents with known ionization energies (IEs) by leaking constant pressures of the compounds of interest into the analyzer side of the instrument. Whenever electron transfer was observed, control experiments were carried out in which cyclopropenyl cation was continually ejected from the analyzer cell (double resonance), c-$C_3H_3^+$ was not transferred to the analyzer cell, and branching ratios were determined to ascertain whether the observed products are due to primary or secondary processes. In addition, reaction conditions were chosen so that if any of the acyclic ion (i.e., propargyl cation) was formed during the EI process, it would react away during the pump out and ion cooling time period since it has a much higher IE (8.67 ± 0.02 eV)[44] than any of the reagents that were used.

Computations. G3[23] and W1[24,25] calculations were carried out as previously described in the literature using Gaussian 09[45] on workstations at the Minnesota Supercomputing Institute for Advanced

Computational Research. All of the resulting energies are given as enthalpies at 298 K and were obtained using scaled Hartree−Fock (0.8929, G3) and B3LYP (0.985, W1) vibrational frequencies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1, calculated structures, energies, and the complete citation to ref 35 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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