

Why Does Cyclopropene Have the Acidity of an Acetylene but the Bond Energy of Methane?

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
Abstract: The gas-phase acidity of 3,3-dimethylcyclopropene (**1**) has been measured by bracketing and equilibrium techniques. Consistent with simple hybridization arguments, our value ($\Delta H_{\text{acid}}^{\circ} = 382.7 \pm 1.3$ kcal mol⁻¹) is indistinguishable from that for methylacetylene (i.e., $\Delta\Delta H_{\text{acid}}^{\circ}(\mathbf{1} - \text{CH}_3\text{C}\equiv\text{CH}) = 1.6 \pm 2.5$ kcal mol⁻¹). The electron affinity of 3,3-dimethylcyclopropenyl radical (**1r**) was also determined (EA = 37.6 ± 3.5 kcal mol⁻¹), and these quantities were combined in a thermodynamic cycle to afford the homolytic C–H bond dissociation energy. To our surprise, the latter quantity (107 ± 4 kcal mol⁻¹) is the same as that for methane, which cannot be explained in terms of the s-character in the C–H bonds. An orbital explanation (delocalization) is proposed to account for the extra stability of **1r**. All of the results are supplemented with G3 and B3LYP computations, and both approaches are in good accord with the experimental values. We also note that for simple hydrocarbons which give localized carbanions upon deprotonation there is an apparent linear correlation between any two of the following three quantities: $\Delta H_{\text{acid}}^{\circ}$, BDE, and EA. This observation could be of considerable value in many diverse areas of chemistry.

Introduction

A large number of carbanions have been generated and studied in the gas phase over the past four decades.¹ From these efforts, it has become clear that there are many similarities to more traditional liquid-phase investigations. For example, direct parallels can be drawn between the reactivity, selectivity, and mechanistic pathways for substitution, elimination, oxidation, reduction, and condensation reactions.^{2,3} Condensed media and gaseous thermodynamic data also tend to mirror each other.^{4,5} This is not surprising for homolytic bond dissociation energies (BDEs),⁶ which are relatively insensitive to solvent changes and differ little from gas-phase values. In contrast, acidities and electron affinities vary considerably with the nature of the solvent, but even in these cases linear correlations can be obtained if one compares gas-phase data to those in polar aprotic media such as dimethyl sulfoxide or *N*-methylpyrrolidin-2-one. The same physical phenomena (e.g., inductive and resonance effects) also can be used to account for the ions' stability as one would expect.

Hybridization is well-known to affect acidities and bond dissociation energies, and both quantities increase with the s-character in a carbon–hydrogen bond. This nicely accounts

Table 1. Acidities, Bond Energies, and Hybridizations of Simple Hydrocarbons^a

cmpd	hybridization (<i>J</i> , Hz) ^b	acidity		BDE
		$\Delta H_{\text{acid}}^{\circ}$ (gas)	p <i>K</i> _A (liq.)	ΔH° (gas)
CH ₄	125	416.8 ± 0.7	48	104.99 ± 0.03
CH ₂ =CH ₂	156	408.8 ± 0.3	44	110.7 ± 0.6
HC≡CH	249	376.86 ± 0.14	24	133.32 ± 0.07
c-C ₃ H ₆	161	411.5 ± 2.0	46	106.3 ± 0.3
	202	398.0 ± 2.0	35 - 37	
	166 ^c	409.7 ± 2.0		109.7 ± 3.3
1	228	382.7 ± 1.3	30	106.7 ± 3.7

^a All energies are in kcal mol⁻¹. See refs 1 and 6 for the cited quantities.
^b ¹³C–H coupling constant. ^c This value is for the parent compound.

for the acidities and BDEs of methane, ethylene, and acetylene as well as small strained-ring compounds such as cyclopropane, bicyclo[1.1.0]butane, and bicyclo[1.1.1]pentane (Table 1).⁷ It also explains why the vinyl hydrogens in cyclopropenes are relatively acidic and undergo hydrogen–deuterium exchange in *tert*-BuOK/*tert*-BuOD⁸ given that they have nearly the same

- (1) For example, see: Bartmess, J. E. NIST Chemistry WebBook, NIST Standard Reference Database Number 69. In *Secondary NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899 (<http://webbook.nist.gov>) and refs therein.
- (2) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146–153.
- (3) For pertinent reviews, see: *Encyclopedia of Mass Spectrometry*; Gross, M. L., Caprioli, R., Eds.; Elsevier: New York, 2001; Vols. 1–10.
- (4) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463–469.
- (5) Bordwell, F. G.; Zhang, X. M. *Acc. Chem. Res.* **1993**, *26*, 510–517.
- (6) In this work, the bond dissociation energy is equivalent to the bond dissociation enthalpy (i.e., BDE(RH) = $\Delta H_{298}(\text{RH})$).

- (7) (a) Ervin, K. M.; DeTuri, V. F. *J. Phys. Chem. A* **2002**, *106*, 9947–9956. (b) Reed, D. R.; Kass, S. R.; Mondanaro, K. R.; Dailey, W. P. *J. Am. Chem. Soc.* **2002**, *124*, 2790–2795. (c) Kass, S. R.; Chou, P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899–7900. (d) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp. 293–296. (e) Battiste, M. A.; Coxon, J. M. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley & Sons: New York, 1987; pp. 255–305.

hybridization as acetylene. The gas-phase acidity and C–H BDE of a cyclopropene, however, have not been reported to date. In this paper, we present measurements of the gas-phase acidity of 3,3-dimethylcyclopropene (**1**) and the electron affinity of 3,3-dimethylcyclopropenyl radical (**1r**) via gas-phase equilibrium and bracketing techniques, respectively. These results are compared to high level ab initio (G3)⁹ and density functional theory (B3LYP)¹⁰ calculations and are combined in a thermodynamic cycle to afford the vinyl C–H BDE of **1**. As expected, the acidity is the same as that of an acetylene, but, surprisingly, the bond energy is 25–30 kcal mol⁻¹ smaller. These apparently contradictory results are explained, and a linear correlation between BDEs and hybridization is noted. The important implications of this latter finding also are noted.

Experimental Section

Cyclopropene and 3,3-dimethylcyclopropene were prepared using literature procedures.¹¹ 1,2-Dideuterio-3,3-dimethylcyclopropene (>90% *d*₂) was synthesized via two successive hydrogen–deuterium exchange reactions with potassium *tert*-butoxide/*tert*-butyl alcohol-OD also as reported.¹² All other reagents were obtained from commercial sources and used as supplied.

The initial gas-phase acidity and labeling studies were carried out at room temperature with a variable temperature flowing afterglow device, which previously has been described.¹³ This work was subsequently reproduced and extended using a dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and controlled by a Sun workstation running the Odyssey version 4.2 software package. Hydroxide ion was generated in the analyzer (first) cell by dissociative electron attachment of water and was allowed to react with 3,3-dimethylcyclopropene to afford the desired *M* – 1 ion. This anion was subsequently transferred to the source (second) cell and collisionally cooled with a pulse of argon (~10⁻⁵ Torr). Neutral reagents were added into the source cell via slow leak valves, and the formation of product ions was monitored as a function of time. Alternatively, methoxide was produced in the analyzer cell by reacting methanol with hydroxide and was transferred into the second cell where it was collisionally cooled and allowed to react with 3,3-dimethylcyclopropene. In this way, both forward and reverse proton-transfer rate constants were measured, and the equilibrium constant ($K = k_1/k_{-1}$) for the acid–base reaction was obtained.

Calculations were carried out using Gaussian 98¹⁴ and GAMESS¹⁵ on IBM and SGI workstations at the Minnesota Supercomputer Institute,

Table 2. Summary of Bracketing Studies for 3,3-Dimethylcyclopropene (**1**)

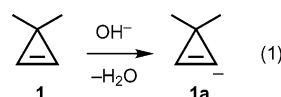
ref. acid (HX)	$\Delta H^\circ_{\text{acid}}$ (kcal mol ⁻¹) ^a	proton transfer	
		forward rxn (1a + HX)	reverse rxn (1 + X ⁻)
NH ₃	404.3 ± 0.30	no	yes
H ₂ O	390.7 ± 0.1	no (0) ^b	yes
MeOH	382.4 ± 0.5	yes (1) ^b	yes
EtOH	379.1 ± 1.2	yes (0) ^b	no ^c
<i>tert</i> -BuOH	376.4 ± 0.7	yes (0) ^b	no

^a Acidity values taken from ref. 1. ^b Parenthetical values correspond to the number of observed H/D exchanges with ROD (R = D, Me, Et, and *tert*-Bu). ^c A small amount of EtO⁻ is observed, but this reaction is inefficient.

and orbitals were visualized using GaussView 2.08¹⁶ and MacMolPlot v5.3.5.¹⁷ R(U)B3LYP optimizations and vibrational frequencies were computed with the 6-31+G(d) basis set, while G3 results were obtained as described in the literature.⁹ The resulting DFT and G3 acidities, bond dissociation energies, and reaction energies, but not the electron affinities, were corrected to 298 K using the B3LYP and HF frequencies, respectively. In the former case, the zero-point energies and vibrational frequencies were left unscaled, whereas these quantities were corrected by a factor of 0.8929 in the latter instance.¹⁸

Results/Discussion

3,3-Dimethylcyclopropene (**1**) is a highly strained but thermally stable hydrocarbon up to ~200 °C.^{11c} Its conjugate base, 3,3-dimethylcyclopropen-1-yl anion (**1a**), was generated in the gas phase by deprotonating **1** with hydroxide ion (eq 1). The



thermodynamic stability of the resulting anion was assessed by measuring its proton affinity and the electron affinity of its corresponding radical (**1r**). The former value was initially obtained using a flowing afterglow device and subsequently reproduced with a FTMS by observing the occurrence or nonoccurrence of proton transfer with a series of standard reference acids and bases (Table 2). In particular, **1a** was found to deprotonate *tert*-butyl alcohol, ethanol, and methanol but not less acidic compounds such as water and ammonia. In the reverse direction, amide, hydroxide, and methoxide readily abstract a proton from **1**, whereas weaker bases such as ethoxide and *tert*-butoxide either abstract a proton very inefficiently or do not abstract a proton at all. Deuterated reagents also were employed, and MeOD induces a single hydrogen/deuterium exchange as expected for **1a**, whereas EtOD and *tert*-BuOD only give deuterium transfer. If **1-d**₂ is used, where the isotopic labels are at the vinyl positions, then **1a-d**₁ is formed upon reaction with hydroxide ion. These results taken together indicate that PA(**1a**) or equivalently $\Delta H^\circ_{\text{acid}}(\mathbf{1}) = 382 \pm 2$ kcal mol⁻¹.¹⁹

- (8) Dorko, E. A.; Mitchell, R. W. *Tetrahedron Lett.* **1968**, 341–343.
 (9) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.
 (10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
 (11) (a) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* **1966**, *31*, 638. (b) Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Dyachenko, A. I.; Savilova, S. F.; Nefedov, O. M. *Synthesis* **1982**, 296–297. (c) Walsh, R.; Untiedt, S.; Stohlmeier, M.; de Meijere, A. *Chem. Ber.* **1989**, *122*, 637–642. (d) Binger, P. *Synthesis* **1974**, 190–192.
 (12) (a) De Mare, G. R.; Panchenko, Y. N.; Abramov, A. V.; Baird, M. S.; Tverezovskii, V. V.; Nizovtsev, A. V.; Bolesov, I. G. *Zh. Fiz. Khim.* **2000**, *74*, 432–440. (b) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53–127.
 (13) (a) Kass, S. R.; Guo, H.; Dahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366–371. (b) Ahmad, M. R.; Kass, S. R. *J. Am. Chem. Soc.* **1996**, *118*, 1398–1407.
 (14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Lui, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Ketih, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revisions A.9–11, Gaussian, Inc.: Pittsburgh, PA, 1998.

- (15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
 (16) GaussView, rev. 2.08, Semichem, Inc. for Gaussian, Inc., 1998.
 (17) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Modell.* **1998**, *16*, 133–138.
 (18) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345–350.
 (19) Cyclopropene was found to be less acidic, and we estimate $\Delta H^\circ_{\text{acid}} = 385 \pm 3$ kcal mol⁻¹, which is in good accord with predicted values of 386.6 (G3) and 384.5 (B3LYP) kcal mol⁻¹.

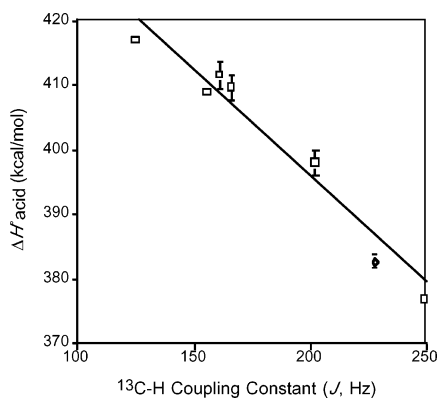
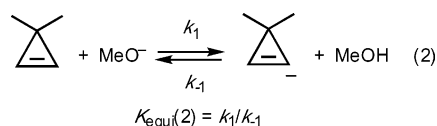


Figure 1. Gas-phase acidities versus hybridization as reflected by ^{13}C – ^1H coupling constants. Reference compounds are indicated by squares and were used to derive the indicated least-squares line ($\Delta H_{\text{acid}}^{\circ} = -0.319J + 460.0$, $r^2 = 0.96$), while **1** is represented by a diamond.

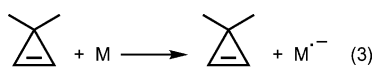
To refine this acidity determination, the forward (k_1) and reverse (k_{-1}) rate constants for proton transfer with methanol were measured in a FTMS to obtain the equilibrium constant (eq 2). Five independent determinations were carried out in the



forward direction and six for the reverse process to afford $k_1 = (1.29 \pm 0.11) \times 10^{-9}$ and $k_{-1} = (4.04 \pm 0.47) \times 10^{-10}$ cm^3 molecule $^{-1}$ s $^{-1}$, where the given uncertainties are the standard deviation in the data. The resulting equilibrium constant ($K_{\text{equi}(2)}$) is 3.20 ± 0.46 , but given the difficulties in measuring neutral gas pressures, a more conservative error for K of $\pm 100\%$ was used for the subsequent data analysis. This leads to $\Delta\Delta G_{\text{acid}}^{\circ}(\text{MeOH}) = -0.7 \pm 0.6$ kcal mol $^{-1}$, which can be combined with $\Delta G_{\text{acid}}^{\circ}(\text{MeOH}) = 375.1 \pm 1.1$ kcal mol $^{-1}$ to give $\Delta G_{\text{acid}}^{\circ}(\mathbf{1}) = 374.4 \pm 1.3$ kcal mol $^{-1}$. B3LYP/6-31+G(d) geometries and vibrational frequencies were used to derive $\Delta S_{\text{acid}}^{\circ}(\mathbf{1}) = 27.6$ eu, which enables us to obtain $\Delta H_{\text{acid}}^{\circ}(\mathbf{1}) = 382.7 \pm 1.3$ kcal mol $^{-1}$. This value is in excellent accord with our bracketing determination and computed 298 K acidities of 381.9 (B3LYP/6-31+G(d)) and 383.6 (G3) kcal mol $^{-1}$.

To put this quantity in perspective, we note that $\Delta H_{\text{acid}}^{\circ}(\text{CH}_2=\text{CH}_2) = 409.4 \pm 0.6$ kcal mol $^{-1}$ and **1** is 26.7 ± 1.4 kcal mol $^{-1}$ more acidic than ethylene. This is consistent with a simple hybridization argument as illustrated in Figure 1 and accounts for the fact that 3,3-dimethylcyclopropene and methylacetylene have the same acidity (i.e., $\Delta\Delta H_{\text{acid}}^{\circ}(\mathbf{1} - \text{CH}_3\text{C}\equiv\text{CH}) = 1.6 \pm 2.5$ kcal mol $^{-1}$).

The electron affinity of 3,3-dimethylcyclopropen-1-yl radical (**1r**) was measured by examining electron-transfer reactions between **1a** and a series of standard reference compounds (eq 3). Each experiment was carried out as a function of time and



carefully monitored to ensure that any observed electron-transfer product was due to the reaction of **1a** with the selected reagent. Electron transfer was observed with *p*-nitrobenzonitrile (EA = 1.691 ± 0.087 eV) and 3,5-bis(trifluoromethyl)nitrobenzene

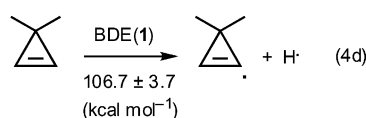
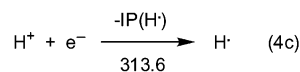
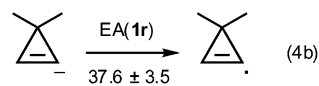
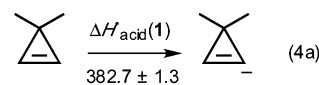
Table 3. Electron Affinity Bracketing Results for 3,3-Dimethylcyclopropen-1-yl Radical (**1r**)

ref. compd	EA (eV) ^a	electron transfer 1r
<i>p</i> -FC ₆ H ₄ NO ₂	1.12 ± 0.10	no
<i>m</i> -CF ₃ C ₆ H ₄ NO ₂	1.41 ± 0.10	no
<i>m</i> -NO ₂ C ₆ H ₄ CN	1.57 ± 0.10	no
<i>p</i> -NO ₂ C ₆ H ₄ CN	1.691 ± 0.087	yes
3,5-(CF ₃) ₂ C ₆ H ₃ NO ₂	1.79 ± 0.10	yes

^a Values taken from ref 1.

(EA = 1.79 ± 0.10 eV), but not with *m*-nitrobenzonitrile (EA = 1.57 ± 0.10 eV) and compounds with lower electron affinities (Table 3). These results enable us to assign EA(**1r**) = 1.63 ± 0.15 eV (37.6 ± 3.5 kcal mol $^{-1}$), which is in good accord with computed values of 1.52 (B3LYP/6-31+G(d)) and 1.62 eV (G3) and a preliminary estimate of 1.56 eV obtained by negative ion photoelectron spectroscopy.²⁰

For comparison purposes, it is interesting to note that EA(CH₂=CH) = 0.667 ± 0.024 eV (15.4 ± 0.6 kcal mol $^{-1}$),²¹ which is 22.2 ± 3.6 kcal mol $^{-1}$ less than the electron affinity of **1r**. This difference is similar to the relative acidities of 3,3-dimethylcyclopropene and ethylene and can be accounted for by a hybridization argument. The electron affinity of **1r**, however, is 1.09 ± 0.15 eV (25.1 ± 3.5 kcal mol $^{-1}$) less than that for 1-propynyl radical (CH₃C≡C).²² This is surprising and cannot be accounted for by the hybridization of 3,3-dimethylcyclopropene and methylacetylene because they have similar s-characters (46–50%) in the bonds of interest. Given the normal acidity of **1**, it appears that **1r** is unusually stable. If this is correct, then the BDE for 3,3-dimethylcyclopropene must be greatly reduced. This quantity was determined using the thermodynamic cycle illustrated in eq 4 (all values in kcal mol $^{-1}$) and is 106.7 ± 3.7 kcal mol $^{-1}$. When this value is refined, we anticipate that it will be ~ 2 kcal mol $^{-1}$ smaller (i.e., 105 kcal mol $^{-1}$) and halfway between the B3LYP and G3 predictions of 103.2 and 107.2 kcal mol $^{-1}$, respectively.



So, **1** has a C–H BDE that is essentially the same as that for methane (104.9 ± 0.1 kcal mol $^{-1}$) and much less than that for acetylene (132.8 ± 0.7 kcal mol $^{-1}$). This finding deviates from the apparent linear dependence of BDEs and heteronuclear ^{13}C –

(20) Polak, M. L.; Lineberger, W. C.; Kass, S. R., unpublished results.

(21) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750–5759.

(22) Robinson, M. S.; Polak, M. L.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc.* **1995**, *117*, 6766–6778.

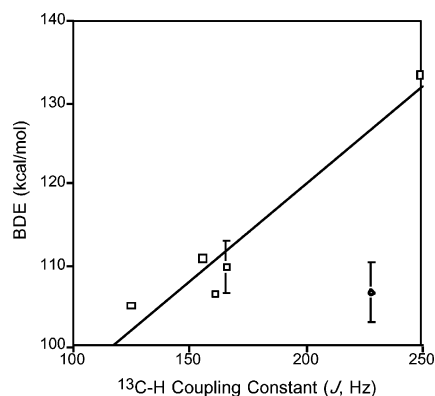
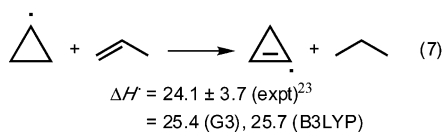
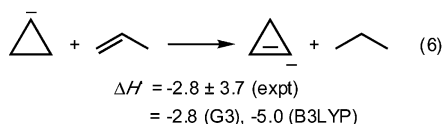
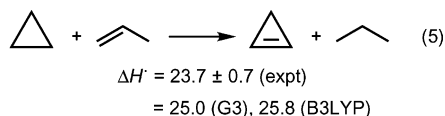


Figure 2. Gas-phase bond dissociation energies versus hybridization as reflected by $^{13}\text{C}-^1\text{H}$ coupling constants. Reference compounds are indicated by squares and were used to derive the indicated least-squares line ($\text{BDE} = 0.237J + 72.3$, $r^2 = 0.93$), while **1r** is represented by a diamond.

^1H coupling constants (Figure 2), but is in accord with **1r** being unusually stable and raises the following question: why does 3,3-dimethylcyclopropene have the acidity of an acetylene but the bond dissociation energy of methane?

To address this apparent paradox, three isodesmic reactions in which the incorporation of a double bond into cyclopropane, cyclopropyl anion, and cyclopropyl radical were examined (eqs 5–7). The first transformation provides a measure of the



differential strain energy (ΔSE) between cyclopropane and cyclopropene (eq 5) and is endothermic as written because the latter compound is more strained. This comparison provides a value for ΔSE ($23.7 \text{ kcal mol}^{-1}$) which is in keeping with G3 and B3LYP calculations and well-accepted results based upon Benson's group equivalents.²⁴ In the second process (eq 6), the additional strain of incorporating a double bond into a three-membered ring is compensated for by the additional stability of having an anion center at a carbon atom with more s-character (i.e., $\sim 33\%$ vs 46%). Consequently, the reaction is slightly exothermic as written. Both of these effects (strain and hybridization) reinforce each other to the detriment of cyclopropenyl radical in the last transformation (eq 7), but this reaction is energetically no worse than the first one. This indicates that there is a stabilizing interaction in **1r** which has not been addressed. An orbital explanation suggests itself, and there is a favorable interaction between the radical center (C1)

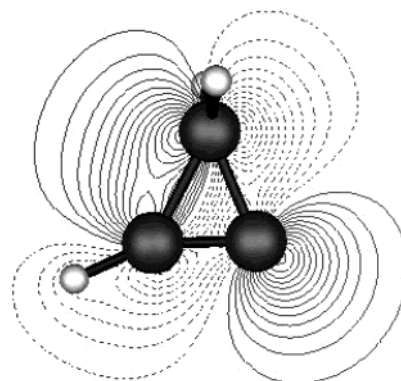


Figure 3. Singly occupied molecular orbital (SOMO) of 1-cyclopropenyl radical.

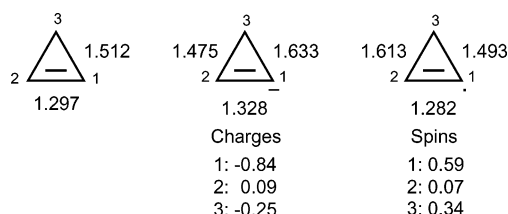


Figure 4. Computed B3LYP/6-31+G(d) geometries and Mulliken population charges and spin densities; hydrogen atom contributions have been summed into the carbon atoms to which they are attached.

and the bonding Walsh orbital between C2–C3 in the singly occupied molecular orbital (SOMO) of **1r** (Figure 3).²⁵ This is akin to allylic conjugation and results in elongation of the C2–C3 bond and delocalization of the radical site on to C3 as reflected in the computed geometry and spin densities (Figure 4).²⁶ The analogous interaction in the anion involves two filled orbitals, which does not lead to stabilization. Consequently, **1r** is differentially stabilized, and this manifests itself in the reduced BDE for **1** and the smaller than expected electron affinity of **1r**.

Figures 1 and 2 indicate that the C–H acidities and bond energies of several hydrocarbons appear to be linearly correlated to the hybridization of the carbon atoms in these bonds as reflected by their heteronuclear $^{13}\text{C}-^1\text{H}$ coupling constants. It follows that $\Delta H^\circ_{\text{acid}}$ and BDE must be linearly related to each other for these species. Given the thermodynamic cycle in eq 8, where $313.6 \text{ kcal mol}^{-1}$ corresponds to the ionization potential of hydrogen atom, it also follows that both of these quantities are linearly correlated with the electron affinity. As a result, the determination of any one of these three quantities ($\Delta H^\circ_{\text{acid}}$, BDE, and EA) can be used to predict the other two. This finding is potentially very useful if it is robust and can be extended to large numbers of compounds. In fact, it can be, but additional details will be provided in a subsequent publication.

$$\text{BDE}(\text{HX}) = \Delta H^\circ_{\text{acid}}(\text{HX}) - 313.6 + \text{EA}(\text{X}^\cdot) \quad (8)$$

Conclusions

As anticipated, 3,3-dimethylcyclopropene is as acidic as methylacetylene, but their C–H bond energies differ by $26.1 \pm 3.8 \text{ kcal mol}^{-1}$! Both of these hydrocarbons have similar hybridizations which accounts for their acidities, but something

(23) This value is based upon the assumption that the vinyl C–H BDE of cyclopropene is the same as that for **1**.

(24) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419–2438.

(25) The same result is obtained for **1r**.

(26) The spin densities for 1-cyclopropenyl radical and **1r** are the same regardless of whether they are computed using Mulliken or natural population analyses.

else must be involved to explain the very different bond strengths. Examination of the SOMO of **1r** reveals that the radical center interacts with the Walsh orbital of the distal carbon-carbon bond so as to delocalize the odd electron and stabilize this species. This results in a smaller bond energy and electron affinity than expected based upon the high s-content in the vinyl C-H bond in **1**. We also have found that for several localized carbanions and their conjugate acids one can obtain two of the following quantities: $\Delta H_{\text{acid}}^{\circ}(\text{HX})$, $\text{EA}(\text{X}^{\cdot})$, and BDE-

(HX) from the third. This observation is potentially of great value.

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