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Phenylcyclopropane Energetics and Characterization of Its Conjugate Base: Phenyl Substituent Effects and the C−H Bond Dissociation Energy of Cyclopropane

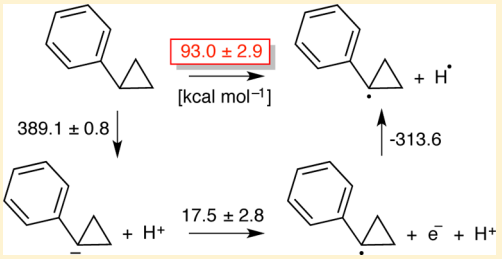
Alireza Fattahi,[†] Lev Lis,[‡] and Steven R. Kass*[,‡]

[†]Department of Chemistry, Sharif University of Technology, Tehran, Iran

[‡]Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

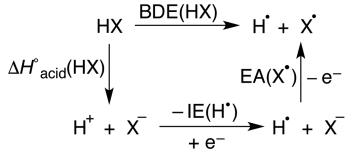
Supporting Information

ABSTRACT: The α-C−H bond dissociation energy (BDE) of phenylcyclopropane (**1**) was experimentally determined using Hess' law. An equilibrium acidity determination of **1** afforded ΔH°_{acid} = 389.1 ± 0.8 kcal mol^{-1}, and isotopic labeling established that the α-position of the three-membered ring is the favored deprotonation site. Interestingly, the structure of the base proved to be a key factor in correctly determining the proper ionization site (i.e., secondary amide ions are needed, and primary ones and OH^- lead to incorrect conclusions since they scramble the deuterium label). An experimental measurement of the electron affinity of 1-phenylcyclopropyl radical (EA = 17.5 ± 2.8 kcal mol^{-1}) was combined with the ionization energy of hydrogen (313.6 kcal mol^{-1}) to afford BDE = 93.0 ± 2.9 kcal mol^{-1}. This enabled the effect of the phenyl substituent to be evaluated and compared to other situations where it is attached to an sp^3- or sp^2-hybridized carbon center. M06-2X, CCSD(T), G4, and W1BD computations were also carried out, and a revised C−H BDE for cyclopropane of 108.9 ± 1.0 kcal mol^{-1} is recommended.



INTRODUCTION

Carbon-based radicals are commonly formed reactive intermediates that play an important role in organic synthesis as well as in atmospheric, biological, combustion, and industrial processes.[1−4] Their energetics are commonly analyzed using carbon−hydrogen bond dissociation energies (BDEs) and are widely used to rationalize the chemical reactivity and selectivity of free radicals.[5] As a result, BDEs are of considerable importance and continued interest. One of the most accurate and reliable methods for determining these quantities is to exploit Hess' law and employ the thermodynamic cycle illustrated in Figure 1. In this approach, experimental measurements of the gas-phase deprotonation enthalpy of HX (ΔH°_{acid}) and the electron affinity of X$^\bullet$ (EA) are combined with the well-known ionization energy of the hydrogen atom (IE = 313.6 kcal mol^{-1}) to obtain the BDE of HX.



$$BDE(HX) = \Delta H^\circ_{acid}(HX) - IE(H^\bullet) + EA(X^\bullet)$$

Figure 1. Negative ion thermodynamic cycle for the determination of a bond dissociation energy via the measurement of a deprotonation enthalpy and an electron affinity; the third term is the ionization energy of hydrogen atom, and a value of 313.6 kcal mol^{-1} is well established.

Styrene (PhCH=CH_2) recently was investigated, and its α-C−H BDE was found to be 100.1 ± 3.4 kcal mol^{-1}.[6] This value is 10.6 ± 3.5 kcal mol^{-1} smaller than that for ethylene and is a direct measure of the stabilizing effect of a phenyl group at an sp^2-hybridized carbon center; the high-level computationally predicted G4[7] energy difference is 6.9 kcal mol^{-1}. At an sp^3 carbon a phenyl ring has a larger impact. That is, BDE(CH_3−H) − BDE($PhCH_2$−H) = 15.2 ± 0.6 kcal mol^{-1},[5] and this difference compares favorably to a G4 theory prediction of 14.7 kcal mol^{-1}. These results reveal that there is a 4.6 ± 3.6 kcal mol^{-1} experimentally determined difference and a corresponding G4 value of 7.8 kcal mol^{-1} for the differential stabilization of a phenyl substituent at sp^2- and sp^3-hybridized carbon atoms.

Cyclopropane is comprised of three tetravalent carbon atoms each of which is bound to four atoms. In an introductory organic chemistry course this commonly would lead to an sp^3 assignment for the carbon centers. It is well-known, however, that the carbon−carbon bonds in a three-membered ring are bent and employ more p-character than in other such situations. Bonding models developed by Coulson and Moffit as well as that by Walsh indicate that the hybridization of the carbon atoms in the C−H bonds of cyclopropane are sp^2.[8,9]

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This assignment is in accord with the enhanced acidity of cyclopropane, its strong C−H BDE, a large $^{13}C-H$ heteronuclear coupling constant of 161 Hz, and the well-known enhanced reactivity of cyclopropanes with electrophiles.[10,11] Consequently, phenylcyclopropane (**1**) offers an opportunity to determine the effect of a phenyl substituent at a different type of sp^2-hybridized carbon center. Experimental and computational results are reported herein, and in the process the acidity of **1** is resolved and the C−H BDE of cyclopropane is revised upward by 3 kcal mol^{-1}. It is also shown how incorrect conclusions can be drawn regarding the favored ionization site of a compound by mass spectrometry.

RESULTS AND DISCUSSION

Phenylcyclopropane was deprotonated by several different bases (NH_2^-, Me_2N^-, and HO^- with proton affinities of 403.4 ± 0.1, 396.4 ± 0.9, and 390.27 ± 0.02 kcal mol^{-1}, respectively),[12] and the resulting conjugate base was found to abstract a proton from H_2O. These results indicate that $\Delta H^\circ_{acid}(\mathbf{1}) \approx 390$ kcal mol^{-1}, and this value was refined by measuring the equilibrium acidity as illustrated in eq 1.

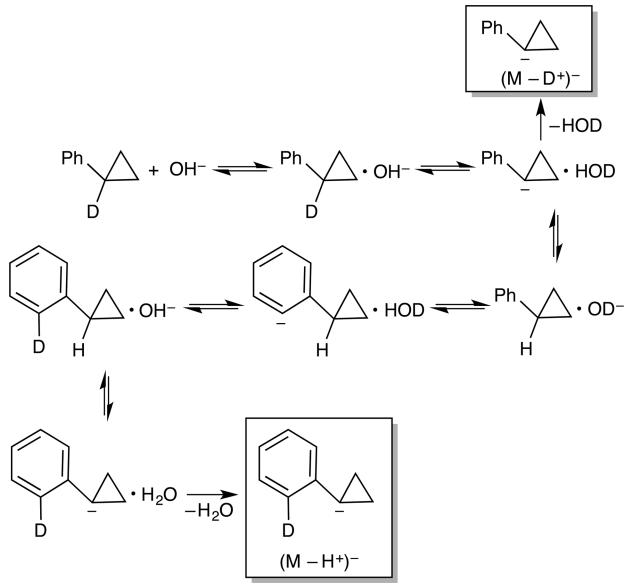
$$1\text{-}c\text{-}C_3H_5Ph + HO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1\text{-}c\text{-}C_3H_4Ph^- + H_2O$$

$$K = k_1/k_{-1} \quad (1)$$

The forward (k_1) and reverse (k_{-1}) rate constants were found to be $k_1 = (2.03 \pm 0.05) \times 10^{-9}$ and $k_{-1} = (1.93 \pm 0.31) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, where the given uncertainties are the standard deviations of the data. This leads to an equilibrium constant of 105 ± 17, but a more conservative uncertainty of ±100% was adopted for the subsequent derivation of the acidity of **1**. Given that $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = \Delta G^\circ_{acid}(\mathbf{1}) - \Delta G^\circ_{acid}(H_2O)$ for eq 1, this leads to $\Delta\Delta G^\circ_{acid} = -2.8 \pm 0.6$ kcal mol^{-1} and can be combined with $\Delta G^\circ_{acid}(H_2O) = 383.68 \pm 0.02$[12a] kcal mol^{-1} to afford $\Delta G^\circ_{acid}(\mathbf{1}) = 380.9 \pm 0.6$ kcal mol^{-1}. Computed entropies for phenylcyclopropane (85.6 e.u.) and its conjugate base (86.9 e.u.) from G4 calculations lead to $T\Delta S^\circ_{acid}(\mathbf{1}) = 8.2$ kcal mol^{-1}. If one assumes an error of ±2 e.u. for $\Delta S^\circ_{acid}(\mathbf{1})$, then $\Delta H^\circ_{acid}(\mathbf{1}) = 389.1 \pm 0.8$ kcal mol^{-1} is obtained.

Benzene is 10.3 kcal mol^{-1} more acidic than cyclopropane (ΔH°_{acid} = 401.2 vs 411.5 kcal mol^{-1}),[12a,13] and consequently it is not immediately clear which of the six different sites in **1** corresponds to the most acidic position. To address this issue experimentally, 1-deuteriophenylcyclopropane (**1D**) was prepared as previously described and reacted with H_2N^-, Me_2N^-, and HO^-. Both amide and hydroxide anions abstracted a proton or a deuterium to afford $(M - H^+)^-$ and $(M - D^+)^-$ ions. The obvious indication is that there are two or more acidic positions in **1**, but this ignores the beautiful mechanistic work carried out by Bierbaum and DePuy et al. on hydrogen−deuterium exchange.[14] In particular, they showed that multiple proton transfers can occur in a single collision between an anion and an acid, and that less acidic sites sometimes undergo isotopic exchange. This takes place when the acid or the conjugate acid of the base possesses two or more exchangeable hydrogens in a process that was termed extraordinary exchange. The "obvious" inference from the labeling results with H_2N^- and HO^- consequently could be incorrect as illustrated in Scheme 1. It is for this reason that Me_2N^- was also used because the conjugate acid of this secondary amide only has one exchangeable hydrogen and cannot undergo extraordinary exchange. That is, it cannot lead to isotopic scrambling. When Me_2N^- was reacted with **1D**, only the $(M - D^+)^-$ ion was observed revealing that the α-position of phenylcyclopropane is the most acidic site in this compound. This result is in keeping with the importance of charge delocalization in the gas phase and previous assumptions about the structure of deprotonated **1** (i.e. **1a**).[15,16]

Scheme 1. Isotopic Label Scrambling Mechanism for the Deprotonation of 1-Deuteriophenylcyclopropane



Several reports on the acidity of **1** have appeared previously.[15] A bracketing result of 390 ± 3 kcal mol^{-1} is in accord with a value of ~392 kcal mol^{-1} based upon hydrogen−deuterium exchange studies, and both of these findings are in agreement with our more accurate determination of 389.1 ± 0.8 kcal mol^{-1}. All three values differ by ~10 kcal mol^{-1}, however, from an equilibrium measurement of 380.5 kcal mol^{-1} by Peerboom et al.[16] A plausible explanation for the latter discrepancy is the presence of a small impurity of 1-phenyl-1-propene, as this could account for the extremely slow deprotonation observed with the methoxide ion. To address this further, M06-2X and G4 computations were carried out. Predicted values of 386.1 (M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ) and 389.2 (G4) kcal mol^{-1} were obtained and are consistent with the higher values (i.e., less acidic determinations); isodesmic reactions using methane, ethylene, and cyclopropane as the reference give M06-2X deprotonation enthalpies of 387.2, 388.4, and 385.8 kcal mol^{-1}. G4 theory has been shown to be especially accurate and reproduces a large well-established energetic data set with an average error of 0.8 kcal mol^{-1}.[7] In this instance our experimental determination is reproduced within 0.1 kcal mol^{-1}. The relative stabilities of the different conjugate bases of **1** were also calculated as indicated in Figure 2, and the α-carbanion is found to be the most stable structure as one would expect. This is in accord with our deuterium-labeling study and that of DePuy et al. but inconsistent with suggestions by Peerboom et al. that deprotonation with OH^- takes place at the ortho position of the aromatic ring.[15,16] That is, this pathway is predicted by G4 theory to be endothermic by 5.2 kcal mol^{-1} and thus energetically unfavorable.

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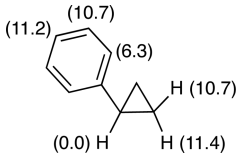
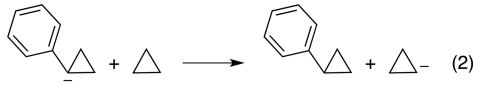


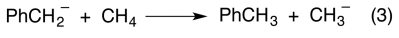
Figure 2. Computed G4 relative deprotonation enthalpies in kcal mol^{-1} for the six different acidic sites in phenylcyclopropane.

The findings above enabled us to determine the substituent effect of a phenyl group on the acidity of phenylcyclopropane at the α- and β-positions as well as the impact of the three-membered ring on benzene. The results are summarized in Table 1, and the G4 values indicate that a cyclopropyl group can enhance the acidity of benzene by up to 5.1 kcal mol^{-1} whereas a phenyl ring increases the acidity of cyclopropane by 12.6 to 24.0 kcal mol^{-1}. The much larger effect in the latter case (eq 2) is significantly less than in the acyclic example given in



(2)

ΔH° = 22.4 ± 2.2 kcal mol^{-1}
25.7 (M06-2X), 24.0 (G4)



(3)

ΔH° = 34.4 ± 0.9 kcal mol^{-1}
36.1 (M06-2X), 36.5 (G4)

eq 3 and can be attributed to differential electron delocalization.To assess the importance of resonance stabilization, the phenyl rotation transition structures for **1a** and benzyl anion were computationally located. In the former case, barriers of 13.7 (M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ) and 10.8 (G4) kcal mol^{-1} were obtained and account for only half of the stabilization due to the phenyl group. That is, additional factors such as polarization and the inductive effect when taken together appear to be as important as the resonance stabilization of **1a**; conjugation between the three-membered ring and the phenyl group also plays a role in the transition structure, but it is worth noting that the rotation barrier for **1** is 1.3 (M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ) and 0.9 (G4) kcal mol^{-1}. For the benzyl anion the rotation barrier is significantly larger (25.1 M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ and 23.2 (G4) kcal mol^{-1}) and the apparent contribution due to resonance delocalization is roughly two-thirds of the substituent effect.

The electron affinity of the 1-phenylcyclopropyl radical (**1r**) was measured by reacting its corresponding anion with reference reagents of known electron affinity and monitoring the occurrence or nonoccurrence of electron transfer. Sulfur dioxide and chloropentafluorobenzene both were found to abstract an electron from **1a** whereas *o*-trifluoromethylcyanobenzene and weaker reagents did not (Table 2). These results

Table 2. Electron Affinity Bracketing Results for 1-Phenylcyclopropyl Radical

ref compd	EA (eV)[a]	electron transfer
SO_2	1.107 ± 0.008	yes
C_6F_5Cl	0.82 ± 0.11	yes
o-$CF_3C_6H_4CN$	0.70 ± 0.10	no
CS_2	0.51 ± 0.10	no
COS	0.46 ± 0.20	no
NO	0.22 ± 0.10	no

[a]All values come from ref 12b.

bracket the electron affinity of **1r** between the values for chloropentafluorobenzene and *o*-trifluoromethylcyanobenzene, so EA(**1r**) = 0.76 ± 0.12 eV (17.5 ± 2.8 kcal mol^{-1}) is assigned.[17] Direct M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ and G4 computations of this quantity give 23.6 and 22.9 kcal mol^{-1}, respectively. Alternatively, if one calculates the electron affinity difference between phenylcyclopropyl and benzyl radicals and uses the experimental value for the latter compound (21.03 ± 0.14 kcal mol^{-1}),[18] then predictions of 21.4 (M06-2X) and 22.2 (G4) kcal mol^{-1} are obtained. These results imply that the electron affinity of **1r** is at the high end of the experimental range.

Hess' law as illustrated in Figure 1 along with the acidity of **1** and the electron affinity of **1r** determined above can be used to derive the C−H BDE of phenylcyclopropane at the α-position. A value of 93.0 ± 2.9 kcal mol^{-1} is obtained which is in reasonable accord with direct predictions of 97.0 (M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ) and 97.4 (G4) kcal mol^{-1} and isodesmic comparisons of 96.7 (M06-2x) and 97.4 (G4) kcal mol^{-1} (eq 4).To assess the impact of the phenyl group on this quantity, it can be compared to the BDE of

Table 1. Experimental and Computed Phenylcyclopropane Acidities and Substituent Effects[a]

	ΔH°_{acid}		substituent effect	
compd	expt	calcd[b]	expt	calcd[b]
C_6H_6	401.2 ± 0.2[c]	399.4 (400.6)		
c-C_3H_6	411.5 ± 2.0[d]	411.8 (413.2)		
$PhCH_3$	382.3 ± 0.5[c]	379.6 (382.8)		
1-Ph-*c*-C_3H_5				
α	389.1 ± 0.8	386.1 (389.2)	22.4 ± 2.2	25.7 (24.0)
β_{cis}		398.5 (399.9)		13.3 (13.3)
β_{trans}		399.3 (400.6)		12.5 (12.6)
o-		394.9 (395.5)		4.5 (5.1)
m-		399.1 (399.9)		0.3 (0.7)
p-		399.7 (400.4)		−0.3 (0.2)

[a]All values in kcal mol^{-1}. [b]These results correspond to M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ and G4 (in parentheses) energies. [c]Reference 12. [d]Reference 13.

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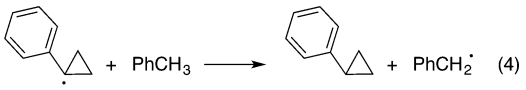


ΔH° = BDE ($PhCH_2$–H) – BDE (**1**)

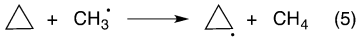
cyclopropane (106.3 ± 0.3 kcal mol^{-1}),[11] and a difference of 13.3 ± 2.9 kcal mol^{-1} is obtained. This compares favorably to M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ) and G4 predictions of 10.3 and 10.8 kcal mol^{-1}, respectively. In this case this difference appears to be largely due to electron delocalization in that the rotation barrier of the phenyl group in **1r** is 9.2 (M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ) and 7.8 (G4) kcal mol^{-1}. Similar effects were noted for toluene and styrene, but the impact of the aromatic ring is 4 kcal mol^{-1} larger in the former case and 3 kcal mol^{-1} smaller in the latter one (Table 3).[6] These results are surprising in that phenyl substitution has the largest impact on methane and the smallest effect on ethylene even though the C–H BDEs follow the order CH_4 < *c*-C_3H_6 < $CH{=}CH_2$. That is, greater stabilization occurs for the more stable radicals (as indicated by their BDEs). This trend can be rationalized by resonance stabilization of the corresponding radicals in that it correlates to their computed C–Ph rotation barriers.

Table 3. Bond Energies and C–Ph Rotational Barriers in kcal mol^{-1}

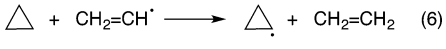
	RCH_3	1-R-*c*-C_3H_5	$RCH{=}CH_2$
BDE (R = H)	104.99 ± 0.03[a]	106.3 ± 0.3[b]	110.7 ± 0.6[a]
BDE (R = Ph)	89.8 ± 0.6[a]	93.0 ± 2.9	100.1 ± 3.4[c]
ΔBDE	15.2 ± 0.6	13.3 ± 2.9	10.6 ± 3.5
ΔBDE (M06-2X, G4)	13.9, 14.7	10.3, 10.8	7.5, 6.9
rotation barrier (M06-2X, G4)	11.1, 10.9	9.2, 7.8	5.1, 3.2

[a]Reference 5. [b]Reference 11. [c]Reference 6.

Previous G3 and W1 calculations indicate that the experimental C–H BDE of cyclopropane is 3 kcal mol^{-1} too small.[19] To address this further, four different computational approaches were employed (i.e., M06-2X/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ, G4, and W1BD) and the BDE was obtained directly and by the isodesmic reactions illustrated in eqs 5 and 6. These results along with new G3 and W1 determinations via eqs 5 and 6 are summarized in Table 4 and lead us to recommend a C–H BDE for cyclopropane of 108.9 ± 1.0 kcal mol^{-1} which corresponds to a 2.6 kcal mol^{-1} upward revision of the currently accepted value.[17]



ΔH° = BDE (*c*–C_3H_6) – BDE (CH_4)



ΔH° = BDE (*c*–C_3H_6) – BDE (C_2H_4)

CONCLUSION

Phenylcyclopropane is slightly more acidic than water in the gas phase, and as in solution the α-position is most labile. The resulting benzylic anion is stabilized by electron delocalization over the aromatic ring, but this accounts for only half of the phenyl substituent effect. By measuring the electron affinity of the 1-phenylcyclopropyl radical and applying Hess' law, the C–H BDE of **1** was found to be 93.0 ± 2.9 kcal mol^{-1}. Resonance stabilization plays a larger role in **1r** and accounts for the observed phenyl substituent effect order: $PhCH_3$ > *c*-C_3H_5Ph > $PhCH{=}CH_2$. High level calculations also indicate that the experimental C–H BDE of cyclopropane is too small by 2.6 kcal mol^{-1}, and we recommend a value of 108.9 ± 1.0 kcal mol^{-1} for this quantity based upon very accurate computational methodologies. An experimental redetermination of this bond energy, however, clearly is warranted.

Table 4. Computed C–H BDEs for Cyclopropane Using Different Theoretical Methods and Chemical Reactions

	BDE(*c*-C_3H_5-H) (kcal mol^{-1})			
method	direct[a]	eq 5	eq 6	avg
M06-2X/aug-cc-pVTZ	107.2	108.3	109.1	108.2
CCSD(T)/aug-cc-pVQZ[b]	108.5	109.5	108.8	108.9
G3	109.2	110.0	109.6	109.6
G4	108.2	108.7	109.0	108.6
W1	109.0	109.7	109.3	109.3
W1BD	109.0	109.0	108.8	108.9
avg	108.5	109.2	109.1	108.9

[a]Direct = *c*-C_3H_6 → *c*-$C_3H_5^{\bullet}$ + $H^{\bullet}$. [b]CCSD(T)/aug-cc-pVTZ optimized structures and unscaled M06-2X/aug-cc-pVTZ vibrational frequencies for zero-point energies and thermal corrections to 298 K were used.

EXPERIMENTAL SECTION

All reagents were obtained from commercial sources and used as supplied except for 1-deuteriophenylcyclopropane. This isotopically labeled compound was prepared by treating phenylcyclopropane with sodium hydride in DMSO-d_6 at 35 °C for 5 days as previously described.[20]

Negative ions were generated by electron ionization in a Fourier transform mass spectrometer (FTMS) equipped with a 3 T magnet and subsequently were allowed to react with **1** or **1D**. The resulting $(M - H^+)^-$ or $(M - D^+)^-$ ions were cooled with a pulse of argon to a pressure of ~10^{-5} Torr and transferred to the second cell of the dual cell instrument. Another argon pulse up to ~10^{-5} Torr was employed, and the ion of interest was mass isolated using a combination of a stored–waveform inverse Fourier transform (SWIFT)[21] and/or chirp excitation pulses.[22] Reactions were monitored using constant amounts of the reagents of interest as a function of time. For the forward direction of the equilibrium acidity determination of **1**, the anionic base (HO^-) was formed from water and transferred to the second reaction region where it was allowed to react with phenylcyclopropane.

Computations were carried out with Gaussian 09[23] at the Minnesota Supercomputer Institute for Advanced Computational Research. Both M06-2X[24] and G4[7] calculations were performed on **1**, all six of its conjugate bases (i.e., the 1-, 2- (cis and trans), and *o*-, *m*-, and *p*-anions) and the 1-phenylcyclopropyl radical (**1r**). Geometry optimizations and vibrational frequencies with the former method and the aug-cc-pVDZ basis set were carried out, and single-point energies were obtained with the larger aug-cc-pVTZ basis set. For methane, ethylene, cyclopropane, methyl, vinyl, and cyclopropyl radicals, M06-2X and CCSD(T) structures were also computed with the aug-cc-pVTZ basis set, and in the former cases vibrational frequencies were computed as well. Coupled cluster single-point energies (i.e., CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ) and the G4 and W1BD[25] methods were employed too. All of the resulting energetic quantities are given at 298 K.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01718.

Computed structures and energies are provided as is the complete citation to ref 23 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kass@umn.edu.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: 2001, 1158 pp.

(2) Zard, S. Z. *Radical Reactions in Organic Synthesis*; Oxford University Press: 2004, 272 pp.

(3) Davies, K. J. A. *Oxidative Damage and Repair*; Pergamon Press: 1991, 899 pp.

(4) *Atmospheric Oxidation and Antioxidants*; Scott, G., Ed.; Elsevier: Vols. *1*−*3*.

(5) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255−263.

(6) Fattahi, A.; Lis, L.; Kass, S. R. *Int. J. Mass Spectrom.*, **2016**, in press (doi: 10.1016/j.ijms.2016.03.009).

(7) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *126*, 084108.

(8) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625−1651.

(9) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809−886.

(10) Morris, D. G. *The Chemistry of the Cyclopropyl Group, Part 1*; Rappoport, Z., Ed.; John Wiley and Sons: 1987; pp 101−172.

(11) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838−2840.

(12) (a) Ervin, K. M.; DeTuri, V. F. *J. Phys. Chem. A* **2002**, *106*, 9947−9956. (b) Bartmess, J. E. *NIST Chemistry WebBook, NIST Standard Reference Database Number 6*; Mallard, W. G., Lustrum, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899 (http://webbook.nist.gov).

(13) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968−1973.

(14) (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650−7653. (b) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921−2922. (c) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256−4258. (d) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565−2571. (e) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185−5192. (f) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384−7389. (g) Kato, S.; DePuy, C. H.; Gronert, S.; Bierbaum, V. M. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 840−847. (h) DePuy, C. H.; Bierbaum, V. M. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel Publishing: 1987; pp 293−303.

(15) (a) Andrist, A. H.; DePuy, C. H.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 845−850. (b) Chou, P. K.; Dahlke, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 315−324.

(16) Peerboom, R. A. L.; de Koning, L.; Nibbering, N. M. M. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 159−168.

(17) The cited error corresponds to 2σ.

(18) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601−620.

(19) Tian, Z.; Fattahi, A.; Kass, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 17087−17092.

(20) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123−2129.

(21) Wang, T. C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1986**, *58*, 2935−2938.

(22) Marshall, A. G.; Roe, D. C. *J. Chem. Phys.* **1980**, *73*, 1581−1590.

(23) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2013.

(24) (a) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2008**, *112*, 1095−1099. (b) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241. (c) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157−167.

(25) Barnes, E. C.; Petersson, G. A.; Montgomery, J. A., Jr.; Frisch, M. J.; Martin, J. M. L. *J. Chem. Theory Comput.* **2009**, *5*, 2687−2693.

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