Gas phase formation of 1-phenylcyclobuten-3-yl and 1-phenylallyl anions and a determination of the allylic C–H acidities and bond dissociation energies of 1-phenylcyclobutene and (*E*)-1-phenylpropene

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1-Phenylcyclobuten-3-yl and 1-phenylallyl anions (**1a** and **2a**, respectively) were prepared in the gas phase by deprotonating their conjugate acids in a Fourier transform mass spectrometer. The acidities of both compounds were measured by determining equilibrium constants with standard reference acids [$\Delta G^\circ_{acid}(\mathbf{1}) = 369.5 \pm 0.7$ kcal mol^{-1} and $\Delta H^\circ_{acid}(\mathbf{1}) = 377.5 \pm 0.7$ kcal mol^{-1}; $\Delta G^\circ_{acid}(\mathbf{2}) = 361.5 \pm 2.1$ kcal mol^{-1} and $\Delta H^\circ_{acid}(\mathbf{2}) = 368.1 \pm 2.1$ kcal mol^{-1}]. Electron affinities of the corresponding radicals were measured by the bracketing technique [EA = 0.94 ± 0.11 (**1r**) and 1.06 ± 0.07 eV (**2r**)] and allylic C–H bond dissociation energies were obtained *via* a thermodynamic cycle [BDE = 85.6 ± 2.6 (**1**) and 78.9 ± 2.6 (**2**) kcal mol^{-1}]. These results are contrasted to density functional theory and *ab initio* calculations on cyclobutene, 1-phenylcyclobutene, (*E*)-1-phenylpropene and propene.

Introduction

Unstable monocyclic 4π electron species are often referred to as antiaromatic compounds and they have been the subject of extensive experimental and theoretical investigations.[1–8] Special attention has been directed towards the smallest representatives of this series, namely cyclopropenyl anion,[9] cyclobutadiene,[10] and cyclopentadienyl cation.[11] Despite their reactive nature some spectroscopic data have been obtained, but thermodynamic information generally is lacking. This makes it difficult to address the antiaromatic destabilization energies of these compounds from an experimental perspective.

Recently, photoacoustic calorimetry was used to estimate the heat of formation of cyclobutadiene (114 ± 11 kcal mol^{-1}),[12] [1 cal = 4.184 J] but this result has been questioned[10a] and has an especially large uncertainty. An alternative approach for determining this quantity which has been successfully employed for a number of fleetingly stable reactive intermediates including benzocyclobutadiene is negative ion gas-phase chemistry.[10a,13] In this particular instance there is a potential problem because cyclobutadiene anion radical is predicted to be unstable with respect to electron detachment or, at best, to have a very low electron binding energy; the electron affinity at the G3 level of theory for the D_{2h} species is −3.3 kcal mol^{-1}. Phenylcyclobutadiene, on the other hand, should give a bound anion radical and therefore is an attractive alternative. Its heat of formation could be determined by measuring the proton affinity and electron binding energy of phenylcyclobutadiene anion radical if the allylic C–H bond dissociation energy of 1- or 3-phenylcyclobutene was known. In this paper we report the latter quantity by measuring the gas phase acidity of 1-phenylcyclobutene (**1**) and the electron affinity of 1-phenylcyclobuten-3-yl radical (**1r**). Since 1-phenylcyclobuten-3-yl anion (**1a**) is a rare example of a stable cyclic allyl anion,[14] we also have explored its acyclic analog for comparison purposes. Density functional theory and *ab initio* calculations on these species and their parent compounds were carried out as well.

Experimental

1-Phenylcyclobutene was prepared by a published method starting from cyclobutanone[15] and phenylmagnesium bromide.[16] It was purified by preparative gas chromatography on a 12′ × 0.25″ 10% SE 30 column at 150 °C before use.

Gas phase experiments were carried out using a dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3.0 T superconducting magnet and controlled by a Sun workstation running the Odyssey version 4.2 software package. 1-Phenylcyclobutene was deprotonated by hydroxide ion which was generated upon ionization of ammonia in the presence of background water. The resulting M − 1 ion at *m*/*z* 129 was isolated in the first (source) cell using a SWIFT waveform[17,18] and then was transferred to the second (analyzer) cell where it was collisionally cooled with a pulse of argon gas (~2 × 10^{-5} Torr). Neutral probe reagents were introduced into the analyzer cell through slow-leak valves and the formation of product ions was measured as a function of time.

Bimolecular reactions typically follow pseudo-first order kinetics in a FTMS because the neutral reagent concentrations are much greater than those of the ions. Rate constants for proton transfer reactions (k_1 or k_{-1}) were determined using eqn. (1), where k_{obs} is the slope of a linear plot of ln [anion] *vs.* time (in seconds), R_x is a compound specific sensitivity correction to the ion gauge (pressure) measurement[19] and is a function of the neutral molecule's polarizability,[20] T is the absolute temperature in kelvin (300 K), and P is the pressure of the reference acid in Torr.[21] Equilibrium constants for acid–base reactions were obtained by taking the ratio of the forward and reverse rate constants ($K = k_1/k_{-1}$), but given the difficulty in obtaining accurate pressure readings, a 50 or 100% error in K was assumed for further data analysis; the statistical uncertainties were approximately 10%.

$$k_1 \text{ or } k_{-1} = k_{obs}R_xT/9.66 \times 10^{18} \times P \qquad (1)$$

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Table 1 Summary of bracketing studies for 1-phenylcyclobuten-3-yl anion (**1a**)

		Proton transfer	
Ref. acid (HX)	$\Delta H^\circ_{\text{acid}}$/kcal mol$^{-1\,a}$	Forward reaction (**1a** + HX)	Reverse reaction (**1** + X$^-$)
H_2O	390.7 ± 0.1	—	Yes
MeOH	381.5 ± 0.4	No (1)^b	Yes
EtOH	378.3 ± 1.0	Yes (1)^b	Yes
i-PrOH	375.9 ± 1.2	Yes	Yes
t-BuOH	374.6 ± 2.1	Yes	—
HF	371.6 ± 0.2	—	No

[a] Acidity values taken from refs. 26 and 27. [b] 1 H–D exchange observed with ROD (R = Me and Et, but not *t*-Bu).

Calculations were carried out using Gaussian 94[22] and GAMESS-US[23] software packages on IBM SP and SGI Origin Supercomputers at the Minnesota Supercomputer Institute and Linux-based Pentium III PC's at the Rudjer Boskovic Institute in Zagreb. Geometry optimizations were carried out at the MP2 and B3LYP levels of theory with the 6-31+G(d) basis set. Diffuse functions were used because they are known to be important for properly describing the electronic structure of anions and for obtaining reliable gas-phase acidities.[8] The nature of each stationary point was subsequently characterized by a vibrational analysis, which also was used to obtain the zero-point vibrational energy (ZPE) and a temperature correction from 0 to 298 K. MP2 frequencies and ZPEs were corrected using scaling factors of 0.9646 and 0.9427, respectively, while no adjustment was made to the corresponding DFT results.[24] Since the two methods end up giving similar results only the B3LYP data will be presented. It is worth noting, however, that **1a** is predicted to have a planar carbon framework at the B3LYP level whereas the phenyl and cyclobutenyl rings are bent with respect to each other in the MP2 structure (Fig. 1). Differences of this sort have been previously noted and lead to few energetic consequences.[25] Unless otherwise stated, all of the computed acidities and bond dissociation energies are given at 298 K, and the electron affinities are reported at 0 K.

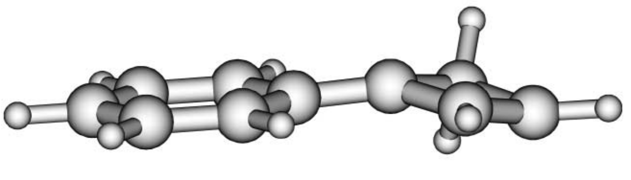
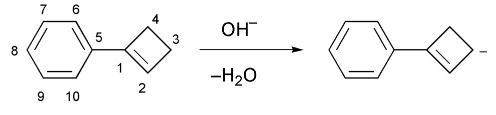


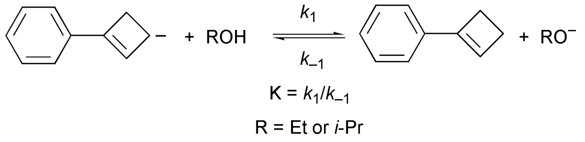
Fig. 1 MP2/6-31+G(d) structure of **1a**.

Results and discussion

1-Phenylcyclobuten-3-yl anion (**1a**) was generated in the gas phase by deprotonation of **1** with hydroxide ion [eqn. (2)]. Its thermodynamic stability can be assessed by measuring the proton affinity of **1a** and the electron affinity of the corresponding radical (**1r**). The former value was initially obtained by observing the occurrence or nonoccurrence of proton transfer with a series of standard reference acids and bases (Table 1).[26,27] In particular, **1a** was found to deprotonate *tert*-butyl alcohol, isopropyl alcohol, and ethanol, but not less acidic compounds. In the opposite direction, methoxide, ethoxide, and isopropoxide ions deprotonate **1** but weaker bases do not. Deuterated reagents also were employed, and MeOD and EtOD induce a single hydrogen–deuterium exchange as expected for **1a** whereas *tert*-BuOD only gives deuteron transfer. These results indicate that PA(**1a**) or equivalently $\Delta H^\circ_{\text{acid}}(\mathbf{1}) \approx 377$ kcal mol^{-1}. To refine this value, equilibrium constants with ethanol and isopropanol were determined by measuring rate constants for the forward (k_1) and reverse (k_{-1}) proton transfer reactions [eqn. (3)].



1 **1a** (2)



(3)

With ethanol as the reference acid, $k_1 = 1.55 \pm 0.01 \times 10^{-10}$ (3) and $k_{-1} = 3.73 \pm 0.28 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} (5), where the parenthetical values represent the number of independent measurements that were carried out and the cited uncertainty is the standard deviation in the data. The resulting equilibrium constant (K) is 0.0416 ± 0.0031, but given the uncertainty in using an ion gauge to measure pressure, a more conservative error for K of ±50% was adopted for further data analysis. This leads to $\Delta\Delta G^\circ_{\text{acid}} = 1.90 \pm 0.30$ kcal mol^{-1}, which was combined with the known $\Delta G^\circ_{\text{acid}}$(EtOH) = 371.7 ± 1.1 kcal mol^{-1} and a calculated $\Delta S^\circ_{\text{acid}}(\mathbf{1}) = 26.6$ eu† using B3LYP/6-31+G(d) geometries and vibrational frequencies to obtain $\Delta G^\circ_{\text{acid}}(\mathbf{1}) = 369.8 \pm 1.1$ kcal mol^{-1} and $\Delta H^\circ_{\text{acid}}(\mathbf{1}) = 377.8 \pm 1.1$ kcal mol^{-1}. In a similar manner, $k_1 = 5.85 \pm 0.31 \times 10^{-10}$ (3) and $k_{-1} = 7.05 \pm 0.88 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (3) when isopropyl alcohol is used as the reference acid. This leads to $\Delta\Delta G^\circ_{\text{acid}} = 0.11 \pm 0.08$ kcal mol^{-1}, which can be combined with $\Delta G^\circ_{\text{acid}}$(*i*-PrOH) = 369.3 ± 1.3 kcal mol^{-1} to obtain $\Delta G^\circ_{\text{acid}}(\mathbf{1}) = 369.2 \pm 1.3$ kcal mol^{-1} and $\Delta H^\circ_{\text{acid}}(\mathbf{1}) = 377.2 \pm 1.3$ kcal mol^{-1}. Both acidity measurements are in excellent accord with each other and their weighted mean provides our final values: $\Delta G^\circ_{\text{acid}}(\mathbf{1}) = 369.5 \pm 0.7$ kcal mol^{-1} and $\Delta H^\circ_{\text{acid}}(\mathbf{1}) = 377.5 \pm 0.7$ kcal mol^{-1}. The latter result, coincidently, matches the predicted 298 K B3LYP/6-31+G(d) acidity exactly (Table 2).

The electron affinity of 1-phenylcyclobuten-3-yl radical (**1r**) was measured to further examine the stability of **1a** by probing electron transfer reactions between this anion and a series of reference compounds [eqn. (4)].[26] Each experiment was carried out as a function of time to ensure that any observed electron transfer product was due to the reaction of **1a** with the selected reagent. In particular, electron transfer was observed with sulfur dioxide (EA = 1.107 ± 0.008 eV) and nitrobenzene (EA = 1.01 ± 0.10 eV), and a small amount was seen with *p*-nitroanisole (EA = 0.91 ± 0.10 eV, Table 3). No electron transfer takes place with perfluorotoluene (EA = 0.86 ± 0.11 eV) and reagents with lower electron affinities, so we use nitrobenzene and perfluorotoluene as the brackets to assign EA(**1r**) = 0.94 ± 0.11 eV (21.7 ± 2.5 kcal mol^{-1}); the reaction with *p*-nitroanisole is ambiguous from a thermochemical standpoint because the slow rate maybe due to a slightly endothermic process or an exothermic reaction with a barrier. This result is in good agreement with a directly calculated value of 0.85 eV (19.7 kcal mol^{-1}) at the UB3LYP/6-31+G(d) level. It can also be combined with the

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† 1 eu = 1 cal K^{-1} mol^{-1}.

Table 2 Comparison of calculated B3LYP/6-31+G(d) electronic energies, zero-point energies, proton affinities, electron affinities, bond dissociation energies, and experimental values

Cmpd	E_{tot}/E_h[a]	ZPE/E_h	PA[b]		EA[b,c]		BDE[b,d]	
			Calc.	Expt	Calc.	Expt	Calc.	Expt
1	−387.05238 (−386.87581)	0.16824					83.3	85.6 ± 2.6
1a	−386.43704 (−386.27656)	0.15157	377.5	377.5 ± 0.7				
1a′	−386.41443 (−386.25436)	0.15159	391.4					
1r	−386.40881 (−386.24571)	0.15472			19.7 [19.4]	21.7 ± 2.5		
2	−348.98143 (−348.81135)	0.16166					79.9	78.9 ± 2.6
2a	−348.38216 (−348.22768)	0.14610	367.7	368.1 ± 2.1				
2r	−348.34343 (−348.18657)	0.14867			25.9 [25.8]	24.4 ± 1.6		
3	−155.97975 (−155.88837)	0.08661					88.3	
3a	−155.32991 (−155.25481)	0.07018	399.0					
3a′	−155.32562 (−155.24955)	0.07126	402.3					
3r	−155.32776 (−155.25030)	0.07258			2.9 [2.8]			
4	−117.91393 (−117.82914)	0.07985					84.6	86.6 ± 1.5
4a	−117.28108 (−117.21238)	0.06342	388.5	389.1 ± 1.5				
4r	−117.26792 (−117.19690)	0.06625			10.0 [9.7]	11.1 ± 0.2		

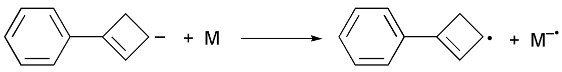
[a] Values in parentheses are thermally corrected to 298 K and include a *RT* work term. [b] PAs (298 K), EAs (0 and 298 K), and BDEs (298 K) are all in kcal mol^{-1}. [c] Values in brackets have been corrected to 298 K. [d] BDEs were calculated using the exact ionization potential for the hydrogen atom (313.6 kcal mol^{-1}).

Table 3 Electron affinity bracketing results for 1-phenylcyclobuten-3-yl radical (**1r**) and 1-phenylallyl radical (**2r**)

Ref. Cmpd	EA/eV[a]	Electron transfer		Additional Products
		1r	**2r**	
CS_2	0.51 ± 0.10	No	—	S-atom transfer[b]
Perfluoropyridine	0.68 ± 0.11	No	No	Adduct–HF_x (x = 1 and 2)[b,c]
p-$C_6H_4[COOCH_3]_2$	0.82 ± 0.09	No	—	Adduct–MeOH[b]
$C_6F_5CF_3$	0.86 ± 0.11	No	No	Adduct–HF_x (x = 1, 2, and 3)[b,c]
p-$NO_2C_6H_4OCH_3$	0.91 ± 0.10	Yes (slow)	—	Adduct–MeOH[b]
$C_6H_5NO_2$	1.01 ± 0.10	Yes	No	
SO_2	1.107 ± 0.008	Yes	Yes	

[a] Values taken from refs. 26 and 27. [b] Observed in reaction with **1r**. [c] Observed in reaction with **2r**, but x = 1 and 2 only.

measured acidity [eqn. (5)] to derive an allylic C–H bond dissociation energy of 85.6 ± 2.6 kcal mol^{-1} for 1-phenylcyclobutene, which not surprisingly is in good accord with the UB3LYP/6-31+G(d) prediction of 83.3 kcal mol^{-1}.

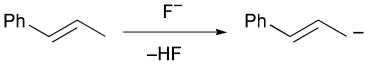


(4)

1r

$$\mathrm{BDE(HX)} = \Delta H^\circ_{\mathrm{acid}}(\mathrm{HX}) - \mathrm{IP(H^\bullet)} + \mathrm{EA(X^\bullet)} \quad (5)$$

To put the above thermodynamic data in perspective, (E)-1-phenylpropene (**2**) was examined. 1-Phenylallyl anion (**2a**) was generated by deprotonating **2** with fluoride ion [eqn. (6)]. Its proton affinity previously has been reported by Chou and Kass (368 ± 4 kcal mol^{-1}),[28] but to refine this quantity we measured the equilibrium constant *via* the forward and reverse rate constants [eqn. (3)] with p-anisidine (p-$MeOC_6H_4NH_2$); k_1 = 4.44 ± 0.16 × 10^{-11} (3), k_{-1} = 2.65 ± 0.22 × 10^{-12} cm^3 molecule^{-1} s^{-1} (3), and K = 16.8 ± 1.5. Since the rate constants are relatively small and subject to greater error, a 100% error in K was assumed in determining the following uncertainties. Our value of K leads to $\Delta\Delta G^\circ_{acid}$ = 1.68 ± 0.60 kcal mol^{-1}, and given ΔG°_{acid}(p-anisidine) = 359.8 ± 2.0 kcal mol^{-1} and a computed ΔS°_{acid}(**2**) = 21.9 eu, we obtain ΔG°_{acid}(**2**) = 361.5 ± 2.1 kcal mol^{-1} and ΔH°_{acid}(**2**) = 368.1 ± 2.1 kcal mol^{-1}. The latter result is in excellent accord with earlier work of Chou and Kass[28] and a B3LYP/6-31+G(d) acidity of 367.7 kcal mol^{-1}.

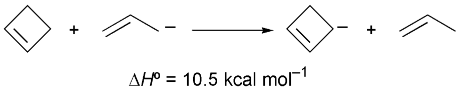


(6)

2 **2a**

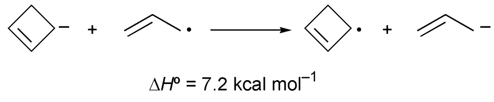
In a similar fashion to **1r**, the electron affinity of 1-phenylallyl radical (**2r**) was bracketed. In particular, electron transfer occurs rapidly with sulfur dioxide [k = 5.0 ± 0.2 × 10^{-10} cm^3 molecule^{-1} s^{-1} (2)] but not with nitrobenzene, perfluorotoluene, and perfluoropyridine (Table 3). These results enable us to assign EA(**2r**) = 1.06 ± 0.07 eV (24.4 ± 1.6 kcal mol^{-1}) and derive an allylic C–H bond dissociation energy of 78.9 ± 2.6 kcal mol^{-1}. Both of these values are well reproduced at the UB3LYP/6-31+G(d) level (*i.e.*, 25.9 and 79.9 kcal mol^{-1}, respectively).

Before comparing the thermodynamic data of 1-phenylcyclobutene and (E)-1-phenylpropene, it is useful to consider the differences between the parent species [eqns. (7)–(9)] and the consequences of adding a phenyl substituent to each system [eqns. (10)–(15)]. Unfortunately, the relevant experimental data are not available for cyclobutene (**3**) since only the vinyl anion (**3a′**) is observed upon proton abstraction.[14] Computational



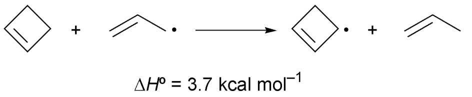
(7)

3 **4a** **3a** **4**



(8)

4r **3r**



(9)

Table 4 Selected B3LYP/6-31+G(d) geometrical parameters for phenylcyclobutene (**1**), (*E*)-1-phenylpropene (**2**), cyclobutene (**3**), propene (**4**), and their conjugate bases[a]

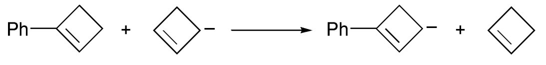
Bond	**1**(C_s) [**1a** (C_s)]	**2**(C_s) [**2a** (C_s)]	**3**(C_{2v}) [**3a** (C_2)]	**4**(C_s) [**4a** (C_{2v})]
C1–C2	1.353 [1.436]	1.344 [1.415]	1.343 [1.415]	1.337 [1.399]
C2–C3	1.516 [1.381]	1.501 [1.378]	1.520 [1.415]	1.503 [1.399]
C3–C4	1.571 [1.540]	—	1.574 [1.548]	—
C4–C1	1.525 [1.541]	1.473 [1.419]	1.520 [1.548]	—
C5–C1	1.462 [1.398]	1.409 [1.439][b]	—	—
C5–C6	1.409 [1.445]	1.393 [1.390]	—	—
C6–C7	1.393 [1.387]	1.400 [1.407]	—	—
C7–C8	1.401 [1.411]	1.397 [1.408]	—	—
C8–C9	1.397 [1.410]	1.396 [1.388]	—	—
C9–C10	1.397 [1.388]	1.407 [1.439][c]	—	—
C10–C5	1.406 [1.443]	—	—	—
C1–C2–C3	94.7 [95.5]	124.5 [128.9]	94.4 [97.1]	125.3 [132.0]
C2–C1–C4	93.6 [88.6]	127.8 [126.9]	94.4 [88.2]	—
C2–C3–C4	85.7 [90.7]	—	85.6 [88.2]	—
C3–C4–C1	86.0 [83.6]	123.5 [125.2][d]	85.6 [86.5]	—
C2–C1–C5	135.5 [137.6]	—	—	—
C1–C2–C3–C4	0.0 [0.0]	180.0 [180.0][e]	0.0 [0.0]	—
C5–C1–C3–C4	180.0 [180.0]	0.0 [0.0][f]	—	—

[a] Bond lengths and angles are in ångström and degrees, respectively. [b] C4–C5. [c] C9–C4. [d] C5–C4–C1. [e] C4–C1–C2–C3. [f] C5–C4–C1–C2.

Table 5 Löwdin atomic charges for phenylcyclobutene (**1**), (*E*)-1-phenylpropene (**2**), cyclobutene (**3**), propene (**4**), and their conjugate bases[a]

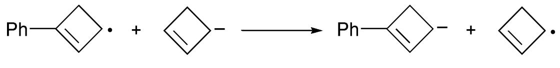
Atom[a]	**1**	**1a**	**1a′**	**2**	**2a**	**3**	**3a**	**4**	**4a**
C1	−0.12	−0.35	−0.12	−0.02	−0.29	−0.05	−0.43	−0.01	−0.47
C2	−0.02	0.01	−0.36	−0.03	0.01	−0.05	−0.08	−0.05	−0.05
C3	0.06	−0.24	−0.02	0.10	−0.28	0.04	−0.43	0.08	−0.47
C4	0.08	0.05	−0.36			0.04	−0.05		
C5	−0.08	−0.03	−0.06	−0.09	−0.03				
C6	0.03	−0.10	0.02	0.01	−0.11				
C7	0.01	−0.01	−0.03	0.01	−0.01				
C8	0.01	−0.20	−0.05	0.00	−0.18				
C9	0.01	−0.01	−0.03	0.01	−0.02				
C10	0.02	−0.11	−0.02	0.01	−0.10				

[a] Charges were calculated using HF/6-31+G(d) wavefunctions and B3LYP optimized geometries. The hydrogen atom contributions have been summed into the carbon atoms to which they are attached.



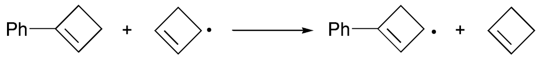
(10)

$\Delta H° = -21.5$ kcal mol^{-1}



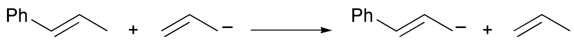
(11)

$\Delta H° = -16.8$ kcal mol^{-1}



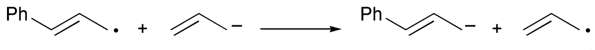
(12)

$\Delta H° = -5.0$ kcal mol^{-1}



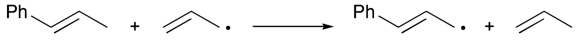
(13)

$\Delta H° = -21.0 \pm 2.6$ kcal mol^{-1} (expt)
$= -20.8$ kcal mol^{-1} (B3LYP)



(14)

$\Delta H° = -13.3 \pm 1.6$ kcal mol^{-1} (expt)
$= -15.9$ kcal mol^{-1} (B3LYP)



(15)

$\Delta H° = -7.7 \pm 3.0$ kcal mol^{-1} (expt)
$= -4.7$ kcal mol^{-1} (B3LYP)

results therefore were used in this case, and for the sake of consistency, in all comparisons with these data. As expected, the allylic position is more acidic (10.5 kcal mol^{-1}) in propene (**4**) than cyclobutene (Table 2). This is a consequence of constraining an allyl anion in a four-membered ring where the central angle of the allylic system cannot expand as it does without this constraint [*i.e.*, C1–C2–C3 = 125.3° (propene) and 132.0° (allyl anion) *vs.* 94.7° (**1**) and 95.5° (**1a**), Table 4] so as to distribute the charge over a greater space and minimize the interactions between the negatively charged ends. In this regard it is interesting to note that if one artificially imposes angle strain on the allyl anion by setting the C1–C2–C3 bond angle to the value for cyclobuten-3-yl anion (97.1°) and sets the analogous bond angle in propene to the value in cyclobutene (94.4°) and then optimizes the rest of the structures, the acidity decreases by 7.7 kcal mol^{-1}. Likewise, if one uses Coulomb's law and a point charge model to calculate the electrostatic repulsion between C1 and C3 upon the deprotonation of propene and its deformed analog, where the charges are obtained from a Löwdin population analysis (Table 5), the difference in energies is 6.7 kcal mol^{-1}. In the corresponding radicals, charge–charge interactions are greatly diminished and the central bond angle does not open up [C1–C2–C3 = 125.1° (**2r**) and 93.6° (**1r**)]. As a result, the allylic C–H bond dissociation energies for cyclobutene and propene are similar (88.3 and 84.6 kcal mol^{-1}, respectively), although the former value is larger despite the fact that **3r** is more substituted than **4r**. Given these acidity and bond dissociation energy differences, it follows that the electron affinity of **3r** is less than for **4r**, and only has a predicted value

Table 6 Hybridizations and π-bond orders as obtained from natural bond order and Löwdin population analyses[a]

	1		**1a**		**1r**	
Bond	s-character	π-BO	s-character	π-BO	s-character	π-BO
C1–C2	35.7–35.9	0.88	32.3–32.7	0.48	32.7–31.6	0.47
C1–C4	27.9–25.2	0.19	27.4–25.2	0.18	28.0–24.0	0.18
C1–C5	36.4–32.5	0.30	40.3–36.2	0.62	39.2–33.5	0.41
C2–C3	29.4–25.0	0.20	36.5–35.2	0.81	33.4–34.9	0.81
C3–C4	23.5–23.5	0.12	24.9–28.7	0.18	29.1–24.0	0.18
C5–C6	33.7–34.5	0.63	31.8–34.2	0.48	33.3–34.0	0.59
C5–C10	33.8–34.4	0.61	31.9–34.2	0.48	33.1–34.1	0.59
C6–C7	35.6–35.0	0.65	36.6–36.2	0.72	36.1–35.2	0.65
C7–C8	35.1–35.0	0.66	35.5–34.8	0.60	34.8–34.8	0.67
C8–C9	34.9–34.8	0.64	35.4–34.8	0.59	34.9–34.9	0.64
C9–C10	35.7–35.1	0.68	36.7–36.3	0.73	35.2–36.0	0.68
	2		**2a**		**2r**	
C1–C2	38.7–38.5	0.91	36.3–36.1	0.54	36.3–34.7	0.49
C1–C4	33.4–32.6	0.30	35.8–36.4	0.57	35.3–33.6	0.39
C2–C3	33.2–28.3	0.22	38.2–38.6	0.81	36.9–38.1	0.85
C4–C5	33.8–34.5	0.62	31.9–34.4	0.51	33.3–34.2	0.60
C4–C9	33.5–34.8	0.63	31.6–34.7	0.51	33.0–34.4	0.60
C5–C6	35.7–35.2	0.68	36.4–36.2	0.71	35.9–35.2	0.68
C6–C7	35.0–34.8	0.64	35.4–34.9	0.61	34.9–34.8	0.64
C7–C8	35.0–35.1	0.66	34.8–35.4	0.60	34.9–34.8	0.71
C8–C9	35.0–35.6	0.66	36.2–36.5	0.72	35.2–35.9	0.67

[a] NBO and Löwdin population analyses were carried out on B3LYP/6-31+G(d) and HF/6-31+G(d) wavefunctions, respectively.

of 2.9 kcal mol^{-1}. This low and possibly negative electron binding energy helps to explain why deprotonation of cyclobutene affords the vinyl anion despite a slight preference for removing the allylic proton. That is, **3a** also is formed but undergoes electron detachment and is not detected.

Phenyl substitution has the same effect on cyclobutene as it does on propene. In particular, the acidities are increased by 21 kcal mol^{-1}, the bond dissociation energies are diminished by 5 kcal mol^{-1}, and the electron affinities are increased by 16 kcal mol^{-1} [eqns. (10)–(15)]. This results because the negative charge in **1a** and **2a** and the odd electron in **1r** and **2r** can be delocalized over the aromatic ring. Consequently, the differences between 1-phenylcyclobutene and (*E*)-1-phenylpropene can be attributed to the differences between the parent (unsubstituted) species. Analysis of the geometries and descriptors of their electronic structures[29] also indicate that the aromatic ring serves to delocalize the charge or the odd electron (Tables 5 and 6). For instance, deprotonation of 1-phenylcyclobutene leads to a shortening of the C1–C5 bond by 0.064 Å and elongation of the C1–C2 bond by 0.087 Å. In addition, the π-bond order of the former bond increases from 0.30 to 0.62 and the latter one decreases from 0.88 to 0.48. There also is a significant build up of negative charge at the *ortho* and *para* positions of the aromatic ring. These trends are as expected for a delocalized carbanion.

Conclusion

1-Phenylcyclobuten-3-yl and 1-phenylallyl anions were generated in the gas phase by deprotonation of 1-phenylcyclobutene and (*E*)-1-phenylpropene, respectively. The measured thermochemistry [$\Delta H^\circ_{\text{acid}} = 377.5 \pm 0.7$ (**1**) and 368.1 ± 2.1 kcal mol^{-1} (**2**) and EA = 21.7 ± 2.5 (**1r**) and 24.4 ± 1.6 kcal mol^{-1}(**2r**)] provides the corresponding allylic C–H bond dissociation energies [85.6 ± 2.6 (**1**) and 78.9 ± 2.6 kcal mol^{-1} (**2**)] *via* the application of a thermodynamic cycle. DFT and MP2 calculations indicate that a phenyl substituent affects cyclobutene and propene to about the same degree so that the differences between 1-phenylcyclobutene and (*E*)-1-phenylpropene can be largely attributed to the differences between the parent species.

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