Thermodynamics

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The Heat of Formation of Cyclobutadiene**

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Cyclobutadiene (**1**) and its derivatives have beckoned to chemists ever since Kekule's deduction of the structure of benzene and his attempt to synthesize **1** in 1872.[1] Pioneering efforts by Willstätter and Finkelstein were followed by a century of studies which produced many remarkable findings. Room temperature stable derivatives such as tri-*tert*-butylcyclobutadiene[2] and tetra-*tert*-butylcyclobutadiene[3] were successfully prepared and spectroscopically characterized, whereas the parent compound was found to be more elusive. It dimerizes in solid matrices at ≥ 35 K, is a transient reactive intermediate in solution, and has a lifetime of only 2 ms at 0.1 Torr in the gas phase.[1a] Nevertheless, trapping[4] and spectroscopic results have revealed that cyclobutadiene has a ground-state singlet configuration and adopts a rectangular D_{2h} structure which rapidly undergoes automerization. An isolable and room temperature stable complex consisting of **1** in the cavity of a spherical crown ether (that is, a hemicarceplex) has even been prepared,[5] but the thermodynamic stability of cyclobutadiene remains experimentally unknown.

Conventional calorimetric methods are precluded when it comes to cyclobutadiene and its simple derivatives because of their high reactivity. Electrochemical,[6] pK_a,[7] and kinetic[8] measurements of model compounds have been carried out and interpreted as indicating that **1** has a negative resonance energy of at least 50–67 kJ mol^{-1}. This conclusion is in accord with many of the early computational findings and a

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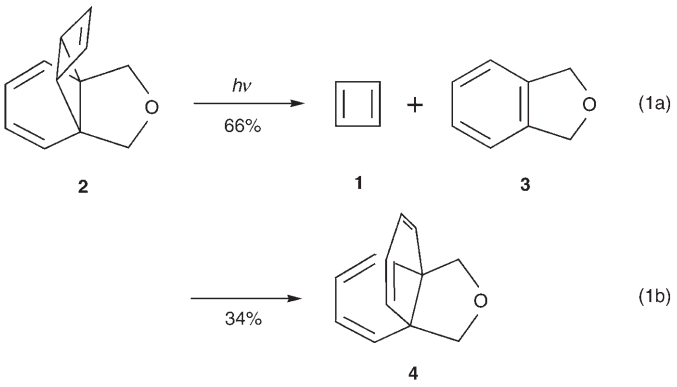
preliminary derivation of $\Delta H_f^\circ(\mathbf{1}) = 377\ kJ\,mol^{-1}$ based on tentative mass spectrometry data.[1a] However, this proposal has been questioned and a small positive resonance energy has been suggested.[9] More recently, a photoacoustic calorimetry study was reported in which the heat liberated in the photochemical generation of cyclobutadiene was measured [Eq. (1)].[10] The resulting reaction enthalpy can be directly



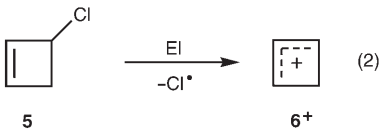
(1a) (1b)

converted into the heat of formation of **1** if the energies of **2**–**4** are known. Unfortunately, these quantities are unavailable, and there is not enough information in the literature to estimate them by using additivity approaches such as the Benson's group equivalents method.[11] To solve this problem, Deniz et al.[10] computed the geometries and energies of **2**–**4** by using molecular mechanics (namely, the MM3 force field) and semiempirical AM1 calculations, respectively. These data enabled $\Delta H_f^\circ(\mathbf{1}) = (477 \pm 46)\ kJ\,mol^{-1}$ to be derived. This value has an unusually large uncertainty and does not represent an experimental determination, despite the claim to the contrary.

Gas-phase measurements in which thermodynamic cycles were employed to provide the heats of hydrogenation of benzocyclobutadiene[12] and phenylcyclobutadiene[13] have also been reported. By comparing these results to **1** by ab initio (MP2) and density functional theory (the Becke 3-parameter hybrid exchange and Lee–Yang–Parr correlation density functional, that is, B3LYP)[14] calculations, $\Delta H_f^\circ(\mathbf{1}) =$ 427 and $(402 \pm 21)\ kJ\,mol^{-1}$ were predicted. Thus, a range of values for the heat of formation of cyclobutadiene spanning from 377 to 477 $kJ\,mol^{-1}$ can be found in the literature.

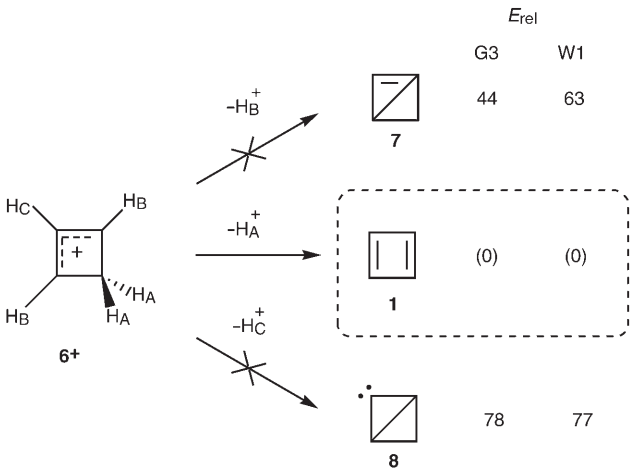
The experimental uncertainty revolving around the energetics of cyclobutadiene is mirrored by computational data which span an even larger range from 364 (BLYP/6-311G-(2d,2p) to 519 $kJ\,mol^{-1}$ (HF/4-31G).[15] More sophisticated methodologies (CCSD(T), CBS-Q, and G2)[15e,j,k,r] lead to predictions of 414–435 $kJ\,mol^{-1}$, but a recent detailed analysis dealing with the factors responsible for the destabilization of cyclobutadiene (σ versus π electrons) is compatible with a heat of formation of 477 $kJ\,mol^{-1}$.[15n] To resolve and settle this issue, we now report the first experimental determination of the heat of formation of cyclobutadiene as well as high level G3[16] and W1[17] computations, which typically are accurate to within 4–8 $kJ\,mol^{-1}$.

Electron ionization (EI) of a static pressure of 3-chlorocyclobutene (**5**) leads to a signal at m/z 53, which was assigned as the cyclobuten-3-yl cation ($\mathbf{6}^+$) [Eq. (2)]. This allylic ion is



(2)

stabilized by delocalization and has no apparent low-energy isomerization pathways available to it that would give more-stable species. To establish the identity of this ion hydrogen–deuterium exchange experiments were carried out. Isopropylamine-ND (iPrND$_2$) was found to induce up to five hydrogen–deuterium exchanges in $\mathbf{6}^+$, as expected for the proposed structure. This result also confirms that the deprotonation of the cyclobuten-3-yl cation affords cyclobutadiene, otherwise five H/D exchanges would not be observed. This finding was anticipated because a π bond is formed on converting $\mathbf{6}^+$ into cyclobutadiene, and its energetic benefit (ca. 272 $kJ\,mol^{-1}$) should outweigh the additional strain energy and antiaromaticity of **1** (ca. 167 $kJ\,mol^{-1}$, see below). High level G3 and W1 computations are in agreement with this result in that they indicate that deprotonation of $\mathbf{6}^+$ to afford the corresponding carbene (**7**, $-H_B$) or allene (**8**, $-H_C$) is much less favorable (Scheme 1).



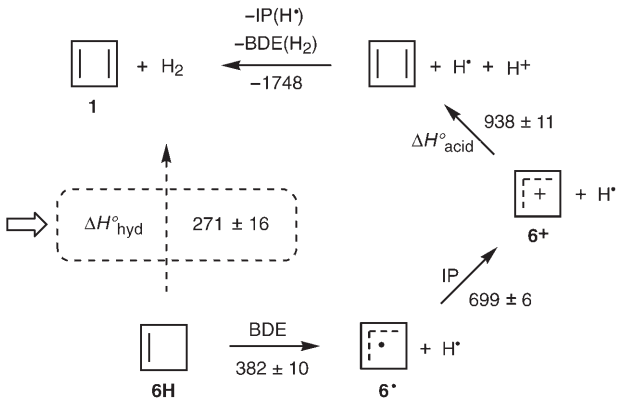
Scheme 1. Computed deprotonation energies of the cyclobuten-3-yl cation [$kJ\,mol^{-1}$].

The acidity of the cyclobuten-3-yl cation corresponds to the proton affinity of cyclobutadiene, and this quantity was measured by treating $\mathbf{6}^+$ with standard reference bases and observing the occurrence or absence of proton transfer. Strong bases such as ammonia (proton affinity (PA) = $(854 \pm 8)\ kJ\,mol^{-1}$) and isopropylamine (PA = $(924 \pm 8)\ kJ\,mol^{-1}$)[18] do not abstract a proton from the cyclobuten-3-yl cation, whereas more basic reagents such as pyrrolidine (PA = $(948 \pm 8)\ kJ\,mol^{-1}$, $k = 5.9 \times 10^{-10}\ cm^3\,molecule^{-1}\,s^{-1}$) and diisopropylamine (PA = $(972 \pm 8)\ kJ\,mol^{-1}$) are rapidly protonated.

Pyridine (PA = (929 ± 8) kJ mol^{-1}) is also observed to abstract a proton, but the rate is modest ($k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} or about 7 in 100 collisions lead to reaction),[19] which indicates that this is a slightly (4–8 kJ mol^{-1}) endothermic process. In bracketing experiments, such a result is taken as a "no" and thus isopropylamine and pyrrolidine are the limiting reagents and PA(**1**) = (938 ± 11) kJ mol^{-1} is assigned. This value is much larger than for other olefins (for example, PA((*Z*)-2-butene) = 753 kJ mol^{-1}, PA(1,3-butadiene) = 783 kJ mol^{-1}, and PA(isobutene) = 802 kJ mol^{-1}), which is not surprising because of the antiaromaticity of cyclobutadiene. It is also in nearly perfect accord with computed results of 937 (G3) and 938 (W1) kJ mol^{-1}.

The ionization potential of the cyclobuten-3-yl radical (**6**$^{\bullet}$) was also measured by bracketing. In particular, **6**$^+$ does not abstract an electron from *N*,*N*,*N*′,*N*′-tetramethyethylenediamine (ionization potential (IP) = (7.59 ± 0.04) eV) or 1,1-dimethylhydrazine (IP = (7.29 ± 0.05) eV), but rapidly does so from diphenylamine (IP = (7.19 ± 0.05) eV, $k = 9.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), *N*,*N*-dimethylaniline (IP = (7.12 ± 0.02) eV, $k = 1.2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}), and reagents with smaller ionization potentials. This finding leads to IP(**6**$^{\bullet}$) = (7.24 ± 0.06) eV, which is in excellent agreement with computed values of 7.29 (G3) and 7.24 eV (W1).

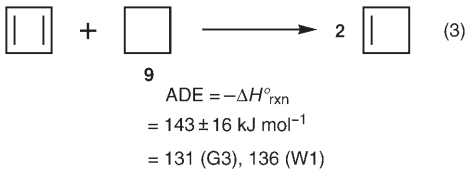
By combining the measured proton affinity of cyclobutadiene and the ionization potential of the cyclobuten-3-yl radical with the recently determined allylic C–H bond dissociation energy (BDE) of cyclobutene (**6H**, (382 ± 10) kJ mol^{-1})[20] and well-known ancillary data (IP(H$^{\bullet}$) = 1312 kJ mol^{-1} and BDE(H_2) = 436 kJ mol^{-1}), one can obtain an experimentally determined heat of hydrogenation for **1** of (271 ± 16) kJ mol^{-1} (Scheme 2). This value compares favor-



Scheme 2. Thermodynamic cycle for the heat of hydrogenation of **1** [kJ mol^{-1}].

ably with predicted values of 266 (G3) and 271 (W1) kJ mol^{-1}. It also leads to an experimentally determined heat of formation for cyclobutadiene of (428 ± 16) kJ mol^{-1}, since the enthalpy of formation of cyclobutene (ΔH_f° = (157 ± 2) kJ mol^{-1})[21] has been determined by combustion calorimetry. The heat of formation of **1** was also computed from its atomization energy, and the G3 and W1 results (435 and 427 kJ mol^{-1}, respectively) are within the experimental uncertainty and the expected accuracy of these methods. This observation provides a high level of confidence both in the experimental and computational results, and should serve to establish the energetics provided herein.

From the data above, the antiaromatic destabilization energy (ADE) of cyclobutadiene can be derived from the definition illustrated in Equation (3). A value of (143 ± 16) kJ mol^{-1} is obtained, which is in good accord with G3



and W1 predictions of 131 and 136 kJ mol^{-1}, respectively. In the latter case, all but 1.7 kJ mol^{-1} of the 7.1 kJ mol^{-1} difference can be attributed to the discrepancy between the experimental and computed heat of formation of cyclobutane (**9**; that is, ΔH_f° = (28.4 ± 0.6) (expt) versus 19.6 kJ mol^{-1} (W1)).[22,23]

It is important to add that the definition of the ADE used here is arbitrary, and that there is no model-free way of obtaining this quantity. Moreover, the implicit assumption made in Equation (3) is that the strain energy (SE) is the same in the reactants and products. This assumption seems reasonable since each species in the comparison is a four-membered ring and the difference in strain between cyclobutene (SE = 125 kJ mol^{-1}) and cyclobutane (SE = 112 kJ mol^{-1}) is only 13 kJ mol^{-1}.[11] Of course, there is no reason why the strain energy of **1** need be additive (that is, SE(**1**) = SE(**6H**) + SE(**6H**–**9**)) and the addition of two formal sp^2 centers to cyclobutene might lead to more than 13 kJ mol^{-1} of additional strain. This would make 137 kJ mol^{-1} a lower limit for the strain energy of cyclobutadiene. Alternatively, one could equate the measured strain energy of 3,4-bismethylenecyclobutene (**10**, 160 kJ mol^{-1})[24] to that of **1** since each ring carbon atom is formally sp^2 hybridized in both compounds. In this case, a 23 kJ mol^{-1} correction would need to be applied to the ADE, but this presumably is an upper limit because of the built in 1,4 hydrogen–hydrogen repulsion in **10**. Consequently, an average value of (149 ± 12) kJ mol^{-1} is adopted for the strain energy of **1**, which leads to a 12 kJ mol^{-1} correction to the ADE derived by way of Equation (3) and a destabilization or delocalization energy of (131 ± 20) kJ mol^{-1}.

An alternative approach to obtaining the ADE of **1** is to compute its heat of formation by an additivity method. Benson's group equivalents were used for this purpose and lead to $\Delta H_f^\circ = 113.5 + x$ kJ mol^{-1}, where x is the sum of the strain energy of cyclobutadiene and its antiaromatic destabilization energy.[11] By substituting the measured heat of formation into this equation one obtains x = (314 ± 16) kJ mol^{-1}, which cannot be separated into its two components in a model-independent way. If SE = (149 ± 12) kJ mol^{-1} is adopted as above, than an ADE or Dewar resonance energy of (165 ± 20) kJ mol^{-1} is obtained. This value is larger than the one derived from Equation (3), but

this is expected since conjugation is built into this model. If a nonconjugated reference is used (that is, C_d-(C)(H) (the energy equivalent for a double-bonded C atom attached to an sp^3-hybridized C atom and an H atom) rather than C_d-(C_d)(H)) than ADE = (136 ± 20) kJ mol^{-1}, which is in excellent accord with the previous determination.

The gas-phase heat of hydrogenation for cyclobutadiene has been determined experimentally by making measurements on the cyclobuten-3-yl cation and applying the results in a thermodynamic cycle. Since the heat of formation of cyclobutene is well established by combustion calorimetry, this provides the first experimental determination of the heat of formation of cyclobutadiene. The resulting value, (428 ± 16) kJ mol^{-1}, is in good accord with previous predictions of 427 and (402 ± 21) kJ mol^{-1} based upon similar energetic determinations of benzocyclobutadiene and phenylcyclobutadiene.[12,13] In contrast, an early estimate of 377 kJ mol^{-1} is significantly too low and a recent photoacoustic calorimetry determination of (477 ± 46) kJ mol^{-1} is too large.[1a,10] The former value is incorrect presumably because the structure of the $C_4H_4^{+\bullet}$ ion formed by the photoionization of pyridine is not ionized cyclobutadiene whereas the latter result is sensitive to the computational approach used to determine the energetics of **2**–**4**. The results reported herein are also in excellent agreement with G3, W1, and other very high level ab initio calculations, and were inspired in part by the G2-computed acidity of $\mathbf{6}^+$ reported by Maksic et al.[25] A very recent detailed analysis of the σ–π separability problem in **1**,[15n] however, leads to energetics (ΔH_f° and ADE) which are too large because electron correlation was thought to be unimportant and was omitted. Finally, a strain energy of (149 ± 12) kJ mol^{-1} is suggested for **1**, and this leads to an ADE value of 131–136 kJ mol^{-1} when a nonconjugated reference model is employed and 165 kJ mol^{-1} when conjugation is included. These findings indicate that the SE is similar in size to the ADE and that the latter is larger but in accord with the electrochemical, pKa, and kinetic measurements carried out on complex model systems.[6–8]

Experimental Section

Gas-phase experiments: A dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and operated with a Sun workstation running Odyssey 4.2 software or a similar instrument controlled by an IonSpec data system running IonSpec99 Ver. 7.0 software were used for these studies. 3-Chlorocyclobutene[26] was added into the first (analyzer) cell at a static pressure of approximately 4×10^{-8} Torr and ionized with 50 eV electrons for 20 ms. All of the resulting ions were transferred to the second (source) cell and translationally and vibrationally cooled with two pulses of argon, each leading to a pressure of about 1×10^{-5} Torr. The desired $[M-Cl]^+$ ion at m/z 53 was subsequently isolated with a stored-waveform inverse Fourier transform (SWIFT) excitation.[27] Neutral reagents were added into the source cell through a solid probe inlet or slow leak valves, and the resulting reactions were monitored as a function of time. To confirm the results of bracketing experiments, the reactions were monitored by continually ejecting the m/z 53 ion and observing the effect on the product ions (that is, double resonance experiments) and by not transferring the reactant ion to the second cell. Rate constants reported in this work are estimated to have an uncertainty of ± 50%, largely because of the uncertainty in measuring reagent gas pressures with an ionization gauge.

Computations: G3[16] and W1[17] calculations were carried out as previously described in the literature using Gaussian 2003[28] on IBM and SGI workstations at the Minnesota Supercomputer Institute. All of the resulting energies are reported as enthalpies at 298 K, and were obtained by using scaled Hartree–Fock (0.8929, G3) and B3LYP (0.985, W1) vibrational frequencies. In both cases, small vibrational frequencies which contribute more than $^1/_2(RT)$ to the thermal energy were replaced by $^1/_2(RT)$.

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