Why Are Methylenecyclopropane and 1-Methylcylopropene More "Strained" than Methylcyclopropane?

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Abstract: *Ab Initio* calculations have been performed in order to investigate why the introduction of each trigonal center into a cyclopropane ring results in an increase in strain energy of 12−14 kcal/mol. Our calculations find that, as is commonly believed, introduction of a trigonal center into a three-membered ring does create some additional angle strain. However, our computational results show that the major source of the additional "strain" that results from the introduction of each trigonal center into cyclopropane is not an increase in angle strain but the loss of a very strong cyclopropane C−H bond.

In 1968, Wiberg and Fenoglio measured the heats of formation of methylenecyclopropane and 1-methylcyclopropene.[1] From their measurements they concluded that introduction of each trigonal center into a cyclopropane ring results in an increase in strain energy of 12−14 kcal/mol.

For example, using Wiberg and Fenoglio's value for the heat of formation of methylenecyclopropane[1] and literature values for the heats of formation of methylcyclopropane,[2,3] isobutylene,[2] and isobutane,[2] the isodesmic reaction in eq 1 is found
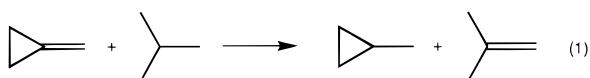
to be exothermic by 14.3 kcal/mol. Equation 1 can be construed as measuring either the difference between the heats of hydrogenation of methylenecyclopropane and isobutylene or the difference between the energies required to convert isobutane and isobutylene into, respectively, methylcyclopropane and methylenecyclopropane. Both interpretations of eq 1 indicate that methylenecyclopropane is ca. 14 kcal/mol more strained than methylcyclopropane.

Quite reasonably, Wiberg and Fenoglio attributed the greater strain energies of methylenecyclopropane and 1-methylcyclopropene to the additional angle strain that results from the presence of, respectively, one and two nominally sp^2, rather than sp^3, carbons in a three-membered ring.[1] This explanation has been widely accepted.[4]

Upon breaking the π bond in methylenecyclopropane, the trigonal ring carbon can pyramidalize, thus relieving the additional angle strain that results from the presence in the three-membered ring of a carbon that is nominally sp^2, rather than sp^3, hybridized. The strain released upon pyramidalization of the trigonal carbon in the transition state should be reflected in an unusually low barrier to rotation about the double bond in methylenecyclopropane.[5] However, Roth and co-workers have

recently found that the barrier to rotation about the double bond in a methylenecyclopropane derivative is only 3.7 kcal/mol less than the rotational barrier in a similarly substituted isobutylene derivative.[6] This very modest lowering of the rotational barrier is only a small fraction of Wiberg and Fenoglio's value of 14 kcal/mol for the additional strain energy in methylenecyclopropane, compared to methylcyclopropane.

In order to reconcile these apparently conflicting experimental results, we have performed *ab initio* calculations. The results of these calculations show that the major source of the additional "strain" energy in methylenecyclopropane and in 1-methylcyclopropene is not angle strain but, rather, the absence of, respectively, one and two unusually strong C−H bonds that are present in methylcyclopropane.

Computational Methodology

All calculations were carried out with the 6-31G* basis set.[7] Geometries were optimized and vibrational frequencies computed using (2,2)CASSCF for alkenes and diradicals, ROHF for radicals, and RHF for alkanes. These calculations were performed with the Gaussian 94 suite of programs.[8]

Single-point energies for alkanes were recalculated at the MP2 level,[9] using Gaussian 94. For single-point calculations on alkenes, radicals, and diradicals the CASPT2N method[10] was employed. The CASPT2N calculations were carried out with MOLCAS.[11] The calculated electronic energies and the vibrational corrections to them are given in Table 1.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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(5) For examples see: Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275. Hrovat, D. A.; Sun, H.; Borden, W. T. *THEOCHEM* **1988**, *163*, 51. Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. Hammons, J. H.; Coolidge, M. B.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468. Coolidge, M. B.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2354. Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 8682.

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Table 1. SCF,[a] MP2,[b] and Zero-Point Energies and Heat Capacities

molecule	SCF (hartrees)[a]	MP2 (hartrees)[b]	ZPE (kcal/mol)	C_v^{298} (cal/(mol K))
methylenecyclopropane	−154.9148	−155.4185	57.0	14.0
methylcyclopropane	−156.0959	−156.6363	73.7	15.0
methylenecyclopropane TS[c]	−154.8167	−155.3231	54.1	14.8
planar methylenecyclopropane TS[d]	−154.8094	−155.3203	53.5	13.1
1-methylcyclopropyl radical	−155.4543	−155.9757	64.6	15.1
planar 1-methylcyclopropyl radical	−155.4446	−155.9697	63.7	13.7
bisected cyclopropylmethyl radical	−155.4616	−155.9841	63.9	15.9
C_s staggered cyclopropylmethyl radical	−155.4601	−155.9806	63.7	15.9
isobutylene	−156.1378	−156.6486	72.0	17.5
isobutane	−157.2990	−157.8472	88.3	18.8
isobutylene TS[c]	−156.0323	−156.5456	68.5	18.9
planar isobutylene TS[d]	−156.0305	−156.5452	67.7	17.4
tert-butyl radical	−156.6707	−157.2007	78.8	19.3
planar C_s *tert*-butyl radical	−156.6673	−157.1985	78.0	17.9
C_s bisected isobutyl radical	−156.6613	−157.1904	77.8	18.5
C_s staggered isobutyl radical	−156.6625	−157.1905	78.5	19.6
1-methylcyclopropene	−154.8943	−155.4004	56.5	15.1
trans-2-methylcyclopropyl radical	−155.4494	−155.9701	64.5	15.0
cis-2-methylcyclopropyl radical	−155.4496	−155.9706	64.5	15.0
planar 2-methylcyclopropyl radical	−155.4414	−155.9655	63.3	14.3

[a] RHF for alkanes, ROHF for radicals, and (2,2)CASSCF for alkenes. [b] MP2 for alkanes and CASPT2N for alkenes, radicals, and diradicals. [c] Transition state for rotation about the double bond. [d] Transition state for rotation about the double bond with the tertiary radical center constrained to planarity.

Results and Discussion

Using the data in Table 1, we computed ΔH^{298} for the isodesmic reaction in eq 1. After correcting the electronic energies for zero-point energies and heat capacities, $\Delta H^{298} = -12.2$ kcal/mol was obtained at the CASSCF-RHF level of theory, and −11.7 kcal/mol was computed at CASPT2N-MP2. Given the sizes of the uncertainties in the experimental heats of formation of the four hydrocarbons in eq 1,[1−3] the agreement between the experimental value of $\Delta H^{298} = -14.3$ kcal/mol and these calculated values is satisfactory.

Next we compared the barrier to rotation about the double bond in methylenecyclopropane (eq 2) with that in isobutylene (eq 3). For the former reaction $\Delta H^{\ddagger} = 58.9$ and 57.2 kcal/mol

(2)
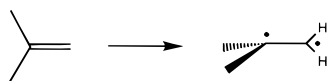
(3)

were calculated at, respectively, the CASSCF and CASPT2N levels of theory. For the latter reaction these values were $\Delta H^{\ddagger} = 63.1$ and 61.6 kcal/mol. In agreement with the experimental results of Roth and co-workers,[6] the barrier to rotation in methylenecyclopropane is calculated to be lower than that in isobutylene by ca. 4 kcal/mol, but this difference between the calculated barrier heights is only one-third of the 12 kcal/mol difference between the calculated heats of hydrogenation.

By constraining to planarity the tertiary radical center in each of the two transition states, the contribution of relief of angle strain to the lower value of $\Delta H^{\ddagger}$ for rotation about the double bond in methylenecyclopropane can be evaluated.[5] At the CASSCF level of theory the resulting increase in the energy of the transition state is 4.6 kcal/mol for methylenecyclopropane but only 1.1 kcal/mol for rotated isobutylene. The CASPT2N transition state energy increases are, respectively, 1.8 and 0.3 kcal/mol. Thus, only 1.5−3.5 kcal/mol of the 4.3 kcal/mol

difference between the rotational barriers is due to selective relief of angle strain on pyramidalization of the tertiary radical center in the transition state for rotation about the double bond in methylenecyclopropane. The balance of the 4.3 kcal/mol difference between the two rotational barriers can be attributed (*vide infra*) to selective stabilization of the primary radical center by the bent bonds of the adjacent cyclopropyl ring in this transition state.[12]

An analysis that uses Benson's "thermodynamic" definition of π BDEs,[13] rather than the "kinetic" definition based on rotational barriers, also shows that relief of angle strain makes only a minor contribution to the exothermicity of the isodesmic reaction in eq 1. The thermodynamic π BDEs of methylenecyclopropane and isobutylene are given, respectively, by the enthalpies of the reactions in eqs 4 and 5.
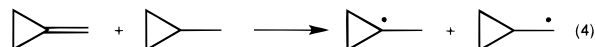
(4)
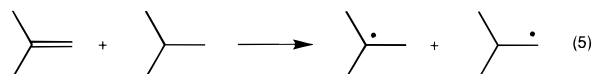
(5)

Using these definitions, the π BDE at 298 K of methylenecyclopropane is calculated to be 57.9 kcal/mol at the CASSCF-RHF-ROHF level of theory and 58.0 kcal/mol when correlation is included at the CASPT2N-MP2-CASPT2N level of theory. The corresponding π BDEs for isobutylene are, respectively, 62.8 and 63.4 kcal/mol. The CASSCF-RHF-ROHF and CASPT2N-MP2-CASPT2N differences between the thermodynamic π BDEs of methylenecyclopropane and isobutylene (eqs 4 and 5) are thus, respectively, 4.9 and 5.4 kcal/mol. These values are close to but slightly larger than the ca. 4.3 kcal/mol

(11) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS-3*; University of Lund: Sweden.

(12) The amount by which (2,2)CASSCF overestimates the barrier to planarity at the tertiary radical center, relative to CASPT2N, is fortuitously nearly the same as the amount by which (2,2)CASSCF underestimates the stabilizing interaction between the primary radical center and the bent bonds of the cyclopropane ring. However, since CASPT2N uses second-order perturbation theory, it tends to overestimate the effects of dynamic correlation. Inclusion of these effects variationally would be expected to yield results that are bracketed by the CASSCF and CASPT2N values but which are closer to the latter.

(13) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63−65.

difference between the kinetic π BDEs (eqs 2 and 3) that is computed at both the CASSCF and CASPT2N levels of theory.[12]

One contributor to the difference between the thermodynamic π BDEs of methylenecyclopropane and isobutylene is the greater stabilization on pyramidalization of the 1-methylcyclopropyl radical than of the *tert*-butyl radical. At the ROHF and CASPT2N levels of theory these pyramidalization energies are, respectively, 6.1 and 3.8 kcal/mol for the former radical[14,15] and 2.1 and 1.4 kcal/mol for the latter. Thus, the difference in pyramidalization energies between the two tertiary radicals in eqs 4 and 5 accounts for only 2.4−4.0 kcal/mol of the 4.9−5.5 kcal/mol difference between the thermodynamic π BDEs of methylenecyclopropane and isobutylene.

Most of the remainder of the difference between the thermodynamic π BDEs of these two alkenes can be accounted for by stabilization of the radical center in the cyclopropylmethyl radical by the bent bonds of the adjacent cyclopropane ring.[16] For example, the "bisected" conformation of the cyclopropylmethyl radical, which provides the best overlap between the ring bonds and the singly occupied AO of the CH_2 group, is lower in energy than the C_s "staggered" conformation by 0.9 kcal/mol at the ROHF level and by 2.2 kcal/mol at the CASPT2N level of theory.

Clearly, the calculated difference of ca. 12 kcal/mol between the heats of hydrogenation of methylenecyclopropane and isobutylene in eq 1 does not reside principally in the calculated difference of 4−5 kcal/mol between the strengths of the two π bonds that are broken upon hydrogenation. Therefore, the exothermicity of the reaction in eq 1 must be due to formation of one or two particularly strong C−H bonds when methylenecyclopropane is hydrogenated. Indeed, our calculations show this to be the case.

The difference between the strengths of the primary C−H bonds formed in the hydrogenation of methylenecyclopropane and of isobutylene is given by the isodesmic reaction in eq 6.
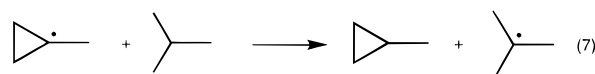

(6)
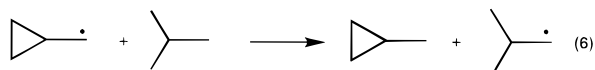
The reaction in eq 6 is calculated to be endothermic by 1.4 kcal/mol at the ROHF-RHF level and by 2.8 kcal/mol when electron correlation is included at the CASPT2N-MP2 level. The lower primary C−H BDE in methylcyclopropane than in isobutane can again be attributed to the selective stabilization of the radical center in the cyclopropylmethyl radical by the bent bonds of the adjacent cyclopropyl group.[16]

The difference between the strengths of the tertiary C−H bonds formed in the hydrogenation of methylenecyclopropane and of isobutylene is given by the isodesmic reaction in eq 7. In contrast to the small endothermicity calculated for the reaction in eq 6, the reaction in eq 7 is computed to be highly exothermic,

(7)

by −8.6 kcal/mol at ROHF-RHF and by −9.1 kcal/mol with inclusion of correlation at the CASPT2N-MP2 level. The exothermicity of this reaction reflects the unusually strong C−H bonds formed by the cyclopropyl ring carbons.[17] Thus, our calculations show that the biggest contributor to making the heat of hydrogenation of methylenecyclopropane considerably larger than that of isobutylene is the greater strength of the tertiary C−H bond in methylcyclopropane than in isobutane.

As noted above, the reaction in eq 1 can be viewed as comparing, instead of the heats of hydrogenation of methylenecyclopropane and isobutylene, the energies required to convert isobutane and isobutylene into, respectively, methylcyclopropane and methylenecyclopropane. From the latter perspective the major contributor to making methylcyclopropane easier to form than methylenecyclopropane is the presence of a tertiary C−H bond in isobutane, which is absent in isobutylene. Our calculations find that this C−H bond is strengthened by ca. 9 kcal/mol on conversion of isobutane to methylcyclopropane. Thus, our calculations show that most of the additional strain energy in methylenecyclopropane, relative to methylcyclopropane, resides, not in angle strain, but in the tertiary C−H bond that is present in methylcyclopropane but absent in methylenecyclopropane.[18]

Our calculations find that the major portion of the higher heat of formation of 1-methylcyclopropene, compared to methylenecyclopropane, has a similar origin. The measurements of Wiberg and Fenoglio yielded a difference in heat of formation of 10.2 kcal/mol between these two isomers.[1] In reasonable agreement with this experimental value, we calculate 1-methylcyclopropene to have the higher heat of formation by 12.7 kcal/mol at the CASSCF level and by 11.2 kcal/mol at CASPT2N.

Because 1-methylcyclopropene and methylenecyclopropane both give methylcyclopropane upon hydrogenation, the difference between the heats of formation of the two alkenes is equal to the difference between their heats of hydrogenation. Thus, by calculating the differences between the energies of the π bonds that are broken and the C−H bonds that are made in the hydrogenation of both compounds, the origin of the difference in heats of formation can be established.[19]

The structural relationship between 1-methylcyclopropene and methylenecyclopropane results in the difference between their thermodynamic π BDEs reducing to the enthalpy of the isodesmic reaction in eq 8. This reaction is calculated to be

(8)

exothermic by 4.8 and 2.4 kcal/mol at, respectively, the

(14) After correcting for differences in zero-point energies and heat capacities, our calculations predict $\Delta H^{\ddagger} = 3.3$ kcal/mol for inversion in the 1-methylcyclopropyl radical at 298 K. This calculated value is in excellent agreement with the experimental value of $E_a = 3.1 \pm 0.2$ kcal/mol, obtained by an EPR study of the rate of inversion of this radical in the temperature range 92−161 K. Deycard, S.; Hughes, L.; Lusztyk, J.; and Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 4954.

(15) For other *ab initio* calculations of barriers to inversion in cyclopropyl radicals see, *inter alia*: Apeloig, Y.; Nakash, M. *J. Am. Chem. Soc.* **1994**, *116*, 10781. Barone, V.; Minichino, C.; Faucher, H.; Subra, R.; Grand, A. *Chem. Phys. Lett.* **1993**, *205*, 324. Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274.

(16) McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*, 359. Danen, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 4835. Radom, L; Paviot, J.; Pople, J. A.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1974**, 58. Walton, J. C. *Magn. Reson. Chem.* **1987**, *25*, 998. Hehre, W. J., *J. Am. Chem. Soc.* **1973**, *95*, 2643.
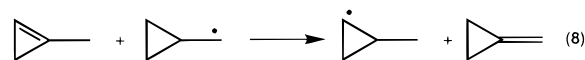
(17) The C−H BDE in cyclopropane at 298 K has been measured to be 106.3 ± 0.3 kcal/mol (Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838), which is nearly 8 kcal/mol larger than the BDE at 298 K of 98.6 ± 0.4 kcal/mol for a secondary C−H bond in propane (Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Kransoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847). Of the several reasons considered by Baghal-Vayjooee and Benson for the unusually high C−H BDE in cyclopropane, the major cause, according to our calculations, is not a large increase in strain on forming a planar cyclopropyl radical but the unusually large amount of carbon 2s character in a cyclopropane C−H bond.

(18) It has previously been noted that the strong C−H bonds in cyclopropane reduce its apparent strain energy. Hamilton. J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.

(19) Calculating these differences in BDEs is the same as calculating separately the changes that occur in the energies of the π C−C and σ C−H bonds in converting one isomer into the other.

CASSCF-ROHF and CASPT2N-CASPT2N levels of theory. Pyramidalization of the secondary radical center in the 2-methylcyclopropyl radical is calculated to lower selectively the π BDE of 1-methylcyclopropene by 5.1 kcal/mol at the RHF level and by 3.2 kcal/mol at CASPT2N.[15] Thus, although this difference in angle strain is responsible for almost all of the difference between the π BDEs of 1-methylcyclopropene and methylenecyclopropane, this difference in angle strain is obviously not responsible for the bulk of the calculated difference of 11−13 kcal/mol between the heats of formation of these two isomers.

Since the difference in π BDEs accounts for less than half of the difference between the heats of formation of 1-methylcyclopropene and methylenecyclopropane, the bulk of the difference in their heats of formation must reside in a difference in C−H bond strengths. The latter difference can easily be shown to be equal to the difference between the heats of formation of the 2-methylcyclopropyl radical and the cyclopropylmethyl radical. We calculate this difference to be 7.9 and 8.8 kcal/mol at, respectively, the ROHF and CASPT2N levels of theory.

The difference between the heats of formation of these two radicals is equal to the difference between the BDEs of a secondary and a primary C−H bond in methylcyclopropane. Therefore, the major reason why 1-methylcyclopropene has a higher heat of formation than methylenecyclopropane is that a secondary cyclopropyl C−H bond in the latter alkene is considerably stronger than a primary methyl C−H bond in the former.[20]

In summary, our calculations find that, as suggested by Wiberg and Fenoglio,[1] introduction of a trigonal center into a three-membered ring does, indeed, create some additional angle strain. However, our computational results show that the major source of the additional strain that results from the introduction of each trigonal center into a cyclopropane ring is not an increase in angle strain but the loss of a very strong cyclopropane C−H bond.

(20) Ordinarily, a primary C−H bond is, of course, stronger than a secondary C−H bond. Our CASSCF/6-31G* calculations indicate that the ca. 2.7 kcal/mol higher experimental heat of formation of 1-butene, relative to *trans*-2-butene,[2] is, in fact, largely due to this difference in C−H bond strengths. Of the computed difference of 2.6 kcal/mol between the heats of formation of these two isomeric butenes at 298 K, only 0.2 kcal/mol is due to the calculated difference between the thermodynamic π BDEs. The remaining 2.4 kcal/mol is accounted for by the ROHF/6-31G* difference between the heats of formation of the 1-butyl and 2-butyl radicals, which is equal to the difference between the primary and secondary C−H BDEs in butane.