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Does Formation of Singlet Propane-1,3-diyl from Propane Deviate from Bond Enthalpy Additivity? Results of Ab Initio Calculations That Bear on the Existence of the Benson Barrier to Diradical Ring Closure[†]

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CISD/cc-pVTZ//CISD/6-31G* calculations have been performed in order to compute the difference between the bond dissociation enthalpies (BDEs) of a C−H bond at C-3 of the 1-propyl radical and a primary C−H bond in propane. The implications of the computational finding that these two BDEs are almost the same are discussed with reference to both the amount of through-bond interaction between the radical centers at the (0,0) geometry of propane-1,3-diyl (**1**) and thermochemical estimates of ΔH_f^{298} of **1**. To compare ΔH_f^{715} of **1** with ΔH_f^{715} of the transition structure for cis−trans isomerization of cyclopropane, the difference between the heat capacities of **1** and cyclopropane, integrated between 298 and 715 K, has also been calculated. This difference is computed to increase the calculated heat of formation of the diradical, relative to that of the transition structure, by ca. 1 kcal/mol. The results of our calculations, when combined with experimental values for the heats of formation of cyclopropane and propyl radical at 298 K and with the literature value for the enthalpy of activation for cis−trans isomerization of cyclopropane at 715 K, place the enthalpy of diradical **1** ca. 2 kcal/mol below that of the activated molecules which undergo this reaction. This result, which is at odds with our finding that the (0,0) geometry of **1** *is* the transition structure for conrotatory ring opening and ring closure of cyclopropane, is discussed in terms of contributions to the activation enthalpy from higher energy pathways for this reaction.

If there is no interaction between the radical centers in a diradical, the enthalpy change in forming the diradical from a closed-shell molecule is equal to the sum of the enthalpy changes for breaking the same two bonds in two closed-shell molecules to form two monoradicals. The heat of formation of the diradical is then said to be given by bond enthalpy additivity (BEA). Because BEA holds only when the presence of one radical center does not affect the bond dissociation enthalpy (BDE) for forming the second radical center, deviations from BEA provide a way of assessing the energy that is associated with interactions between the two radical centers in a diradical.[1]

For example, the deviation from bond enthalpy additivity (ΔBEA*)* for forming propane-1,3-diyl (**1**) from propane is given by the enthalpy of the reaction in eq 1, which is equal to the difference between the C−H BDE in eq 3 and C−H BDE in eq 2.

$$2\mathrm{CH_3CH_2CH_2^\bullet} \rightarrow \mathrm{CH_3CH_2CH_3} + {}^\bullet\mathrm{CH_2CH_2CH_2^\bullet} \quad (1)$$

$$\mathrm{CH_3CH_2CH_3} \rightarrow \mathrm{CH_3CH_2CH_2^\bullet} + \mathrm{H^\bullet} \quad (2)$$

$$\mathrm{CH_3CH_2CH_2^\bullet} \rightarrow {}^\bullet\mathrm{CH_2CH_2CH_2^\bullet} + \mathrm{H^\bullet} \quad (3)$$

The value of ΔBEA in forming **1** from propane provides a measure of the extent to which hyperconjugation of the radical centers with the adjacent CH_2 groups in two 1-propyl radicals provides more (or less) stabilization than hyperconjugation of the pair of radical centers in **1** with the CH_2 group that is adjacent to both of them. A positive ΔBEA for forming singlet **1** would mean that two different CH_2 groups are better than one common CH_2 group at hyperconjugatively stabilizing two radical centers. A negative ΔBEA would mean that interaction of both radical centers in **1** with the bonds of the adjacent CH_2 group provides greater hyperconjugative stabilization of the singlet diradical than that which is available in two propyl monoradicals.

The question of the sign and size of ΔBEA is especially important for **1**, because Benson's thermochemical estimates of the heats of formation of diradicals, such as **1**, rely on the assumption that ΔBEA = 0.[2] For example, Benson calculated the heat of formation of **1** at 298 K using ΔH_f^{298} of propane and twice the value for the BDE of a primary C−H bond in ethane at this temperature. The resulting value of 67.0 kcal/mol for the heat of formation of **1** placed it 54.3 kcal/mol above ΔH_f^{298} for cyclopropane but ca. 9 kcal/mol below the heat of formation of the transition structure (TS) for cis−trans isomerization of cyclopropane-d_2.[2] The enthalpy of the TS was obtained by adding $\Delta H^\ddagger$ for this reaction, measured by Rabinovitch and co-workers,[3] to ΔH_f^{298} for cyclopropane.

If the Benson analysis were correct, singlet diradical **1** would be an energy minimum, and its cyclization to cyclopropane would require passage over a TS that is 9 kcal/mol higher in enthalpy than **1**. However, neither the extended Hückel (EH) calculations of Hoffmann,[4] nor the first ab initio calculations on the ring opening of cyclopropane by Salem and co-workers,[5] nor many subsequent ab initio calculations on this reaction[6] have found a significant energy minimum corresponding to **1**, much less an energy minimum with a ca. 9 kcal/mol barrier to ring closure. The apparent disagreement between the results of thermochemical and quantum chemical calculations has been

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discussed in several reviews published by Berson.[7] The assumption of ΔBEA $= 0$ for the formation of **1** from propane was mentioned as one possible source of the apparent disagreement.

In 1981, Doering[8] identified the major source of the apparent disagreement as being the value for the primary C−H BDE used by Benson. An upward revision by 2.6 kcal/mol in the accepted value for the C−H BDE in ethane led to an increase in the estimated heat of formation of **1** to $\Delta H_f^{298} = 72.2$ kcal/mol and to the disappearance of >5 kcal/mol of the 9 kcal/mol Benson barrier to ring closure.

Doering claimed a further reduction of about 4 kcal/mol in the size of the Benson barrier by arguing for $\Delta H^{\ddagger} = 60$ kcal/mol for cis−trans isomerization of cyclopropane-1,2-d_2, in place of the higher value of $\Delta H^{\ddagger} = 63.6 \pm 0.5$ kcal/mol, derived directly from the rate data of Schlag and Rabinovitch.[3b,9a] Doering concluded, "The Benson activation energy [for ring closure] bids to be disappearing in response to revisions in the Arrhenius parameters for geometrical isomerization of cyclopropane and in the heat of formation of the ethyl radical."[8]

Because Doering's value for the heat of formation of **1** is based on the assumption of bond enthalpy additivity, the good agreement, claimed by Doering, between the estimated values of $\Delta H_f = 72.2$ kcal/mol for **1** and $\Delta H_f = 72.8$ kcal/mol for the TS for cis−trans isomerization of cyclopropane-1,2-d_2 might suggest that ΔBEA for formation of **1** from propane actually is zero, or very close to it. However, the two heats of formation may actually be farther apart than comparison of Doering's values would suggest.

For example, the current experimental value for the BDE of a primary C−H bond in propane is ca. 0.5 kcal/mol higher than the value used by Doering,[10] and the higher BDE raises Doering's value for the heat of formation of **1** by about 1.0 kcal/mol. In addition, Berson has argued that the value of $\Delta H^{\ddagger} = 60$ kcal/mol for cis−trans isomerization of cyclopropane-1,2-d_2, used by Doering, is also too low, but possibly by as much as 3−4 kcal/mol.[7c,9b] Consequently, the difference between the values of ΔH_f for **1** and for the TS for cis−trans isomerization of cyclopropane-1,2-d_2 could easily be as large as 3 kcal/mol. Therefore, comparison of the two heats of formation does not show that ΔBEA ≈ 0 for formation of **1**; it only suggests that ΔBEA is probably not larger than 3 kcal/mol.

An additional uncertainty in the comparison of the heats of formation is introduced by the need to compare them at a common temperature. To obtain the heat of formation of the TS at 715 K, the middle of the temperature range in which Rabinovitch's kinetic measurements were made, the heat capacity of cyclopropane has to be integrated from 298 to 715 K. Using the NIST Chemistry WebBook values for the heat capacity in this temperature range,[11] the size of this correction to the heat of formation of the TS at 715 K is not trivial; it amounts to 8.8 kcal/mol.

To compare ΔH_f^{715} for the TS with the estimated value of ΔH_f^{715} for diradical **1**, the heat capacity of diradical **1** must also be integrated from 298 to 715 K and added to ΔH_f^{298} for **1**. Unfortunately, the heat capacity of **1** has not been, and probably cannot be measured. Nevertheless, Benson has estimated it to be 17.6 cal/(mol K) at 298 K, 4.3 cal/(mol K) greater than that of cyclopropane at this temperature.[2a]

Assuming that the 4.3 cal/(mol K) difference in heat capacities is temperature independent and integrating this difference from 298 to 715 K, Benson calculated that at 715 K the difference between the heat capacities of **1** and cyclopropane would contribute 1.7 kcal/mol toward increasing the heat of formation of **1**, relative to that of the TS for cis−trans isomerization of cyclopropane-d_2.[2a] A correction for the greater heat capacity of **1** was not included in Doering's comparison of the two estimated heats of formation.[8]

Because cyclopropane is more rigid than diradical **1**, there is little doubt that **1** does have the higher heat capacity. However, Benson's estimate of the heat capacity of **1** at 298 K required some assumptions about the methylene rotational barriers in the diradical, and it is highly unlikely that the difference between the heat capacities of **1** and of cyclopropane really is temperature independent over a range of more than 400°. To establish whether there really is a difference between the heat of formation of **1** and that of the TS for cis−trans isomerization of cyclopropane-1,2-d_2, it is necessary to know whether Benson's value for the integrated difference between the heat capacities is accurate.

The calculations described here were carried out in order to obtain two quantitities, both of which are necessary for an accurate comparison of the heats of formation of **1** and the TS. First, we have addressed the question of the size of ΔBEA for formation of **1**. Not only is knowing the difference between the BDEs for breaking the first and second primary C−H bonds in propane essential for obtaining ΔH_f^{298} of **1**, but the answer to the 40-year old question of whether ΔBEA ≈ 0 is of significant interest in its own right.

We have previously computed the energy of the reaction in eq 1, which defines ΔBEA for formation of **1** from propane, with (2/2)CASSCF/6-31G* calculations. We obtained $\Delta E = 1.6$ kcal/mol, but without corrections for differences in zero-point energies or heat capacities.[12] Here we report the results of calculations of ΔE, performed with a much better basis set and with inclusion of dynamic electron correlation.[13] We also report the calculated zero-point and thermal corrections that are necessary to obtain ΔBEA at 298 K from ΔE.

Second, we have calculated the difference between the heat capacities of **1** and cyclopropane, integrated from 298 to 715 K. As discussed above, this integrated difference between the heat capacities is necessary to make the comparison between the estimated ΔH_f^{298} for **1** and the sum of ΔH_f^{298} for cyclopropane and $\Delta H^{\ddagger}$ for cis−trans isomerization of cyclopropane-1,2-d_2 at 715 K. Here we report the calculated size of this integrated difference.

Finally, we discuss how the results of both sets of calculations affect the size of the "Benson barrier"; i.e., the difference between ΔH_f^{715} of **1** and ΔH_f^{715} of the TS for cis−trans isomerization of cyclopropane-1,2-d_2. We conclude that the enthalpy of the diradical really is slightly lower than the average enthalpy of the activated molecules that undergo cis−trans isomerization, and we discuss the reason for the existence of this enthalpy difference.

Computational Methodology

Geometries were optimized and vibrational analyses performed with configuration interaction calculations that included all single and double excitations (CISD). The CISD calculations were carried out using RHF reference wave functions for propane and cyclopropane, an ROHF wave function for propyl radical, and (2/2)CASSCF calculations for diradical **1**. The 6-31G* basis set[14] was employed for all of these calculations. The CISD/6-31G* vibrational frequencies were used, without scaling, to compute the zero-point energies and heat capacities that were necessary to convert energy differences into enthalpy differences. Gaussian 98[15] was used to perform the calculations

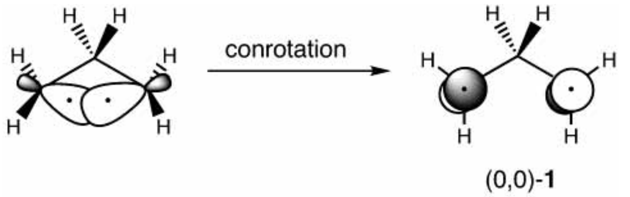

Figure 1. Depiction of the highest occupied (HO)MO in the conrotatory opening of cyclopropane to the (0,0) geometries of propane-1,3-diyl (**1**).

on propane and cyclopropane, and MOLCAS[16] was used for the calculations on 1-propyl radical and propane-1,3-diyl.

Single-point CISD calculations were performed at the CISD/6-31G* optimized geometries using Dunning's cc-pVTZ basis set.[17] The effects of quadruple excitations were approximated by the Davidson correction.[18] These single-point calculations were carried out with MOLCAS.

Results and Discussion

Geometry of Diradical 1. Hoffmann's landmark EH study found singlet propane-1,3-diyl (**1**) to prefer the so-called (0,0) geometry,[4] which is shown in Figure 1. The (0,0) geometry of **1** maximizes hyperconjugative interaction of the weakly electron-donating C−H bonds at C-2 with the in-phase combination of the 2p-π AOs at C-1 and C-3. This through-bond interaction[19] favors occupancy of the out-of-phase combination of 2p-π AOs at C-1 and C-3 by the pair of nonbonding electrons, because this AO combination does not interact with the C−H orbitals at C-2. This led Hoffmann to predict that, as depicted in Figure 1, ring opening to the (0,0) geometry of **1** would occur in a conrotatory fashion.[20−22]

In contrast to Hoffmann's EH results,[4] ab initio calculations, which correlated the pair of electrons in the breaking C−C bond, found (0,0)-**1** to be a mountaintop on the potential energy surface for cyclopropane ring opening, with negative force constants for both conrotation and disrotation.[5,6] The reaction path around the C_{2v} mountain top for (0,0)-**1** involves sequential, rather than simultaneous, passage of the terminal methylene groups through the C−C−C plane, and this circuitous reaction path passes through C_2 and C_s intermediates and over pairs of C_2 and C_1 TSs. All of these stationary points lie within 1 kcal/mol of each other in energy,[6] but which of them should be identified as being diradical **1**?

On the basis of the results of a few (2/2)CISD calculations, it was conjectured inclusion of dynamic electron correlation[13] might provide enough stabilization for the (0,0) geometry of **1** to make the force constant for disrotation positive.[6a] With a negative force constant only for conrotation, the (0,0) geometry would then become the TS for conrotatory ring opening and ring closure of cyclopropane. The only other stationary points on the potential surface for **1** would then be the TS for disrotatory cyclopropane ring opening and closure and the (0,90) TS for rotation of just one methylene group of cyclopropane.[4−6] Because both of these TSs are higher in energy than the TS for conrotatory ring opening and ring closure of cyclopropane, it would then be proper to use the (0,0) geometry of **1** for computing the size of ΔBEA in the formation of **1** from cyclopropane.

To test the hypothesis that the (0,0) geometry really is the TS for conrotation on the (2/2)CISD/6-31G* potential energy surface, we optimized the C_{2v} geometry of **1** at this level of theory and carried out a (2/2)CISD/6-31G* vibrational analysis. The vibrational analysis confirmed that this geometry has a single imaginary mode of 139i cm^{-1}, which has a_2 symmetry and which corresponds to conrotation. The b_1 vibrational mode for disrotation was computed to have a small but positive frequency of 61 cm^{-1}.

TABLE 1: Energy (kcal/mol) of the Reaction in Eq 1, Computed at the CISD Level of Theory, with the 6-31G* and cc-pVTZ Basis Sets at CISD/6-31G* Optimized Geometries and with CISD/6-31G* Vibrational Corrections

basis set	ΔE(CISD)	ΔE(CISD+Q)[a]	ΔBEA(0 K)[b]	ΔBEA(298 K)[c]
6-31G*	1.1	1.0	0.6	0.4
cc-pVTZ	1.0	0.8	0.4	0.2

[a] Including the Davidson correction for quadruple excitations. [b] ΔE(CISD + Q) plus the correction for zero-point energy differences. [c] ΔBEA(0 K) plus the correction for heat capacity differences, integrated from 0 to 298 K.

The very small size of the frequency computed for disrotation leaves open the possibility that the force constant could easily change sign upon expansion of the basis set from 6-31G* to cc-pVTZ. Unfortunately, carrying out a CISD vibrational analysis with the larger basis set was beyond our computational capabilities.

Nevertheless, we did check the effect of basis set on the size of the energy increase for rigid disrotation of the terminal methylene groups by 5° and 10° at the CISD/6-31G* optimized (0,0) geometry of **1**. With the 6-31G* basis set the CISD energy increased by, respectively 8.3 and 32.1 × 10^{-5} hartrees, whereas with the cc-pVTZ basis set the energy increases were 9.0 and 36.0 × 10^{-5} hartrees. Therefore, it would appear that with both basis sets the (0,0) geometry has a small positive force constant for disrotation and is, therefore, the lowest energy TS for ring opening of cyclopropane.

ΔBEA for Formation of Singlet 1 from Propane. To obtain the sign and size of ΔBEA for formation of the (0,0) geometry of **1** from propane, we computed the energy of the disproportionation reaction in eq 1 with both the 6-31G* and cc-pVTZ basis sets, using CISD wave functions, and performing calculations at geometries optimized at the CISD/6-31G* level. The energies for the reaction in eq 1, with and without the Davidson correction for quadruple excitations and before and after inclusion of zero-point and heat capacity differences, are given in Table 1. The CISD energies of the three molecules in eq 1, which were used to compute the reaction energies in Table 1, are available as Supporting Information.

Comparisons of the CISD/6-31G* results in Table 1 with the previous RHF-ROHF-(2/2)CASSCF/6-31G* value of $\Delta E = 1.6$ kcal/mol shows that inclusion of dynamic electron correlation lowers the value of ΔE by 0.5 kcal/mol. Inclusion of the Davidson correction, expansion of the basis set and correction for zero-point energy and heat capacity differences all result in further small reductions. On the basis of our best set of calculations (CISD + Q/cc-pVTZ//CISD/6-31G*), it appears that ΔBEA(298 K) is within a few tenths of a kcal/mol of being zero.

Our finding that ΔBEA(298 K) ≈ 0 for formation of propane-1,3-diyl (**1**) from propane means that the presence of the radical center at C-1 in 1-propyl radical is computed to have a negligible effect on the BDE of a hydrogen at the other terminal carbon atom. This result might be construed as indicating that there is no interaction between the radical centers in the (0,0) geometry. However, evidence for through-bond interaction between the radical centers at this geometry comes from the 1−2 kcal/mol preference, computed at many different levels of theory,[4−6] for conrotatory ring opening of cyclopropane to the (0,0) geometry of **1**, rather than disrotatory opening to the (0,0) geometry or monorotatory opening to the (0,90) geometry.[23]

The resolution of the apparent paradox that (a) ΔBEA ≈ 0 for formation of (0,0)-**1** from propane but (b) there is significant through-bond interaction between the radical centers in **1** at this geometry comes from the finding that different types of substituents, attached to C-2 of propane, give ΔBEA values of opposite sign for formation of the corresponding singlet propane-1,3-diyls.[12] For example, a π bond, formed between C-2 of propane and a methylene group attached to it, is neither a net electron donor or acceptor, because the π and π* orbitals of the double bond both interact to the same extent with the in-phase combination of the 2p-π AOs at C-1 and C-3 in the trimethylenemethane diradical. Although formation of the triplet ground state of trimethylenemethane from isobutylene has ΔBEA ≈ 0,[24] formation of the singlet has a large, positive ΔBEA.[12]

In contrast, attachment of a pair of fluorine substituents to C-2 provides a low-lying, C−F antibonding orbital that can accept a pair of electrons from the in-phase combination of 2p-π AOs at C-1 and C-3 in 2,2-difluoropropane-1,3-diyl.[12,21a] Hyperconjugation of the in-phase combination of 2p-π AOs at C-1 and C-3 with the C−F bonds at C-2 is calculated to provide more than twice as much stabilization for the pair of nonbonding electrons in the singlet diradical as the analogous interaction provides for the unpaired electron in the monoradical. Therefore, formation of this singlet diradical from 2,2-difluoropropane is predicted to have a negative ΔBEA.[12]

Similarly, hyperconjugative electron donation from a high-lying, filled C−Si bonding orbital into the in-phase combination of 2p-π AOs at C-1 and C-3 is calculated to stabilize singlet 2,2-disilylpropane-1,3-diyl by more than twice as much as the analogous interaction stabilizes the monoradical.[25] In this diradical the MO formed from the out-of-phase combination of 2p-π AOs at C-1 and C-3 has a node at C-2; therefore, occupancy of this MO allows the pair of nonbonding electrons to avoid being destabilized by the electron donating C−Si bonds. It is the occupancy of this MO by the pair of nonbonding electrons in 2,2-disilylpropane-1,3-diyl that results in formation of this diradical from 2,2-silylpropane being calculated to have a negative ΔBEA.[12]

The C−H bonds at C-2 in **1** are much weaker hyperconjugative electron donors than the C−Si bonds in 2,2-disilylpropane-1,3-diyl, and the electronic structure of **1** is intermediate in type between that of 2,2-disilylpropane-1,3-diyl and that of trimethylenemethane. Because formation of the lowest singlet state of 2,2-disilylpropane-1,3-diyl from 2,2-disilylpropane has a negative ΔBEA, whereas formation of the lowest singlet state of trimethylenemethane from isobutylene has a positive ΔBEA, ΔBEA for formation of **1** from propane could be either positive or negative, but it should be much smaller in magnitude than ΔBEA for formation of either 2,2-disilylpropane-1,3-diyl or singlet trimethylenemethane. Thus, the reason that our calculations find ΔBEA for formation of **1** from propane to be nearly zero is *not* because through-bond interaction between the 2p-π AOs at C-1 and C-3 is absent in the (0,0) geometry of **1**. Instead, ΔBEA ≈ 0 for formation of **1** because the nature of this interaction of the 2p-π AOs at C-1 and C-3 with the C−H bonds at C-2 is intermediate in type between the through-bond interaction in 2,2-disilylpropane-1,3-diyl and that in singlet trimethylenemethane.

Size of the Integrated Difference between the Heat Capacities of 1 and of Cyclopropane. Because our calculations find the enthalpy of the reaction in eq 1 to be nearly zero, the assumption that ΔBEA ≈ 0 for formation of the (0,0) geometry of singlet **1** from propane appears to be valid. In addition, because our (2/2)CISD calculations also find the (0,0) geometry of singlet **1** to be the lowest energy TS for cis−trans isomerization of cyclopropane-1,2-d_2,[26] thermochemical estimates of ΔH_f^{715} of **1** and ΔH_f^{715} of the TS might be expected, within the limits of experimental error, to be the same.

However, as discussed in the Introduction, comparison of thermochemical estimates of these two heats of formation must include a correction for the difference between the heat capacities of **1** and of cyclopropane, integrated from 298 to 715 K. To establish how large this integrated heat capacity correction is, we computed it using the vibrational analyses from our CISD calculations on **1** and on cyclopropane.

The CISD/6-31G* heat capacity of cyclopropane, integrated from 298 to 715 K, was computed to be 8.6 kcal/mol. This calculated value is in very good agreement with the value of 8.8 kcal/mol, obtained by integrating the heat capacities published by NIST.[11]

As expected, the CISD/6-31G* heat capacity of **1**, integrated over the same temperature range is larger, amounting to 9.7 kcal/mol.[27] Thus, the difference between the integrated heat capacities of **1** and of cyclopropane amounts to 1.1 kcal/mol. This difference is about 70% of the size of that estimated by Benson.[2a]

Comparison of ΔH_f^{715} for (0,0)-1 and for the Transition Structure. To obtain the difference between ΔH_f^{715} for (0,0)-**1** and ΔH_f^{715} for the TS for cis−trans isomerization of cyclopropane-1,2-d_2, the difference of 1.1 kcal/mol between the integrated heat capacities of the diradical and cyclopropane must be added to the difference between the estimated ΔH_f^{298} of **1** and the sum of ΔH_f^{298} of cyclopropane and $\Delta H^{\ddagger}$ for the cis−trans isomerization of cyclopropane-1,2-d_2. Using Doering's thermochemical estimate of $\Delta H_f^{298} = 72.2$ kcal/mol for **1** and his value of $\Delta H_f = 72.8$ kcal/mol for the sum of ΔH_f^{298} of cyclopropane and $\Delta H^{\ddagger}$,[8] the difference between the ΔH_f^{715} values is $72.2 - 72.8 + 1.1 = 0.5$ kcal/mol. This difference has almost exactly the same magnitude but the opposite sign as Doering's uncorrected difference of −0.6 kcal/mol.

On the other hand, $\Delta H_f^{298} = 73.0 \pm 1.0$ kcal/mol is probably a more realistic value for **1**.[10] Also, if Schlag and Rabinovitch's value[3b] of $\Delta H^{\ddagger} = 63.6 \pm 0.5$ kcal/mol for cis−trans isomerization of cyclopropane-1,2-d_2, rather than Doering's preferred value of $\Delta H^{\ddagger} = 60$ kcal/mol,[8] is added to $\Delta H_f^{298} = 12.8$ kcal/mol for cyclopropane, the sum is 76.4 kcal/mol.[9] Then, even after including the 1.1 kcal/mol for the integrated difference between the heat capacities of **1** and cyclopropane, the ΔH_f^{715} value for the diradical is 2.3 kcal/mol below that for the TS.

Any combination of errors (including the deviation from bond enthalpy additivity for formation of diradical **1** not being completely negligible, our calculated difference between the integrated heat capacities being too low, and Schlag and Rabinovitch's activation enthalpy being too high) that totaled 2.3 kcal/mol would bring the estimate of ΔH_f^{715} for **1** into near perfect agreement with ΔH_f^{715} for the TS. However, it seems quite likely that the enthalpy of **1** really is lower than the average enthalpy of the thermally activated molecules of cyclopropane-1,2-d_2 that undergo cis−trans isomerization, because at 715 K many of the molecules that react do so by passage through TSs that are higher in energy than the (0,0) TS for conrotation.

It is possible to effect cis−trans isomerization of cyclopropane-1,2-d_2 by cleavage of either the C1−C3 or C2−C3 bond and by passage through not only a conrotatory but also a disrotatory or (0,90) monorotaory TS. However, cleavage of the C1−C2 bond can only effect cis−trans isomerization by a

(0,90) monorotaory TS.[26] Two (0,90) TSs are possible, because either of the two CHD groups can rotate. Therefore, statistically, cis–trans isomerization is twice as likely to occur via a (0,90) TS as via either the conrotatory or the disrotatory TSs.

The (0,0) conrotatory TS is 1.6 kcal/mol lower in energy than the disrotatory TS and 2.3 kcal/mol lower than the monorotatory TSs.[23] A 1.6 kcal/mol lower energy at 715 K corresponds to a factor of 3 advantage in rate, and 2.3 kcal/mol corresponds to a factor of 5 advantage. Combining the statistical and energetic factors, the fraction of cis–trans isomerization occurring via passage through the (0,0) conrotatory TS would be equal to $1/(1 + 1/3 + 2/5) = 1/1.73 = 58\%$. Another $0.4/1.73 = 23\%$ of the reaction would occur via passage through the (0,90) monorotatory TSs, and another $0.33/1.73 = 19\%$ would occur via passage over the disrotatory TS.

The average enthalpy of the molecules of cyclopropane-1,2-d_2 that undergo cis–trans isomerization would then be $23\% \times 2.3$ kcal/mol $+ 19\% \times 1.6$ kcal/mol $= 0.8$ kcal/mol higher than that of the (0,0) TS, which we identify with diradical **1**. At 715 K the rate constant would be larger by a factor of 1.73 than that for pure conrotation, because, although the disrotatory and monorotatory pathways would increase the apparent activation enthalpy by 0.8 kcal/mol, they would also increase the preexponential term by a factor of $1.73 \exp(0.8/1.98 \times 715) = 3.0$.

A contribution to the rate constant for cis–trans isomerization of cyclopropane-d_2 from transition structures with higher enthalpies than that for pure conrotation would explain qualitatively why the effective enthalpy of those activated molecules that go onto product is slightly higher than that which we estimate for **1**. In addition, such a contribution would explain qualitatively why the difference between the energy of activation (E_a) and the threshold energy for reaction (E_0) is much larger for cis–trans isomerization than for rearrangement of cyclopropane to propene and why the preexponential factor associated with E_a for cis–trans isomerization is considerably larger than that associated with E_0.[3c] Finally, if pathways that pass through higher energy TSs contribute to the enthalpy of activation for cis–trans isomerization, measured by Schlag and Rabinovitch,[3b] this would explain why the 5.6 kcal/mol difference between their value of $\Delta H^{\ddagger} = 63.6 \pm 0.5$ kcal/mol and that of $\Delta H^{\ddagger} = 58.0$ kcal/mol, computed by us at the CISD+Q/cc-pVTZ//CISD/6-31G* level of theory for conrotatory opening of cyclopropane to (0,0)-**1**, is surprisingly large.[28]

Conclusions

Our CISD calculations have confirmed the conjecture[6a] that, with the inclusion of dynamic electron correlation, the (0,0) geometry of propane-1,3-diyl (**1**) would be calculated to be the TS for conrotatory ring opening of cyclopropane. The (0,0) geometry is both the lowest energy conformation of **1** and the lowest energy TS for cis–trans isomerization of cyclopropane-1,2,-d_2.[26] Therefore, thermochemical estimates of the heat of formation of **1** and of the TS might be expected to give the same value.

A crucial assumption in the thermochemical estimate of the heat of formation of **1** is that the BDE of a C–H bond at C-3 in 1-propyl radical is the same as the BDE of a C–H bond at C-1 in propane. Our CISD+Q/cc-pVTZ calculations find that the assumption of bond enthalpy additivity in estimating the heat of formation of **1** is valid to within a few tenths of a kcal/mol.

However, the finding that $\Delta\text{BEA} \approx 0$ for formation of **1** from propane does not mean that the radical centers at C-1 and C-3 do not interact. The calculated preference of cyclopropane for conrotatory ring opening to the (0,0) geometry of **1**, rather than either disrotatory ring opening to the same geometry or monorotatory ring opening to the (0,90) geometry,[4–6,23] clearly shows that the radical centers at C-1 and C-3 do interact through the C–H bonds at C-2. It is the fact that the nature of this interaction is of a type that is intermediate between the through-bond interactions in singlet trimethylenemethane ($\Delta\text{BEA} > 0$)[12] and in 2,2-disilylpropane-1,3-diyl ($\Delta\text{BEA} < 0$)[24] that makes $\Delta\text{BEA} \approx 0$ for formation of **1** from propane.

A comparison of ΔH_f^{715} of **1** with ΔH_f^{715} of the TS for cis–trans isomerization of cyclopropane-1,2-d_2 requires that ΔH_f^{298} for **1** be corrected by the heat capacity of **1**, integrated between 298 and 715 K and that the sum of ΔH_f^{298} for cyclopropane and $\Delta H^{\ddagger}$ for cis–trans isomerization of cyclopropane-1,2-d_2 be corrected by the heat capacity of cyclopropane, integrated between the same temperature limits. Our CISD calculations give a value of 1.1 kcal/mol for the integrated difference between these two heat capacities.

It is possible that some combination of errors, which make the estimated ΔH_f^{715} of **1** too low and ΔH_f^{715} of the TS too high is responsible for the 2.3 kcal/mol difference between the estimated ΔH_f^{715} values of the diradical and the TS. However, there is good reason to believe that $\Delta H^{\ddagger} = 63.6 \pm 0.5$ kcal/mol, measured by Schlag and Rabinovitch,[3b] really is greater than the difference in enthalpy between cyclopropane and the TS for conrotation, because passage of molecules through the disrotatory and monorotatory TSs is calculated to contribute to the activation enthalpy measured for this reaction.

Although the contributions from these latter two reaction pathways raise the average activation enthalpy, they also increase the preexponential factor over the value that it would have if the only reaction pathway were passage through the (0,0) geometry of the conrotatatory TS. At the elevated temperatures that are necessary to observe cis–trans isomerization of cyclopropane-d_2, the effect on the rate constant of the greater activation entropy, associated with multiple reaction pathways, more than compensates for the contributions of the higher energy reaction paths to raising the average activation enthalpy for this reaction.

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Supporting Information Available: Optimized geometries, energies, vibrational frequencies, and thermal corrections for propane-1,3-diyl (**1**), 1-propyl radical, propane, and cyclopropane. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For a critical discussion of the significance of ΔBEA values see: Zhang, D. Y.; Borden, W. T. *J. Org. Chem.* **2002**, *67*, 3989.

(2) (a) Benson, S. W. *J. Chem. Phys.* **1961**, *34*, 521. (b) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 117–120.

(3) (a) Rabinovitch, B. S.; Schlag, E. W.; Wiberg, K. B. *J. Chem. Phys.* **1958**, *28*, 504. (b) Schlag, E. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1960**, *82*, 5996. (c) Waage, E. V.; Rabinovitch, B. S. *J. Phys. Chem.* **1972**, *76*, 1695.

(4) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

(5) (a) Jean, Y.; Salem, L.; Wright, J. S.; Horsely, J. A.; Moser, C.; Stevens, R. M. *Pure Appl. Chem., Suppl. (23rd Congr.)* **1971**, *1*, 197. (b) Horsely, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 5996.

(6) (a) Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085. (b) Yamaguchi, Y. Schaefer, H. F., III; Baldwin, J. E. *J. Phys. Chem.* **1994**, *98*, 7513. (c) Doubleday, C., Jr. *J. Phys. Chem.* **1996**, *100*, 3520. (d) The many earlier calculations, cited in these three papers.

(7) (a) Berson, J. A. *Annu. Rev. Phys. Chem.* **1977**, *28*, 111. (b) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 324−334. (c) Berson, J. A. *Science* **1994**, *266*, 1338.

(8) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1695.

(9) (a) Doering chose to use the Kistiakowski value of $E_a = 65.0$ kcal/mol for the rearrangement of cyclopropane to propene, and he employed the estimate by Waage and Rabinovitch,[3c] based on a combination of RRKM calculations and their experimental data, that at very low pressures the critical energy (E_0) for cis−trans isomerization of cyclopropane-1,2-d_2 is smaller by 3.7 kcal/mol than E_0 for rearrangement.[8] After subtracting RT and rounding, Doering obtained $\Delta H^{\ddagger} = 60$ kcal/mol for cis−trans isomerization. (b) However, Berson has pointed out that the Waage and Rabinovitch low-pressure value of $\Delta E_0 = 3.7$ kcal/mol cannot be equated with the difference between the E_a values for rearrangement and cis−trans isomerization of cyclopropane-1,2-d_2 at high pressures.[7c] Based on the kinetics measured by Schlag and Rabinovitch,[3b] the latter difference is $\Delta E_a = 65.9 \pm 0.4 - 65.1 \pm 0.5$ kcal/mol ≈ 1 kcal/mol. Berson's critique suggests that Schlag and Rabinovitch's value of $\Delta H^{\ddagger} = 63.6 \pm 0.5$ kcal/mol for cis−trans isomerization should be used in place of Doering's value of $\Delta H^{\ddagger} = 60$ kcal/mol; this substitution would raise the heat of formation of the TS state by 3.6 kcal/mol above Doering's value of $\Delta H_f = 72.8$ kcal/mol.

(10) A recent review (Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255) favors BDE$^{298} = 101.1 \pm 0.4$ kcal/mol for the primary C−H bond in ethane, which is 0.5 kcal/mol higher than the value used by Doering.[8] The data available from the NIST Chemistry WebBook[11] gives BDE$^{298} = 101.0 \pm 0.5$ kcal/mol for the primary C−H bond in propane, which is 0.4 kcal/mol higher than the value used by Doering. Assuming ΔBEA $= 0$, so that BDE$^{298} = 101.0 \pm 0.5$ kcal/mol is used for both of the primary C−H bonds in propane that are broken in forming **1**, the heat of formation of **1** would increase to $\Delta H_f^{298} = 73.0 \pm 1.0$ kcal/mol, which is 0.8 kcal/mol higher than the value employed by Doering.

(11) http://webbook.nist.gov/chemistry/

(12) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689.

(13) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(14) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(15) Frisch, M. J.; Trucks, G. W.;. Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A Gaussian 98, Revision A.11.4; Gaussian, Inc., Pittsburgh, PA, 2002.

(16) Andersson, K.; Barysz, M.; Bernhardsson, A.; Blomberg, M. R. A.; Cooper, D. L.; Fülscher, M. P.; de Graaf, C.; Hess B. A.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Nakajima T.; Olsen, J.; Roos, B. O.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stålring, J.; Thorsteinsson, T.; Veryazov, V.; Widmark, P.-O. MOLCAS, version 5.4; Department of Theoretical Chemistry, Chemical Centre: University of Lund, P.O.B. 124, S-221 00 Lund, Sweden, 2002.

(17) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(18) Davidson, E. R. In *The World of Quanhtum Chemistry*; Daudel, R., Pullman, B., Eds.; Dordrecht: The Netherlands, 1974.

(19) This term was not used by Hoffmann in ref 4, but he subsequently applied it to interactions of this type: (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(20) Despite numerous attempts, this prediction has never been confirmed experimentally.[6,7] However, the related prediction, that hyperconjugative electron donation into the low-lying, C−F, σ^* orbitals in 2,2-difluoropropane-1,3-diyl should result in disrotatory opening to and closure of this diradical,[12,21a] has been confirmed by experiments.[21b,22]

(21) (a) Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1521. (b) Tian, F.; Lewis, S. B.; Bartberger, M. D.; Dolbier, W. R., Jr.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 6187.

(22) For the most recent review of studies of cyclopropane stereomutations see: Borden, W. T. In *Contemporary Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S.; Jones, M., Jr., Eds.; Wiley: New York, 2003; Chapter 22.

(23) Our CISD+Q/cc-pVTZ//(2,2)CASSCF/6-31G* calculations place the (0,0) TS for conrotation of both terminal methylene groups 1.6 kcal/mol lower in energy than the TS for disrotation of both terminal methylene groups and 2.3 kcal/mol lower in energy than the (0,90) TS for rotation of just one methylene.

(24) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.

(25) Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079.

(26) Conrotatory cleavage of the bond between C-1 and C-2 of *trans*-cyclopropane-1,2-d_2, followed by conrotatory closure of the (0,0)-**1** thus formed, results in enantiomerization. However, the same process, but involving either of the C−C bonds to C-3, results in isomerization to the cis isomer.

(27) Replacing the harmonic oscillator partition function for the 61 cm^{-1} disrotatory vibration at the (0,0) geometry of **1** with the partition function for a hindered rotor with a barrier height of 1.6 kcal/mol[23] was calculated to reduce the integrated heat capacity of **1**, but by only 0.1 kcal/mol.

(28) For comparison, at the same level of theory, our calculated BDE at 298 K for butane dissociating to two ethyl radicals is 84.7 kcal/mol. This calculated value is not 5.6, but only 3.3 kcal/mol smaller than the value of BDE $= 88.0 \pm 0.8$ kcal/mol, which is based on the experimental heats of formation of butane and of two ethyl radicals.