

electron redistribution can occur upon going from a PDZ to a NHF basis, and (3) the fact that, for these molecules, d functions seem to be equally important for a description of the density, even though one of the molecules contains a third row atom.

It should be emphasized that the basis set and electron correlation effects described here are very small compared to the total densities themselves. But the necessity to use adequate basis sets and to include electron correlation to describe many molecular properties correctly is well known. This draws our attention once more to the fact that it is indeed by examining such minute variations of electron distributions that a deeper understanding of chemical bonding is to be reached. Such a circumstance is to be expected, since chemical bonding is a distinctly quantum mechanical phenomenon, arising from a delicate balance of small energy shifts and minute electronic rearrangements.

Acknowledgments. This work was partially funded by the National Science Foundation. The authors thank Dr. R. M. Stevens for the use of his computer programs and for helpful discussions.

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Accurate ab Initio Calculations on the Singlet-Triplet Separation in Methylene

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Abstract: Configuration interaction (CI) calculations which include all single and double excitations have been performed for the 3B_1 and 1A_1 states of methylene. The basis sets used were of better than triple- ζ quality and included two sets of polarization functions. The separation is computed to be 10.6 kcal/mol. A trend is shown to exist from the carbon atom through CH to CH₂, which suggests that the actual splitting is less than 10 kcal/mol. This is in disagreement with the interpretation of the latest experimental data, but agrees with earlier experimental work.

I. Introduction

In recent years, there have been a large number of experiments and calculations to determine the singlet-triplet ($^1A_1 - ^3B_1$) separation for methylene, CH₂. Until recently, there have been two distinct sets of experimental values for this quantity. The high values²⁻⁵ cluster around 7-8 kcal/mol (with the triplet being the ground state), and the lower set⁶⁻⁸ report 0-3 kcal/mol. The best configuration interaction (CI) results⁹ to date have computed the separation to be 14.1 kcal/mol. Other recent calculations¹⁰⁻¹³ have also supported the "high" value for the singlet-triplet separation. (An excellent review of earlier work has been given by Harrison.¹⁴)

Very recently, new experimental work by Zittel et al.,¹⁵ based on laser photodetachment spectrometry of CH₂⁻, has produced a separation of 19.5 ± 0.7 kcal/mol. Unlike previous experiments, this experiment does not rely on any thermochemical data, but its interpretation depends on the identifi-

cation and assignment of a peak in the photoelectron spectrum of CH₂⁻ which is 300 times less intense than the principal peak.

Since the best existing theoretical estimate (14.1) lies between the approximately 8 kcal/mol of the previous "high" value and the 19.5 ± 0.7 kcal/mol of Zittel et al., it is unable to help resolve this difference. For this reason, a new series of high-accuracy ab initio calculations were performed on CH₂.

II. Theoretical Approach

The previous theoretical work (see, e.g., ref 9 and 16) indicates that the triplet state is well described by a single configuration

$$1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1 (^3B_1)$$

The singlet state has been found to have two important con-

figurations,

$$\left. \begin{array}{l} 1a_1^2 2a_1^2 1b_2^2 3a_1^2 \\ 1a_1^2 2a_1^2 1b_2^2 1b_1^2 \end{array} \right\} ({}^1A_1)$$

Meadows and Schaefer¹⁶ have computed single-determinant Hartree-Fock wave functions for 3B_1 and 1A_1 . These produce a singlet-triplet separation of 24.8 kcal/mol. When they include the second configuration in the singlet wave function, the separation was reduced to 10.9 kcal/mol. The second configuration helps compensate for the difference in correlation between the singlet and triplet states, but if the interpretation of the photodetachment spectra of Zittel et al.¹⁵ is correct, it suggests that the two-configuration result overcompensates for the difference in correlation energy. Since our aim is to compute the singlet-triplet separation reliably, no built-in biases should be included, and for this reason we chose to use and compare both the single and double configuration approaches for the singlet. The correlation correction for both states is then determined by configuration interaction (CI).

The carbon inner-shell orbital ($1a_1$) is held doubly occupied in all configurations in the present CI calculations. Otherwise, all single and double excitations from one principal configuration (denoted (CI(SD))) are included for the 3B_1 state and for the single reference configuration treatment of the 1A_1 state (denoted 1A_1 -1Ref). Effects of higher than double excitations are added in two ways; for the smaller basis set all triple excitations were also included, CI(SDT), while the effect of the quadruple excitations was included by the Davidson formula¹⁷

$$\Delta E_Q = (1 - C_0^2)\Delta E_D \quad (1)$$

where C_0 is the coefficient of the SCF function in the normalized all-double-excitations CI wave function and ΔE_D is the all-doubles correlation energy. This formula was originally proposed for closed-shell states, but was applied here to the open-shell single reference configuration calculations without change.

The CI programs used in this work are those developed and implemented by Shavitt and co-workers.¹⁸ In these programs, a list of spatial occupancies is generated. The configuration functions (CF) correspond to all possible spin couplings for each spatial occupancy. For an open-shell state, however, the CFs may be more appropriately divided into spin-orbital differences with the reference CF rather than spatial occupancy difference. The division would then be spin-orbital single replacements (extended Brillouin theorem CFs), spin-orbital double replacements, and spin-orbital triple replacements arising from some spin couplings of spatial occupancies which differ from the reference CF by two orbitals. For the ΔE_D in eq 1, we used the correlation energy obtained with all single and double spatial excitations, and C_0 was taken from the same wave functions. Ideally only the spin-orbital double replacement CFs (same as spatial double replacements for closed shells) should be used; however, the effect of the singles for both open- and closed-shell cases will be small, and Schaefer and Bender¹⁹ have shown the very small effect of including the spin-orbital triple replacements arising from some spin couplings of spatial doubles. These effects will increase the quadruples estimate (QE) by a small amount relative to the exact application of eq 1.

While error bounds cannot be given for these calculations, the singlet-triplet separation in methylene is closely related to excitation energies in the carbon atom and the CH radical. These quantities have been measured and can serve to calibrate the methylene calculations.

The Mulliken population analysis for the 3B_1 state of methylene²⁰ suggests a carbon hybridization of sp^2 , with the $2p_x$ (π) orbital singly occupied. The approximately 130° bond

Table I. Carbon Atom Results^{a,d}

	DZ C(9s5p/4s2p)			
	SCF	CI(SD)	QE	
3P	-37.6845	-37.7229	0.83	
5S	-37.5945	-37.6055	0.05	
Δ	-56.5	-73.7	(-74.5) ^b	
	DZP C(9s5p1d/4s2p1d)			
	SCF	CI(SD)	CI(SDT)	QE
3P	-37.6846	-37.7623	-37.7629	2.48
5S	-37.5949	-37.6182	-37.6184	0.17
Δ	-56.3	-90.4	-90.7	(-93.0) ^b
	Big Basis C(12s4p2d/6s4p2d)			
	SCF	CI(SD)	QE	
3P	-37.6876	-37.7775	3.07	
5S	-37.5985	-37.6304	0.26	
Δ	-55.9	-92.3	(-95.1) ^b	
	Sasaki and Yoshimine ^c			
	SCF	CI(SD)	CI(SDTQ)	
3P	-37.6886	-37.8355	-37.8393	
5S	-37.5992	-37.6886	-37.6893	
Δ	-56.1	-92.2	-94.1	

^a The experimental separation (ref 27) is -96.4 kcal/mol. ^b Separation energy including the quadruples estimate. ^c Reference 26. ^d CI(SD) indicates configuration interaction with all single and double excitations, while CI(SDTQ) adds selected triple and quadruple excitations. QE is the estimated correction for quadruple excitations from eq 1 (in kcal/mol). Total energies are in hartrees and energy differences [$\Delta = E({}^3P) - E({}^5S)$] are in kcal/mol.

angle is consistent with the expected 120° for this hybridization. The population analysis for the singlet state²⁰ indicates that the carbon atom is largely unhybridized in that state, and the approximately 100° bond angle is close to the expected 90° for this case. This suggests that the 1A_1 state is associated with the 3P ($1s^2 2s^2 2p^2$) state of the carbon atom, while the 3B_1 state is more closely associated with 5S ($1s^2 2s^1 2p^3$). These correlations are also supported by the analysis of Harrison and Allen.²¹

In CH, the ground state is ${}^2\Pi$, and a low-lying excited ${}^4\Sigma^-$ state exists. The ${}^2\Pi$ ($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^1$) state has the carbon atom essentially unhybridized, with one carbon p electron in the CH σ bond and the other p electron as the lone π electron. In the ${}^4\Sigma^-$ ($1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$) state, carbon can be considered hybridized sp (with two additional $p\pi$'s singly occupied). One sp hybrid is involved in the CH bond, while the other is the 3σ lone electron; the two additional p electrons are in the π orbitals. As in methylene, one state in CH, ${}^2\Pi$, is related to the 3P state of carbon, while the other, ${}^4\Sigma^-$, is related to the 5S state. Thus, by computing the ${}^3P - {}^5S$ atomic separation, the ${}^2\Pi - {}^4\Sigma^-$ separation in CH, and the ${}^3B_1 - {}^1A_1$ separation in methylene, some trends may be observed which should help in estimating the true separation in methylene.

III. Basis Sets

The initial (smallest) basis set used was the Dunning double- ζ (DZ) contraction²² of the Huzinaga primitive set,²³ with carbon (9s5p/4s2p) and hydrogen (4s/2s) (with a scale factor of 1.2).

This was augmented in the second (DZP) basis set with carbon d and hydrogen p polarization functions. In previous work on carbenes²⁰ it was observed that the optimum d exponent was different for the singlet and triplet states. The optimum d exponents for CH_2 are 0.74 for the triplet and 0.51 for the two-configuration singlet. These exponents were used in the DZP basis for the 3B_1 and 1A_1 (both 1Ref and 2Ref) calculations, respectively. All six Cartesian d components (including the 3s formed from $d_{xx} + d_{yy} + d_{zz}$) were added to the

Table II. CH Radical Results^{a,c}

	DZ		
	R_c	SCF	
² Π	2.12	-38.2584	
⁴ Σ ⁻	2.04	-38.2768	
Δ		11.5	
	DZP		
	R_c	SCF	
² Π	2.10	-38.2727	
⁴ Σ ⁻	2.04	-38.2844	
Δ		7.3	
	Lie et al. ^b		
	R_c (SCF)	SCF	CI (extended)
² Π	2.085	-38.2798	-38.4104
⁴ Σ ⁻	2.023	-38.2902	-38.3865
Δ		6.5	-15.0

^a Experimental separation (ref 29) is -17.1 kcal/mol. ^b Reference 28. ^c Total energies in hartrees, energy differences [$\Delta = E(^2\Pi) - E(^4\Sigma^-)$] in kcal/mol, and bond lengths (R_c) in bohrs.

initial basis set, as well as a set of p functions on H with exponent 1.0.

The largest basis set used was based on the 12s7p basis for carbon and 6s for hydrogen of van Duijneveldt.²⁴ These were contracted (12s7p/6s4p) and (6s/3s). To this two d sets were added on carbon and two p sets were added on hydrogen. The exponents of the p functions were 1.4 and 0.25, as recommended by van Duijneveldt.²⁴ The optimum single d from the previous work was expanded into two d functions using Dunning's²⁵ one- and two-Gaussian fits to a single Slater 3d function. The exponents obtained were 1.82 and 0.54 for ³B₁ and 1.26 and 0.37 for ¹A₁.

IV. Results

A. Carbon Atom. The total energies for ⁵S and ³P for all basis sets, along with the very accurate work of Sasaki and Yoshimine,²⁶ are included in Table I. The d exponents for the DZP basis set were optimized in a CI(SD) calculation, giving 0.55 for ³P and 0.59 for ⁵S. The d exponents for the largest basis set were those used for the methylene calculations (as described above). The Sasaki and Yoshimine SCF results reproduce the numeric Hartree-Fock total energies, and all basis sets closely reproduce the numeric Hartree-Fock separation of 56.1 kcal/mol. The DZ basis set is about 20 kcal/mol in error at the CI(SD) level, compared to the experimental separation energy, but once the polarization functions are added, the error becomes much smaller. The largest calculation is in error by only 4 kcal/mol at the CI(SD) level, producing a separation of 92.3 kcal/mol, compared with the experimental value²⁷ of 96.4. The triple excitations were also included in calculations with the DZP basis, but their effect was negligibly small. The quadruples contribution was estimated from eq 1, and lowered the ³P state relative to the ⁵S by 2 kcal/mol for the interme-

diate basis and by 2.8 kcal/mol for the largest basis. This is in essential agreement with the CI(SDTQ) results of Sasaki and Yoshimine, who included only selected triples and quadruples.

B. CH Molecule. The calculations on CH were all performed at the SCF level and are summarized in Table II. The very large calculation of Lie et al.²⁸ (using an STO basis set) is included, along with the experimental value of Kasdan et al.²⁹ The internuclear separation was optimized, and the optimum d exponent was computed. As in the case of methylene, the addition of the polarization functions causes a greater lowering in the ²Π state, which is associated with the ³P atomic state. The optimum d exponent is 0.50 (compared to 0.51 in CH₂) for the state correlated with carbon ³P (for which the d exponent is 0.55) and 0.70 (compared with 0.74 in CH₂) for the state correlated with carbon ⁵S (for which the d exponent is 0.59). The CI results of Lie et al.²⁸ produce a much larger correlation correction for the state associated with carbon ³P. This agrees with the previous CI calculations⁹ on methylene, where ¹A₁ shows the larger correlation.

C. CH₂ Molecule. The DZ basis was first used to compute CI(SD) wave functions for ³B₁, ¹A₁-1Ref, and ¹A₁-2Ref. The molecular geometry was optimized for each case. This work is similar to that of O'Neil et al.,³⁰ the difference being that the ¹A₁-1Ref was also computed at the CI(SD) level. A calculation was also carried out including all triple excitations, in addition to the singles and doubles, denoted CI(SDT). These calculations are summarized in Table III.

Although the singlet-triplet separation is very different at the SCF level for ¹A₁-1Ref and ¹A₁-2Ref, the CI results are much more similar. The triple excitations produce a very small differential lowering between the singlet and triplet states.

The ¹A₁-1Ref and ³B₁ CI(SD) calculations allow the use of Davidson's formula,¹⁷ eq 1, for the quadruples effect (QE). The differential quadruples effect is computed to be 1.4 kcal/mol. The difference between ¹A₁-1Ref and ¹A₁-2Ref is 1.5 kcal/mol. It appears that including the singles and doubles relative to the second important configuration (which is itself a double excitation relative to the original reference configuration and has a CI coefficient of ~0.14) helps to account for the quadruples differential.

The DZP basis set was next used to compute the CI(SD) wave functions. The geometry was optimized for the ³B₁ and for the ¹A₁-2Ref. The ¹A₁-1Ref wave function was computed at the ¹A₁-2Ref CI(SD) optimum geometry, since the DZ geometry optimization showed the ¹A₁-1Ref and ¹A₁-2Ref CI calculations to give almost identical geometries, the angles differing by only 0.1°. The separation energy was obtained as ~12 kcal/mol for ¹A₁-2Ref, with the same result for the ¹A₁-1Ref case if the quadruples correction is taken into account. This separation is lower than the previous CI result of Schaefer and co-workers,⁹ mainly because different d exponents were used for the different states. These results are summarized in Table IV.

Table III. CH₂ ³B₁ and ¹A₁ Results for the DZ Basis Set^b

	SCF			CI				
	∠HCH	R_{CH}	E_{SCF}	∠HCH	R_{CH}	CI(SD)	CI(SDT)	QE
³ B ₁	130.5°	2.03	-38.9137	133.7°	2.07	-38.9825	-38.9836	1.86
¹ A ₁ -1Ref	106.1°	2.09	-38.8620	105.1°	2.14	-38.9447	-38.9462	3.20
¹ A ₁ -2Ref	104.6°	2.09	-38.8770	105.2°	2.14	-38.9472	-38.9480	
Δ (³ B ₁ - ¹ A ₁ -1Ref)			32.4			23.7	23.4	(22.0) ^a
Δ (³ B ₁ - ¹ A ₁ -2Ref)			22.8			22.2	22.3	

^a Separation energy including the quadruples estimate. This is in excellent agreement with the CI(SD) and CI(SDT) separation energies based on the ¹A₁-2Ref calculation. ^b The SCF and CI optimum geometries are reported separately. The CI(SDT) energies were computed at the CI(SD) geometry. The bond lengths are in bohrs, the total energy in hartrees, and the energy differences and quadruples estimate (QE) in kcal/mol.

Table IV. CH₂ ³B₁ and ¹A₁ Results for the DZP Basis^c

	SCF			CI			
	ZHCH	R _{CH}	E _{SCF}	ZHCH	R _{CH}	CI(SD)	QE
³ B ₁	129.4°	2.03	-38.9282	132.4°	2.045	-39.0416	3.37
¹ A ₁ -1Ref ^a	102.4°	2.11	-38.8863	102.4°	2.11	-39.0183	5.61
¹ A ₁ -2Ref	102.8°	2.08	-39.9079	102.4°	2.11	-39.0222	
Δ (³ B ₁ - ¹ A ₁ -1Ref)			26.2			14.6	(12.4) ^b
Δ (³ B ₁ - ¹ A ₁ -2Ref)			12.8			12.2	

^a The ¹A₁-2Ref CI(SD) optimum geometry was used. ^b Separation energy including the quadruples estimate. This is in excellent agreement with the CI(SD) separation energy based on the ¹A₁-2Ref calculation. ^c The optimum geometries and total energies are reported for SCF and CI(SD) calculations. The bond lengths are in bohrs, the total energy in hartrees, and the energy differences and quadruples estimate in kcal/mol.

Table V. CH₂ ³B₁ and ¹A₁ Results for the Large Basis Set, C(12s7p2d/6s4p2d) and H(6s2p/3s2p)^b

	SCF	CI(SD)	QE
³ B ₁	-38.9333	-39.0622	4.15
¹ A ₁ -1Ref	-38.8935	-39.0411	6.46
¹ A ₁ -2Ref	-38.9157	-39.0453	
Δ (³ B ₁ - ¹ A ₁ -1Ref)	25.0	13.2	(10.9) ^a
Δ (³ B ₁ - ¹ A ₁ -2Ref)	11.1	10.6	

^a Separation energy including the quadruples estimate. This is in excellent agreement with the CI(SD) separation energy based on the ¹A₁-2Ref calculation. ^b The geometry is taken from the DZP CI(SD) calculations. The total energy is in hartrees; the energy differences and quadruples estimate are in kcal/mol.

The optimum geometries of these calculations were then used for the CI calculations with the largest basis set. At the SCF level, the results are very similar to the larger calculations of Meadows and Schaefer,¹⁶ giving 11.1 vs. 10.9 kcal/mol for the ³B₁ - ¹A₁-2Ref separation and 25.0 vs. 24.8 kcal/mol for the ³B₁ - ¹A₁-1Ref separation. As with the DZP basis, the different d exponents for the different states allow a more equal description of the two states, and result in agreement with the results obtained with a larger basis set in which the same d exponents were used for both states. The separation at the CI(SD) level is 10.6 kcal/mol for the ¹A₁-2Ref and 10.9 kcal/mol for ¹A₁-1Ref when the quadruples correction is used. The large basis results are reported in Table V. The ¹A₁-1Ref CI(SD) calculation used the orbitals of the ¹A₁-2Ref SCF wave function. Similar calculations for the DZP CI(SD) case showed that using the ¹A₁-2Ref orbitals for the ¹A₁-1Ref CI lowered the energy by only 0.06 kcal/mol.

D. Trends and an Estimate of the Singlet-Triplet Separation in CH₂. In the carbon atom, as the basis set size and the level of CI increase, the ³P state is lowered relative to the ⁵S state. In CH and CH₂ the optimum d exponents for the states which correspond to an unhybridized carbon atom (³P) are different from those for the state associated with carbon atom hybridizations sp (CH ⁴Σ⁻) and sp² (CH₂ ³B₁), but the optimum d exponents for the corresponding states are almost the same in CH and CH₂. The addition of polarization functions causes a greater lowering for the states associated with carbon ³P, and

CI causes a lowering in the same direction. For the C atom and for CH the best calculations still have ³P and the CH state associated with it too high by about 2 kcal/mol relative to ⁵S and its associated CH state (⁴Σ⁻), respectively (Table VI). When applied to CH₂, this implies that ¹A₁ is still too high relative to the ³B₁ state. The quadruples correction shows that the two-configuration approach for ¹A₁ is useful, since it appears to account for the differential quadruples effect. On the basis of these trends, summarized in Table VI, it would appear that the singlet-triplet separation is no greater than 10 kcal/mol, and possibly as low as 9 kcal/mol. This is in remarkable agreement with the estimate of 9.7 kcal/mol given by Harrison¹⁴ on the basis of a reinterpretation of spectroscopic data on the ¹B₁ ← ¹A₁ transition¹¹ and an evaluation of previous theoretical results.

V. Discussion

In their paper, Zittel et al.¹⁵ used some ab initio calculations to analyze their experimental results. They computed bending potential curves for CH₂ ¹A₁ and CH₂ ²B₁ at the CI(SD) level with a DZ basis. The ³B₁ curve was computed at the SCF level with a DZP basis set. They then adjusted these curves to reproduce their spectra. The exact nature of the changes needed in order to reproduce their spectra, other than the shifts in the position of the minimum, was not described. If one or two of the very weak peaks are left out (A, or A and B), it is quite possible that a new potential curve could be fitted equally well to the remaining peaks. The inclusion of correlation in ³B₁ will change the shape of their bending potential curve. With our DZP basis, SCF calculations yield a ³B₁ barrier to linearity of 4110 cm⁻¹ (R_{CH} not reoptimized) compared to the value of 3900 cm⁻¹ used by Zittel et al., but the barrier height at the CI(SD) level is only 2620 cm⁻¹. Such changes could alter the computed vibrational spectra substantially. It must be concluded that unlike the case of NH₃, for which the basis set limit gives the same inversion barrier height at the SCF level as at the CI level,³¹ there is a substantial correlation contribution to the barrier to linearity in CH₂. The only alternative is that the basis set used is not yet large enough. The difference in zero point energy for the ³B₁ and ¹A₁ states is ~0.5 kcal/mol, and therefore can be neglected relative to the difference between

Table VI. Summary of CI Energy Differences (kcal/mol) for C, CH, and CH₂^e

Basis set	C (³ P - ⁵ S)	CH (² Π - ⁴ Σ ⁻)	CH ₂ (¹ A ₁ - ³ B ₁)	
			1Ref	2Ref
DZ	-73.7 (-74.5)		23.4 (22.3)	22.0
DZP	-90.4 (-93.0)		14.6 (12.2)	12.4
Large basis	-92.3 (-95.1)	-15.0 ^a	13.2 (10.6)	10.9
Experimental	-96.4 ^b	-17.1 ^c	(~9) ^d	

^a Extended CI result of Lie et al., ref 28. ^b Reference 27. ^c Reference 29. ^d Theoretical estimate based on trends shown. ^e The computed differences are from the CI(SD) calculations, with the value obtained using the quadruples correction estimate given in parentheses.

our calculation (~ 10 kcal/mol) and the experimental value (~ 20 kcal/mol) of Zittel et al. In any case, the results of the calculations presented here cannot be reconciled with a singlet-triplet separation in methylene of 19.5 ± 0.7 kcal/mol deduced by Zittel et al. from their experiments.

VI. Conclusion

The use of the two-configuration singlet reference state is shown to produce results in agreement with those of the one-configuration singlet, if the estimated quadruple excitations corrections are taken into account. A trend is observed which indicates that the 3P carbon atom, the $^2\Pi$ CH radical, and 1A_1 methylene are all related, while 5S carbon, $^4\Sigma^-$ CH, and 3B_1 CH₂ are also related. Accurate calculations for C and CH show C(3P) and CH($^2\Pi$) too high by ~ 2 kcal/mol relative to C(5S) and CH($^4\Sigma^-$), respectively. This indicates that the computed large-basis 1A_1 state of methylene is still too high relative to 3B_1 . Therefore, the correct separation is most likely somewhat smaller than our lowest computed value of 10.6 kcal/mol, and may possibly be as low as 9 kcal/mol.

Acknowledgments. We would like to thank Dr. George Purvis for many helpful comments and Dr. William P. Reinhardt for an interesting discussion. This work was supported by Battelle Memorial Institute.

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The Transition State for the Epoxidation of Ethylene with Peroxyformic Acid. An ab Initio Molecular Orbital Study

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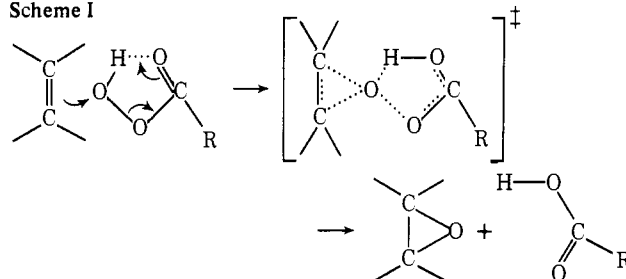
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Abstract: Ab initio molecular orbital theory (STO-2G and STO-4G) is used to study various plausible transition states (**1-5**) for epoxidation of ethylene with peroxyformic acid. Unsymmetric transition states, **3** and **4** (1,1-addition mechanism), are found to be energetically more favorable than symmetric ones, i.e., **1** and **2**, with the transition state **5** (1,3-dipolar addition) being somewhere in between. Previously reported nonequivalency of both olefinic carbon atoms in epoxidation of substituted styrenes seems to be not just simply a consequence of a choice of an unsymmetric olefin.

Introduction

The reaction of olefins with peroxy acids to produce epoxides (oxiranes) has been known for almost 70 years (Prilezhaev, 1908). Although a large volume of literature on the subject exists,¹⁻⁴ the question of the mechanism of this reaction is still not settled. Several mechanisms, which can accommodate the experimental data, have been proposed. The so-called "butterfly" mechanism, first proposed by Bartlett,⁵ involves nucleophilic attack of the olefin on peroxy acid according to Scheme I. Waters⁶ suggested initial attack of a hydroxyl cation, OH⁺ (not necessarily as a free ion), on the olefin via the transition state depicted in Scheme II. A recent study of the secondary deuterium isotope effect for the epoxidation of *p*-phenylstyrene and three deuterated derivatives revealed a clear

Scheme I



distinction between the α and β carbon atoms of the olefin in the transition state. On the basis of these observations, an unsymmetric transition state, as shown in Scheme III, has been