

Rate Constant and Activation Energy for Et· Re-combination. Since yields of $\text{EtH}_{\text{combination}}$ are not experimentally verifiable under the circumstances, it is necessary to use the PrH and BuH yields as in the 142° work; that is,⁶ from eq 1-4 and the experimentally observed value $k_{\text{ME}} = 2(k_{\text{M}}k_{\text{E}})^{1/2}$

$$\frac{2[\text{BuH}][\text{MeI}]}{[\text{PrH}][\text{EtI}]_{\text{av}}} = K_{\text{ME}} \left(\frac{k_{\text{E}}}{k_{\text{M}}} \right)^{1/2} \quad (10)$$

The data (Table I) show the left-hand side of eq 10 to be constant over a fivefold range of MeI/EtI ratio and to equal 8.38 ± 0.05 .

The equilibrium constant, K_{ME} , calculated from the same thermochemical quantities used previously⁶ equals 66.6, so that $k_{\text{M}}/k_{\text{E}} = 63.6$.

To ascertain the temperature dependence of k_{E} , the activation energy for the measured quantity, $W = (k_{\text{E}}/k_{\text{M}})K_{\text{ME}}^2$ can be calculated from the Arrhenius relation

$$\log \frac{W_1}{W_2} = \frac{\Delta H_w \Delta T}{4.576 T_1 T_2} \quad (11)$$

where W_2 at $354^\circ\text{K} = (8.38 \pm 0.05)^2$ and W_1 at $415^\circ\text{K} = (4.6 \pm 0.2)^2$

$$\Delta H_w = 4.576 \frac{T_1 T_2}{\Delta T} \log \frac{W_1}{W_2} = -5.7 \text{ kcal} \quad (12)$$

Then, since $E_{\text{M}} = 0$

$$E_{\text{E}} = \Delta H_w - 2\Delta H_{\text{ME}(\text{mean})} \quad (13)$$

ΔH_{ME} at 354 and 415°K is, respectively, -2.9 and -2.8 kcal, so that $E_{\text{E}} = 0$.

The uncertainty in this calculation introduced from the measured quantities may be equated to twice the spread observed for $W_1^{1/2}$ and $W_2^{1/2}$ or about $\pm 10\%$ each. This gives rise to a joint error of ± 0.6 kcal in ΔH_w .

The uncertainty introduced from ΔH_{ME} is considerably larger, of course, on the order of ± 1 kcal.⁶ However, the data now at hand impose narrower constraints. In our first report,⁶ the value obtained for k_{E} , $10^{8.6} M^{-1} \text{sec}^{-1}$ (from the accepted value for $k_{\text{M}} = 10^{10.4} M^{-1} \text{sec}^{-1}$), was judged too low, and an apparently more reasonable value, $10^{9.6} M^{-1} \text{sec}^{-1}$, was shown to lie within the error limits for K_{ME} as calculated from thermochemical quantities. It now becomes evident that any such arbitrary adjustment of K_{ME} downwards (which in effect is to make ΔH_{ME} less negative) will result in a negative activation energy for ethyl radical recombination (eq 13). In particular, if K_{ME} is chosen so that $k_{\text{E}} = 10^{9.6} M^{-1} \text{sec}^{-1}$, then $E_{\text{E}} = -2$ kcal. Conversely, for E_{E} to equal $+1$ or $+2$ kcal^{2,3} requires a more negative ΔH_{ME} and an impossibly low value for k_{E} .

Singlet-Triplet Energy Separation, Walsh-Mulliken Diagrams, and Singlet d-Polarization Effects in Methylene

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Abstract: The singlet-triplet ($^1\text{A}_1 \leftrightarrow ^3\text{B}_1$) energy separation in methylene has been computed by correlated *ab initio* wave functions of the highest accuracy yet reported. Results from these wave functions plus additional small corrections lead to a prediction of 11.0 ± 2 kcal/mol for the singlet-triplet energy difference. Other independent theoretical estimates also lend support to a value in this range. This relatively small separation arises primarily from the differential lowering effect produced by basis functions of d symmetry. Walsh-Mulliken (orbital energy vs. bond angle) diagrams are constructed and shown to be qualitatively valid representations for this molecule. Their topology is also the same for both the $^1\text{A}_1$ and $^3\text{B}_1$ states. Interpretation of these diagrams leads to a simple physical picture of the orbital distortions in the $^1\text{A}_1$ state generated by the d-polarization functions. It is demonstrated that methylene insertion and addition reactions are facilitated by d polarization. An argument as to why methylene insertion is not observed in carbon-carbon single bonds is also given.

The principal unresolved physical problem underlying carbene chemistry is the magnitude of the singlet-triplet energy separation in methylene. Because this quantity is inaccessible to direct experimental determination,² it has been the subject of much theoret-

ical effort. Electronic structure theory has been notably successful in predicting a variety of properties for methylene such as geometry,³ but the singlet-triplet

(1) (a) Lawrence Radiation Laboratory, University of California; (b) Department of Chemistry, University of California; (c) Department of Chemistry, Princeton University.

(2) Herzberg and collaborators have carried out the most definitive study of the methylene energy level structure, and their indirect estimates led them to conclude that "... the singlet is above the triplet state, probably by less than 1 eV": G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, pp 491, 584.

(3) On the basis of early spectroscopic studies by Herzberg [G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961); "Electronic Spectra and Electronic Structure of Polyatomic Molecules," ref 2], it was thought for some years that the triplet ground state was linear. High-accuracy theoretical calculations [J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969); C. F. Bender and H. F. Schaefer, *ibid.*, **92**, 4987 (1970)], however, gave a bent ground state. Recent experimental evidence [E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970); R. A. Berheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970); E. Wasserman, V. J. Kuck, R. S. Hutton and W. A. Yager, *J. Amer. Chem. Soc.*, **92**,

Table I. Molecular Orbital Total Energies for CH₂^a

	θ , deg	2.0 bohrs		2.1 bohrs ^b		2.2 bohrs	
		s,p	s,p,d	s,p	s,p,d	s,p	s,p,d
³ B ₁	80	38.8482		38.8467	38.8575	38.8439	
	100	38.8835		38.8860	38.8959	38.8815	
	120	38.9010	38.9110	38.9024	38.9117	38.8968	38.9055
	140	38.9016		38.9020	38.9103	38.8954	
	160	38.8925		38.8918	39.8989		
	180	38.8862		38.8847			
¹ A ₁	80	38.8282		38.8362	38.8572	38.8368	
	100	38.8488		38.8543	38.8727	38.8527	
	120	38.8465		38.8501	38.8658	38.8468	38.8613
	140	38.8307		38.8328	38.8446	38.8270	
	160	38.8133		38.8128	38.8214		
	180	38.8059		38.8046			

^a Hartree units, all numbers negative. ^b This calculation is designated SCF 1 in the text and on Figure 1. Basis sets given in ref 3 and 4.

energy separation has proved to be very difficult and there is little confidence in existing predictions. Detailed analysis of the previous failures and further developments in computational techniques leads us to believe that the present paper goes a long way toward resolving this question.

In addition to an accurate estimate of the singlet-triplet separation, our research has revealed the existence of an important d-orbital mixing in the ¹A₁ state. This d-polarization of the singlet p orbitals has a significant effect on the efficiency and reaction path for insertion and addition reactions. If one thinks of molecular orbital states made from an optimized s,p basis set as a calculational reference for ³B₁ and ¹A₁, then it turns out that approximately two-fifths of the relative energy lowering is due to the d-polarization effect and three-fifths due to instantaneous electron-electron correlation.

Insight into the nature of the individual molecular orbitals, how they are modified upon excitation from ³B₁ to ¹A₁, and the d-polarization influence on them has been obtained by constructing and interpreting the appropriate Walsh-Mulliken diagrams. Our results for CH₂ also check and strengthen the validity of the assumptions made in the use of these diagrams.

Calculational Methods and Results

Several *ab initio* molecular orbital wave functions were constructed by the well-known finite expansion (Roothaan) self-consistent-field (SCF) method. The results are shown in Figure 1 and Table I. SCF 1, s,p employed a basis set consisting of Whitten's s-type Gaussian group for carbon,^{4a} Huzinaga's carbon p's,^{4b} and Whitten's hydrogen 1s.^{4a} In the SCF procedure the carbon s's were contracted into four groups and the carbon p's and hydrogen s's into two groups. Computations were performed at $R(\text{CH}) = 2.0, 2.1,$ and 2.2 bohrs for HCH angles of 180 through 80°. The optimum bond length for both states is near 2.1 bohrs with an HCH angle of 129° (total energy -38.9041 hartrees) for the triplet, and 105° (total energy -38.8547 hartrees) for the singlet. The minimum-to-minimum separation for this s,p basis set is 29.31 kcal/mol. The second series of calculations (SCF 1, s,p,d) used the same s,p

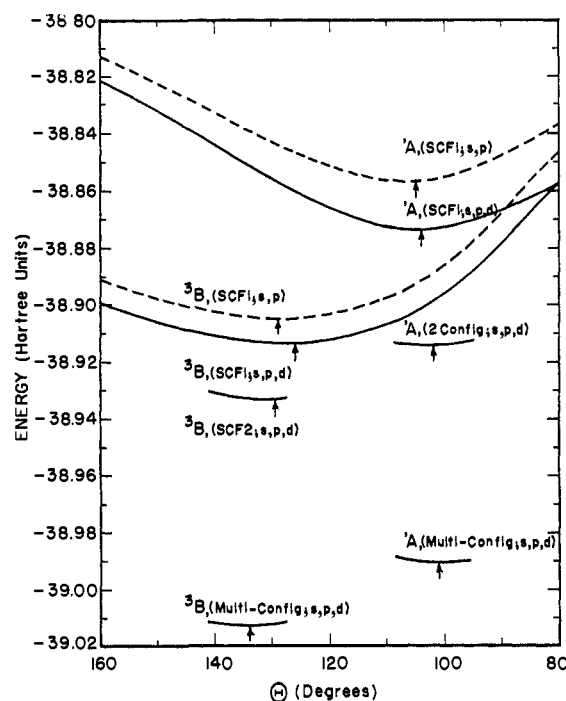


Figure 1. Total energy vs. bond angle for the ¹A₁ and ³B₁ states of methylene at four different levels of accuracy. Arrows designate angles of minimum energy.

basis set plus a single component d function with orbital exponent 0.7969.⁵ At 2.1 bohrs the potential minima of the triplet occurs at 126° (total energy -38.9123 hartrees) and at 101° (total energy -38.8726 hartrees) for the singlet. The minimum-to-minimum separation is now 24.92 kcal/mol (0.0397 hartrees). SCF 2, s,p,d (for the ³B₁ state) employed Huzinaga's 10s,5p Gaussian set with Dunning's⁶ five s, three p contraction. Dunning's single Gaussian p_x, p_y, p_z polarization functions⁷ were used on the hydrogens along with a two-Gaussian fit to a carbon single exponential d-polarization function of exponent 2.00. The total energy (-38.19327 hartrees) and other details regarding this wave function have been reported elsewhere.⁸

(5) The value of this exponent was taken from the extensive optimization computations on the methyl cation and anion by R. E. Kari and I. G. Csizmadia, *ibid.*, 50, 1443 (1969).

(6) T. H. Dunning, *ibid.*, 55, 716 (1971).

(7) T. H. Dunning, *ibid.*, 55, 3958 (1971).

(8) D. R. McLaughlin, C. F. Bender, and H. F. Schaefer, *Theor. Chim. Acta*, in press.

7491 (1970); G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, 54, 2276 (1971)] has shown the cited theoretical calculations to have been accurate within 2° of the currently accepted new experimental value (136°).

(4) (a) J. L. Whitten, *ibid.*, 39, 349 (1963); 44, 359 (1966); (b) S. Huzinaga, *ibid.*, 42, 1293 (1965).

Two varieties of correlated wave functions were constructed. For the 1A_1 state a two-configuration ($1a_1^2 2a_1^2 1b_2^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2 1b_1^2$) wave function was set up with the same basis as SCF 2, s,p,d. This two-configuration SCF function is used in place of a single determinant 1A_1 because the two configurations lie close in energy. It was constructed by performing natural orbital iterations on a configuration interaction wave function that included all single excitations from both configurations.⁹ Iterations were continued until the coefficients of the singly excited configurations vanished, and the extended Brillouin's theorem¹⁰ then guarantees an optimized two-configuration wave function. Table II gives total energies

Table II. Configuration Interaction Total Energies for the 1A_1 State of CH_2^a

$R(C-H)$, bohrs	θ , deg	E (2 config) ^b	E (419 config) ^b
2.05	96	38.91239	38.98714
2.10		38.91273	38.98895
2.15		38.91146	38.98919
2.20		38.90880	38.98808
2.05	100	38.91357	38.98801
2.10		38.91372	38.98963
2.15		38.91228	38.98968
2.20		38.90945	38.98839
2.00	104	38.91201	
2.05		38.91384	38.98807
2.10		38.91382	38.98950
2.15		38.91221	38.98938
2.20		38.90924	38.98792
2.00	108	38.91161	
2.05		38.91326	38.98736
2.10		38.91308	38.98861
2.15		38.91131	38.98832
2.20		38.90819	38.98671

^a Hartree units, all numbers negative. ^b Basis set given in ref 6 and 7

for the four C-H distances and four bond angles investigated using the SCF 2, s,p,d basis set. The lowest energy curve is plotted in Figure 1. The minimum energy bond distance, bond angle, stretching force constant, bending force constant, and interpolated total energy (SCF 2, s,p,d basis) are 1.099 Å, 102.2°, 4.62 m/Å, 0.61 mdyn/Å, and -38.9140 hartrees, respectively. The highest accuracy configuration interaction wave functions are approximate "first-order" wave functions.¹¹ The configurations in this type of wave function are determined by symmetry considerations, and, in principle all configurations are included in which no more than a single electron occupies an orbital beyond the valence shell. For CH_2 the valence orbitals for this purpose are $2a_1$, $1b_2$, $3a_1$, $1b_1$, $4a_1$, and $2b_2$, and Table III gives the configurations employed. Restrictions placed on the configurations are that the $1a_1$ orbital be at all times doubly occupied and that only configurations differing by one or two orbitals from the two reference configurations $1a_1^2 2a_1^2 1b_2^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2 1b_1^2$ be included. This leads to a 419-configuration wave function,¹² and an optimized solution

(9) C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966).

(10) L. Brillouin, *Actual. Sci. Ind.*, No. 71 (1933); No. 159 (1943); B. Levy and G. Berthier, *Int. J. Quantum. Chem.*, **2**, 307 (1968).

(11) H. F. Schaefer, *J. Chem. Phys.*, **54**, 2207 (1971).

(12) Further characteristics of this type of wave function are described in a water molecule calculation by H. F. Schaefer and C. F. Bender, *ibid.*, **55**, 1720 (1971).

is achieved by employing the iterative natural orbital method. This allows the $4a_1$ and $2b_2$ orbitals, not occupied in the two-configuration SCF wave function, to take on their optimum form. Typically, four natural orbital iterations were required to obtain energy convergence. Calculated total energies are given in Table II. The minimum energy bond distance, bond angles, stretching force constant, bending force constant, and interpolated total energy are 1.125 Å, 101.0°, 4.51 mdyn/Å, and -38.9898 hartrees, respectively, compared to the experimental bond distance and bond angle of 1.11 Å and 102.4°.¹³ Comparable calculations employing 617 configurations over an s,p,d basis for the 3B_1 ground state yield a "first-order" energy of -39.0121 hartrees.⁸

Discussion

A. The Singlet-Triplet Energy Separation. A review and analysis of all previous theoretical work on the singlet-triplet energy separation, except the current papers to be noted here, has been given by Harrison and Allen.¹⁴ Four recent investigations employ single-determinant, SCF molecular orbital wave functions for representing the 1A_1 and 3B_1 states. Lathan, Hehre, Curtiss, and Pople¹⁵ obtain 40 and 37 kcal/mol for s,p bases at the STO-3G and 4-31G level, respectively. Del Bene,¹⁶ using a closely related s,p basis, obtained 33 kcal/mol. The s,p basis employed for the simplest SCF calculation reported here is slightly superior to these and, as noted previously, yields a separation of 29 kcal/mol. Adding a d orbital to our basis brings this down to 25 kcal/mol. The trend observed from this collection of single-determinant SCF results is toward a smaller singlet-triplet separation as the wave function is improved, but the available data do not permit an accurate determination of the energy difference at the Hartree-Fock limit. Rough extrapolation, however, points to a 19-21 kcal limit. This number can be combined with a crude estimate of the differential correlation energy to yield the range of values to be expected for the actual singlet-triplet separation. An empirical correlation energy estimate derived from Huo's¹⁷ near Hartree-Fock wave function for isoelectronic NH ($^3\Sigma^1 \leftrightarrow ^1\Delta$ separation = 1.8 eV) plus the experimental separation of 1.2 eV observed by Florent and Leach¹⁸ leads to a differential instantaneous electron-electron correlation energy of 0.6 eV.¹⁹ On the other hand, a united-atom calculation by Cade²⁰ gives 0.2 eV for the net $^3\Sigma^- \leftrightarrow ^1\Delta$ correlation energy in NH. We thus obtain a first crude singlet-triplet separation estimate as 11 ± 6 kcal/mol.

In addition to the present work, there have been four recent studies in which configuration interaction wave functions for 3B_1 and 1A_1 were constructed. A rather extensive valence-bond treatment with an s,p basis by Harrison and Allen¹⁴ yielded 41 kcal/mol. Starting

(13) G. Herzberg and J. W. C. Johns, *Proc. Roy. Soc., Ser. A*, **295**, 107 (1966).

(14) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969).

(15) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971).

(16) J. E. Del Bene, *Chem. Phys. Lett.*, **9**, 68 (1971).

(17) W. Huo, *J. Chem. Phys.*, **49**, 1482 (1968).

(18) R. Florent and S. Leach, *J. Phys. Radium*, **13**, 377 (1952).

(19) Neither calculation considers the mixing of $^1\Delta$ with $^1\Sigma^+$ and this could increase this value.

(20) P. E. Cade, *Can. J. Phys.*, **46**, 1989 (1968).

Table III. Configurations Included in the Approximate "First-Order" Wave Functions for 1A_1 CH₂^a

	Excitation	No. of 1A_1 eigenfunctions per orbital occupancy		Excitation	No. of 1A_1 eigenfunctions per orbital occupancy
1st ref confign	$1a_1^2 2a_1^2 1b_2^2 3a_1^2$	1	2d ref confign	$1a_1^2 2a_1^2 1b_2^2 1b_1^2$	1
	$2a_1 \rightarrow 4a_1$	1		$2a_1 \rightarrow 4a_1$	1
	$1b_2 \rightarrow 2b_2$	1		$1b_2 \rightarrow 2b_2$	1
	$3a_1 \rightarrow 4a_1$	1		$2a_1^2 \rightarrow 3a_1 4a_1, 4a_1^2, 2b_2^2$	1
	$2a_1^2 \rightarrow 1b_1^2, 4a_1^2, 2b_2^2$	1		$2a_2 1b_2 \rightarrow 3a_1 2b_2, 4a_1 2b_2$	2
	$2a_1 1b_2 \rightarrow 4a_1 2b_2$	2		$1b_2^2 \rightarrow 3a_1 4a_1, 4a_1^2, 2b_2^2$	1
	$2a_1 3a_1 \rightarrow 1b_1^2, 4a_1^2, 2b_2^2$	1		$2a_1^2 \rightarrow 3a_1 ma_1, 4a_1, ma_1$	1
	$1b_2^2 \rightarrow 1b_1^2, 4a_1^2, 2b_2^2$	1		$2a_1^2 \rightarrow 2b_2 mb_2$	1
	$1b_2 3a_1 \rightarrow 4a_1 2b_2$	2		$2a_1 1b_2 \rightarrow 3a_1 mb_2, 4a_1 mb_2$	2
	$3a_1^2 \rightarrow 4a_1^2, 2b_2^2$	1		$2a_1 1b_2 \rightarrow 2b_2 ma_1$	2
	$2a_1 \rightarrow ma_1$	1		$2a_1 1b_1 \rightarrow 4a_1 mb_1$	2
	$1b_2 \rightarrow mb_2$	1		$2a_1 1b_1 \rightarrow 2b_2 ma_2$	2
	$3a_1 \rightarrow ma_1$	1		$1b_2^2 \rightarrow 3a_1 ma_1, 4a_1 ma_1$	1
	$2a_1^2 \rightarrow 1b_1 mb_1$	1		$1b_2^2 \rightarrow 2b_2 mb_2$	1
	$2a_1^2 \rightarrow 4a_1 ma_1$	1		$1b_2 1b_1 \rightarrow 4a_1 ma_2$	2
	$2a_1^2 \rightarrow 2b_2 mb_2$	1		$1b_2 1b_1 \rightarrow 2b_2 mb_1$	2
	$2a_1 1b_2 \rightarrow 1b_1 ma_2$	2			
	$2a_1 1b_2 \rightarrow 4a_1 mb_2$	2			
	$2a_1 1b_2 \rightarrow 2b_2 ma_1$	2			
	$2a_1 3a_1 \rightarrow 1b_1 mb_1$	2			
	$2a_1 3a_1 \rightarrow 4a_1 ma_1$	2			
	$2a_1 3a_1 \rightarrow 2b_2 mb_2$	2			
	$1b_2^2 \rightarrow 1b_1 mb_1$	1			
	$1b_2^2 \rightarrow 4a_1 ma_1$	1			
	$1b_2^2 \rightarrow 2b_2 mb_2$	1			
	$1b_2 3a_1 \rightarrow 1b_1 ma_2$	2			
	$1b_2 3a_1 \rightarrow 4a_1 mb_2$	2			
	$1b_2 3a_1 \rightarrow 2b_2 ma_1$	2			
	$3a_1^2 \rightarrow 1b_1 mb_1$	2			
	$3a_1^2 \rightarrow 4a_1 ma_1$	2			
	$3a_1^2 \rightarrow 2b_2 mb_2$	2			

^a ma_1 includes $5a_1-16a_1$, ma_2 includes $1a_2-2a_2$, mb_1 includes $2b_1-5b_1$, and mb_2 includes $3b_2-9b_2$.

with single determinant SCF solutions at the same level as the s,p basis set calculations reported here, Harrison²¹ added configuration interaction with the four lowest states and obtained 39 kcal/mol for the separation. O'Neil, Schaefer, and Bender,²² employing the same technique described above in the Calculation Methods section, but with an s,p basis and considerably fewer configurations, got 22 kcal/mol. Recent work by Hay, Hunt, and Goddard²³ employs an antisymmetrized product of optimized, singlet-coupled, strongly orthogonal, Heitler-London-like pair functions augmented by a configuration interaction. The three pair functions housing the six valence electrons can be expanded as six orthogonal natural orbitals, and this forms the basis for their configuration interaction treatment (with the carbon 1s always kept doubly occupied). Using the same double ζ s,p basis set as O'Neil, Schaefer, and Bender,²² they find a singlet-triplet separation of 22.4 kcal/mol. When they include a d orbital, the singlet-triplet separation drops to 11.5 kcal, a value strikingly close to that which we have obtained (their 1A_1 total energy, -38.9414 hartrees, is approximately 1.3 eV higher than that reported here).

It is clear from these results that the d basis function is playing a key role in differentially correlating the electrons in 1A_1 more than those in 3B_1 . The increased opportunity for orbital flexibility is conceptually similar to the d-polarized orbital effect schematically shown in

Figure 5, but a simple pictorial representation is not possible. The principal shortcoming of our lowest total energy wave functions is the degree of flexibility allowed the d functions. Only one orbital exponent has been used, but it has been strongly indicated by work on NH₃²⁴ that two sets of d functions, each with different orbital exponents, are required. Taking into account the expected effect of additional d functions as well as additional s and p functions plus truncation in the configuration interaction expansion leads us to predict a further differential lowering of approximately 0.10–0.15 eV, thus a singlet-triplet separation of 11 ± 2 kcal/mol.

Further insight into the physical nature of the 1A_1 and 3B_1 states can be obtained from a conceptually simpler pair of wave functions than the elaborate configuration interaction ones given above. These two are the 3B_1 (SCF 2, s,p,d) and 1A_1 (2 configuration, s,p,d) wave functions of Figure 1. The single-determinant 3B_1 function is near the Hartree-Fock limit (estimated to be within 0.015 hartree unit). For 1A_1 , two configurations, $1a_1^2 2a_1^2 1b_2^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2 1b_1^2$, are mixed and the orbitals optimized over the same s,p,d basis as employed for the 3B_1 . The singlet-triplet separation for this pair of wave functions is 11.7 kcal/mol. The physical situation is clear and simple. For the 1A_1 state the two close-lying $3a_1$ and $1b_1$ levels obviously must be mixed, and the resulting splitting contributes to a differential lowering of the 1A_1 relative to the 3B_1 in addition to that produced by the d orbitals. In

(21) J. F. Harrison, *J. Amer. Chem. Soc.*, **93**, 4112 (1971).

(22) S. V. O'Neil, H. F. Schaefer, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971).

(23) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972).

(24) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970).

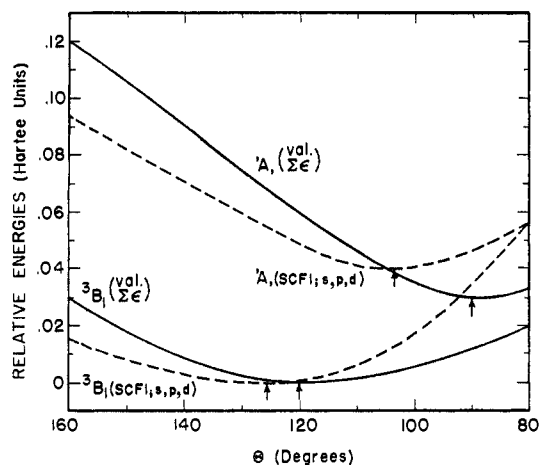


Figure 2. Comparison of 1A_1 and 3B_1 potential energy curves produced by total energies and sum of valence electron one-electron eigenvalues for molecular orbital wave functions. Arrows designate angles of minimum energy

terms of the generalized valence-bond wave function of Goddard, *et al.*,²³ this splitting may be pictured as dividing the lone pair into sp-hybridized lobes pointing above and below the molecular plane and bent back from the hydrogens.

Finally, it is important to note two pieces of experimental work that suggest a dramatically small separation. Halberstadt and McNesby²⁵ estimate 2.5 kcal/mol from the 3130-Å photolysis of ketene in the presence of methane and propane. This estimate contains large uncertainties because of the assumption that CH_2 suffers many collisions before C-H bond insertion and because it depends on the accuracy of RRKM calculations for the rate of dissociation of chemically activated ethane. Carr, Eder, and Topor²⁶ propose a value of 1–2 kcal/mol from experiments on the 3500-Å photolysis of ketene. This value is based on their estimate of the singlet-triplet ratio which is then used in conjunction with the Boltzmann factor to obtain the energy separation. There are at least three unresolved uncertainties which could make singlets appear more numerous than they actually are: ketene may selectively scavenge triplet, some of the observed singlet product may come directly from ketene, or triplets may suffer more unproductive collisions with propane (or other molecules used as molecular state detectors) than singlets. Overall, we feel that these two experimentally derived estimates are much less certain than the theoretical calculations.

B. Walsh-Mulliken Diagrams. Because of their simplicity and intuitive appeal, orbital energy *vs.* angle plots (Walsh-Mulliken diagrams)^{27, 28} have helped to organize many results from organic and inorganic chemistry. In his original article Walsh²⁷ incorrectly predicted the 1A_1 (or a linear 3B_1) as the methylene ground state. It is important to note, however, that this failure to predict a bent 3B_1 ground state was due to his well-known omission of s,p mixing in a_1 orbitals²⁹ and not to

(25) M. L. Halberstadt and J. R. McNesby, *J. Amer. Chem. Soc.*, **89**, 3417 (1967).

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(27) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953); *Progr. Stereochem.*, **1**, 1 (1954).

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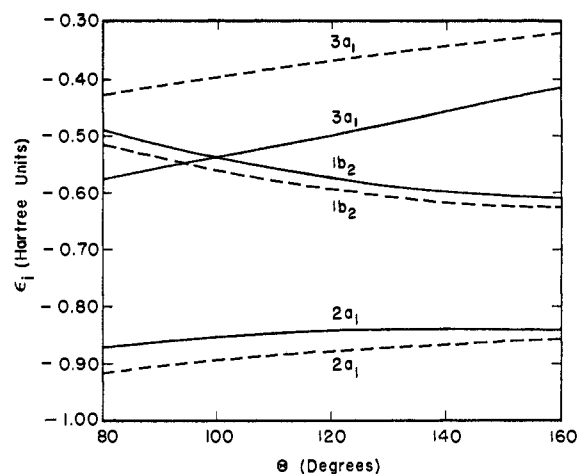


Figure 3. Walsh-Mulliken diagrams for valence orbitals of CH_2 to illustrate relative invariance of diagram topology for different electronic states: solid lines, 3B_1 ; dashed lines, 1A_1 .

a breakdown of the sum of valence orbital energies as a molecular shape criterion. Figure 2 shows that for CH_2 the sum of valence orbital energies does yield a respectable first estimate of the equilibrium angles, potential energy curve shape, and even singlet-triplet energy separation (18.5 kcal). The $\Sigma^{val}\epsilon$ criterion works well here because CH bonds have small dipole moments.³⁰

In recent years a large number of Walsh-Mulliken diagrams have been generated by *ab initio* molecular orbital calculations, and these results support the generality and simple, semiquantitative utility that Walsh originally ascribed to them. In particular it has been shown that the topology of these diagrams is sensibly independent of the central atom (*e.g.*, A in AH_2 systems).³⁰ Less is known about their invariance under change of molecular state. Figure 3 shows this type of curve shape invariance for the 3B_1 and 1A_1 states in CH_2 . It is also apparent from the gross features of Figure 4 that these diagrams are unaffected by basis set choice to a first approximation (the detailed differences, however, yield much additional information, and this is analyzed in the paragraphs below).

As noted previously in Figure 1, d-polarization of the basis set differentially lowers the 1A_1 relative to the 3B_1 , particularly near the equilibrium 1A_1 angle. Detailed understanding of the d-polarization is obtained from the orbital *vs.* angle decomposition plotted in Figure 4. In 1A_1 the outer two electrons are both in $3a_1$, but in 3B_1 they occupy the configuration $1b_1 3a_1$. $3a_1$ is made up of atomic orbital contributions from the two hydrogens plus the 2s and 2p carbon orbitals, the latter hybridizing to form a lone pair. As schematically illustrated in Figure 5, a carbon-centered d_{yz} mixes with and improves the shape of the sp lone-pair hybrid as well as enhancing the H-C-H bonding. It follows that this type of mixing decreases the orbital energy more for small angles (down to about 60°). At 80° the decrease for the singly occupied $3a_1$ in 3B_1 (0.0036 hartree) is almost exactly half that for the doubly occupied $3a_1$ in 1A_1 (0.0076 hartree). The p orbital perpendicular to the molecular plane is $1b_1$ and d_{yz}

(30) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

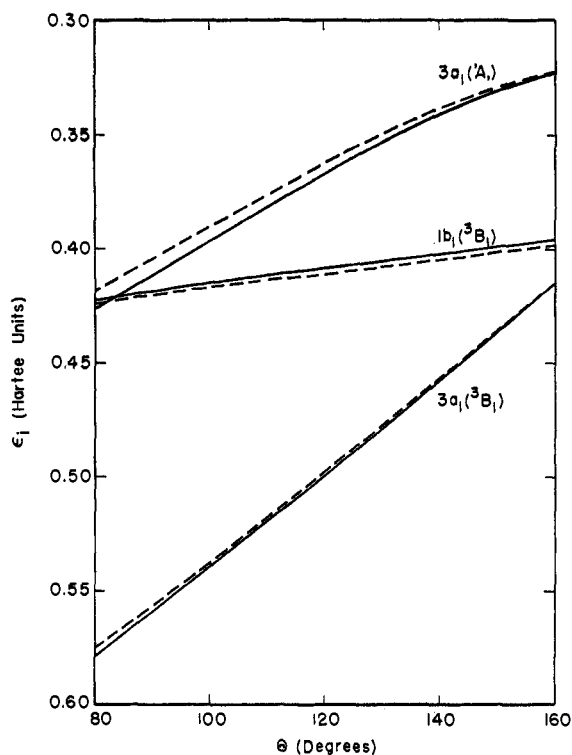


Figure 4. d-Polarization effect on orbital energies vs. bond angle for those orbitals which differ between the 3B_1 and 1A_1 states: solid lines, s,p,d basis set; dashed lines, s,p basis set.

polarizes it toward the lone pair. The charge increase in the H-C-H region produced by d_{yz} in $3a_1$ creates an effective potential that causes this polarization direction and raises the $1b_1$ orbital energy. Since the orbital energy change in $1b_1$ is roughly equal and opposite to that in $3a_1$ (3B_1), the net effect is a differential polarization in 1A_1 . The existence of a distinctive d contribution to energies and orbital shapes for the light atoms should not now be surprising in view of several recent demonstrations of their influence (e.g., the origin of the inversion barrier in ammonia).²⁴ d effects will show up particularly when comparing conformations with strongly differing local symmetries.

C. Consequences for Methylene Reactions. Because insertion and addition reactions of singlet methylene are believed to be largely direct, theory can be applied more easily, and all of our conclusions here are concerned solely with them.³¹ Three previous papers by Hoffmann and collaborators also bear on these two types of reactions.³²⁻³⁴ His conclusions are based on extended Hückel calculations for the combined system of CH_2 plus its reactants. Although this computation scheme is relatively crude, the conclusions are sub-

(31) Fortunately, complete and up-to-date reviews of carbene chemistry are available, and therefore this background need not be repeated here. See P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235; W. R. Moss, *Chem. Eng. News*, 47, 60 (June 1969); W. Kirmse, "Carbene Chemistry," 2d ed, Academic Press, New York, N. Y., 1971.

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(33) R. Hoffmann, R. Gleiter, and F. B. Mallory, *ibid.*, 92, 1460 (1970).

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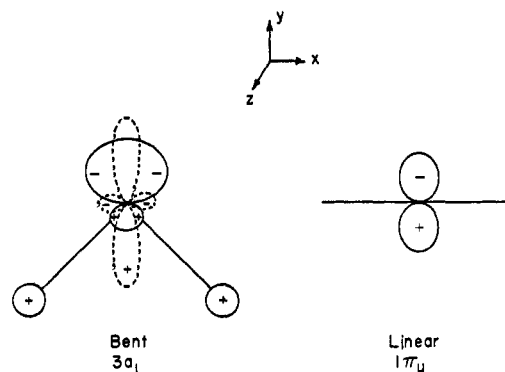


Figure 5. Schematic of orbital mixing in $3a_1 \rightarrow 1\pi_u$ of CH_2 : solid line around $3a_1$ is sp hybrid representing lone pair; dashed line, d_{yz} mixing.

stantially correct. The results reported here are based on a much higher accuracy wave function for methylene by itself, and they serve to extend and suggest small modifications in Hoffmann's work. Thus for singlet addition to double bonds the d-polarization effect discussed above modifies reaction paths and enhances its electrophilic nature for two reasons. First, the d_{yz} orbitals polarize the empty p orbital perpendicular to the molecular plane away from the C-H bonds and presumably toward the attracted double bond. Secondly, d_{yz} allows a path-dependent shape change in the methylene lone pair and in the H-C-H region charge, thus providing an optimum accommodation to electron repulsion between CH_2 and the double bond.

There is another feature of methylene insertion reactions for which an explanation has not yet been proposed, and this is the generally observed failure of methylene to insert in a carbon-carbon single bond. Detailed examination of *ab initio* ethane wave functions³⁵ and those for CH_2 reported here leads to the conclusion that methylene insertion is prevented by an electron repulsion dominated interaction for all directions of approach to the carbon-carbon single bond.³⁶ This situation is in sharp contrast to insertion in C-H where electron repulsion around H is low and to glide formation where there exist paths for avoiding excess repulsion.³⁷

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(35) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, 46, 2261 (1967).

(36) Because extended Hückel theory does not include electron-electron repulsion terms, this level of theory is inapplicable to this problem.

(37) Since submission of this work, another calculation on the 3B_1 and 1A_1 states of CH_2 has been reported by S. Y. Chu, A. K. Siu, and E. F. Hayes, *J. Amer. Chem. Soc.*, 94, 2969 (1972). An s,p basis set was employed to construct both SCF and SCF + CI wave functions. Computed total energies are slightly lower than Harrison's²¹ but higher than those obtained by O'Neil, Schaefer, and Bender.²² The singlet-triplet energy separation is calculated to be 20.3 kcal/mol.