Ab Initio MCSCF and CI Calculations of the Singlet–Triplet Energy Differences in Oxyallyl and in Dimethyloxyallyl

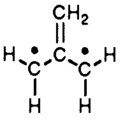
Michael B. Coolidge,† **Koichi Yamashita,**‡ **Keiji Morokuma,**‡ **and Weston Thatcher Borden***,†

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195, and the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

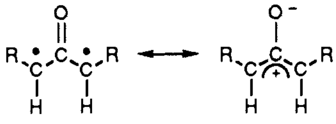
Received July 27, 1989

Abstract: Ab initio MCSCF and multireference CI calculations predict a very small singlet–triplet energy splitting in oxyallyl (**2**). The largest calculations find the triplet to be the ground state by 1–2 kcal/mol. The reason for the small singlet–triplet energy difference in **2** is discussed. The pair of alkyl substituents in dimethyloxyallyl (**3**) are computed to confer a singlet ground state on this diradical. Multireference CI calculations, which include correlation between σ and π electrons, give a singlet–triplet energy separation in **3** of ~5 kcal/mol.

Oxyallyl (**2**) may be viewed as being derived from trimethylenemethane (**1**) by replacement of a methylene group by oxygen. The formation of oxyallyls as intermediates in the equilibration of allene oxides with the isomeric cyclopropanones[1,2] and the chemical trapping of oxyallyls in cycloaddition reactions[3] have obvious parallels in trimethylenemethane chemistry.[4] However, although **1**[5] and derivatives[4,6] have been shown experimentally to be ground-state triplets, we are unaware of any experimental evidence for a triplet ground state for **2** or a derivative thereof.



1



2a, R = H
3a, R = CH_3

2b, R = H
3b, R = CH_3

In agreement with experiment, ab initio calculations predict a triplet ground state for **1**.[7] A triplet ground state has also been predicted for **2** by an ab initio, π MCSCF study.[8-10] The energy difference between the triplet ground state ($^3B_2$) and the lowest singlet state ($^1A_1$) was computed to be 12.3 kcal/mol with the split-valence 3-21G basis set, which decreased to 5.6 kcal/mol when polarization functions were included in the basis set.[8]

The substantial change in the singlet–triplet splitting, caused by inclusion of polarization functions, suggests that their inclusion might also have a differential effect on the optimized geometries for the two states. Unfortunately, the computer resources that were available at the time these MCSCF calculations were performed precluded geometry reoptimization with the polarized basis set. Moreover, although the four π electrons were correlated in the MCSCF wave function, the effect of including σ–π correlation was not investigated.

Recent calculations of the singlet–triplet splitting in 2,4-dimethylenecyclobutane-1,3-diyl and in its mono- and dioxo derivatives have shown that inclusion of σ–π correlation provides selective stabilization of the singlet states of these diradicals.[11] The magnitude of this selective singlet-state stabilization was found to increase with increasing oxygen substitution. This finding suggested that inclusion of σ–π correlation would decrease and, perhaps, even change the sign of the singlet–triplet splitting computed for oxyallyl (**2**).

The calculations described in this paper were performed in order to assess the effects of both geometry reoptimization with a better basis set and inclusion of σ–π correlation on the singlet–triplet splitting computed for **2**. In addition, we were interested in investigating the possible effect of alkyl substituents on selectively stabilizing the singlet state in derivatives of **2**. While our calculations on **2** were in progress, Professor Paul Lahti informed us that he was performing calculations on cyclic derivatives of

Table I. Energies of the $^1A_1$ and $^3B_2$ States of Oxyallyl at Their MCSCF Optimized Equilibrium Geometries,[a] Computed at Various Levels of Theory

calculation	$^1A_1$, hartrees	$^3B_2$, hartrees	ΔE_{S-T}, kcal/mol
CAS-π MCSCF[b]	−190.7580	−190.7650	4.4
MR-SD CI[c]	−191.2072	−191.2110	2.4
MR-SDQ CI[d]	−191.2703	−191.2729	1.6
TCSCF/RHF[e]	−190.7464	−190.7382	−5.1
CAS-π CI[e]	−190.7684	−190.7720	2.3
MR-π-SD CI[e]	−190.7811	−190.7881	4.4
MR-σ-S CI[e]	−190.8606	−190.8601	−0.3
MR-σ-S,π-SD CI[e]	−190.8727	−190.8739	0.8

[a] For $^1A_1$ R(C–O) = 1.214 Å and R(C–C) = 1.471 Å. For $^3B_2$ R(C–O) = 1.254 Å and R(C–C) = 1.444 Å. [b] At the CAS-π MCSCF geometries, optimized with the 3-21G basis set, $E(^1A_1) = -190.7574$ hartrees, $E(^3B_2) = -190.7618$ hartrees, and $\Delta E_{S-T} = 2.8$ kcal/mol. [c] All single and double excitations from CAS multireference wave functions, using the contracted CI method of Werner and Knowles.[15] [d] MR-SD CI with the Davidson correction[16] for quadruples added. [e] A better basis set on hydrogen was used for these calculations.[18]

---

† University of Washington.

‡ Institute for Molecular Science.

(1) Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7347. Camp, R. L.; Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 7349. Chan, T. H.; Ong, B. S. *J. Org. Chem.* **1978**, *43*, 2994. *Tetrahedron* **1980**, *36*, 2269.

(2) Oxyallyls have also been postulated as intermediates in Favorskii rearrangements (review: Chenier, P. J. *J. Chem. Educ.* **1978**, *55*, 286) and in the photorearrangements of 2,5-cyclohexadienones (review: Schaffner, K.; Demuth, M. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 281–319.

(3) Turro, N. J. *Acc. Chem. Res.* **1969**, *2*, 25; *Pure Appl. Chem.* **1971**, *27*, 679. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819. Chan, T. H.; Li, M. P.; Mychajlowskij, W.; Harpp, D. N. *Tetrahedron Lett.* **1974**, *39*, 3511. Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. Samuel, C. J. *J. Chem. Soc. Perkin Trans. 2* **1981**, 736.

(4) Review: Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 151–194.

(5) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.

(6) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725.

(7) Review: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1–72.

(8) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 5112.

(9) Two ab initio studies of oxyallyl have been performed at the SCF level (Liberles, A.; Greenberg, A.; Lesk, A. *J. Am. Chem. Soc.* **1972**, *94*, 8685. Schaad, L. J.; Hess, B. A.; Zahradnik, R. *J. Org. Chem.* **1981**, *46*, 1909), and a third included electron correlation via the use of Møller–Plesset perturbation theory (Ortiz, J. V. *J. Org. Chem.* **1983**, *48*, 4744). The results of CI calculations with the semiempirical INDO/S method have also been reported: Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273.

(10) For an MCSCF study of thioxyallyl and leading references to the experimental literature on thio derivatives of **2**, see: Ando, W.; Furuhata, T. *Tetrahedron* **1986**, *27*, 4035.

0002-7863/90/1512-1751$02.50/0

2.[12] Therefore, we restricted ourselves to investigating the effect of just the two methyl groups in dimethyloxyally **3**.

Computational Methodology

All the calculations reported in this paper were carried out with the Dunning double-ζ basis set,[13] augmented by a set of polarization functions on carbon ($\zeta = 0.75$) and on oxygen ($\zeta = 0.85$). Multiconfiguration (MC)SCF calculations were performed with this DZP basis set for $^3\mathrm{B}_2$ and $^1\mathrm{A}_1$ wave functions that consisted of all the symmetry-adapted configurations (9 for $^3\mathrm{B}_2$ and 12 for $^1\mathrm{A}_1$) that arise from four electrons occupying the lowest four π orbitals. These complete active space (CAS) MCSCF calculations were carried out at the Institute for Molecular Science with the MOLPRO package of ab initio programs.[14]

The polarized basis set proved too large to allow convenient calculation of analytical gradients of the MCSCF energy for use in geometry optimization. Therefore, the CH bond lengths and the bond angles from the previous MCSCF study[8] were used, and only the C–O and C–C bond lengths were reoptimized by fitting six single-point MCSCF energies for each state to a quadratic potential function. The reoptimized bond lengths and the corresponding MCSCF energies for the lowest singlet and triplet states are given in Table I.

Configuration interaction (CI) calculations were performed at the MCSCF optimized geometries. The 8 electrons in 1s orbitals were cored, and all single and double excitations were allowed for the 22 valence electrons from each of the two CAS reference wave functions. The resulting multireference (MR)-SD CI wave functions consisted of 1 480 927 configurations for $^3\mathrm{B}_2$ and 812 362 configurations for $^1\mathrm{A}_1$. The energies of these wave functions were calculated with the internally contracted CI method of Werner and Knowles.[15]

These MR-SD CI energies are given in Table I. Also listed are the energies obtained by adding the Davidson correction for quadruple excitations.[16] The latter energies are labeled MR-SDQ CI in Table I.

Another set of strictly variational CI calculations was performed at the University of Washington, using the MELD package of ab initio programs.[17,18] Starting from both the RHF wave function for $^3\mathrm{B}_2$ and the two-configuration (TC)SCF wave function for $^1\mathrm{A}_1$, the orbitals of the virtual space were transformed into K orbitals.[19] CI calculations were then performed in the complete active π space (CAS-π CI), using the same 9 configurations for $^3\mathrm{B}_2$ and 12 configurations for $^1\mathrm{A}_1$ as were employed in the MCSCF calculations.

With the π CAS configurations as references, all single and double excitations were performed in the π space. These MR-π-SD CI calculations involved 923 spin-adapted configurations for $^3\mathrm{B}_2$ and 738 spin-adapted configurations for $^1\mathrm{A}_1$. Essentially the same energies were obtained when complete π CI calculations (3600 configurations for $^3\mathrm{B}_2$ and 2760 for $^1\mathrm{A}_1$) were performed.

Table II. p–π Orbital Total and (Unpaired) Electron Populations[a,b] in the $^1\mathrm{A}_1$ and $^3\mathrm{B}_2$ States of Oxyallyl at Various Levels of Theory

calculation	state	O	$C_1(C_3)$	C_2
TCSCF	$^1\mathrm{A}_1$	1.42	0.93	0.68
RHF	$^3\mathrm{B}_2$	1.33 (0.22)	0.94 (0.87)	0.77 (0.03)
MR-π-SD CI	$^1\mathrm{A}_1$	1.39	0.91	0.77
MR-π-SD CI	$^3\mathrm{B}_2$	1.21 (0.48)	0.96 (0.85)	0.86 (–0.18)
MR-σ-S,π-SD CI	$^1\mathrm{A}_1$	1.38	0.89	0.82
MR-σ-S,π-SD CI	$^3\mathrm{B}_2$	1.20 (0.45)	0.96 (0.83)	0.87 (–0.13)

[a] See ref 23. [b] Because there is some electron density in d–π orbitals, the p–π total populations do not sum to 4.0; nor do the unpaired electron populations in the $^3\mathrm{B}_2$ state sum exactly to 2.0.

Correlation between the σ and π electrons was included by allowing all possible σ single excitations from the π CAS configurations. These MR-σ-S CI calculations involved 10 809 configurations for the triplet and 7419 for the singlet. Allowing either π-SD or σ-S excitations from the π CAS configurations gave 11 723 and 8145 configurations, respectively, for $^3\mathrm{B}_2$ and for $^1\mathrm{A}_1$.

The calculations on dimethyloxyallyl (**3**) were also performed in C_{2v} symmetry at the same geometries as the calculations on the parent (**2**). The H_3C–C bond length of 1.499 Å and the other geometrical parameters for the methyl groups were taken from the results of 6-31G* UHF calculations on the ethyl radical.[20] The unique hydrogen on each methyl group in **3** was oriented transoid to the hydrogen on the adjacent carbon. UHF calculations on the $^3\mathrm{B}_2$ state of **3** found this geometry to be 0.0004 hartree lower than the methyl group conformation with a cisoid orientation of hydrogens.

The size of **3** precluded MCSCF calculations, and so only CI calculations with K orbitals were performed on this diradical. Preliminary π CI calculations indicated the inadequacy of four electron/four orbital reference wave functions for **3**. Therefore, all eight electrons in orbitals of π symmetry were correlated in the reference wave functions for **3**, using a total of eight π orbitals. The reference π wave functions consisted of 1192 configurations for $^3\mathrm{B}_2$ and 900 configurations for $^1\mathrm{A}_1$.

Allowing all single and double π excitations from these reference wave functions generated 592 325 $^3\mathrm{B}_2$ configurations and 350 472 $^1\mathrm{A}_1$ configurations. The large numbers of configurations in the reference wave functions prevented the inclusion of all single σ excitations from them. Therefore, a partial CI in the σ space was performed in which single excitations of the 26 valence electrons in orbitals of σ symmetry were permitted into the lowest 13 virtual K orbitals. The resulting MR-σ-S CI wave functions consisted of 600 942 configurations for $^3\mathrm{B}_2$ and 345 176 for $^1\mathrm{A}_1$.

Results and Discussion

Reoptimization with the Dunning DZP basis set of the MCSCF geometries for the singlet and triplet states of **2** results in a significantly shorter C–O bond length for both states. For the $^3\mathrm{B}_2$ state, the C–O bond shortens from the 3-21G optimized bond length by fully 0.059 Å, which is accompanied by an increase in the length of each of the equivalent C–C bonds of 0.029 Å. In the $^1\mathrm{A}_1$ state, the C–O bond shortens by 0.020 Å, and the optimized C–C bond length remains unchanged.

At the 3-21G optimized geometries, the CAS-π MCSCF energy difference of 2.8 kcal/mol between the singlet and triplet with the Dunning DZP basis set is only half of the 5.6 kcal/mol computed with the 3-21G* basis set.[8] Because geometry reoptimization has a larger effect on $^3\mathrm{B}_2$ than on $^1\mathrm{A}_1$, as shown in Table I, the MCSCF value of $\Delta E_{\mathrm{S-T}}$ increases to 4.4 kcal/mol upon geometry reoptimization.

The MCSCF value of 4.4 kcal/mol for $\Delta E_{\mathrm{S-T}}$ is slightly larger than the 2.3 kcal/mol obtained from the CAS-π CI calculations, which used the same number of configurations. However, $\Delta E_{\mathrm{S-T}} = 4.4$ kcal/mol was also found by the MR-π-SD CI calculations,

---

(11) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 3773.

(12) Ichimura, A.; Lahti, P. M.; Matlin, A. R. *J. Am. Chem. Soc.*, in press. We thank Professor Lahti for informing us of his study, for agreeing to simultaneous publication, and for sending us a preprint of his manuscript.

(13) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F. III, Ed.; Plenum: New York, 1977; Vol. 2.

(14) Knowles, P. J.; Werner, H.-J.; Elbert, S. T., 1988. The MCSCF methodology is described in: Werner, H. J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053. Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259.

(15) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803. We thank Dr. Knowles for providing us with a version of MOLPRO that incorporates internally contracted CI, as well as MCSCF methodology.

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

(17) Developed at the University of Washington by McMurchie, L.; Elbert, S., Langhoff, S., and Davidson, E. R. and modified by Feller, D. and Rawlings, D.

(18) A triple-ζ basis set for hydrogen, which is built into the Dunning DZP basis set for heavy atoms in MELD, was used for these CI calculations. The hydrogen basis set is described in: Stenkamp, L. Ph.D. Thesis, University of Washington, 1975.

(19) Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3977.

(20) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie Mellon University: Pittsburgh, PA, 1983.

which allowed all single and double π excitations from these configurations. As noted in the preceding section, the energies from the latter CI calculations are essentially the same as those obtained from complete CI in the π space.

Since the triplet has a more delocalized π wave function than the singlet,[21] as expected,[11] inclusion of correlation between the nonbonding and bonding pair of π electrons selectively stabilizes the triplet. Thus, on going from the RHF/TCSCF level, where only the nonbonding electrons are correlated, to either the CAS-π MCSCF or the MR-π-SD CI level, where all four π electrons are correlated, ΔE_{S-T} increases by 9.5 kcal/mol.

Also as expected,[11] inclusion of σ–π correlation selectively stabilizes the more ionic singlet state. With the inclusion of excitations of electrons in σ orbitals, ΔE_{S-T} decreases to between 1 and 2 kcal/mol.[22] The fact that these calculations predict $^3B_2$ to be the ground state of oxyallyl is less significant than the fact that ΔE_{S-T} in **2** is computed to be very small, roughly an order of magnitude smaller than in **1**.[7]

Since, as shown by the π AO population analyses[23] for **2** in Table II, the $^1A_1$ state has more π charge separation than $^3B_2$, it is tempting to explain the decrease in ΔE_{S-T} on going from **1** to **2** on the basis of an important contribution from resonance structure **b** to the $^1A_1$ state of **2**. The 0.09–0.18 greater electron density in the π AO on oxygen in $^1A_1$, compared to $^3B_2$, is consistent with this explanation; but the shorter C–O and longer C–C bond lengths in the singlet than in the triplet are not.

We have suggested previously[8] that the major difference between **1** and **2** is the greater strength of a C–O compared to a C–C double bond. The significant stabilization of the $^1A_1$ state, relative to $^1B_1$ and $^1B_2$, on going from **1** to **2** was attributed to the fact that the $^1A_1$ wave function in **2** allows a full C–O π bond; whereas, the wave functions for the other two low-lying singlet states of **2** have little or no C–O π bonding. Since the wave function for the $^3B_2$ state of **2** can be regarded as a hybrid of three covalent resonance structures, only one of which (**2a**) places a double bond between C and O, the stabilization of $^1A_1$, relative to $^3B_2$, on going from **1** to **2** can be similarly explained.

It should be noted that, although symmetry mandates that the three resonance structures for the triplet contribute equally in **1**, this is not the case in **2**. For example, in triplet **1** the ratio of unpaired electrons on any two peripheral carbons is, by symmetry, 1.00. However, Table II shows that in triplet **2** the ratio of unpaired π electron density on carbon to oxygen ranges from 1.77 at the MR-π-SD CI level to 1.84 at the MR-σ-S,π-SD CI level of theory.[24] From the ratio of the unpaired electron densities on oxygen and carbon it can be calculated that structure **2a** contributes ~2.6 times more to triplet oxyallyl than do either of the two resonance structures that place one unpaired electron on carbon and one on oxygen.[26]

Table III. Energies of the $^1A_1$ and $^3B_2$ States of Dimethyloxyallyl, Computed at Various Levels of Theory

calculation	$^1A_1$, hartrees	$^3B_2$, hartrees	ΔE_{S-T}, kcal/mol
TCSCF/RHF	−268.8456	−268.8300	−9.8
CAS-π CI[a]	−268.8775	−268.8730	−2.8
MR-π-SD CI[a]	−268.9067	−268.9047	−1.3
MR-σ-S CI[a,b]	−268.9721	−268.9636	−5.3

[a] Complete active space consists of eight electrons in eight π orbitals. [b] All single σ excitations into the 13 lowest K orbitals.

Based on the foregoing discussion, a reasonable perspective from which to understand the near degeneracy of $^3B_2$ and $^1A_1$ in oxyallyl is that, to a first approximation, structure **2a** represents the bonding in both states. Of course, the two other covalent resonance structures for **2** do make some contribution to $^3B_2$; and the more delocalized wave function for $^3B_2$ than for $^1A_1$[21] accounts for the differences between the optimized bond lengths for the two states. On the other hand, structure **2b** makes a contribution to $^1A_1$ but not to $^3B_2$,[27] thus explaining the differences in the π electron densities in the two states.

The more delocalized π wave function for $^3B_2$ stabilizes it, relative to $^1A_1$. However, the greater electron density on oxygen in $^1A_1$ selectively stabilizes it. These two effects are apparently of about the same magnitude, which results in the approximate degeneracy between the energies of $^3B_2$ and $^1A_1$ in **2**.

Because $^1A_1$ has less π bonding to the two equivalent carbons of **2** than does $^3B_2$ and because $^1A_1$ has more cationic character at these atoms, methyl substitution at these two carbons would be anticipated to stabilize selectively the singlet state. This expectation is confirmed by the computational results contained in Table III. At each level of theory ΔE_{S-T} for **3** is smaller than the comparable number for **2** in Table I. The negative sign for every value of ΔE_{S-T} in Table III shows that at all these levels of theory, a singlet ground state is predicted for **3**.

Comparison of the values of ΔE_{S-T} in Tables I and III, computed at similar levels of theory, shows that the pair of methyl groups in **3** stabilizes $^1A_1$, relative to $^3B_2$, by about 5–6 kcal/mol. This suggests that at the MR-SDQ CI or the MR-σ-S,π-SD CI level, ΔE_{S-T} in **3** would be in the range of −4 to −5 kcal/mol. In fact, extrapolations, based on comparisons of CI calculations with partial and complete σ single excitations from a smaller set of reference configurations, indicate that use of the full set of σ virtual orbitals for correlation would find the singlet to be selectively stabilized, relative to the triplet, by another 1–2 kcal/mol. Therefore, 5 kcal/mol would appear to be a conservative estimate of the magnitude of the energy by which $^1A_1$ lies below $^3B_2$ in **3**.

In conclusion, although our calculations predict a very small preference for a triplet ground state in the parent oxyallyl (**2**), our computational results unequivocally predict a singlet ground state for dimethyloxyallyl (**3**). This finding is consistent with the prediction by Lahti and co-workers of singlet ground states for cyclic derivatives of oxyallyl.[12] Our results indicate that the constraints on the C–C–C bond angle at the carbonyl carbon, which are imposed by incorporation of oxyallyl into a four- or

---

(21) Wave functions for singlet diradicals are usually less delocalized than those for the corresponding triplets.[7] Since electrons of opposite spin are not correlated by the Pauli exclusion principle, in order to avoid high-energy ionic terms in the wave functions for singlet diradicals, the nonbonding electrons tend to be confined to different regions of space.

(22) If the TCSCF and RHF configurations are used as references for SD CI calculations, ΔE_{S-T} is calculated to be −1.9 kcal/mol, instead of the 2.4 kcal/mol that is obtained with CAS multireference SD CI calculations (Table I). As discussed in the text, the configurations that are required to correlate the nonbonding with the bonding π electrons are more important in the triplet wave function than in that for the singlet. Therefore, failure to include these configurations in the reference space spuriously tends to favor the singlet. Application of the Davidson correction remedies this problem, but only partially. With the TCSCF and RHF configurations as references, adding the Davidson correction for quadruples to the SD CI energies gives a value for ΔE_{S-T} of 0.2 kcal/mol, compared to the value of 1.6 kcal/mol in Table I for MR-SDQ CI calculations.

(23) Populations were obtained by projecting the wave functions onto a minimal basis set of AOs, using the method of: Davidson, E. R. *J. Chem. Phys.* **1967**, *46*, 3319.

(24) At the RHF level this ratio is 3.95. Because RHF wave functions provide no correlation between electrons of opposite spin, such wave functions tend to overestimate the extent to which unpaired electrons are localized.[25]

(25) For a discussion, see: Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

(26) The opposite changes in the optimized lengths of the C–O and the C–C bonds in $^3B_2$ on going from 3-21G to the Dunning DZP basis set can be attributed to a change in the contributions of the three covalent resonance structures for triplet **2**. The polarized basis set provides a more accurate description of the greater strength of C–O, compared to C–C, double bonds, than does 3-21G. Consequently, going from 3-21G to Dunning DZP increases the contribution of structure **2a**, relative to the two resonance structures that have C–C double bonds.

(27) In terms of molecular orbital theory, this fact can be explained as follows. In the $^3B_2$ state one electron must occupy the a_2 nonbonding MO. This NBMO has a node along the C–O bond. Thus, unlike the $2b_1$ NBMO, which may be described as a mixture of the p–π orbitals on the two equivalent carbons and the π^* C–O orbital,[11] a_2 has very little density on oxygen (exactly zero in the absence of d orbitals in the basis set). Because the $^1A_1$ wave function has the form, $^1A_1 = c_1|...2b_1^2\rangle - c_2|...a_2^2\rangle$, in going from $^3B_2$ to $^1A_1$, electron density can be transferred from C to O, if the coefficient of the first configuration is larger than that of the second. Indeed, this is the case. For example, in the π MCSCF wave function for the $^1A_1$ state of **2** the ratio of the squares of these two coefficients is 2.36, which increases to 2.78 in the MR-SD CI wave function.

five-membered ring, are not required to ensure a singlet ground state for dialkyl derivatives of **2**.

Acknowledgment. We thank the National Science Foundation for support of this research and for a grant, which made possible the purchase of the Convex C-2 computer, on which many of these calculations were performed. Some of these calculations were carried out at the San Diego Supercomputer Center, which we thank for a generous grant of time on the Cray XMP-48. This study was initiated while W.T.B. was a Visiting Scientist at IMS and being supported by a fellowship from the Japanese Society for Promotion of Science. W.T.B. expresses his gratitude to JSPS and to the Computer Center at IMS for use of the HITAC M-680H and S-820/80 Computers.

Registry No. 2, 102265-42-9; **3**, 17805-06-0.

Carbenoid Character in Transition Structures for Reactions of Ketenes with Alkenes

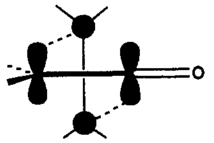
Xuebao Wang and K. N. Houk*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024. Received August 4, 1988

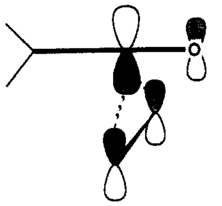
Abstract: The reactions of ketene and methylketene with ethylene and of ketene with propene were studied with ab initio molecular orbital calculations, with the STO-3G, 3-21G, and 6-31G* basis sets and correlation energy corrections at the MP2 level. The cycloadditions proceed via geometries that indicate that the reaction is of the 2 + 2 + 2 type, rather than a [$_{\pi}2_s + {}_{\pi}2_a$] cycloaddition. It is a quasi-pericyclic reaction, like carbene cycloadditions and hydroborations, with appreciable interaction of carbon ketene central carbon with both termini of the alkene. Bond formation is very asynchronous, with bond lengths of 1.78 and 2.43 Å. There is appreciable charge separation in the transition structure. The stereochemical preferences of the methylketene and propene reactions are consistent with experimental results on related substituted cases.

Cycloadditions of ketenes to alkenes to form cyclobutanones have been known for most of this century[1] and are probably the most complex and intriguing of the reactions classified by Woodward and Hoffmann as pericyclic.[2] The electronic interactions and geometry of the transition state have been the subject of much speculation.[3] The mechanism of the reaction is considered to be either concerted[4,5] or stepwise,[5] depending upon the electronic character and bulkiness of the ketene and alkene substituents.[4-9] Unsymmetrical ketenes add to cyclic alkenes to give the sterically more hindered product.[4,5] Ketenes add [2 + 2] even when allowed [4 + 2] possibilities appear attractive, as for example with cyclopentadiene.[5a]

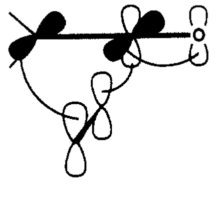
Woodward and Hoffmann speculated about a variety of electronic interactions.[10] They considered the possibility that the reaction was a concerted $_{\pi}2_s + {}_{\pi}2_a$ cycloaddition, suprafacial on the alkene and antarafacial on the ketene because of the low steric hindrance of the "sideways" approach shown in **A**. They also emphasized that the carbonyl group LUMO is the "spearhead of reactivity".[2] Thus, the additional interaction shown in **B** could occur. Gompper proposed that the interaction of the ketene LUMO occurs unsymmetrically on the alkene HOMO, leading



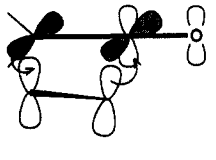
A



B



C



D

---

[1] Staudinger, H.; *Die Ketene*; Enke: Stuttgart, 1912.

[2] Woodward, R. B; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Academic Press: New York, 1970; p 163.

[3] For reviews: (a) Holder, R. W. *J. Chem. Educ.* **1976**, *53*, 81. (b) Ghosez, L.; O'Donnell, M. J. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1976; Vol. 2. (c) Bartlett, P. D. *Pure Appl. Chem.* **1971**, *27*, 597.

[4] (a) Rey, M.; Roberts, S.; Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 417. (b) Brook, P. R.; Harrison, J. M.; Duke, A. *J. Chem. Soc. D* **1970**, 589. (c) Brady, W. T.; Roe, R., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 1662. (d) Brady, W. T.; Hoff, E. F., Jr. *J. Org. Chem.* **1970**, *35*, 3733. (e) Hassner, A.; Corey, M.; Sartoris, N. *J. Am. Chem. Soc.* **1976**, *98*, 7698. (f) Wagner, H. U.; Gompper, R. *Tetrahedron Lett.* **1970**, 2819.

[5] (a) Huisgen, R.; Otto, P. *J. Am. Chem. Soc.* **1969**, *91*, 5922. (b) Duncan, W. G.; Weyler, W., Jr.; Moore, H. W. *Tetrahedron Lett.* **1973**, 4391. (c) Bartlett, P. D.; Cohen, G. M.; Elliott, S. P.; Hummel, K.; Minns, R. A.; Sharts, C. M.; Fukunaga, J. Y. *J. Am. Chem. Soc.* **1972**, *94*, 2899. (d) Bertrand, M.; Gras, J. L.; Gore, J. *Tetrahedron Lett.* **1972**, 2499. (e) Bampfield, H. A.; Brook, P. R. *Chem. Commun.* **1974**, 172. (f) Houk, K. N.; Strozier, R. W.; Hall, J. A. *Tetrahedron Lett.* **1974**, 897.

[6] Isaacs, N. S.; Stanbury, P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 166.

[7] Huisgen, R.; Feiler, L. A.; Otto, P. *Tetrahedron Lett.* **1968**, 4485.

[8] Baldwin, J. E.; Kapecki, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4868.

[9] (a) Katz, T. J.; Dessau, R. *J. Am. Chem. Soc.* **1969**, *85*, 2172. (b) Baldwin, J. E.; Kapecki, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4874. (c) Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1978**, *100*, 2570.

[10] Zimmerman, H. E. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. I, p 77. In the mid-1960s before the publication of the Woodward–Hoffmann treatise,[2] there were extensive speculations about all of these possible mechanisms at the Woodward group seminars.

0002-7863/90/1512-1754$02.50/0