

Table IX. Hydrogen Bond and Neighbor Analyses for Solvent Shells around the Perpendicular Allyl Cation^a

$r(\text{CF}), \text{\AA}$	(HB)	(N_{sx})	(e_{ss})
0.0-3.5	0.91	4.83	0.1
3.5-4.5	1.16	4.14	-2.5
4.5-5.5	1.65	9.24	-8.2
5.5-6.5	1.74	12.30	-10.0
6.5-7.5	1.90	21.96	-12.2
7.5-8.5	1.87	26.36	-12.2
8.5-9.5	1.88	43.59	-13.1
solution	1.82		-12.5
pure HF	1.82		-13.1

^a (HB) is the average number of hydrogen bonds, (N_{sx}) is the average number of hydrogen fluoride monomers in the shell, and (e_{ss}) is the average total solvent-solvent bonding energy (kcal/mol) for monomers in the shell.

the disruption is somewhat greater for the perpendicular ion for which the nearest solvent molecules actually have slightly net repulsive solvent-solvent interactions. This has been observed previously for other ionic solutions and results from repulsive interactions between molecules in the first shell that are oriented for maximum bonding with the solute.^{24,25} The average hydrogen bond strengths and hydrogen bond angles were also computed for each shell. No significant differences were found in comparison to the results for the pure solvent.

Conclusion

This work significantly extends a series of theoretical investigations of the solvation of carbonium ions and of solvent effects on their relative energies. Initially, a simple model for specific solvation of carbonium ions by HF was presented. Besides generating results that were consistent with experimental observations, the model proved to be a qualitative gauge for the solvation energy difference between isomeric carbonium ions.^{7,15} For example, the difference in energy between the planar and perpendicular conformers of the allyl cation is calculated to be lowered by 6 kcal/mol when the ions are solvated by one HF and 13 kcal/mol for two HF's. This is consistent with recent analyses of NMR data for substituted allyl cations.¹¹ Furthermore, the above findings support

the idea that given substantially different charge delocalization for isomeric cations, the relative energies should vary from the gas phase to solution.^{4,7}

Of course, the concern remains that interactions with additional solvent molecules are needed before an adequate account of differential solvation of carbonium ions can be obtained. In this regard, the results of the statistical mechanical calculations presented in this work complete the analyses. The most striking outcome is that the qualitative trends provided by the quantum mechanical models for specific solvation are upheld. In particular, the more localized perpendicular allyl cation is found to be better solvated than the planar species. The formally charged carbon of the former is strongly coordinated with two HF monomers, while the planar ion is primarily solvated only through hydrogen bonds. Although the solvent disruption caused by the perpendicular conformer is greater than for the planar cation, the difference is not large enough to offset the weaker solvation of the resonant ion. Specifically, the difference in ion-solvent interaction energies (E_{sx}) is 25 kcal/mol, while there is only 4 kcal/mol more solvent disruption (ΔE_{ss}) caused by the perpendicular ion.

Besides demonstrating the importance of solvent effects on the relative energies of isomeric carbonium ions, the present work also provided detailed insights into the solvation of the allyl cation in liquid HF. The importance of hydrogen bonding in the solvation of carbonium ions is particularly notable. It was also found that the solvent disruption is primarily localized in the first shell of solvent molecules around the ions. Normal solvent-solvent hydrogen bonding is rapidly reestablished beyond this region. Furthermore, the present studies have well illustrated the utility of statistical mechanics methods for examining organic liquids and solutions at the molecular level. Though computationally demanding, such studies should become an increasingly valuable source of information on the solvation of molecules and intermediates and on the origin of solvent effects.

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Registry No. Allyl cation, 1724-44-3; hydrogen fluoride, 7664-39-3.

Structure and Stability of Oxyallyl. An MCSCF Study

Yoshihiro Osamura,^{1a} Weston T. Borden,^{1b} and Keiji Morokuma*

*Contribution from the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.
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Abstract: The structures of several low-lying states of oxyallyl ($\cdot\text{CH}_2\text{COCH}_2\cdot$) have been determined by ab initio MCSCF calculations. The ground state of oxyallyl is found to be $^3\text{B}_2$, but the first excited state ($^1\text{A}_1$) is located only 6 kcal/mol higher in energy. The $^1\text{A}_1$ state is best described as a diradical, with a strong C-O π bond and an electron largely localized at each of the peripheral carbon atoms. Two other singlet states, $^1\text{B}_2$ and $^1\text{B}_1$, lie 10-20 kcal/mol above $^1\text{A}_1$. The vibrational analysis of $^1\text{A}_1$ shows all real frequencies; therefore, oxyallyl appears to be a true intermediate of the ring opening of cyclopropanone.

Oxyallyl, $\cdot\text{CH}_2\text{COCH}_2\cdot$, has been widely discussed as a possible transition state or an intermediate in several reactions,^{2,3} for example, in the isomerization of cyclopropanone⁴ and in the

Favorskii rearrangement.^{5,6} Semiempirical and ab initio studies^{4,6} using the closed-shell SCF method suggest that the oxyallyl singlet is the transition state of disrotatory ring opening of cyclopropanone. However, as discussed below, the electronic state for this system

(1) (a) Present address: Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Yokohama 223, Japan. (b) Permanent address: Department of Chemistry, University of Washington, Seattle, WA 98195.

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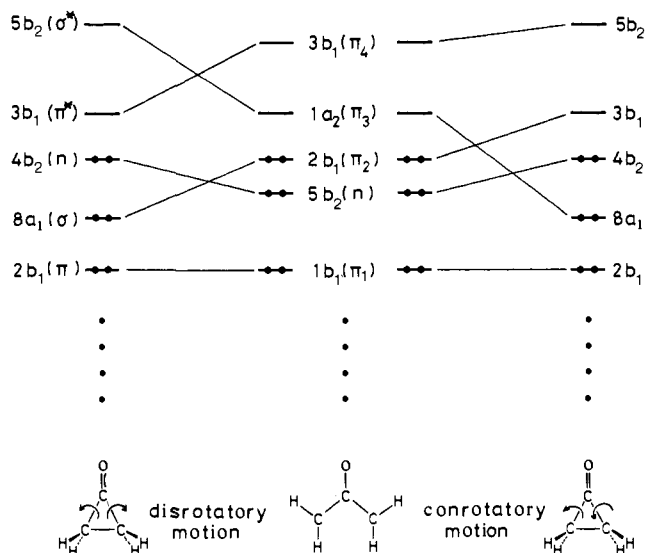


Figure 1. Orbital correlation diagram for conrotatory and disrotatory ring opening processes of cyclopropanone to oxyallyl.

is not necessarily best described by a one-configuration wave function. The lowest singlet state is often written as being zwitterionic (**1**), but theoretical calculations suggest that the triplet state is the ground state.⁷

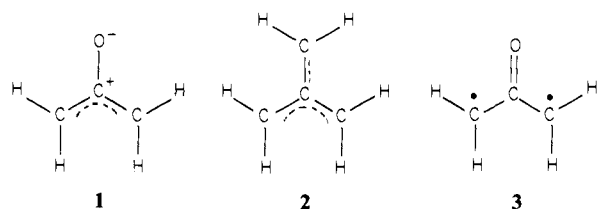
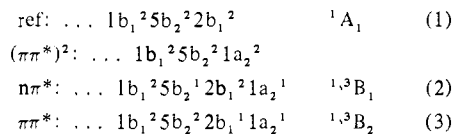


Figure 2. Optimized geometries in angstroms and degrees of oxyallyl for five low-lying states with the 3-21G basis set. Values in parentheses are those determined with the STO-3G basis set.

Since oxyallyl may be viewed as a derivative of trimethylenemethane (TMM) (**2**), in which one methylene group is replaced by oxygen, it is reasonable to expect the structure of oxyallyl to resemble that of TMM. Numerous theoretical studies have been published for TMM,⁸⁻¹⁰ which has been found to have a ${}^3A_2'$ (in D_{3h} ; 3B_2 in C_{2v}) ground state. The lowest singlet state (1B_1) has one methylene group twisted out of conjugation. The lowest planar singlet state is 1A_1 .

Although oxyallyl is isoelectronic with TMM, two C-H bonds in TMM are replaced by an oxygen lone pair in oxyallyl. Therefore, an $n\pi^*$ excitation in oxyallyl corresponds to the twisted (${}^1,{}^3B_1$) states of TMM. Possible low-lying states of oxyallyl are described principally by the following electron configurations



where $1b_1$ (π_1) and $2b_1$ (π_2) are π orbitals symmetric with respect to the reflection along the CO axis, $1a_2$ (π_3) is an antisymmetric π orbital, and $5b_2$ (n) is the oxygen p lone-pair orbital.

The state suggested to be involved in the ring opening of cyclopropanone is 1A_1 , which is usually depicted as a closed-shell zwitterion (**1**). The key questions that we sought to answer computationally in this study were as follows: (1) What is the ground state of oxyallyl? (2) Is 1A_1 an intermediate or transition state in the ring opening of cyclopropanone? (3) Is 1A_1 (in the

gas phase) best represented as a zwitterion (**1**) or as a diradical (**3**) with a strong C-O π bond?

Methods

If one assumes that the energy separation between HOMO ($2b_1$, π_2) and LUMO ($1a_2$, π_3) of oxyallyl is large, Woodward-Hoffmann rules predict that the conrotatory motion of cyclopropanone is forbidden because of the avoided crossing between the first and the second 1A_1 state and that the disrotatory path is allowed, as shown in Figure 1. In fact, the results of closed-shell RHF calculations suggest that oxyallyl should have substantial zwitterionic character and is the transition state and that disrotation is preferred. However, with TMM where the HOMO and LUMO are degenerate at D_{3h} geometries, HOMO and LUMO of oxyallyl might be expected to be close in energy. Were this the case, the configuration in which a pair of electrons is excited from $2b_1$ (π_2) to $1a_2$ (π_3) would contribute significantly to 1A_1 , and a one-configuration wave function would be insufficient to describe such a diradical state.

The best way to treat such a diradical species is the multiconfiguration self-consistent-field (MCSCF) method.¹¹ The two-configuration SCF (TCSCF) or generalized valence bond (GVB) method¹² is the simplest MCSCF wave function that can describe

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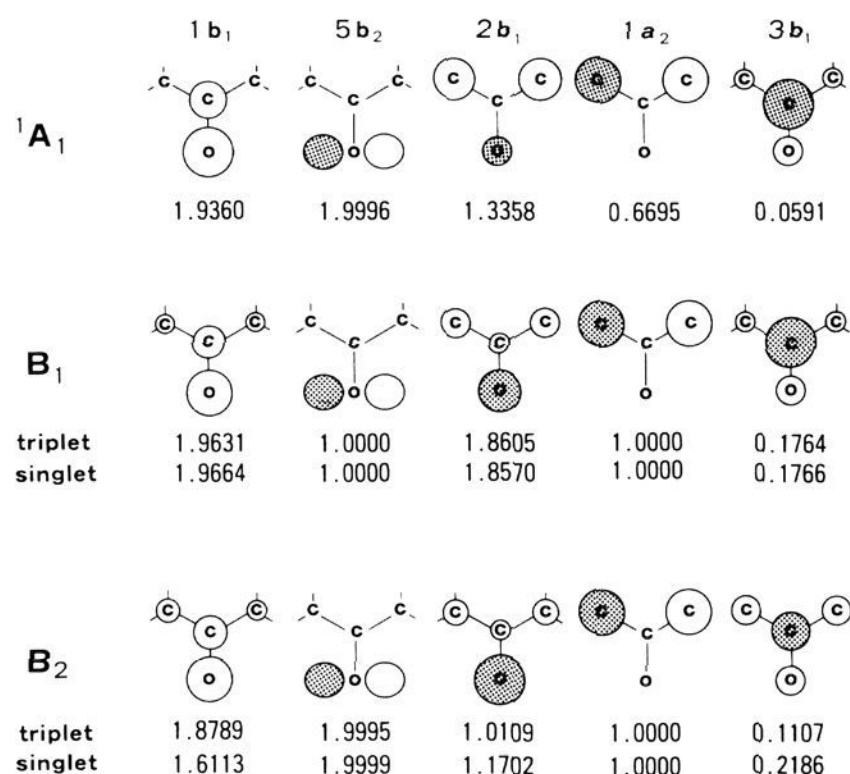


Figure 3. Shapes and electron occupation numbers of active MO's in MCSCF wave functions with the 3-21G* basis set.

typical diradicals such as trimethylene and twisted ethylene. However, systems having delocalized unpaired electrons (e.g., TMM) should be described with more general MCSCF methods, which can treat larger numbers of configurations necessary to provide adequate correlation between all the π electrons.¹¹ General and practical MCSCF methods and programs have recently become available.¹³ In this paper, we used the program GAMESS developed by Dupuis et al.¹⁴ to determine electronic structures and geometries. The electron configurations used in MCSCF calculations were of CAS (complete active space) type and consist of all the configurations generated from all possible occupations of six electrons in a p lone-pair orbital on oxygen, $5b_2$ (n), and four π orbitals, $1b_1$ (π_1) and $2b_1$ (π_2), $1a_2$ (π_3) and $3b_1$ (π_4). The number of configurations for singlet states is 50 without symmetry restriction. Geometry optimizations were carried out by using the MCSCF energy gradient method built into the GAMESS program.

Geometries and Relative Energies

The molecular geometries of oxyallyl were optimized for five low-lying states, 1A_1 , 1B_1 , and 1B_2 , with two different basis sets (STO-3G minimal basis¹⁵ and split-valence 3-21G basis¹⁶) under the constraint of C_{2v} symmetry. As are illustrated in Figure 2, the differences in the optimized geometries between the basis sets are small. Shapes of active molecular orbitals and their electron occupation numbers are shown in Figure 3.

The geometry of the 1A_1 state clearly shows the existence of a strong C–O double bond and one electron largely localized at each peripheral carbon. Thus, at least in the gas phase, 1A_1 is predicted to be a diradical but not to be a zwitterion. The triplet and singlet B_1 states are found to have almost identical structures and energies, because two singly occupied molecular orbitals (SOMO's) are localized to different regions of space. The oxygen lone pair orbital ($5b_2$, n) is spatially removed from the antisymmetric π orbital ($1a_2$, π_3) which spans only two peripheral carbon atoms. Consequently, the exchange integral between these orbitals is small, making the singlet and the triplet nearly identical.

Table I. Atomic Electron Population and Dipole Moment (in debye) of Singlet States of Oxyallyl at Respectively Optimized Geometries^a

state	1A_1	1B_1	1B_2
O σ	7.2301	6.4671	7.3818
π	1.3102	1.9114	0.9967
C_1^b σ	4.6398	4.6003	4.6318
π	0.8369	0.9975	1.0162
C_2 σ	5.5290	5.4148	5.4430
π	0.9266	1.0455	0.9936
H_1^b σ	0.7567	0.7726	0.7652
H_2 σ	0.7792	0.7789	0.7850
dipole moment	2.9595	1.4909	1.7785

^a 3-21G* values are at the 3-21G optimized geometries. ^b C_1 is in carbonyl, C_2 is in methylene, and H_1 and H_2 are cis and trans to oxygen, respectively.

Table II. MCSCF Relative Energies (in kcal/mol) for Five Low-Lying States of Oxyallyl at Respectively Optimized Geometries

basis set	STO-3G	3-21G	3-21G* ^a
3B_2	0.0 ^b	0.0 ^b	0.0 ^b
1A_1	20.9	12.3	5.6
3B_1	6.2	13.1	15.9
1B_1	6.4	13.5	16.5
1B_2	18.1	20.6	26.0

^a At the 3-21G optimized geometries. ^b Absolute energies are -188.331538, -189.685754, and -189.818499 hartrees for STO-3G, 3-21G, and 3-21G*, respectively.

In contrast, there are significant geometrical differences between the singlet and triplet B_2 states, in which the SOMO's are both π orbitals. 3B_2 has a delocalized wave function, whereas 1B_2 has one electron localized in a π orbital on oxygen and a second in the allylic nonbonding orbital. The situation in the $^1,^3B_2$ states in oxyallyl is identical with that in this pair of states in TMM. Atomic electron population in σ and π orbitals and dipole moments are summarized in Table I. Charge distribution for neither B_1 nor B_2 state shows an ionic character. This fact is understood by considering that the difference in the number of π electrons, five in B_1 and four in B_2 states, is to a large extent a reflection of the oxygen atomic orbital occupation (one σ and two π electrons for B_1 states and two σ and one π electrons for B_2 states). Consequently, 1A_1 has the largest dipole moment among low-lying states because of its polar CO double bond.

The relative energies of the states in oxyallyl are summarized in Table II. It should be noted that the energies of five low-lying states are rather close to each other, although their structures are quite different. The ground state is calculated to be 3B_2 with all basis sets. However, the identity of the lowest singlet depends on the basis set used, with better basis sets favoring 1A_1 over 1B_1 . Since 1A_1 contains a strong C–O π bond, the relative energy of 1A_1 depends on the ability of the basis set to describe this bond. Polarization functions have been found to be necessary to describe properly C–O π bonds.¹⁷ In order to test the effect of polarization functions on the relative energies of the states in oxyallyl, we calculated the MCSCF energies with the 3-21G* basis set,¹⁸ using the geometries optimized with the 3-21G basis. As shown in Table II, inclusion of polarization functions leads to the unequivocal prediction that 1A_1 is the lowest singlet state. In fact, its energy is computed to be only 5.6 kcal/mol above that of 3B_2 . This is less than half of the singlet–triplet splitting calculated in TMM, where the lowest singlet is 1B_1 . Indeed, the energy separation between 3B_2 and 1B_1 in oxyallyl is computed to be about the same as that in TMM. It is the strong C–O π bond in 1A_1 that is responsible for the rather small singlet–triplet splitting that is calculated for oxyallyl. Geometry reoptimization with the 3-21G*

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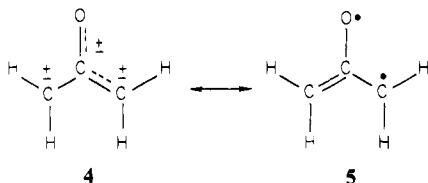
basis set might further decrease the energy difference.

As discussed above, the electronic structure of the 1A_1 state must be described with at least a two-configuration self-consistent-field (TCSCF) wave function.

$$\Psi(^1A_1) \approx C_1 | \dots 1b_2^2 5b_1^2 2b_2^2 | - C_2 | \dots 1b_2^2 5b_1^2 1a_2^2 | + \dots$$

The coefficients of these two configurations in the MCSCF wave function were found to be $C_1 = 0.786$ and $C_2 = 0.580$. The large magnitude of C_2 shows that the 1A_1 state of oxyallyl is a diradical, **3**, instead of **1**. This is, of course, consistent with the fact that the optimized geometry has a C–O double bond and long C–C bond lengths.

There are other possible structures for oxyallyl, such as **4** and **5**, which have C_s rather than C_{2v} symmetry. Although we tried,



we were unable to find such optimized structures. They probably do not correspond to any equilibrium structure; the C–O double bond diradical structure (**1**) and the O–allyl⁺ zwitterion structure (**2**) are probably more stable than corresponding **5** and **4**, respectively.

In order to examine whether 1A_1 is a true intermediate or a transition state, we determined the normal vibrational frequencies on the basis of the force constant matrix obtained by taking numerical differences of analytical MCSCF energy gradients. As in the case of TMM,¹⁰ the vibrational analysis with the STO-3G basis set gives two imaginary frequencies corresponding to pyramidalization of two CH₂ groups. However, calculations with the 3-21G basis set show all the vibrational frequencies to have real values. This strongly suggests that the 1A_1 state of oxyallyl is the intermediate of the ring-opening reaction of cyclopropanone. This 1A_1 intermediate has a vibrational frequency of 170 cm⁻¹ with the 3-21G basis (also 170 cm⁻¹ with STO-3G) for a b₁ normal coordinate corresponding to disrotatory ring closure and 230 cm⁻¹ (240 cm⁻¹) for an a₂ normal coordinate corresponding to conrotatory ring closure. Though we have not located transition states, these frequencies suggest that the barrier for the disrotatory ring closure from the 1A_1 intermediate to cyclopropanone would be lower than that for the conrotatory ring closure, a conclusion consistent with Woodward–Hoffmann rules.

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Registry No. •CH₂COCH₂, 17440-65-2; cyclopropanone, 5009-27-8.

Equilibrium Geometries for Triplet Trimethylene, $\dot{C}H_2CH_2\dot{C}H_2$

Yukio Yamaguchi and Henry F. Schaefer III*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received January 16, 1984

Abstract: One of the lowest lying triplet electronic states for the C₃H₆ system is triplet trimethylene, a much-discussed diradical. Previous theoretical work has identified several triplet stationary points of CH₂CH₂CH₂ with one or more imaginary vibrational frequencies. Here are located and characterized two genuine minima on the triplet trimethylene potential energy hypersurface. Single-configuration self-consistent-field theory is used in conjunction with a standard Huzinaga–Dunning double- ζ basis set. These minima are of C₂ and C_s symmetry, respectively, and are separated by only 0.14 kcal. By reference to three other triplet stationary points, the potential surface for trimethylene internal rotation and pyramidalization is discussed.

In recent years there has been considerable interest, both experimental¹⁻⁷ and theoretical,⁸⁻¹⁷ in the trimethylene biradical,

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$\dot{C}H_2CH_2\dot{C}H_2$. Most of this interest has been rightly directed at the stereoisomerization of cyclopropane, a process with which is associated an activated energy of 59.8 kcal/mol.¹⁸ Although earlier there was considerable support¹⁹ for the idea that trimethylene might be a true intermediate (i.e., a minimum on the C₃H₆ energy surface), more recently the weight of theoretical evidence is for trimethylene as a transition state.^{11,12,14,17,18} Following the classic work of Woodward and Hoffmann,²⁰ the question of conrotatory vs. disrotatory singlet pathways has attracted much attention, with the consensus now being that the conrotatory pathway to ring closure of the "π cyclopropane" should

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