Solvent Effects on the Ring Opening of Cyclopropanones to Oxyallyls: A Combined ab Initio and Monte Carlo Study

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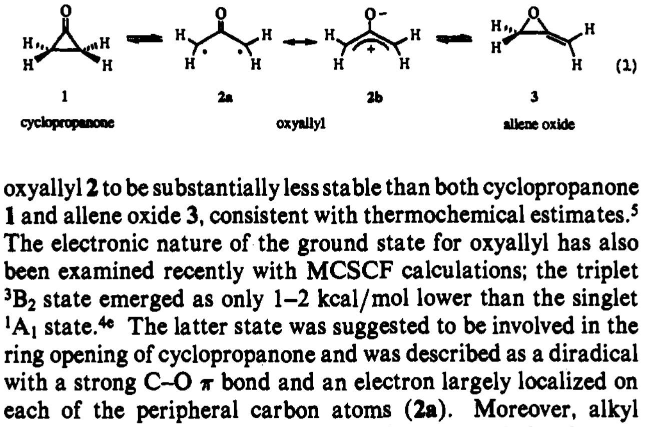
Abstract: Solvent effects on the disrotatory ring opening of cyclopropanone and 2,2-dimethylcyclopropanone have been computed by Monte Carlo simulations at 25 °C. Geometries for the cyclopropanones, the transition state for the rearrangement of cyclopropanone, and the oxyallyls were obtained from ab initio (4/4) CASSCF calculations with the 6-31G* basis set. For each geometry, CHELPG and Mulliken charges were determined for use in the fluid simulations. Statistical perturbation theory yielded the changes in free energies of solvation in four solvents for the ring openings. The modest computed solvent effects are in good accord with experimental data of Greene and co-workers. Our results support the intermediacy of oxyallyls in cyclopropanone stereomutations, indicate the proximity of the oxyallyls to the transition states for the ring openings, and confirm the principally diradical rather than zwitterionic nature of the oxyallyls.

Introduction

Oxyallyls have been proposed as reactive intermediates or transition states in the equilibrium between cyclopropanones and allene oxides (eq 1)[1] as well as in other reactions[2] including Favorskii rearrangements.[3] Ab initio calculations[4] have indicated oxyallyl 2 to be substantially less stable than both cyclopropanone 1 and allene oxide 3, consistent with thermochemical estimates.[5] The electronic nature of the ground state for oxyallyl has also been examined recently with MCSCF calculations; the triplet $^3B_2$ state emerged as only 1–2 kcal/mol lower than the singlet $^1A_1$ state.[4e] The latter state was suggested to be involved in the ring opening of cyclopropanone and was described as a diradical with a strong C–O π bond and an electron largely localized on each of the peripheral carbon atoms (**2a**). Moreover, alkyl substitution strongly stabilizes the singlet state such that for 1,3-dimethyloxyallyl the singlet is computed to be the ground state, ca. 5 kcal/mol lower than the triplet.[4e,f] This trend is supported by the recent photochemical generation of 3-oxobicyclo[3.2.0]hept-6-ene-2,4-diyl, whose reactivity and EPR characteristics were interpreted as reflecting a singlet ground state with zwitterionic character.[6]


(1)

1 cyclopropanone

2a 2b oxyallyl

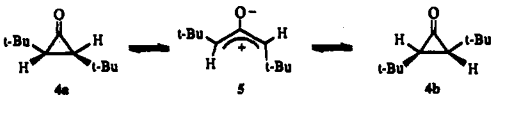
3 allene oxide

Table 1. Experimental Data for the Racemization of (+)-*trans*-2,3-Di-*tert*-butylcyclopropanone

solvent	$k \times 10^4$, s^{-1} [a]	k_{rel}	$\Delta G^{‡}$ [b]	$\Delta\Delta G^{‡}$	$E_T(30)$[c]
isooctane	0.27	1.0	29.11	0.00	30.9
tetrahydrofuran	0.80	3.0	28.35	–0.76	37.4
benzene	0.86	3.2	28.30	–0.81	34.3
pyridine	1.78	6.6	27.79	–1.32	40.5
acetonitrile	3.35	12.4	27.34	–1.77	45.6

[a] Data from ref 7 at 79.6 °C. [b] $\Delta G^{‡}$ in kcal/mol, calculated as $-RT(\ln k_{rac}/4 - \ln RT/Nh)$. See ref 8. [c] Data from ref 9.

The energy separation between a cyclopropanone and its corresponding oxyallyl has been estimated experimentally by measuring the rate of stereomutation of cyclopropanones.[7,8] This was first done in 1970 by Greene and co-workers, who studied the racemization of enantiomerically enriched *trans*-2,3-di-*tert*-butylcyclopropanone (eq 2).[7] Notably, they studied solvent effects on the racemization and obtained $\Delta G^{‡}$ values of 27–29 kcal/mol, as summarized in Table 1. The authors stated that "the most attractive possibility for the racemization is disrotatory ring opening to the oxyallyl species" (**5**).


(2)

4a 5 4b

If this is the case, then the solvent effects in Table 1 seem modest. The reaction rate increases by only a factor of 12 in going from isooctane to acetonitrile as solvent. In other instances, creation of a zwitterion is accompanied by much larger rate effects.[9] For example, the corresponding rate ratios for [2 + 2] cycloadditions of tetracyanoethylene and vinyl ethers are 10^3–10^4.[10] Several explanations of the modest solvent effects on cyclopropanone ring opening are possible, including: (1) cyclopropanone **4** is nearly as polar as zwitterionic oxyallyl **5**; (2) the transition state for the rearrangement of **4** is not **5**, but an earlier, less-polar structure; and (3) the oxyallyl is better represented by

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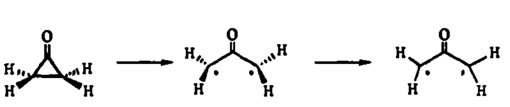
a diradical structure analogous to **2a**, which is much less polar than zwitterion **5**.

The present study was undertaken to clarify these issues. Principally, the intention was to compute the solvent effects on the parent rearrangement of cyclopropanone through a combined quantum and statistical mechanical approach. This required ab initio calculations to characterize the structures and charge distributions for cyclopropanone, a possible disrotatory transition state, and oxyallyl (eq 3), followed by fluid simulations in several solvents to determine the changes in free energies of solvation.

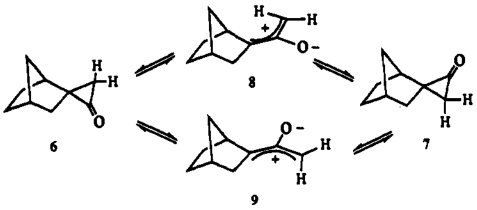


cyclopropanone transition state oxyallyl (3)

Comparison of the results with the trends in Greene's data would then either reveal a fundamental discrepancy between the calculations and experiments or help clarify the origin of the modest solvent effects found by Greene and co-workers. A substituted case has also been considered computationally, the ring opening of 2,2-dimethylcyclopropanone to 1,1-dimethyloxyallyl (eq 4). This system has relevance as a simple model for the

2,2-dimethylcyclopropanone 1,1-dimethyloxyallyl (4)

spirocyclopropanones **6** and **7**, which have recently been studied by Cordes and Berson.[8] The barriers to stereomutation measured



by them are 7–9 kcal/mol lower than those measured by Greene and co-workers. The lower barriers for the spiro systems are not surprising in view of the anticipated reduction in steric strain in the transition states of oxyallyl species **8** and **9** as compared to the di-*tert*-butyl-substituted oxyallyl **5**.[8] Cordes and Berson also reported preliminary results indicating a significant solvent dependence for the rate of stereomutation; the half-life for stereomutation of **7** or **8** was about the same at 244 K in diethyl ether and at 195 K in dichloromethane.

Computational Methods

Ab Initio Calculations. The gas-phase geometries for the cyclopropanones, singlet oxyallyls, and the transition state for ring opening in eq 3 were obtained from (4/4)CASSCF optimizations with the 6-31G* basis set.[11] These are multiconfiguration (MC) SCF calculations in the complete active space (CAS). In the case of the oxyallyls, the CAS consists of all configurations that come from placing four electrons in four π molecular orbitals. For consistency, four electrons were also correlated in four orbitals for the cyclopropanones using the π and π^* orbitals of the carbonyl bond and the σ and σ^* orbitals of the C2–C3 bond. The chosen orbitals for the transition state are naturally the ones that correlate with those chosen for cyclopropanone and oxyallyl and which give the lowest CASSCF energy. Harmonic vibrational frequencies were calculated at the (4/4)CASSCF/6-31G* level. They were used to characterize stationary points as minima or first-order saddle points (transition states) and to calculate the contributions of the zero-point vibrational energies to the total relative energies. The CASSCF calculations also gave the Mulliken and CHELPG[12] charges for the molecules, which were needed for the potential functions in the Monte Carlo simulations (vide infra). All ab initio calculations were carried out with the GAUSSIAN 92 program.[13]

Fluid Simulations. Monte Carlo calculations were performed for the interconversions in eqs 3 and 4 using statistical perturbation theory to compute the changes in free energies of solvation in four solvents, propane, tetrahydrofuran (THF), dichloromethane, and acetonitrile. The intermolecular interactions are described by potential functions with the potential energy, ΔE_{ab}, consisting of Coulomb and Lennard-Jones terms between the atoms i in molecule a and the atoms j in molecule b, which are separated by a distance r_{ij} (eq 5). For the solutes, the partial charges

$$\Delta E_{ab} = \sum_i \sum_j \{q_i q_j e^2/r_{ij} + 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6]\} \qquad (5)$$

(q) were obtained from the ab initio calculations, and standard all-atom Lennard-Jones parameters (σ, ϵ) were adopted with geometric combining rules. Specifically, σ in Å and ϵ in kcal/mol are 2.96 and 0.210 for oxygen, 3.75 and 0.105 for carbonyl carbon, 3.50 and 0.066 for other carbons, and 2.50 and 0.030 for hydrogens.[14] It should be noted that we have previously demonstrated that 6-31G* CHELPG charges yield average errors of 1.1 kcal/mol for the free energies of hydration for 13 diverse organic molecules in TIP4P water.[15] Established potential function parameters for the solvents, propane,[16] THF,[17] and acetonitrile,[18] were adopted. For dichloromethane, previously unreported parameters have been employed that reproduce the experimental density and heat of vaporization of the liquid at 25 °C.[19] The solvent models used united atoms for the CH_2 and CH_3 groups.

The individual molecules were kept rigid in the simulations; only translations and rigid body rotations were sampled. In each case, the systems consisted of a single solute plus 125 solvent molecules in a cubic cell roughly 25 Å on a side with periodic boundary conditions. The simulations were run in the isothermal isobaric (*NPT*) ensemble at 25 °C and 1 atm with Metropolis and preferential sampling.[20] Cyclopropanone was mutated to oxyallyl via the transition state using statistical perturbation theory.[21] As discussed below, there was little difference between the transition state and oxyallyl, so the transition-state stage was skipped for the dimethylcyclopropanone simulations. For both systems, about 10 separate simulations were used to gradually mutate by disrotation the reactant to product using double-wide sampling, which yielded ca. 20 free energy increments. All calculations were performed with the BOSS program.[22] With BOSS, initial and final *Z*-matrices (r, θ, ϕ internal coordinate representations) are input for a mutation, and the program scales the r, θ, and ϕ values linearly between the two as the coupling parameter λ goes from 0 to 1. Selecting the proper correspondence between the hydrogens allows either disrotatory or conrotatory motion to be followed. Each simulation consisted of 1×10^6 configurations of equilibration followed by 2×10^6 configurations of averaging. The calculations were straightforward and proceeded with high precision, as evidenced by the smoothness of the free energy curves and the small statistical uncertainties obtained from the batch means procedure.[20] The intermolecular interactions were truncated at 11 Å, based on the shortest distance between a solute atom and the central atom of the solvent molecule with quadratic feathering to zero over the last 0.5 Å.

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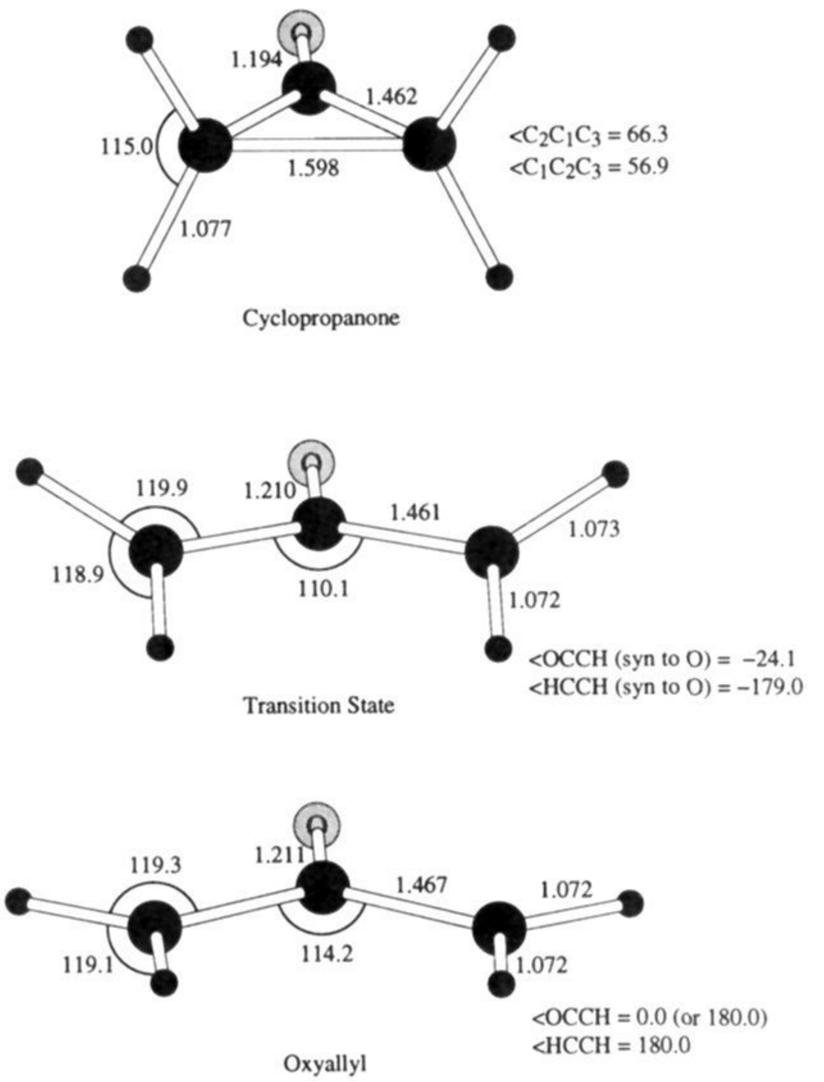

Figure 1. Computed structures for cyclopropanone, the transition state for disrotatory ring opening, and oxyallyl from (4/4)CASSCF/6-31G* calculations. Distances in angstroms and angles in degrees throughout.

Results and Discussion

Ab Initio Results. The (4/4)CASSCF/6-31G* geometries of cyclopropanone, singlet $^1A_1$ oxyallyl, and the transition state connecting these two energy minima are illustrated in Figure 1. For cyclopropanone, the computed structure agrees well with the experimental one from a microwave study.[23] The experimental C═O, C1—C2, and C2—C3 bond lengths are 1.191, 1.475, and 1.575 Å, while the computed values are 1.194, 1.462, and 1.598 Å, respectively. Additionally, the experimental C1–C2–C3 and C2–C1–C3 bond angles are 57.7° and 64.6° versus 56.9° and 66.3° in Figure 1.

The vibrational frequencies for $^1A_1$ oxyallyl at the (4/4)CASSCF/6-31G* level are all real, indicating the structure is a true intermediate. The lowest frequency is 131.5 cm^{-1} for a b_1 normal coordinate corresponding to disrotatory ring closure. A b_2 normal coordinate corresponding to conrotatory closure has a much higher frequency, 411.0 cm^{-1}, consistent with the Woodward–Hoffmann rules. The imaginary frequency for the transition state (179.3*i* cm^{-1}) corresponds to disrotatory ring closure, as expected.

The transition state is structurally (Figure 1) and energetically (Table 2) very similar to oxyallyl. The principal difference is the rotation of the CH_2 groups ca. 24° out-of-plane in the transition state. It is also notable that the C═O bond length increases by less than 0.02 Å in progressing from cyclopropanone to the transition state or oxyallyl. This bond length is particularly short in cyclopropanone, the textbook explanation being the enhanced s-character in bonds exo to 3-membered rings. The calculated value of 1.21 Å for the transition state and oxyallyl is normal for an acyclic ketone, e.g., the microwave value is 1.22 Å for the C═O bond in acetone.[24] The computed C—C bond lengths in oxyallyl are also normal for sp^2—sp^2 single bonds such as the C1—C2 separation of 1.470 Å observed for acrolein.[25] This is considerably longer than the C—C bond length of 1.37 Å that is obtained for the allyl cation at both the 6-31G* and 6-311++G(D,P) levels.[26] Thus, the structural results support the description of oxyallyl as primarily a diradical (**2a**) rather than a zwitterion (**2b**).[4d,e]

Table 2. (4/4) CASSCF/6-31G* Thermodynamic Results for Cyclopropanone and Oxyallyl[a]

property	cyclopropanone	transition state	$^1A_1$ oxyallyl
E, hartrees	−190.775 930	−190.734 304	−190.734 826
ZPE, kcal/mol	36.08	31.93	31.93
ΔE^0, kcal/mol	0.0	21.97	21.64
S^{298}, cal/mol-K	63.57	66.56	68.41
C_v^{298}, cal/mol-K	13.69	15.40	17.39
ΔH^{298}, kcal/mol	0.0	22.52	22.48
ΔG^{298}, kcal/mol	0.0	21.63	21.04

[a] Vibrational frequencies were scaled by 0.91. Scaled frequencies below 500 cm^{-1} were treated as classical rotations ($E_{vib} = RT/2$). The imaginary frequency for the transition state was ignored in all calculations.

The energetic results in Table 2 reveal a predicted energy barrier at 0 K of 22.0 kcal/mol and a free energy barrier of 21.6 kcal/mol at 298 K for the disrotatory ring opening of cyclopropanone. The energy difference between the transition state and oxyallyl is found to be only 0.33 kcal/mol. In order to compute the energy difference between cyclopropanone and oxyallyl with the inclusion of more electron correlation, we also performed CASPT2N/6-31G* calculations, using the (4/4)CASSCF/6-31G* geometries, with the MOLCAS program.[27] CASPT2N uses the equivalent of second-order Møller–Plesset perturbation theory to obtain the correlation energy with a CASSCF reference wave function.[28] The energies of cyclopropanone (−191.2963 au) and oxyallyl (−191.2446 au) yield a difference of 32.4 kcal/mol, which would translate to a free energy difference at 298 K of about 27.6 kcal/mol based on the results in Table 2.

The approximately 6 kcal/mol larger barrier from the CASPT2N calculations comes from the provision of electron correlation for all three ring bonds in cyclopropanone, not just the one bond that is correlated at the (4/4)CASSCF level. A similar increase is found in the ring opening of cyclopropane on going from the GVB to SD-CI level.[29] It may be coincidental that the CASP2TN value of about 28 kcal/mol for the free energy of activation for the parent reaction in the gas phase is close to the observed range of solution-phase activation free energies for the reaction in eq 2 (Table 1).

The (4/4)CASSCF/6-31G* geometries of 2,2-dimethylcyclopropanone in C_s symmetry and 1,1-dimethyloxyallyl in C_1 symmetry are shown in Figure 2. The substitution of the two methyl groups causes only slight modifications to the cyclopropanone ring. The electronic energy difference between the two structures in Figure 2 is 24.0 kcal/mol, which is 1.8 kcal/mol smaller than for the unsubstituted case. A calculation was originally performed on a planar, C_s structure for 1,1-dimethyloxyallyl. No imaginary frequencies were found; but the CASSCF normal mode analysis was not performed analytically, so the existence of two very low frequency modes led to the search for a C_1 structure. The one illustrated in Figure 2 was found, which is only 0.8 kcal/mol lower in energy than the C_s alternative. The nonplanar structure undoubtedly benefits from relief of steric interactions that involve the methyl groups. However, there may

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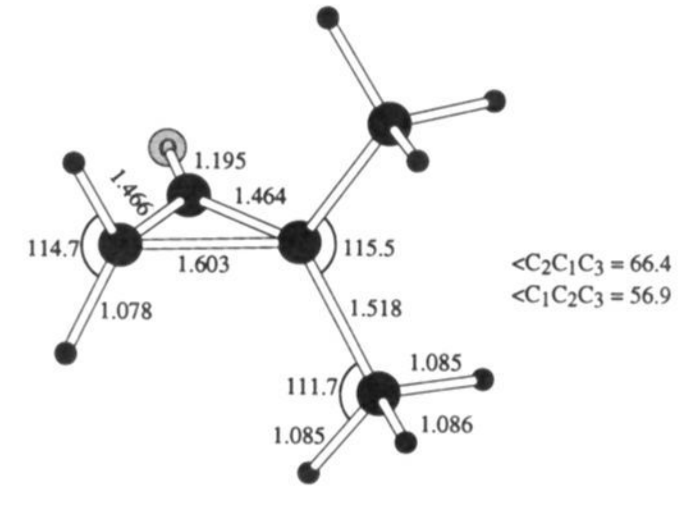
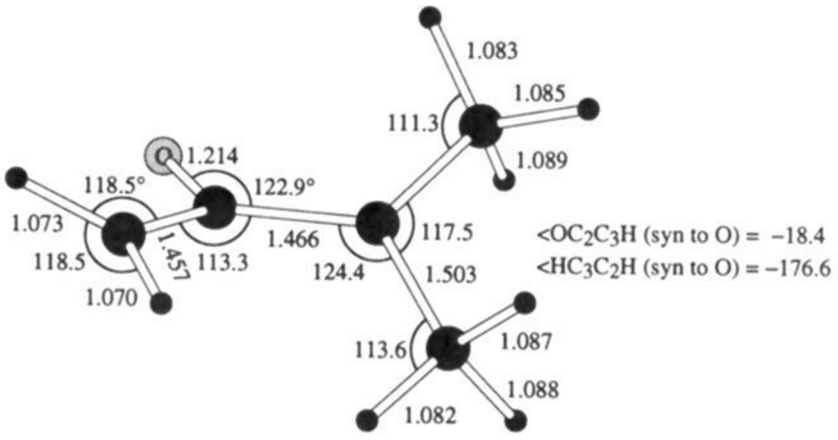
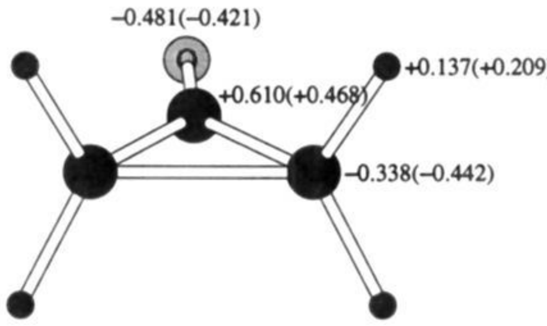


2,2-Dimethylcyclopropanone

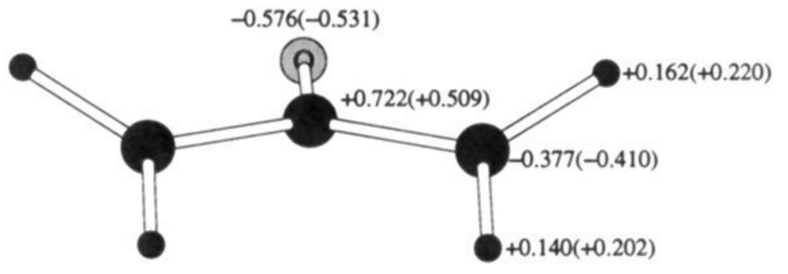


1,1-Dimethyloxyallyl

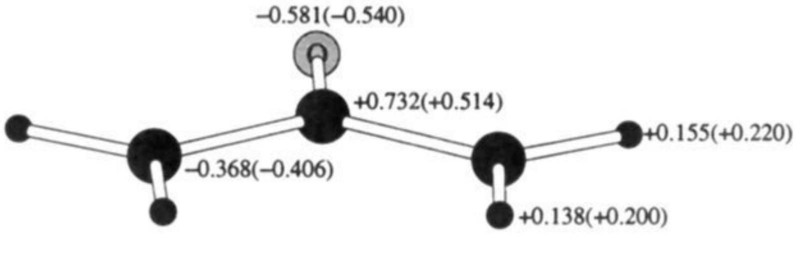
Figure 2. Computed structures for 2,2-dimethylcyclopropanone and 1,1-dimethyloxyallyl from (4/4)CASSCF/6-31G* calculations.



Cyclopropanone



Transition State



Oxyallyl

Figure 3. Computed CHELPG and Mulliken (in parentheses) charges for cyclopropanone, the transition state, and oxyallyl from (4/4)CASSCF/6-31G* calculations.

also be an electronic component related to observations on the conformation of pentane-2,4-diyls that are discussed elsewhere.[30] Clearly, the potential energy surface in the vicinity of the planar structure is relatively flat. Since the differences in energy and structure between unsubstituted oxyallyl and the transition state leading to it were also found to be small (Table 2), the transition state leading to 1,1-dimethyloxyallyl was not sought.

The (4/4)CASSCF/6-31G* calculations yielded the CHELPG and Mulliken charges for the species in eqs 3 and 4 that are given in Figures 3 and 4. Our previous experiences indicate that 6-31G* CHELPG charges in an all-atom format are far superior to Mulliken charges for use in fluid simulations.[15] However, results with the Mulliken charges are also reported below to test the sensitivity of the solvation effects to the charge model. In Figure 3, several points are notable: (1) the polarization of the C═O bond is less with the Mulliken charges than with the CHELPG charges; (2) there is virtually no change in the charges between the transition state and oxyallyl, so a difference in solvation of the two similar structures is unlikely; (3) the net CHELPG charge for the C═O unit changes only slightly upon disrotation from +0.129 for cyclopropanone to +0.151 for oxyallyl; the qualitative direction of the shift is inconsistent with the development of significant zwitterionic character, although the oxygen does become more negative by 0.100 e upon ring opening; and (4) the CHELPG charges on the methylene carbon and hydrogens change little during the reaction and do not reveal a tendency toward developing allyl cation character. Thus, the charges are also supporting the diradical description for oxyallyl (**2a**).

The situation for the dimethyl analog in Figure 4 is similar. The charge variations are modest, and the net CHELPG charge change for the carbonyl group is only –0.02 e, though the C═O bond does become more polarized upon ring opening. The enhanced polarization may be expected to promote stronger solvation at the carbonyl oxygen. This is also reflected in the dipole moments computed from the charge distributions, which increase by 0.7–0.9 D upon ring opening of both cyclopropanones (Table 3). These are not large changes, but they should lead to some preferential stabilization of the oxyallyls in more polar solvents. The magnitude of the solvation effects is addressed through the fluid simulations. It should be noted that the dipole moment of 2.79 D for cyclopropanone, computed with the CHELPG charges, is close to the experimental value of 2.67 ± 0.10 D.[23]

Monte Carlo Results. The ab initio calculations have provided structures and charge distributions for the oxyallyls as diradicals. The question addressed by the fluid simulations is, Do these structures and charge distributions lead to predictions of solvent effects in accord with Greene's data? If they do, then a consistent picture emerges giving confidence that the diradical description of the oxyallyls is appropriate both in the gas phase and in the examined solvents. Otherwise, an inconsistency arises that may reflect inaccuracies in the computed structures and electronic characters of the oxyallyls and possibly the cyclopropanones, or the structures and charge distributions may be medium-dependent with an anticipated tendency toward more zwitterionic character in more polar solvents.[31]

The results of the calculations for the changes in free energies of solvation corresponding to eqs 3 and 4 are illustrated in Figures 5–8. For the ring opening of cyclopropanone, the results with the CHELPG and Mulliken charges are shown in Figures 5 and 6, respectively. In this case, λ = 0.0, 1.0, and 2.0 correspond to cyclopropanone, the transition state, and oxyallyl, respectively. It is apparent that there was no appreciable change in the calculated free energy of solvation between the transition state and oxyallyl in any solvent with either charge model. The CHELPG and Mulliken results for the ring opening of 2,2-

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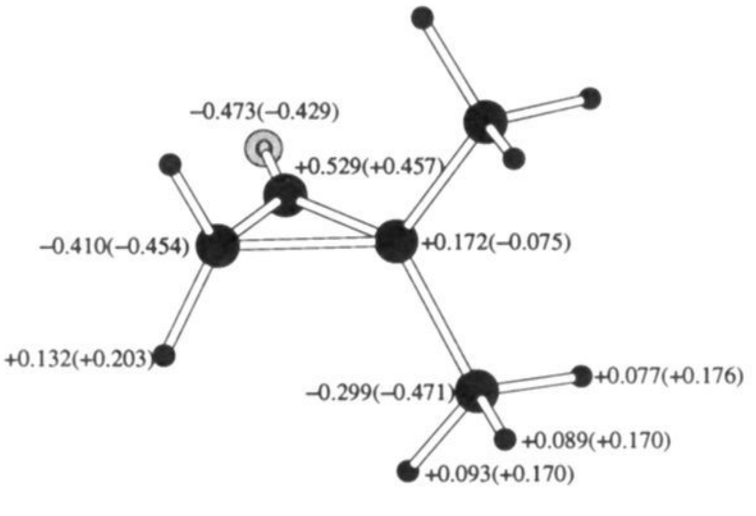
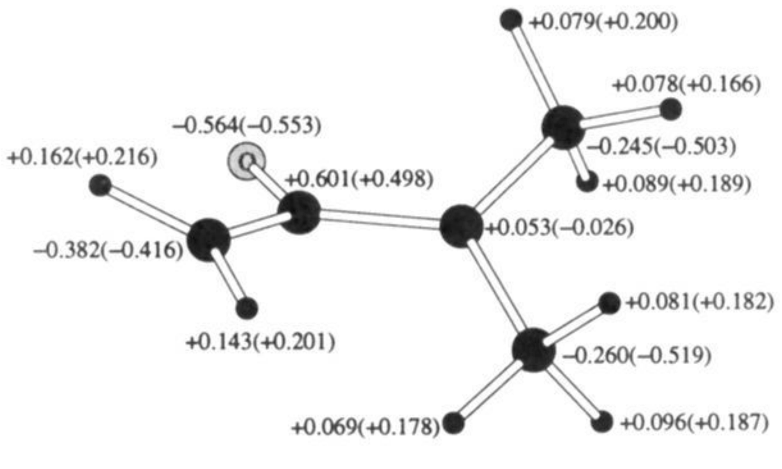
[30] Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, submitted. Getty, S. J.; Hrovat, D. A.; Xu, D. J.; Barkers, S. A.; Borden, W. T. *Discuss. Faraday Soc.*, in press.



2,2–Dimethylcyclopropanone



1,1–Dimethyloxyallyl

Figure 4. Computed CHELPG and Mulliken (in parentheses) charges for 2,2-dimethylcyclopropanone and 1,1-dimethyloxyallyl from (4/4)CASSCF/6-31G* calculations.

Table 3. Computed Dipole Moments (D) from the Charge Distributions[a]

molecule	CHELPG	Mulliken
cyclopropanone	2.79	3.34
transition state	3.52	4.30
oxyallyl	3.47	4.24
2,2-dimethylcyclopropanone	2.93	3.61
1,1-dimethyloxyallyl	3.59	4.31

[a] The charge distributions are illustrated in Figures 3 and 4 and were obtained from (4/4) CASSCF/6-31G* wave functions.

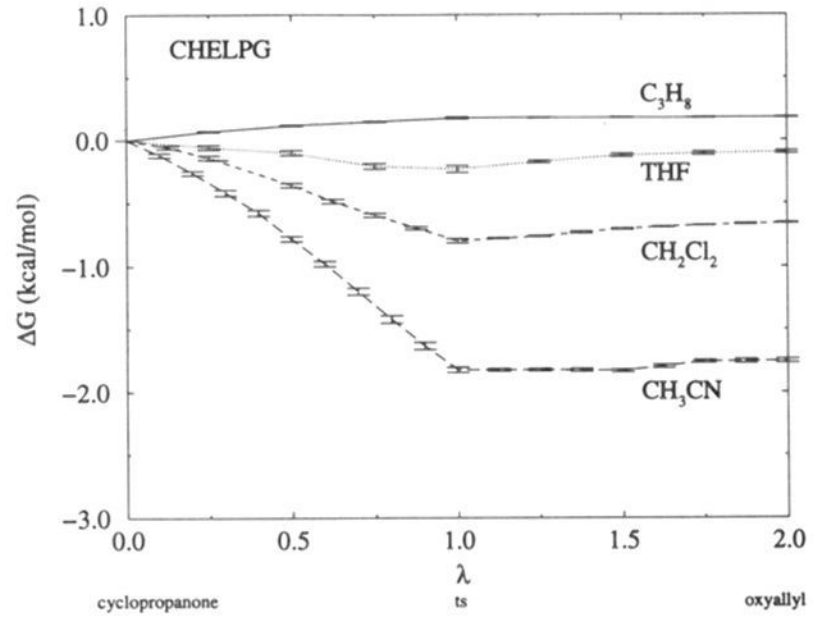


Figure 5. Computed changes in free energies of solvation (kcal/mol) for the ring opening of cyclopropanone using the CHELPG charges.

dimethylcyclopropanone are given in Figures 7 and 8, respectively, with λ = 0.0 and 1.0 corresponding to the cyclopropanone and oxyallyl derivatives, respectively. The overall changes in free energies of solvation are summarized in Table 4 for both systems.

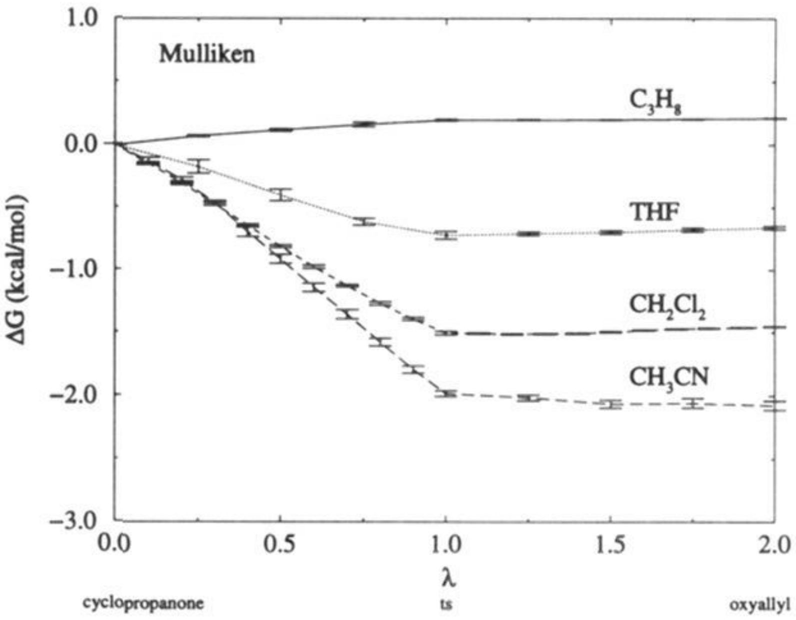


Figure 6. Computed changes in free energies of solvation (kcal/mol) for the ring opening of cyclopropanone using the Mulliken charges.

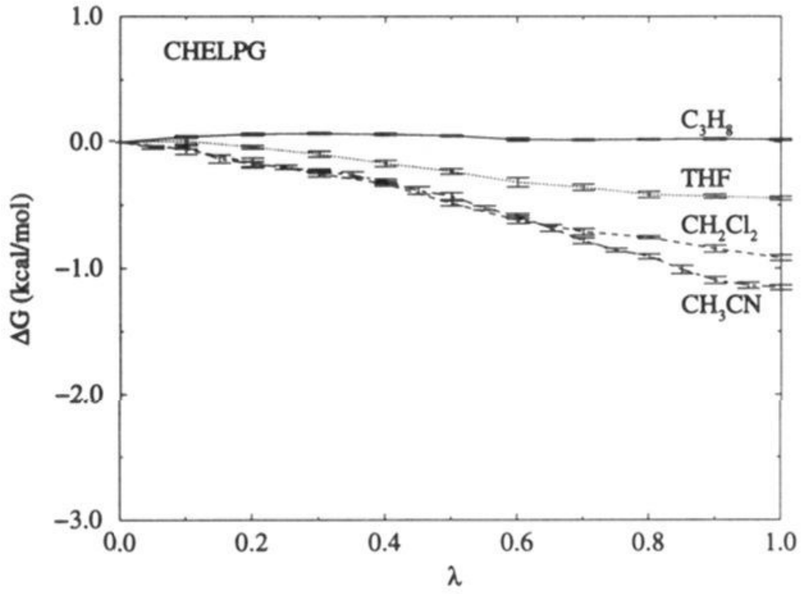


Figure 7. Computed changes in free energies of solvation (kcal/mol) for the ring opening of 2,2-dimethylcyclopropanone (λ = 0) to 1,1-dimethyloxyallyl (λ = 1) using the CHELPG charges.

First, it should be noted that the precision of the Monte Carlo results for simple mutations of this type in aprotic solvents is high with overall statistical uncertainties (1σ) of about 0.1 kcal/mol. Then, it is apparent that the predicted solvent effects for both systems are not large. The expected stabilization of the oxyallyl species in the more polar solvents is indeed found. The results from the two charge models are quite similar; the somewhat larger effects from the Mulliken charges are consistent with the correspondingly larger changes in dipole moments (Table 3). The accord is rather surprising in view of the significantly poorer results that are obtained for free energies of hydration with 6-31G* Mulliken charges,[15] though the previous comparisons involved far more diverse structures than those represented by the present mutations.

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(31) This notion received some testing. (4/4)CASSCF/6-31G* calculations using the dipolar SCRF theory[32] implemented in GAUSSIAN 92[13] with a dielectric constant of 36 (acetonitrile) were performed for cyclopropanone, the transition state, and oxyallyl to recompute the Mulliken and CHELPG charges in the presence of the solvent reaction field. This is a low-level SCRF treatment that only includes the response of the continuum solvent to the solute's dipole moment.[32] Reoptimization of the geometry of the oxyallyl intermediate in the presence of the reaction field resulted in bond length changes of less than 0.01 Å. The charge changes versus those in the gas phase are 0.00–0.03 e for all three solutes without geometry reoptimization. The computed dipole moments for cyclopropanone and oxyallyl with the CHELPG charges are 2.79 and 3.47 D in the gas phase and 3.09 and 3.86 D for $\epsilon = 36$ without geometry reoptimization. With the geometry reoptimization, the dipole moment for oxyallyl increases by 0.03 D to 3.89 D. The similar increases in both dipole moments and their values between the gas-phase CHELPG and Mulliken results in Table 3 indicate that use of SCRF charges would have little impact on the present differences in free energies of solvation (Table 4).

(32) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776.

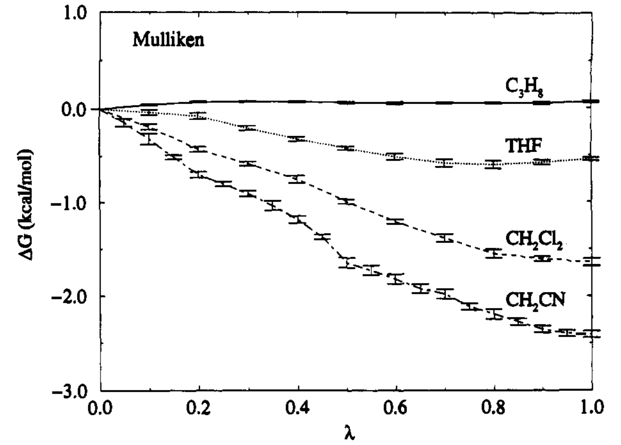

Figure 8. Computed changes in free energies of solvation (kcal/mol) for the ring opening of 2,2-dimethylcyclopropanone (λ = 0) to 1,1-dimethyloxyallyl (λ = 1) using the Mulliken charges.

Table 4. Computed Differences in Free Energies of Solvation (kcal/mol) at 25 °C

solvent	CHELPG ΔG_{sol}	CHELPG $\Delta\Delta G_{sol}$	Mulliken ΔG_{sol}	Mulliken $\Delta\Delta G_{sol}$
	Cyclopropanone → Oxyallyl			
propane	0.18 ± 0.01	0.00	0.21 ± 0.02	0.0
THF	–0.10 ± 0.05	–0.28	–0.66 ± 0.09	–0.87
dichloromethane	–0.66 ± 0.04	–0.84	–1.45 ± 0.04	–1.67
acetonitrile	–1.75 ± 0.08	–1.93	–2.08 ± 0.12	–2.29
	2,2-Dimethylcyclopropanone → 1,1-Dimethyloxyallyl			
propane	0.02 ± 0.03	0.0	0.07 ± 0.03	0.0
THF	–0.45 ± 0.08	–0.47	–0.55 ± 0.09	–0.61
dichloromethane	–0.92 ± 0.09	–0.94	–1.64 ± 0.10	–1.71
acetonitrile	–1.15 ± 0.10	–1.17	–2.11 ± 0.18	–2.18

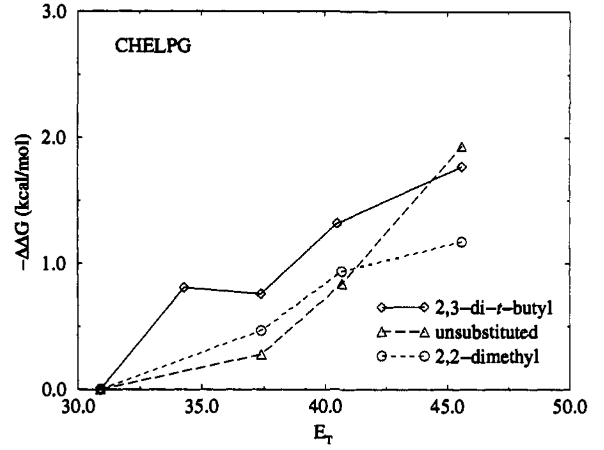

Figure 9. Computed changes in free energies of solvation for the ring openings of the cyclopropanones and the differences in experimental $\Delta G^‡$ values for various solvents relative to an alkane solvent (data from Table 1) plotted versus the experimental $E_T(30)$ values for the solvents. Computed results with the CHELPG charges.

Strikingly, the quantitative predictions of $\Delta\Delta G_{sol}$ relative to the alkane solvent are also close to the values observed by Greene and coworkers, summarized as $\Delta\Delta G^‡$ in Table 1. This is emphasized in Figures 9 and 10, which contrast the CHELPG (Figure 9) and Mulliken (Figure 10) results with the experimental data (solid lines) as a function of the solvatochromic solvent polarity index $E_T(30)$.[9] The choice of charge model has greater effect on the calculated results than do the alkyl substituents. The relatively smaller increment between dichloromethane and acetonitrile as solvents for the opening of 2,2-dimethylcyclopropanone than for the parent compound with both charge models probably reflects some hindrance to solvation of the carbonyl dipole in 1,1-dimethyloxyallyl by the methyl groups.

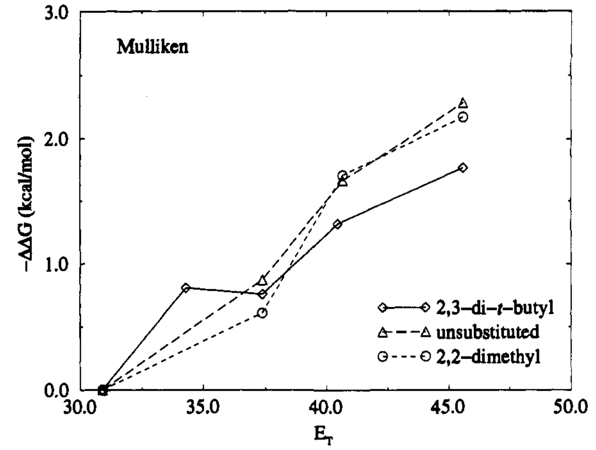

Figure 10. Computed changes in free energies of solvation for the ring openings of the cyclopropanones and the differences in experimental $\Delta G^‡$ values for various solvents relative to an alkane solvent (data from Table 1) plotted versus the experimental $E_T(30)$ values for the solvents. Computed results with the Mulliken charges.

It may be noted that the results for dichloromethane ($E_T(30)$ = 40.7)[9] in Figures 9 and 10 are not anomalous. The predicted solvent effects for the two charge models bracket the experimental data for pyridine ($E_T(30)$ = 40.5). However, all of the curves in Figures 9 and 10 appear to dip somewhat for the ether solvent, THF, reflecting a lower isomerization rate in this solvent than might have been expected from its $E_T(30)$ of 37.4. Cordes and Berson reported that the half-lives for the stereomutation of **6** or **7** were the same at 244 K in diethyl ether and at 195 K in dichloromethane.[8] Qualitatively, the present computations concur with the significantly faster isomerization rate in dichloromethane. A quantitative comparison awaits more complete kinetic data. Nevertheless, the present results predict a lower free energy of activation by 1.0–1.5 kcal/mol in dichloromethane than in diethyl ether ($E_T(30)$ = 34.5).[9] If one makes the unlikely assumption that $\Delta S^‡ = 0$, so that log *A* is the same at the two experimental temperatures, then the experimental data suggest a larger lowering of the free energy or energy of activation, ca. 3 kcal/mol, in dichloromethane compared to diethyl ether. Of course, **6** and **7** are structurally different from the simple cyclopropanones considered here.

Cordes and Berson also mentioned that the measured log *A* of 10 ± 1.4 for the reaction of **6** in diethyl ether was surprisingly low.[8] Given their E_a of 15.8 kcal/mol, the data imply a $\Delta S^‡$ = –9.8 cal/mol-K at 244 K. In contrast, the frequency calculations predict a $\Delta S^‡$ of ca. +3 cal/mol-K for the ring opening of the parent cyclopropanone in the gas phase (Table 2). If this discrepancy is real, it could suggest that there is substantial solvent restriction in the transition states for ring opening of **6** and **7**.

Conclusion

The computed solvent effects for the reactions in eqs 3 and 4 are very similar to those observed for eq 2 by Greene and coworkers.[9] This provides strong support for the present description of the structures and charge distributions for the species in eqs 3 and 4, which were obtained from the (4/4)CASSCF/6-31G* calculations. Our results indicate that the oxyallyls are very close in structure and energy to the transition states for the ring openings. Furthermore, the modest solvent effects for the reactions arise from the similar polarities for the cyclopropanones and oxyallyls, which reflects the primarily diradical rather than zwitterionic nature of the oxyallyls.

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