in the absence of oxygen a pale yellow species, **5**, is formed. If air is allowed into a hot solution of this complex, **2** is rapidly generated. If, however, the solution is cooled and O_2 admitted, the major product is **3** as indicated by a return of a deep blue coloration. These observations suggest that upon heating **1** in DMF in the absence of O_2 the ligand is oxidatively decarboxylated and the V(V) reduced to V(III).[14] The V^{III} (EHGS) complex thus formed can then be oxidized by molecular oxygen to **3**. These transformations are outlined in Scheme I. The proof of such speculation awaits further characterization of **5** and the completion of our kinetic studies with these complexes.

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Registry No. 1, 89890-27-7; **2**, 36913-44-7; **3**, 89890-28-8; $Na_4 \cdot CH_3OH \cdot 1.5H_2O$, 89890-30-2; **5**, 89890-31-3; EHPG, 1170-02-1; EHGS, 89890-32-4.

Supplementary Material Available: Table of atomic positional parameters with estimated standard deviations (1 page). Ordering information is given on any current masthead page.

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[14] Physical evidence for the vanadium(III) formulation of **5** comes from Evans solution magnetic moments and the similarity in chemistry of **5** with synthesized V^{III}(EHPG) complexes.

Ab Initio Calculation of the Transition State for the Cope Rearrangement

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The mechanism of the Cope rearrangement has been the subject of numerous experimental studies.[2] In addition to a concerted pericyclic process, two distinct, nonconcerted pathways are possible a priori. One involves σ-bond cleavage to afford two allyl radicals; the other involves σ-bond formation to give cyclohexane-1,4-diyl.

σ-Bond cleavage is ruled out by labeling studies[3] and by the fact that the activation energy of 56 kcal/mol for dissociation of 1,5-hexadiene to two allyl radicals[4] is substantially higher than that of 34 kcal/mol for its Cope rearrangement.[5] Formation of cyclohexane-1,4-diyl as an intermediate has received much more serious consideration.[2] Although revised estimates of the heat of formation of this diradical now place it about 7 kcal/mol above the transition state for the Cope rearrangement,[6] MINDO calculations have found that cyclohexane-1,4-diyl is a metastable intermediate on the potential surface for this reaction.[7] Dewar has used these MINDO results to support his general contention that multibond reactions cannot normally be synchronous.[8]

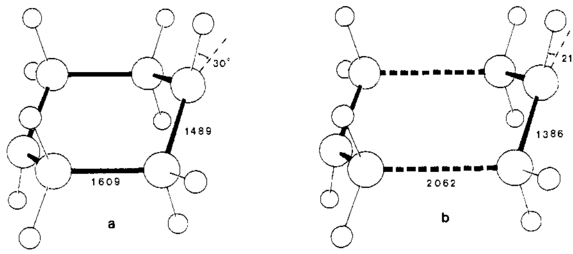

Figure 1. Optimized C_{2h} geometry found using the 3-21G basis set and (a) the TCSCF wave function and (b) the MCSCF wave function, described in the text.

In this communication we report the findings of our ab initio studies of the Cope rearrangement. In contrast to the MINDO results, we find that the lowest energy chair (C_{2h} symmetry) species is the transition state for a concerted pericyclic process. However, this ab initio result is obtained only when a flexible basis set is used and when electron correlation is properly treated.

Calculations were carried out using both STO-3G[9] and 3-21G[10] basis sets. A two-configuration (TC) SCF wave function appropriate for cyclohexane-1,4-diyl was employed, as well as a multiconfiguration (MC) SCF wave function. The latter involved all 52 ^1A_g spin adapted configurations that are possible when the three orbitals occupied by the six "active" electrons are correlated with three virtual orbitals. For the TCSCF wave functions geometries were optimized with the aid of analytically evaluated gradients, using a program written by Kato and Morokuma.[11] For the MCSCF calculations with the STO-3G basis set, GAMESS[12] was employed.

Unfortunately, MCSCF calculations with the 3-21G basis required more computer memory than was available at either IMS or at the University of Washington. Consequently, with this basis set six-electron, six-orbital MCSCF calculations were simulated by using ALIS[13] to find the optimal orbitals for an MCSCF wave function consisting of the 12 most important configurations. These optimized orbitals were then used to perform a full six-electron, six-orbital CI. A test of this procedure was provided by the calculation of the energy of two allyl radicals at a large internuclear separation (14 Å). The energy of −231.6788 hartrees that was computed was only 0.0016 hartrees above twice the three-electron, three-orbital π MCSCF energy for allyl.

With the STO-3G basis set both the TCSCF and MCSCF calculations found cyclohexane-1,4-diyl to be the lowest energy structure of C_{2h} symmetry. The optimized structures with this basis set resembled closely the optimal C_{2h} structure that was found using the 3-21G basis set and a TCSCF wave function. The diradical nature of the latter structure was indicated not only by the bond lengths, shown in Figure 1a, but also by the large size (0.52) of the second coefficient in the wave function. Evaluation of the Hessian matrix showed that the structure was a minimum on the TCSCF potential surface. The energy of −231.6597 hartrees for the diradical was computed to be 6.4 kcal/mol below that of the transition state that was found to connect it with 1,5-hexadiene.

That these predictions of a diradical intermediate in the Cope rearrangement were spurious was suggested by comparison of the MCSCF energy of the structure shown in Figure 1a with that of a TCSCF optimized structure in which the two equivalent bond lengths, *r*, in the six-membered ring were each constrained to be

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1.971 Å. At the TCSCF level of theory this latter structure was computed with the 3-21G basis set to be 12.0 kcal/mol above the one in Figure 1a with $r = 1.609$ Å. However, with the six-electron, six-orbital MCSCF wave function the relative energies were reversed, indicating that the MCSCF wavefunction gives an optimal value of r that is considerably larger than that given by the TCSCF wave function.

Since the minimum energy C_{2h} geometry for the 3-21G MCSCF wave function appeared to have an optimal value of r close to that of the SCF wave function ($r = 2.023$ Å), several geometries with fixed values of r in this neighborhood were optimized at the SCF level of theory. Energies were then calculated using the MCSCF wave function; and the minimum MCSCF energy was found to occur at $r = 2.062$ Å. The structure thus optimized is shown in Figure 1b. Its MCSCF energy of −231.6997 hartrees is 14.1 kcal/mol below that of the structure in Figure 1a.

Both the geometry of the MCSCF optimized structure and the fact that the second largest coefficient in the MCSCF wave function is only 0.18 show that this structure is not a diradical. That the structure is, indeed, the transition state in a concerted pericyclic reaction is indicated by the fact that upon simultaneously lengthening one of the two equivalent C–C bonds and shortening the other in 0.01-Å increments, the energy falls smoothly with both SCF and MCSCF wave functions. The MCSCF energy of the transition state is 29.4 kcal/mol above that of 1,5-hexadiene, whose geometry in the all-transoid conformation was optimized at the SCF level. This energy difference is in reasonable agreement with the activation energy of 34 kcal/mol that is measured for the Cope rearrangement.[5]

Our 3-21G MCSCF results provide strong computational evidence that the preferred pathway for the Cope rearrangement of the parent 1,5-hexadiene is via a concerted pericyclic reaction. The reason that a diradical structure is found at lower levels of theory is that the STO-3G basis set and a TCSCF wave function each prejudice the calculations by selectively stabilizing cyclohexane-1,4-diyl relative to two allyl radicals. The single p function used for both σ and π bonds in STO-3G biases this basis set toward the former type of bond, and a TCSCF wave function that correlates the nonbonding pair of electrons in cyclohexane-1,4-diyl provides no correlation for the nonbonding pair in two allyls.

Since cyclohexane-1,4-diyl and two allyl radicals may be viewed as contributors to the resonance hybrid that represents the concerted pericyclic transition state,[14] the correct determination of the lowest energy C_{2h} structure depends critically on the ability of a calculation to describe both these contributors equally well. Otherwise, the result obtained will be biased toward the nonconcerted alternative that is favored by the computational method employed.[15]

Our 3-21G MCSCF finding that the Cope rearrangement proceeds via a concerted pericyclic transition state of C_{2h} symmetry is in disagreement with the previous MINDO results, which found the lowest energy C_{2h} species to be a metastable diradical intermediate.[7] Our 3-21G MCSCF results indicate that in the Cope rearrangement bond making and bond breaking occur in unison, thus also contradicting Dewar's general assertion that multibond reactions cannot normally be synchronous.[8]

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Registry No. 1,5-Hexadiene, 592-42-7.

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[15] Similarly, an SCF calculation would be biased toward finding a concerted pericyclic pathway, since diradicals cannot be adequately described with a single-determinantal wave function. Because both diradical contributors to the resonance hybrid for the concerted transition state are described equally poorly with an SCF wave function, the optimal C_{2h} geometry at the SCF level is similar to that found at the MCSCF level, where both contributors are described equally well. Nevertheless, the poor description at the SCF level of the diradical contributors to the transition state results in the calculated energy of activation being 12.3 kcal/mol higher at the SCF than at the MCSCF level of theory.

Energetics and Dynamics of Radical Pairs in Micelles. Measurement of the Average Singlet–Triplet Energy Gap by means of the Magnetic Field Dependence of ^{13}C CIDNP

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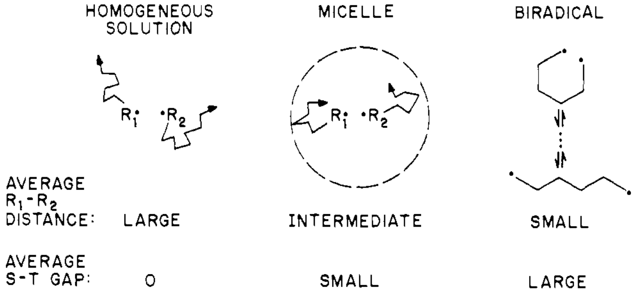
Among species with homolytically broken bonds, radical pairs and biradicals occupy opposite structural and dynamical extremes, as illustrated below.



The radical fragments of a geminate pair are free to diffuse independently in solution, but the two ends of a biradical are severely constrained. Intuitively one expects that radical pairs generated within a micelle occupy a position intermediate between these two extremes. Several aspects of the chemistry of radical pairs in micelles have in fact been found to be unique to the micellar medium.[1] What is lacking is a structural/dynamical scale that allows a quantitative measure of the position occupied by radical pairs in micelles. We wish to report the first such measurements.

A reasonable definition for such a scale is the singlet–triplet energy gap E_{ST}, and the easiest way to measure it is by the magnetic field dependence of CIDNP.[2-4] For radical pairs in homogeneous solution E_{ST} is typically zero.[2b] For biradicals E_{ST} is nonzero and can be either positive (triplet ground state) or negative (singlet ground state).[3] The above diagram illustrates the approximate inverse relation between E_{ST} and the spatial separation of the radical centers. In biradicals there is experimental[3b-d] and theoretical[5] evidence that other factors, such as through-bond coupling and the mutual orientation of the two ends, strongly affect E_{ST}.

Consider a biradical with $E_{ST} < 0$. In an external magnetic field the triplet sublevels T_{+1}, T_0, T_{-1} are split by the Zeeman energy while E_{ST}, the energy difference between the S and T_0 states, is unaffected. If we adjust the magnetic field to produce a T_{-1}–S degeneracy the intersystem crossing rate—and hence the CIDNP intensity—will exhibit a local maximum[2-4] at this field

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