from the solvent-swelling measurements described in the Experimental Section. S is the chronoamperometric slope (A cm^{-2} s$^{-1/2}$), d is the film thickness (cm), $(\Gamma_{Fe})_{obsd}$ is the quantity of electroactive complex in the film (mol cm^{-2}), and F is the faraday. Values of D_{eff} obtained in this way for several coatings are given in Table I. The uniformly smaller values observed with the coatings resulting from procedure I are in accord with the smaller voltammetric peak currents obtained with these films. The systematic increase in D_{eff} with thinner films formed by procedure II is in the direction expected from the increase in the fraction of Fe(CN)$_5$py^{3-} groups that are electroactive in thinner films. However, the correlation is not a straightforward one; a 20-fold increase in the concentration of electroactive centers produces only a twofold increase in the measured value of D_{eff}. The large uncertainties associated with the estimated values of d for these films discourages us from attempting more detailed analysis of the trends. The approximate values of D_{eff} estimated in this study fall within the range of previously reported values.[11-13,15] However, this range encompasses several orders of magnitude and it seems clear that the rates of diffusive charge transport through polymer films containing redox centers vary much more extensively than do the rates of diffusion of small molecules in liquid solutions.

Conclusions

By exploiting the coordination chemistry and solubility properties of mixtures of PVP and Fe(CN)$_5$OH$_2$$^{3-}$ it proved possible to incorporate redox active Fe(CN)$_5$$^{3-}$ groups into PVP either before or after films of the polymer were cast on electrode surfaces. The markedly different electrochemical responses of the two types of films, even when their nominal compositions and dimensions are the same, shows that the spatial distribution as well as the total number of redox centers within such films determines the rate at which charge can be transported through them. The now generally accepted proposal[9] that the mechanism of charge transport involves electron exchange between adjacent pairs of (oxidized and reduced) redox centers is supported by our observation of a sharp decrease in this rate when the concentration of redox centers falls below a critical value.

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Theoretical Study of Concerted vs. Stepwise Fragmentation of 2-Carbena-1,3-dioxolane

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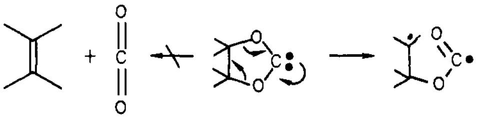
Abstract: The transition state for concerted fragmentation of the lowest singlet state of 2-carbena-1,3-dioxolane to ethylene plus carbon dioxide has been located at the restricted Hartree–Fock (RHF) level of ab initio theory, using a 4-31G basis set. The transition state is calculated to lie 30.4 kcal/mol above the optimized geometry for the reactant at this level of theory. This energy difference is rather insensitive to expansion of the basis set or to reaction, of CI. The STO-3G basis set is shown, however, to be very unsatisfactory for treating this reaction, since STO-3G gives the correct magnitude but the wrong sign for the energy difference between the reactants and products. The energy of the diradical formed by cleavage of just one C–O bond in carbenadioxolane is computed to lie at least 8.8 kcal/mol below the transition state for concerted fragmentation. Since a previous theoretical study of dihydroxycarbene suggests that the energy of the transition state for formation of the diradical should not be significantly higher than the energy of the diradical itself, it is concluded that cleavage of one C–O bond in carbenadioxolane is a lower energy process than concerted fragmentation. This theoretical finding rationalizes the experimental results in the pyrolysis of carbonate tosylhydrazone salts.

Pyrolysis of carbonate tosylhydrazone salts gives products whose formation can be most easily rationalized as involving one-bond cleavage in presumed 2-carbena-1,3-dioxolane intermediates.[1] That such intermediates do not decompose to alkene plus CO$_2$ in a concerted ${}_{\sigma}2_2 + {}_{\sigma}2_s + {}_{\omega}2_s$ process is somewhat surprising, since in the lowest singlet state of the carbene this reaction pathway is "allowed" by orbital symmetry.[2] However, a computational study of an analogous reaction, fragmentation of singlet dihydroxycarbene [C(OH)$_2$] to H$_2$ plus CO$_2$, showed that, although a transition state for concerted fragmentation exists, cleavage of just one OH is energetically preferable.[3]



The high energy of the transition state for concerted fragmentation of C(OH)$_2$ was attributed principally to the fact that at the transition state the incipient CO$_2$ fragment remains highly bent (OCO bond angle = 121.8°). This small angle is necessary for decreasing the H–H distance from that in C(OH)$_2$ toward that in H$_2$ while maintaining a modicum of OH bonding. Since the force constant for bending CO$_2$ is large, a high-energy transition state results.

The 1.33-Å C–C bond in ethylene is considerably longer than the 0.74-Å H–H bond in H$_2$. We speculated, therefore, that at the transition state for concerted fragmentation of carbenadioxolane the incipient CO$_2$ molecule might be less bent than at the transition state for concerted decomposition of C(OH)$_2$. Consequently, we suggested that the calculated barrier height for concerted carbenadioxolane fragmentation might be lower than that for the analogous process in C(OH)$_2$. In order to test these

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(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

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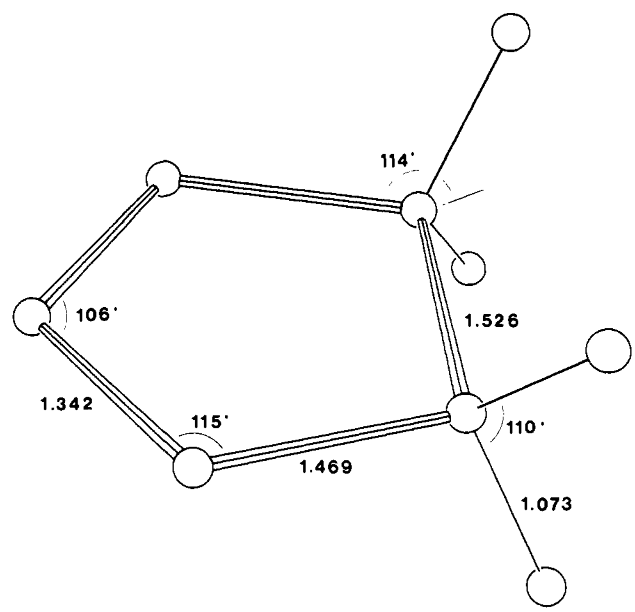

Figure 1. Optimized geometry for the lowest singlet state of 2-carbena-1,3-dioxolane with bond lengths in Å. The total energy calculated at the RHF level of theory with the Dunning DZ basis set is −265.4876 hartrees. CI reduces this to −265.9602 hartrees.

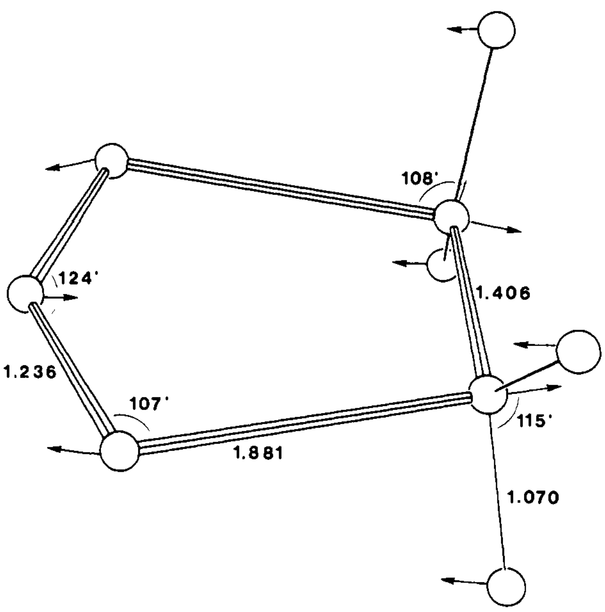

Figure 2. Geometry of the transition state for concerted fragmentation of 2-carbena-1,3-dioxolane. Bond lengths are in Å, and the mass weighted reaction coordinate is indicated by the arrows.

predictions and to determine whether one-bond cleavage in carbenadioxolane would also be more favorable than concerted fragmentation, we have undertaken additional ab initio calculations, the results of which we report herein.

Results and Discussion

The geometry of the lowest singlet state of carbenadioxolane and that of the transition state for concerted fragmentation were both determined at the restricted Hartree–Fock (RHF) level of theory with the 4-31G basis set.[4] Previous calculations on C(OH)$_2$[3] have shown that enlargement of the basis set to include polarization functions or the use of a correlated wave function have a negligible effect on the corresponding geometries. In locating the $^1A_1$ optimal geometry of both the reactant and the transition state, use was made of the GAMESS[5] program at the National Resource for Computation in Chemistry. The Hessian matrix for distortions that maintained the C_{2v} symmetry of the reactant was produced by numerical differencing of analytically evaluated first derivatives. The Newton–Raphson[6] technique was used to reduce the magnitude of the gradient to about 0.5 kcal/(mol Å). The full mass-weighted second-derivative matrix, including distortions which lowered the symmetry, was then diagonalized to yield a normal mode analysis for both the reactant and the transition state.

The geometry of the reactant is shown in Figure 1. Figure 2 shows the transition state and the reaction coordinate, the single vibrational mode with a negative force constant. The transition state is not as "late" as that for C(OH)$_2$. Although both of the CO bonds being broken are quite long, the C–C bond length is about midway between its value in carbenadioxolane and in ethylene. As in the case of C(OH)$_2$ decomposition, the CO$_2$ fragment remains quite bent at the transition state, and the reaction coordinate corresponds largely to linearizing this fragment. At the transition state the OCO angle is, as anticipated, larger than the corresponding angle at the transition state for concerted C(OH)$_2$ fragmentation, but only by 2.2°.

The calculated RHF barrier, corrected for the computed difference in zero-point energies between the reactant (50.5 kcal/mol) and transition state (47.1 kcal/mol), is 30.4 kcal/mol with the 4-31G basis and 33.0 kcal/mol with the slightly larger Dunning [4s, 2p/2s] basis.[7] By way of comparison, a minimal STO-3G basis[11] predicts the barrier to be 86.0 kcal/mol, nearly three times larger. This discrepancy is presumably due to the relatively poor description of multiple vs. single bonds with STO-3G. This basis set finds CO$_2$ plus ethylene to be ***higher*** in energy than carbenadioxolane by 37.0 kcal/mol, whereas the larger Dunning basis finds the two fragments to be ***lower*** than carbenadioxolane by about the same amount of energy. As we have discussed previously,[3] the STO-3G basis set is clearly inadequate for treating this type of reaction.

In order to assess the effect of electron correlation on the reaction barrier, CI calculations were carried out with the Dunning double ζ (DZ) basis set, including all single and double excitations from two reference configurations.[12] The correlation energies in the reactant and transition state proved to be almost identical, the CI barrier being only 1.7 kcal/mol less than the RHF value. The CI barrier of 31.6 kcal/mol is considerably smaller than that of 51.7 kcal/mol computed for concerted fragmentation of C(OH)$_2$ at the CI level with a DZ basis set augmented by polarization functions.[3]

Only a small part of the 20-kcal/mol difference in barrier heights can be attributed to a difference in overall reaction energetics. At the DZ-RHF level of theory, fragmentation of carbenadioxolane is computed to be only 6 kcal/mol more exothermic than that of C(OH)$_2$.[13] We believe that the major part of the difference in barrier heights is due to the small change required of the C–C bond length in carbenadioxolane fragmentation, compared to the large change in the H–H bond distance demanded for concerted decomposition of C(OH)$_2$. However, as noted above, the smaller bond-length change required for carbenadioxolane fragmentation results in only a small increase in the OCO angle at the transition state.

The 20-kcal/mol reduction in the barrier to concerted fragmentation on going from C(OH)$_2$ to carbenadioxolane does not

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(5) Dupuis, M.; Spangler D.; Wendolosky, J. J., "The Generalized Atomic and Molecular Structure System", 1980.

(6) See, for example: Wilde, D. J.; Beightler, C. S. "Foundations of Optimization"; Prentice Hall: Englewood Cliffs, N.J., 1967.

(7) Dunning's[8] [4s,2p] contraction of Huzinaga's[9] [9s,5p] primitive set was employed for C and O. For H a [2s] contraction of the Huzinaga (4s) basis was used.[10]

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(12) See ref 3 for details.

(13) A thermochemical calculation also suggests that the two reactions should have very similar exothermicities.

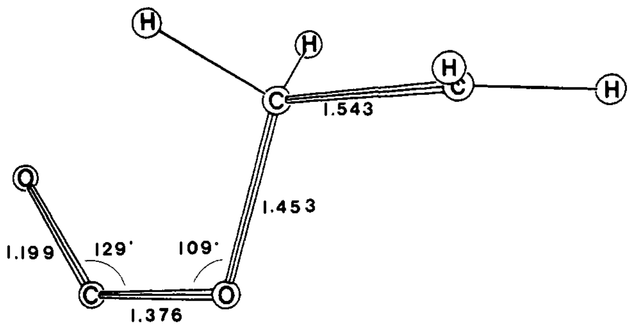

Figure 3. Geometry assumed for the diradical resulting from cleavage of one C–O bond in carbenadioxolane. Bond lengths are in Å.

necessarily imply that this reaction channel should be favored over one-bond cleavage in the latter molecule. One-bond cleavage in the carbenadioxolane would be expected to require on the order of 20 kcal/mol less energy than in $C(OH)_2$ because of the lower bond dissociation energy for O–C than O–H. In order to test whether one-bond cleavage would actually be favored over concerted fragmentation by about the same amount in the former carbene as in the latter,[14] we calculated the energy of the diradical resulting from one-bond cleavage in carbenadioxolane.

Optimization of the geometry of this diradical is no easy matter, since (a) it has many degrees of freedom; (b) it is probably prevented by only small barriers from re-forming carbenadioxolane,[3] closing to the β-lactone,[15] fragmenting to ethylene plus CO_2,[15] or losing CO;[16] (c) the proper description of the singlet diradical requires a high-quality basis set and at least a two-configuration wave function. Fortunately it proved sufficient for our present purposes simply to assume a reasonable geometry for the diradical.

Since this geometry, shown in Figure 3, is unoptimized, the energy calculated at it represents an upper bound to the true energy of the diradical. At both the DZ–RHF and DZ–CI levels of theory the energy was found to be 8.8 kcal/mol below that of the transition state for concerted fragmentation. This figure is quite comparable to the 6.3-kcal/mol energy difference found between the transition state for concerted fragmentation of $C(OH)_2$ and the radical pair formed by one-bond cleavage.[14]

Calculations on $C(OH)_2$ show little or no barrier to recombination of $H\cdot + \cdot CO_2H$ to the carbene.[3] Thus, it would be quite surprising if the diradical that results from one-bond cleavage in carbenadioxolane were separated from the carbene by an appreciable barrier. If, as seems likely, this barrier is less than 8.8 kcal/mol, the lower limit calculated for the energy difference between the diradical and the transition state for concerted carbenadioxolane fragmentation, the transition state for one-bond cleavage is lower in energy than that for concerted fragmentation.

A complete exploration of the energy surface for the diradical formed by one-bond cleavage in singlet carbenadioxolane is necessary before one can claim to have shown computationally that the intermediacy of this species can account completely for the products formed on pyrolysis of carbonate tosylhydrazone salts. Nevertheless, our finding that this diradical is lower in energy than the transition state for concerted carbenadioxolane fragmentation provides a very attractive explanation for the unexpected experimental result[1] that the orbital symmetry allowed pathway from the singlet carbene is not the one followed.

Carbenadioxolanes can be written as possible intermediates in several other olefin-forming reactions.[17-21] The theoretical results reported here suggest that the free carbenes are not the species that fragment in reactions where olefin formation is concerted. There is experimental evidence that ylides may be the reactive intermediates in at least some of these cycloreversions.[19,22] Concerted fragmentation of such stabilized 2-dioxolane anions is well precedented.[23,24]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank NRCC and NSF for grants and Bernie Santarsiero for help with the ORTEP plotting routines.[25]

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[14] The number for this energy difference at the DZP–CI level is given incorrectly in the text of ref 3, but the energy difference is shown correctly in Figure 3 of the reference. The DZP–CI energy difference between $H\cdot$ plus $\cdot CO_2H$ and the "S" form of $C(OH)_2$ is also given incorrectly in the text. The correct value is 54.0 kcal/mol. The energy of the "S" form should be raised for the DZP–CI entry in Figures 3, so the energy difference between "S" and "U" remains constant with the DZP basis set.

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