related to the enzyme-catalyzed hydrolysis of the phosphate. Two major lines of evidence are consistent with this conclusion. When the enzyme concentration is varied over a factor of 4, the rate constant changes only slightly (<20%), suggesting that the reaction is nonenzymatic. In addition, the observed general-base catalysis by acetate ion ($k_{\mathrm{OAc^-}} = 3.6\ \mathrm{M^{-1}\ s^{-1}}$) is expected for ketonization but not for an enzymatic process.

In order to confirm that the k_2 process is not phosphatase-catalyzed hydrolysis of **2b**, the reaction was run at pD 4.70 and 1 mM acetate and quenched at various times by the addition of sodium hydroxide to give a pD $>$12. Addition of base inactivates the enzyme and causes both the product of ketonization, **3**, and the dienol intermediate **2a** to form 2-cyclohexenone (**4**) ($\lambda_{\max} =$ 232 nm). Thus, monitoring the adsorbance at 232 nm as a function of time of quenching gives an estimate of the rate constant for phosphatase-catalyzed hydrolysis of **2b**. At 0.05 mg/mL of phosphatase, the rate constant is about 0.10 $\mathrm{s^{-1}}$. This value is greater than 5-fold larger than the measured rate constant for ketonization (k_2) under these conditions.

Rate constants for ketonization were obtained at pD 4.70, 5.14, and 5.62 (μ = 0.1, NaClO$_4$, acetate buffer, 25 °C). Extrapolation to zero acetate concentration gives values of $1.37 \times 10^{-2}\ \mathrm{s^{-1}}$ (pD 4.69), $1.58 \times 10^{-2}\ \mathrm{s^{-1}}$ (pD 5.14), and $1.40 \times 10^{-2}\ \mathrm{s^{-1}}$ (pD 5.62). Since these values are invariant with pD in this range they represent water-catalyzed ketonization (k_0). In order to compare the rate constants for ketonization of **1b** and **2a**, we multiply the rate constant of **2a** by an assumed solvent isotope effect of 5–10 to correct for the different solvents (D$_2$O vs. H$_2$O).[9] In addition, if we assume that we could have detected 5% of the conjugated isomer **4** in the product, the rate constant for protonation at the γ-carbon of **2a** can be calculated to be 10^3- to 10^4-fold slower than it is for **1b**. This large rate difference is probably due to the availability of a mechanism for **1b** which is unavailable to **2a**, presumably the 1,5-sigmatropic hydrogen shift, suggested by Duhaime and Weedon.[5d]

Acknowledgment. This work was supported by Grant GM 33059 from the National Institutes of Health.

(9) The solvent isotope effect has been measured for the water-catalyzed ketonization of vinyl alcohol ($k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}} = 12$).[4c]

Correlated Transition Structure for the 1,5-Sigmatropic Hydrogen Shift

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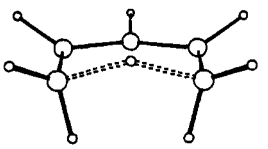
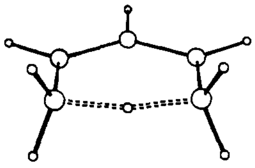
Received September 2, 1986

It was recently proposed that the 1,5-sigmatropic hydrogen shift in 1,3-pentadiene occurs via a "planar nonfacial" C_{2v} geometry.[1a] We wish to report extensive calculations that show that this claim is incorrect. We have also determined the influence of basis sets and electron correlation on the transition structure of this typical pericyclic reaction.

Ab initio transition structures obtained at the RHF level[2-5] for the 1,5-sigmatropic hydrogens shift of 1,3-pentadiene predict that the reaction occurs via a C_s suprafacial transition structure, **1**, consistent with experimental data.[6] MINDO/3 calculations also give a similar C_s transition structure,[7] but the activation energy is much higher than the experimentally observed value,[8] while the calculated isotope effects were too low. Vibrationally assisted tunneling was proposed for this reaction.



1



2

Dormans and Buck (DB) reported that a C_{2v} transition state, **2**, has a lower unrestricted Hartree–Fock (UHF) energy than the C_s transition state restricted Hartree–Fock (RHF) energy. They also propose that vibrationally assisted tunneling from this C_{2v} geometry is the mechanism for the 1,5-sigmatropic hydrogen shift.[1]

There are several clear lines of evidence that show that the C_{2v} geometry is not a transition structure. First, the experimental suprafacial stereochemistry of substituted cases[6] is not consistent with a planar transition structure. Second, the lower energy of the C_{2v} structure in the DB work is an artifact of the use of the UHF method for **2** and RHF for **1**. As shown in Tables I and II, when these two structures are reoptimized at the same computational level, the C_s structure is always lower in energy than the C_{2v}.[9] Third, the optimized UHF C_{2v} structure has two imaginary frequencies at the UHF/3-21G level; thus, it is not a transition state.[10] The second imaginary frequency (337i) corresponds to an distortion of the C_{2v} structure to the C_s structure. The C_s transition structure has only a single imaginary frequency.[3,4] In addition, the activation energies reported by DB are relative to the s-cis conformation of 1,3-pentadiene, instead of the more stable s-trans conformation.

We have carried out a systematic investigation of the influence of basis sets and electron correlation on the transition structure of the 1,5-sigmatropic shift. The large discrepancy between the calculated activation energy for the C_s structure and the experimental one is, indeed, due to neglect of correlation energy and not to location of an incorrect geometry. As seen in Table II, even including correlation energy only at the MP2/6-31G*//HF/3-21G level gives a calculated activation energy that is very close to the observed value of 36.1 kcal/mol.[8] At the single determinant level, the UHF energy is lower than the RHF energy. However, when electron correlation is included by the MP2 method, the restricted procedure gives a lower energy than the unrestricted. This is expected since the UHF wavefunction is heavily contaminated by higher spin states as seen from the $\langle S^2 \rangle$ value ($\langle S^2 \rangle$ = 0 for a pure singlet).[11]

Table III shows additional results obtained for optimized reactant and C_s transition state calculations. There are only very small differences in geometries between RHF/3-21G and RMP2/6-31G* optimized structures. These structures are at most only 0.04 Å different in bond lengths and only a few degrees different in angles. Although there are not large changes in activation energies, improvements in the basis set at the RHF level result in an increase in the ΔE, which appear to be converging

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0002-7863/87/1509-3139$01.50/0

Table I. Comparison of Total Energies (hartrees) of C_{2v} and C_s Structures at 3-21G Geometries[a]

	RHF/3-21G (6-31G*)	UHF/3-21G (6-31G*)	RMP2/6-31G*	UMP2/6-31G*	$\langle S^2 \rangle$
C_s	−192.792 54 (−193.862 67)	−192.800 72 (−193.87128)	−194.529 32	−194.484 79	0.8
C_{2v}	−192.684 67 (−193.759 08)	−192.793 30 (−193.86410)	−194.401 01	−194.454 01	1.3

[a] MP2 calculations with frozen core. $\langle S^2 \rangle$ values from UHF/6-31G* calculations.

Table II. Comparison of Energies (kcal/mol) of C_{2v} and C_s Structures (3-21G) Relative to (*Z*)-1,3-Pentadiene

	RHF/3-21G (6-31G*)	UHF/3-21G (6-31G*)	RMP2/ 6-31G*	UMP2/ 6-31G*
C_s	54.8 (58.7)	49.6 (53.6)	37.6	65.5
C_{2v}	122.5 (123.8)	54.3 (57.8)	118.1	84.8

Table III. Total Energies and Activation Energies for the 1,5-Sigmatropic Shift

computational level	$-E_{TS}$, hartree	ΔE, kcal/mol
RHF/STO-3G	191.501 70	64.3
RHF/3-21G	192.792 54	54.8
RHF/6-31G	193.795 45	56.5
RHF/6-311G	193.829 37	57.2
RHF/6-31G*	193.862 79	58.7
RHF/6-31G**	193.877 47	58.1
RHF/6-311G**//RHF/6-31G**	193.912 50	58.5
RMP2/STO-3G	192.818 33	50.1
RMP2/3-21G	193.270 41	39.3
RMP2/6-31G	194.272 44	40.1
RMP2/6-311G	194.418 26	37.7
RMP2/6-31G*	194.555 27	37.7
RMP2/6-31G**//RMP2/6-31G*	194.597 53[a]	36.5
RMP2/6-311G**//RMP2/6-31G*	194.665 70[a]	34.1
RMP2/3-21G//RMP2/6-31G*	193.261 43[a]	39.4
RMP3/3-21G//RMP2/6-31G*	193.287 66[a]	44.6
RMP4(SDTQ)/3-21G//RMP2/6-31G*	193.320 57[a]	42.1
RMP2/6-31G*	194.531 27[a]	37.7
RMP3/6-31G*//RMP2/6-31G*	194.561 88[a]	44.7
RMP4(SDTQ)/6-31G*//RMP2/6-31G*	194.602 67[a]	41.1
ΔH^{b} (RHF/3-21G, T = 200 °C)[12]	−3.6 kcal/mol	
$\Delta S^{\ddagger}$ (RHF/3-21G, T = 200 °C)[12]	−9.3 eu	
exptl $\Delta H^{\ddagger}$ (T = 200 °C)[8]	35.2 ± 2.2 kcal/mol	
exptl $\Delta S^{\ddagger}$ (T = 200 °C)[8]	−9.5 ± 4.6 eu	

[a] MP calculations used the frozen core approximation. [b] ZPE and finite temperature correction.

at 58–59 kcal/mol. Thus the HF limit gives an activation energy which is about 25 kcal/mol too high for this reaction. Inclusion of correlation energy, even at the RMP2 level with the 3-21G basis set, gives an activation energy close to the experimental value. Further improvement of the basis set at the RMP2 level (from 3-21G to 6-311G**) lowers the calculated ΔE to 34.1 kcal/mol, which, when corrected for zero-point energy and finite temperature, is significantly below the experimental result. MP2 often overestimates the effect of electron correlation on activation energies. Inclusion of more terms in the perturbation expansion (RMP3 and RMP4) results in oscillations in the ΔE, which appears to be converging around 42 kcal/mol with the 6-31G* basis. As judged from the MP2 and MP4 results with the 6-31G* and 6-311G** basis sets, the activation energy with the 6-311G** basis would probably be ~3 kcal/mol lower than with the 6-31G* basis. We estimate that the activation energy at infinite order MP with the 6-311G** basis would be approximately 39 kcal/mol. When corrected for ZPE and finite temperature using RHF/3-21G frequencies[12] scaled by a factor of 0.89,[13] this is within experimental uncertainty of the observed value of 35.2 kcal/mol. The calculated $\Delta S^{\ddagger}$ is also in good agreement with the experimental value. The isotope effect calculated for this reaction at the RHF/3-21G level is 2.52,[3b] which is in poor agreement with the experimental result of 4.97.[8a] The isotope effects are calculated from harmonic vibrational frequencies and the molecular geometry. Although improvement is expected with more accurate frequencies, it is currently impractical to calculate the frequencies at a correlated level. These high-level quantum mechanical calculations and classical transition state theory are able to account quite accurately for the observed activation parameters for this typical pericyclic reaction.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research through a research grant and computer time at the San Diego Supercomputer Center and to the Harris Corporation and the UCLA Computer Center for the additional computer time used in this work.

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Generation of Oxoiron(IV) Porphyrin Complexes by Amine *N*-Oxide Oxo-Transfer Reactions

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Received August 26, 1986

Oxoiron(IV) porphyrin prosthetic groups are now recognized as intermediates for peroxidase enzymes,[1] and such high-valent states are also suggested for cytochrome P-450[2] and cytochrome oxidase.[3] Synthetic iron(IV) porphyrin compounds have been prepared in situ at low temperature by indirect autoxidation,[4] by use of chemical oxidants,[5] by electrochemical oxidation,[6] and by photodissociation reactions.[7] Proton NMR spectroscopy has provided the major method for characterization of the iron(IV) porphyrins in solution.[4a–c,f,5]

Bruice and co-workers have investigated the kinetics and mechanism of a novel iron(III) porphyrin mediated *N*-demethylation reaction of *N*,*N*-dimethylaniline *N*-oxide.[8] Evidence favors

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