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A Quantum Chemical Study on the Mechanism of a Photochemical [1,3]-OH Shift in 2-Propen-1-ol

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Abstract: For the photochemical [1,3]-OH shift in 2-propen-1-ol a mechanism is proposed on the basis of the relaxation of the excited double bond toward a twisted geometry, accompanied by a separation of charge, leading to a planar [1,3]-OH shift. By means of semiempirical MNDO calculations followed by a limited (3 × 3) CI, one-dimensional potential energy surfaces for ground and excited states are calculated. It is shown that the proposed mechanism is strongly preferred to the mechanism predicted by the rules of conservation of orbital symmetry. It is to be expected that the presented results may be of general value in alkene photochemistry.

During our investigations on the photochemistry of rigid 1,5-dienes it was found that irradiation of 8-hydroxygermacrene B leads to an exclusive [1,3]-OH shift.[1] The rules of conservation of orbital symmetry[2] predict a concerted shift to proceed in a suprafacial fashion. However, orbital symmetry controlled reactions deal only with strictly concerted conversions and no attention is paid to local geometry changes which effectuate the course of the overall process. Still it is well-known in alkene photochemistry that twisting of the excited double bond occurs in order to diminish electronic repulsion between the antibonding p orbitals. In unsymmetrically substituted alkenes this twist will be accompanied by a complete charge separation in the orthogonal situation. This effect, which occurs in a small area of the angle of twist (known as "Sudden Polarization"), invoked an overwhelming number of publications[3] in order to establish its physical significance. Until this moment, however, no complete reaction path for a photochemical reaction involving this phenomenon is known to us. Such a calculation would offer a possibility for comparison of a similar reaction path with a concerted reaction as predicted by conservation of orbital symmetry. Relatively little attention has been paid to the stereochemical aspects of photochemical sigmatropic rearrangements. Most of this work was directed to [1,3]-C shifts which were described in detail by Cookson and co-workers.[4] They demonstrated that the photochemical [1,3]-benzylic shift in *cis*- and *trans*-3-methyl-5-phenyldicyanocyclohexylidene is completely stereospecific with retention of configuration of the migrating benzylic center (see Figure 1), which is consistent with the orbital symmetry.

Irradiation of the cyano-3-phenylcyclohexylidene methyl ester of acetic acid showed that no information could be obtained regarding the stereochemical fate of the allylic terminus (see Figure 2). It was found that cis-trans equilibration was faster than the [1,3]-benzylic shift. Cis-trans isomerization is known to proceed via a relaxed twisted state of the excited double bond. Regarding the highly unsymmetrical substitution, charge separation is likely to occur. From this polarized twisted geometry a planar shift (vide infra) might occur which would offer an explanation for the stereochemical outcome of the reaction.

Mechanism

Taking into account the amount of computer time needed for the calculations, 2-propen-1-ol is chosen as a model system since it is the smallest molecule that may exhibit a [1,3]-OH shift. For this shift the rules of conservation of orbital symmetry predict a concerted $[\sigma_2 + \pi_2]$ reaction to proceed in a suprafacial fashion with retention of configuration of the migrating oxygen orbital due to the symmetry of the HOMO of the allylic fragment. Using the knowledge concerning alkene photochemistry, we suggest a mechanism as depicted in Figure 3. *Not the symmetry of the HOMO but the geometrical relaxation of the excited double bond determines the stereochemical outcome of the reaction.* Excitation of 2-propen-1-ol is expected to result in a twist around the π bond accompanied by charge separation. Regarding the strong polarity invoked by the hydroxyl function, it has to be expected that the charge separation will be effectuated on a rather large interval of the angle of twist. This polarization is expected to result in the formation of a negative charge on the central carbon atom which is stabilized by the partially positive charge of the neighboring carbon atom due to the electronegative character of the oxygen atom. The terminus of the allylic fragment will be positively charged. When the hydroxyl group is situated in the plane of the three carbon atoms, a highly symmetrical transition state results from a shift of the partially negatively charged hydroxyl function toward the positively charged terminus of the allylic fragment.

Method of Calculation

Theoretical investigations concerning the sudden polarization effect employed ab initio procedures with limited or large-scale configuration interaction. Only small molecules, e.g., propylene and butadiene, can be handled in this way. Especially when a reaction path has to be calculated geometry optimizations should be carried out, requiring large amounts of computer time. The importance of correct geometries is emphasized by the work of Suzuki et al.[5] Their studies concerning the photochemical behavior of the retinylidene chromophore led to a charge distribution that is opposite to the results obtained by Salem.[6] These contradictory results are explained by their different approaches. In Salem's ab initio calculations only a fixed averaged geometry is used throughout the reaction, while Suzuki performed geometry optimizations at each point of the energy surface with the LCAO-ASMO-SCF-CI method. Regarding the important role of the optimizations, a cautious exploration of the excited-state profiles with the semiempirical MNDO-SCF-MO method[7] with inclusion of (3 × 3) CI seems relevant. Semiempirical methods like MNDO have proved to be successful for the calculation of ground-state reactions. For calculations involving open-shell singlets and triplets, the standard closed-shell SCF procedure is adapted with the *half-electron* method.[8] Though this program has rarely been applied to calculations

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(1) Fransen, H. R.; Buck, H. M. *J. Chem. Soc., Chem. Commun.* **1982**, 786.

(2) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395, 2046.

(3) Bonačić-Koutecký, V.; Bruckmann, P.; Hiberty, P.; Koutecký, J.; Leforestier, C.; Salem, L. *Angew. Chem.* **1975**, *87*, 599. For reviews see, e.g.: Salem, L. *Acc. Chem. Res.* **1979**, *12*, 87. Malrieu, J. P. *Theor. Chim. Acta* **1981**, *59*, 251.

(4) Brown, R. F. C.; Cookson, R. C.; Hudec, J. *Tetrahedron* **1968**, *24*, 3955. Cookson, R. C.; Hudec, J.; Sharma, M. *J. Chem. Soc., Chem. Commun.* **1971**, 107, 108. Sharma, M. *J. Am. Chem. Soc.* **1975**, *97*, 1153.

(5) Suzuki, H.; Ishikawa, K.; Yoshihara, T. *J. Phys. Soc. Jpn.* **1982**, *51*, 3643.

(6) Salem, L.; Bruckmann, P. *Nature (London)* **1975**, *258*, 526.

(7) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899. MNDO: Thiel, W. J. *QCPE* **1978**, *11*, 353.

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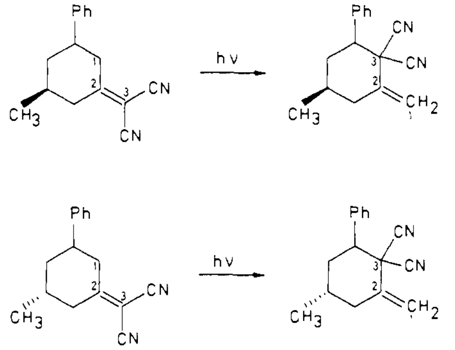


Figure 1. Photochemistry of *cis*- and *trans*-3-methyl-5-phenyldicyanocyclohexylidene.

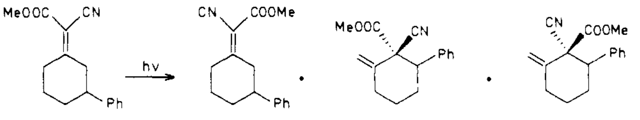


Figure 2. Photochemistry of the cyano-3-phenylcyclohexylidene methyl ester of acetic acid.

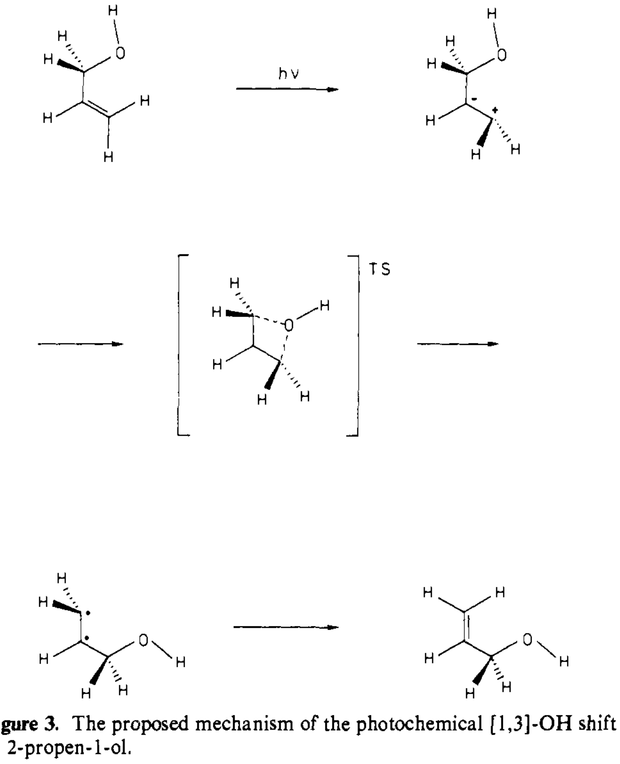


Figure 3. The proposed mechanism of the photochemical [1,3]-OH shift in 2-propen-1-ol.

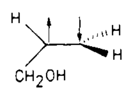
of excited-state surfaces, in a few cases it proved to be valuable for describing photochemical reactions.[9]

Excitation of 2-propen-1-ol results in a diradicaloid species with two markedly unequal radical sites. Previous investigations have shown that three low lying singlet states are important for describing both planar and twisted geometries, i.e., one covalent structure $\{a(1)b(2) + a(2)b(1)\}/(2 + 2S_{ab}^2)^{1/2}$ and two ionic structures a(1)a(2) and b(1)b(2) (structures **1–3**), where a and b represent the orthogonalized 2p orbitals on the two carbon atoms of the double bond. Mixing of these three structures corresponds with a (3 × 3) CI between the three singlet MO configurations ψ_+^2, ψ_-^2, and $\psi_+\psi_-$ (structures **4–6**) where $\psi_+ = \{a(1) + b(1)\}/(2 + 2S_{ab})^{1/2}$ and $\psi_- = \{a(1) - b(1)\}/(2 - 2S_{ab})^{1/2}$.

Table I. Optimized Structures of the Initial Configuration (START) and the Transition State (TS) of the Suprafacial Shift for S_0 and S_1 [a]

	S_0		S_1	
	START	TS	START	TS
C2C1	1.5145	1.5067	1.4915	1.3953
C3C2	1.3593	1.5067	1.4422	1.3953
C3C2C1	125.8	113.5	126.1	117.4
H4C1	1.1241	1.0809	1.1366	1.0903
H4C1C2	110.8	112.4	107.0	124.9
H4C1C2C3	32.2	20.7	52.7	37.3
H5C1	1.1242	1.0819	1.1252	1.0867
H5C1C2	109.2	120.3	109.6	120.6
H5C1C2C3	147.6	−160.6	166.2	−155.2
H6C2	1.0930	1.0943	1.0926	1.0989
H6C2C1	114.6	115.6	113.8	119.7
H6C2C1C3	179.9	137.1	158.6	−159.7
H7C3	1.0878	1.0809	1.0858	1.0867
H7C3C2C1	124.0	122.4	122.9	120.6
H7C3C2C1	−1.1	−20.7	0.0	−37.3
H8C3	1.0881	1.0819	1.0852	1.0903
H8C3C2	121.8	120.3	121.0	124.4
H8C3C2C1	178.7	160.6	180.0	155.2
O9C1	1.3967	2.3212	1.3998	2.1840
O9C1C2	109.4	65.0	113.9	77.5
O9C1C2C3	−90.6	−67.6	−68.7	−44.6
H10O9	0.9467	0.9458	0.9464	0.9444
H10O9C1	110.9	120.0	110.0	106.9
H10O9C1C2	179.1	−149.0	176.0	−127.3

[a] Distances are in angstroms and angles and dihedral angles are in degrees.



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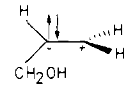

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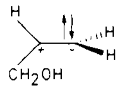

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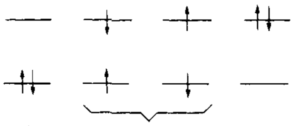

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For a proper description of the three corresponding potential energy surfaces it is required that they are simultaneously well treated. The half-electron method replaces the electron in a single occupied MO by two "half electrons" with opposite spin. In this way both ground and excited states can be handled by the same standard closed-shell procedure. After the SCF calculation a simple energy correction is carried out to compensate these approximations.[8] The subsequent (3 × 3) CI, involving the three structures **4–6**, mimics well the four-state diradical model, and therefore the essential qualitative features of the diradical are reproduced in an acceptable manner. In this way the method guarantees an equivalent description of the three singlet states.

Results and Discussion

The suprafacial and planar [1,3]-OH shifts were described by calculating one-dimensional potential energy surfaces of the ground state (S_0) and the excited states (S_1 and S_2). Energies of the distinct singlet states were calculated independently as a result of separate geometry optimizations with the Davidon–Fletcher–Powell algorithm.[10] To describe the suprafacial shift the geometry of the initial configuration and the transition state[11] were fully

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(8) With use of the HE method the energy of the excited singlet (S) and the triplet (T) states can be abstracted from the general expression:

$$E = \sum_{\delta} n_\delta E_\delta^c + {}^1\!/_4 \sum_{\delta,\epsilon} n_\delta n_\epsilon (2J_{\delta\epsilon} - K_{\delta\epsilon})$$

in which n_δ and n_ϵ are 2 for double-occupied MOs and 1 for single-occupied MOs. Comparing the HE energy with the correct energies, the energies of the individual states (ϵ_S^{HE} and ϵ_T^{HE}) are then obtained by adding and/or subtracting appropriate multiples of integrals between single-occupied MOs:

$$\epsilon_S^{HE} = E_S^{HE} + {}^3\!/_2 K_{\rho\sigma} - {}^1\!/_4(J_{\rho\rho} + J_{\sigma\sigma})$$

$$\epsilon_T^{HE} = E_T^{HE} - {}^1\!/_2 K_{\rho\sigma} - {}^1\!/_4(J_{\rho\rho} + J_{\sigma\sigma})$$

Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953. Dewar, M. J. S.; Trinasjtic, N. *J. Chem. Soc. A* **1971**, 1220. Dewar, M. J. S.; Olivella, S. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 829.

(9) Dewar, M. J. S.; Doubleday, C. *J. Am. Chem. Soc.* **1978**, *100*, 4935.

(10) Davidon, W. C. *Comput. J.* **1968**, *10*, 406. Fletcher, R. *Ibid.* **1965**, *8*, 33. Fletcher, R.; Powell, M. J. D. *Ibid.* **1963**, *6*, 163.

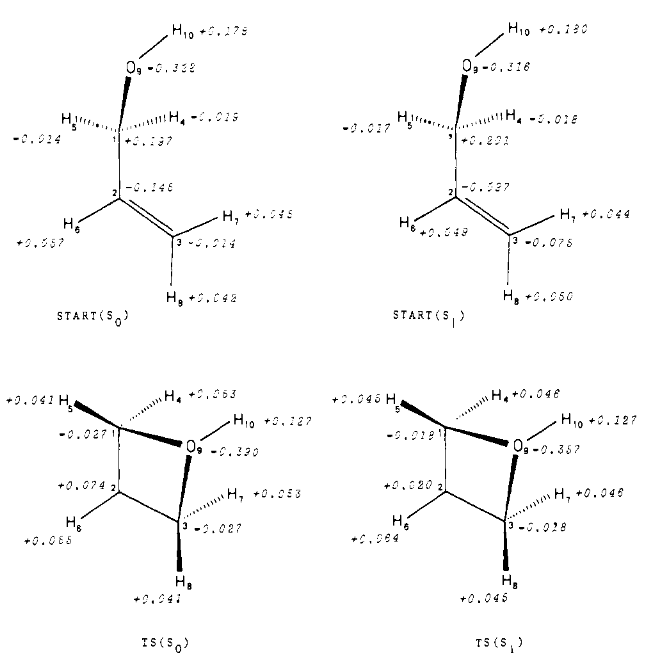

Figure 4. Electron densities of the initial configuration (START) and the transition state (TS) of the suprafacial shift for S_0 and S_1.

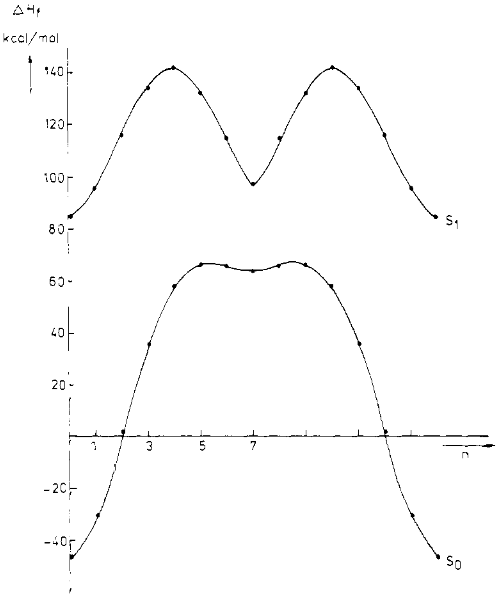

Figure 5. Enthalpy of formation (ΔH_f) vs. the arbitrary reaction coordinate (n)[12] of a suprafacial [1,3]-OH shift in 2-propen-1-ol.

optimized (see Table I and Figure 4).

To get an insight in the course of the suprafacial shift the energies of a number of intermediate geometries were calculated.[12] These results are depicted in Figure 5. As can be seen from this figure the suprafacial shift exhibits a very high activation enthalpy ($\Delta H^{\ddagger}$) barrier in both S_0 ($\Delta H^{\ddagger} = 112.5$ kcal/mol) and S_1 ($\Delta H^{\ddagger} = 56.8$ kcal/mol), making this shift under thermal and photochemical conditions highly improbable.[13] In order to calculate the potential surfaces for a planar reaction the calculation was split into two parts. First the twisting motion of the double bond was calculated (see Figure 6). Geometries were fully optimized

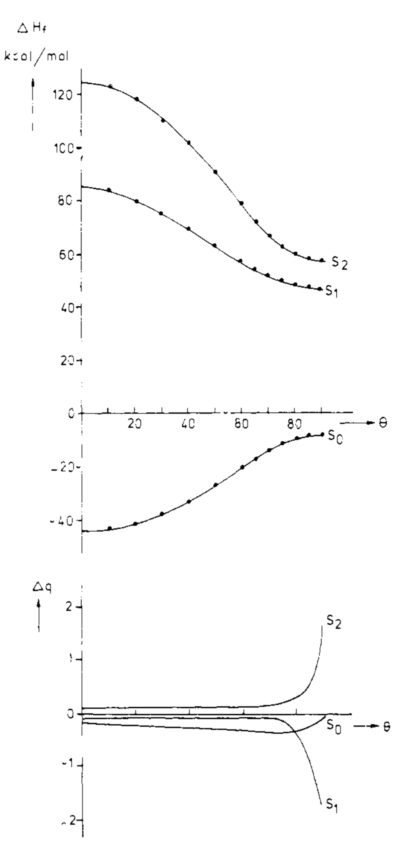

Figure 6. Enthalpy of formation (ΔH_f) and charge separation (Δq) between the central carbon atom and the terminal carbon atom vs. the rotation angle (θ) in 2-propen-1-ol for S_0, S_1, and S_2.

Table II. Optimized Structures of the Initial Configuration (START), the Twisted Configuration (TWIST), and the Transition State (TS) of the Planar Shift for S_0 and S_1[a]

	S_0			S_1		
	START	TWIST	TS	START	TWIST	TS
C2C1	1.5121	1.4970	1.4695	1.4816	1.4884	1.4687
C3C2	1.3594	1.4403	1.4695	1.4308	1.3561	1.4687
C3C2C1	129.6	127.1	96.9	123.0	127.8	97.0
H4C1	1.1238	1.1269	1.1106	1.1323	1.1272	1.1077
H4C1C2	108.2	108.4	120.8	109.2	110.2	121.2
H4C1C2C3	122.6	122.8	104.5	123.4	122.1	108.8
H5C1	1.1238	1.1269	1.1078	1.1323	1.1272	1.1140
H5C1C2	108.2	108.4	117.8	109.2	110.2	119.3
H5C1C2C3	−122.6	−122.8	−118.7	−123.4	−122.1	−111.1
H6C2	1.0957	1.0901	1.0734	1.0897	1.0919	1.0694
H6C2C1	111.7	115.6	126.0	114.6	114.1	131.5
H6C2C1C3	180.0	180.0	145.2	180.0	180.0	−178.9
H7C3	1.0867	1.0828	1.1106	1.0839	1.1034	1.1141
H7C3C2	125.0	121.2	120.8	123.9	125.1	119.3
H7C3C2C1	0.0	−90.0	−104.5	0.0	−90.0	−108.8
H8C3	1.0906	1.0828	1.1078	1.0878	1.1034	1.1077
H8C3C2	121.1	121.2	117.8	120.1	125.1	121.2
H8C3C2C1	180.0	90.0	118.7	180.0	90.0	111.1
O9C1	1.3969	1.3963	1.5443	1.3974	1.4039	1.5259
O9C1C2	112.4	112.3	86.2	113.1	110.7	85.3
O9C1C2C3	0.0	0.0	0.0	0.0	0.0	0.0
H10O9	0.9466	0.9460	0.9616	0.9466	0.9461	0.9602
H10O9C1	110.8	110.8	125.9	110.8	110.8	124.8
H10O9C1C2	180.0	180.0	137.2	180.0	180.0	136.4

[a] Distances are in angstroms and angles and dihedral angles are in degrees.

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(11) For a better understanding of the mechanism, we prefer to use the term "transition state" for these geometries although we recognize them sometimes as local minima. Within the symmetry constraints of the transition state the geometries calculated are real minima.

(12) These geometries were obtained by linear interpolation for all parameters (p_i):

$$p_{in} = p_{ib} + n(p_{ia} - p_{ib})/7;\ n = 0, 1, ..., 7$$

where a represents the transition state and b the starting configuration for the suprafacial shift and the twisted configuration for the planar shift. The reaction profiles are symmetric with respect to the transition state ($n = 7$). This approach offers the possibility of getting an impression about the enthalpy barriers although we do not describe the real reaction path.

(13) The potential surface for the second excited state was not calculated because no stable geometry for the transition state could be found.

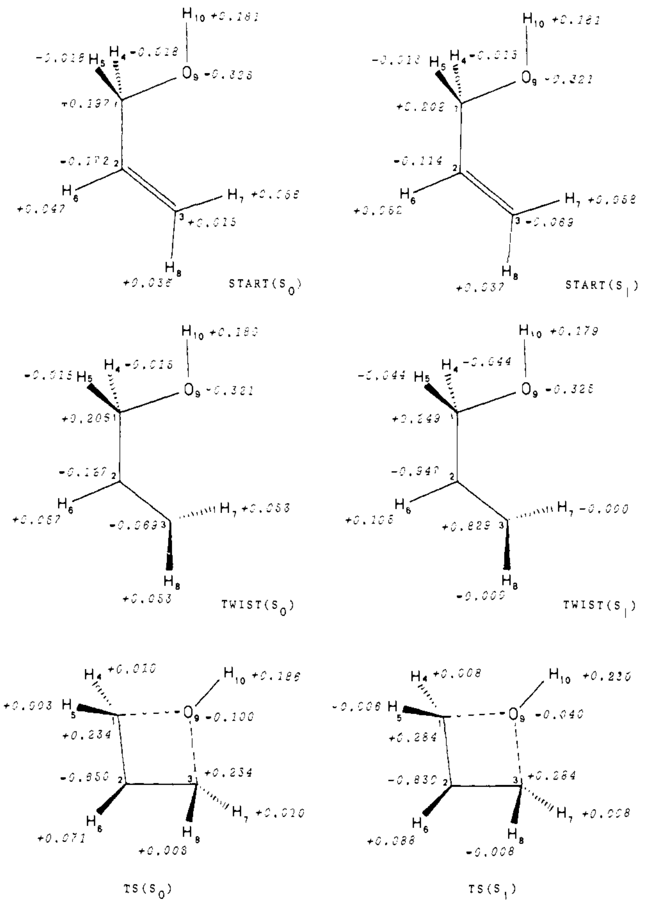

Figure 7. Electron densities of the initial configuration (START), the twisted configuration (TWIST), and the transition state (TS) of the planar shift for S_0 and S_1.

with the hydroxyl group situated in the plane of the three carbon atoms. The initial energy gap between S_0 and S_1 is reduced from 130.8 kcal/mol to 55.1 kcal/mol going from $\theta = 0°$ toward $\theta = 90°$. Charge separation is found to occur in an interval of 20° around the orthogonal geometry. For the S_1 the polarization results in a positive charge at the terminal carbon atom and a negative charge at the central carbon atom which is in agreement with qualitative chemical arguments (vide supra). The polarization in S_2 is opposite, whereas S_0 remains essentially covalent. Starting from the twisted geometry the planar shift of the hydroxyl group is described. The 90°-twisted geometry (C_s symmetry) and the transition state (C_s symmetry[14]) were fully optimized (see Table II and Figure 7).

The intermediate geometries were obtained by linear interpolation.[12] The results are shown in Figure 8. The energy gap between S_0 and S_1 is reduced from 55.1 kcal/mol for the twisted geometry to 9.8 kcal/mol for the transition state. $\Delta H^{\ddagger}$ for S_1 is 26.8 kcal/mol (compare with 56.8 kcal/mol for the suprafacial shift, vide supra).[15] The complete energy profiles for the planar shift are outlined in Figure 9.

Instead of a suprafacial shift, which is highly unfavorable, relaxation of the double bond results in an orthogonal geometry accompanied by charge separation. From this point on the energy surface a radiationless transition to the S_0 surface is possible, resulting in the starting material. For the strongly competitive photochemical [1,3]-OH shift the energy barrier is 26.8 kcal/mol. However, the relative maximum on the S_1 surface is still 12.2 kcal/mol below the energy of the initial vertical excited molecule. A highly symmetrical transition state then results with only a small energy gap of 9.8 kcal/mol between S_1 and S_0.

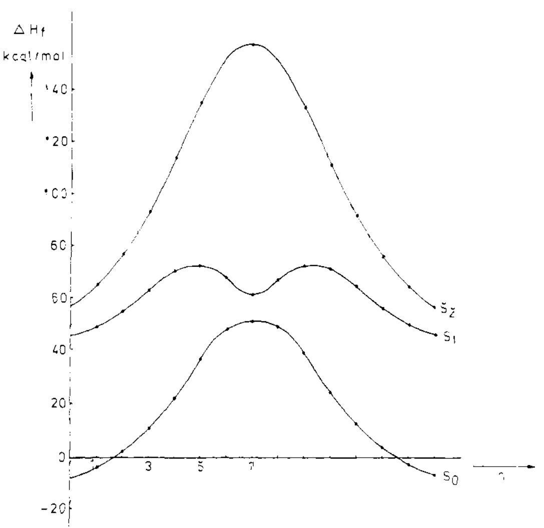

Figure 8. Enthalpy of formation (ΔH_f) vs. the arbitrary reaction coordinate (n)[12] of the planar [1,3]-OH shift in 2-propen-1-ol starting from a 90°-twisted geometry for S_0, S_1, and S_2.

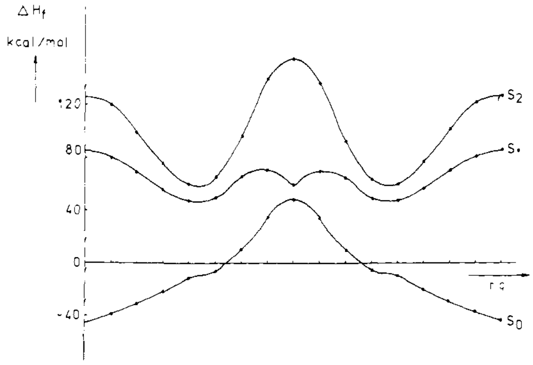

Figure 9. Enthalpy of formation (ΔH_f) vs. the reaction coordinate (r.c.) of a planar [1,3]-OH shift in 2-propen-1-ol for S_0, S_1, and S_2.

For the suprafacial shift the corresponding energy difference amounts to 32.7 kcal/mol. Since this energy gap appears in the denominator of the expression for the coupling between two electronic states,[16] the $S_1 - S_0$ transition probability will be much greater for the planar shift than for the suprafacial shift. *Evidently both the height of the energy barrier and the energy gap between S_1 and S_0 favor the planar mechanism above the suprafacial shift predicted by orbital symmetry.* From these calculations it may be concluded that the substantial gain in energy caused by the geometrical relaxation of the double bond determines the course of the reaction rather than orbital symmetry considerations. It is to be expected that this model description may be of general value in alkene photochemistry.

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[14] For the transition state a C_s symmetry was chosen rather than a C_{2v} symmetry since it lowered the energy of the configurations by 6.4 kcal/mol for S_0, 3.0 kcal/mol for S_1, and 0.1 kcal/mol for S_2.

[15] It may be of interest that for S_0 also a considerable reduction of $\Delta H^{\ddagger}$ is calculated. $\Delta H^{\ddagger}$ is 112.5 kcal/mol for the suprafacial shift and 95.8 kcal/mol for the planar shift.

[16] The probability for the radiationless transformation from S_1 to S_0 is determined by the coupling between the S_1 and S_0 potential energy surfaces. The electronic coupling element is given by:

$$C_{10}(Q) = \frac{-\sum_k \langle \phi_1(q,Q_k)|\delta U/\delta Q_k|\phi_0(q,Q_k)\rangle_q \cdot \delta/\delta Q_k}{E_0(Q) - E_1(Q)}$$

The summation is over the normal coordinates k while $\phi_0(q,Q_k)$ and $\phi_1(q,Q_k)$ are the electronic wave functions of the ground and first excited state. The subscripts q and Q denote the electron and nuclear coordinates, while $E_0(Q)$ and $E_1(Q)$ represent the potential energy of S_0 and S_1. (Kemper, M. J. H.; van Dijk, J. M. F.; Buck, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 784.)