Tetrahedron Vol. 35, pp. 397–407
© Pergamon Press Ltd., 1979. Printed in Great Britain

A QUANTITATIVE STUDY ON THE STEREOSELECTIVITY OF SIGMATROPIC SHIFT REACTIONS IN ACYCLIC SYSTEMS[1]

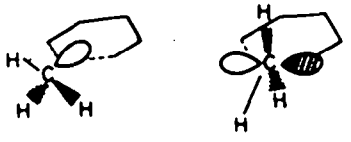
W. A. M. CASTENMILLER*† and H. M. BUCK
Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

(*Received in UK 28 March 1978*)

Abstract—The semiempirical MINDO/3 method has been used to study sigmatropic [1,3] shifts in propene, [1,5] shifts in pentadiene and [1,7] shifts in heptatriene, occurring in the suprafacial and antarafacial way. Hydrogen, fluorine and methyl (with retention or inversion of configuration) were taken as the shifting groups. For the [1,3] shifts some STO-3G and 4-31G calculations have also been performed. Good correspondence has been obtained with the stereoselectivity predictions of the Woodward–Hoffmann theory. The activation energy for the allowed reactions is 8–21 kcal/mol lower than the value for the forbidden modes. The shift of a F atom proceeds via an inversion-type mechanism.

The stereochemistry of sigmatropic shift reactions in unsaturated hydrocarbon systems can be predicted in a qualitative way using the principle of Conservation of Orbital Symmetry.[2] The reactions can occur in two distinct stereochemical modes: in a suprafacial way, when the migrating group remains on the same side of the plane of the π-electron system (at left), or in an antarafacial way, when the shifting group moves to the other side of the plane (at right).

A sigmatropic shift of an sp^3-hybridized group like CH_3 can occur with either retention (at left) or inversion (at right) of configuration of the tetragonal atom.



It is imperative that all these reactions occur in an uncatalysed concerted process in which the bond-breaking and bond-formation are taking place simultaneously, and not in a two-step pathway via an ionic or biradical intermediate. Several reviews on sigmatropic reactions have been published.[2-5]

The transition state (TS) of a sigmatropic reaction can be characterized by the presence of an element of symmetry. For a suprafacial TS this is the mirror plane through the shifting group and the middle of the conjugated carbon chain, which is perpendicular to the chain (C_s symmetry). In an antarafacial TS a two-fold rotational axis is present through the shifting group and the centre of the carbon system (C_2 symmetry).

From the theory of Woodward and Hoffmann[2] the following selection rules can be derived: the thermal suprafacial [1,5] hydrogen shift reaction is allowed, while the antarafacial shift is forbidden. The allowed [1,3] and [1,7] shifts occur in the antarafacial way. The stereoselectivity of methyl shifts occurring with retention of configuration is similar to that of a hydrogen shift, while the reactions with inversion of configuration show the opposite stereochemistry because of the introduction of a negative overlap in the cyclic conjugated transition state.

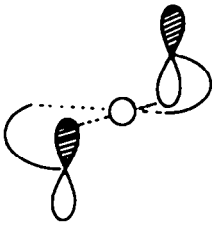
So far, only a few quantitative results have been published from Molecular Orbital calculations on sigmatropic reactions in linear alkenes. Some MINDO/CI calculations including geometry optimizations have been performed[6] on the suprafacial [1,3] H shift in propene (activation energy 49.2 kcal/mol) and on the suprafacial and antarafacial [1,5] H shifts in 1,3-pentadiene (activation energies 28.3 and 37.0 kcal/mol, respectively). Similar MINDO/2 calculations without CI were reported to give unsatisfactory results.[7]

Two papers have appeared with results from calculations on the suprafacial [1,3] shifts of a fluorine substituent[8] and of a methyl group with retention of configuration[9] in propene. The INDO and STO-4G methods have been employed, but no geometry optimization has been included. For the allyl fragment a planar geometry was assumed and the shifting group was situated in a parallel plane at a fixed distance from the allyl fragment. No reaction energies have been reported. A similar model has been used in INDO/CI calculations on the suprafacial methyl and chlorine [1,3] shifts in propene.[10]

In the qualitative model of Woodward and Hoffmann and also in the quantitative studies[6-10] only the π orbitals of the alkene system are being taken into account. Usually the interaction between only one orbital of the shifting group with these π orbitals is being studied to predict the stereoselectivity of the reactions. Some crude geometrical assumptions are being made about suprafacial and antarafacial transition states or about retention and inversion of configuration. No serious attention was given to the question how the shifting group is bound to the terminal atoms in the TS. The geometrical arrangement at the terminal C atoms has not been considered. With one (ill-documented) exception,[6] only a rather vague suggestion has been made on the possible occurrence of antarafacial shifts in linear sys-

†Present address: Unilever Research Laboratory, Vlaardingen, The Netherlands.

tems. Usually a Möbius-type arrangement of the carbon chain is suggested.



The theoretical work reported so far is not in line with the wealth of experimental data available.

Computational model. In this study we have undertaken a systematic quantitative investigation of sigmatropic reactions in order to obtain a consistent picture for a large series of [1,j] shifts. MO calculations have been performed for the hydrogen, methyl and fluorine shifts in a series of hydrocarbon systems. The semiempirical MINDO/3 method[11] has been used throughout. This method has been selected because it has given good results in the predictions of heats of formation, geometry data, vibration frequencies, etc. for a large series of molecules, and because it also has given good predictions on the activation energies for a series of model reactions.

Moreover, the MINDO/3 computer program[12] contains a very efficient geometry optimization procedure using the gradients of the energy with respect to all the coordinates to locate a stationary point on the potential energy hypersurface. Some reviews have been given on the results obtained from the MINDO/3 method.[1,13,14] The results obtained for the H and F shifts in propene have been supported by performing STO-3G[15] and 4-31G[16] *ab initio* calculations using the GAUSSIAN70 computer program.[17]

Our purpose was to obtain uniformly consistent quantitative results for the shifts of various substituents by using the same calculational method including geometry optimization throughout. The results of the calculations are used to test the adequacy of the qualitative model that has been given to explain the stereoselectivity of these reactions. It was also investigated if reliable quantitative predictions could be obtained from semiempirical and *ab initio* methods. The reactions that have been studied are the H, Me and F shifts in linear conjugated systems: [1,3] shifts in 3-substituted propene, [1,5] shifts in 5-substituted (Z)-1,3-pentadiene and [1,7] shifts in 7-substituted (Z,Z)-1,3,5-heptatriene. Both suprafacial and antarafacial reactions have been studied, and methyl shifts occurring both with retention and inversion of configuration on the shifting Me carbon atom have been taken into account.

For all these reactions we have studied the ground states and transition states on the potential energy hypersurface. A geometry optimization study generally leads to a stationary point on the surface, i.e. a point where the gradient of the energy with respect to all the coordinates equals zero. To decide upon the nature of the stationary point it is necessary to evaluate the force constants in this point.[18] When all eigenvalues of the force constant matrix are positive, the stationary point is a local or global minimum. When there is just one negative eigenvalue, we are dealing with a saddlepoint on the surface representing a transition state (TS). When there are two or more negative eigenvalues, we are dealing with an energy maximum. In this study, however, we have not evaluated the force constants.

The theory of Woodward and Hoffmann[2] deals with reactions where orbital symmetry is preserved. For sigmatropic reactions this implies the presence of a symmetry element in the TS, either a mirror plane or a twofold rotational axis. Then it is possible to locate such a transition state on the energy surface from a geometry optimization study within the appropriate symmetry point group. The minimum within this symmetry subspace then is a transition state on the overall surface.[18] We have not determined explicitly if all the symmetric minima found are genuine transition states by evaluating the force constant matrix. When the reaction would take place over an asymmetric TS instead of a symmetric stationary point, this would imply that stereoselectivity is lost during the reaction. An asymmetric TS could eventually occur in the avoided ("forbidden") reaction. Because we are studying the stereochemistry in the reactions based on the Woodward–Hoffmann theory, we may assume the reactions to proceed via a symmetrical transition state.

It sometimes occurs that, in the search for a C_2 energy minimum (for an antarafacial reaction), for instance, the minimum structure is found to have in fact even C_{2v} symmetry. Starting the geometry optimization within the C_s subspace from this C_{2v} structure then could lead to a lower C_s minimum (the TS for the suprafacial reaction). When this feature is observed, we can conclude that there is no genuine TS for the antarafacial reaction. The C_{2v} structure is a stationary point with more than one negative eigenvalue of the force constant matrix, not a transition state. This situation is found to exist for some of the model reactions studied (*vide infra*).

In this investigation we have only studied the reactants and products (ground states) and the symmetrical transition states. We have not performed any calculations on the complete reaction paths. By the choice of the transition state model we have implicitly chosen the substituent which is the shifting group and we have not made any direct comparison between the migratory aptitudes of two different geminal substituents.

Unless indicated otherwise, the following general assumptions have been made in the geometry optimization studies:

(a) For a suprafacial transition state C_s symmetry was assumed and for an antarafacial TS C_2 symmetry. No attention was paid to asymmetrical reaction paths for forbidden reactions.

(b) Local C_{2v} symmetry was assumed for a methyl group in the TS of a reaction with inversion of configuration, and local C_s symmetry for a reaction with retention of configuration. This corresponds to a "trigonal-bipyramidal" or a "tetrahedral" configuration, respectively.

(c) Local C_{2v} symmetry was assumed for sp-hybridized CH groups and for CH_2 groups in ground state molecules or in an sp^3 hybridization.

(d) Local C_s symmetry was assumed for CH_2 groups in the transition states of the alkene systems.

(e) C–H bond lengths were set equal to 1.10 Å (1.08 Å in *ab initio* calculations). This assumption was based on the results from geometry optimizations reported in the literature.

It is expected that all the assumptions concerning the geometry of the hydrogen atoms only have a small effect on the total heats of formation of the molecules studied.

The heats of formation and the energy differences given in this work are always reported in kcal/mol, where

1 kcal/mol = 4.18400 × 10^3 J/mol. Interatomic distances are given in Å (1 Å = 10^{-10} m), angles in degrees. Dihedral angles are reported using the notation A-B-C-D for the dihedral angle of atom A rotated clockwise around the vector B→C out of the plane (B, C, D): the angle is zero when A and D are at same side of B–C. Difference charge densities are corrected for the number of electrons in the valence state of the free atom (a positive number indicates a positively charged atom).

RESULTS AND DISCUSSION

Ground states of the alkene systems. For the MINDO/3 calculations on the ground states of linear alkenes substituted with a group X=H, Me or F we have taken the planar all-*cis* conformation of the carbon chain which can be assumed to form the initial conformation for the sigmatropic reaction. The C—X bond was situated perpendicular on the plane of the carbon chain to avoid repulsion effects from the terminal vinyl group. This conformation is intermediate between the *syn* and *gauche* rotational isomers. For systems with X=H and for 1-butene the *syn* conformation was assumed to be the starting point for the reaction, because of the diminished repulsion between the terminal atoms. It should be stressed that the lowest energy all-*trans* conformation was not selected to represent the ground state of the alkenes in these reactions. All parameters with respect to the carbon skeleton have been optimized, except for 4 parameters in heptatriene (taken from pentadiene) and 5 parameters in the substituted heptatrienes (taken from the parent heptatriene).

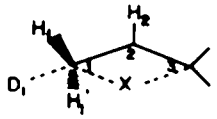
The C–C distances in the carbon chain have values of about 1.350 Å for double bonds, 1.330 Å for terminal vinyl bonds and 1.460 Å for $C(sp^2)$–$C(sp^2)$ single bonds. The values for the $C(sp^2)$–CH_2X bond lengths are 1.480, 1.465 and 1.500 Å for X=H, F and Me, respectively, while the C–X bond lengths are 1.517 Å for X=Me and 1.383 Å for X=F. A value of 111.3° is found for the F–C–C angle. For the vinyl methylene group the H–C–C angle was always found to be very close to 124°, the other sp^2 hydrogen atoms are situated near the appropriate bisector. All these data are in good agreement with MINDO/3 results in the literature.[19,20]

As expected, the only notable deviation from standard data is seen in the carbon skeleton angles as a direct consequence of the assumed planar all-*cis* conformations. The angle of 131.9° in propene (3.0° larger than the reported MINDO/3 value[19]) increases to 136.8° in 1-butene upon introduction of the *syn* Me group. The average angle in the pentadiene systems equals 135.3° and in the heptatriene molecules the average value is 137.0° for the two outer angles and 142.5° for the three inner angles. The heptatriene angles are too large as a result of the geometry assumptions. It is found that the angles in 1,3-hexadiene with the Me group in the *syn* conformation are about 5° larger than in the perpendicular arrangement, leading to a rise in energy of 7.1 kcal/mol. Similarly, the heat of formation of *syn*-1-butene is 5.6 kcal/mol larger than the reported MINDO/3 value for the *anti*-isomer.[19]

These features are caused by the increased nonbonded repulsions in the planar all-*cis* models. However, the discrepancies are small compared to the activation energies found for the sigmatropic reactions, as will be seen below. One could argue that the carbon skeleton angles in heptatriene could be reduced by allowing deviations from planarity in the carbon chain. This would certainly result in lower heats of formation; however, this extension of the model has not been considered.

Transition state geometries. The most important MINDO/3 geometry parameters for the transition states are given in Tables 1–3, together with the numbering system of the atoms. D_1 is a dummy atom on the bisector of the H_1–C_1–H_1' angle. Geometry optimization was complete (including the Me groups) within the C_s or C_2

Table 1. MINDO/3 geometry of transition states for sigmatropic [1,3] shifts of a group X in propene, where X=H, CH_3, F



	H		CH_3.[a]		F	
	S	A	R	I	S	A[b]
C_1–C_3	2.561	2.128	1.689	2.324	2.323	2.224
C_1–C_2	1.409	1.403	1.473	1.452	1.411	1.408
X–C_1	1.714	1.376	1.715	1.657	1.464	1.493
C_1–C_2–C_3	130.8	98.6	70.0	106.4	110.8	104.4
C_1–X–C_3	96.7	101.2	77.9	89.0	105.0	96.4
X–C_3–C_1–C_2	78.7	180	173.1	160.0	129.3	180
D_1–C_1–C_2	172.4	158.9	143.5	143.2	155.7	163.2
D_1–C_1–C_2–C_3	91.4	149.3	177.9	159.0	135.3	180.0
a[c]	-3.6	0	-27.9	43.0	30.9	0

[a] See text

[b] Stationary point, see text

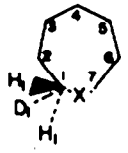
[c] H_2 out of plane bending angle, see text

Table 2. MINDO/3 geometry of transition states for sigmatropic [1,5] shifts of a group X in 1,3-pentadiene, where X=H, CH_3, F

	H		CH_3,S		CH_3,A		F	
	S	A[a]	R	I[a]	R	I	S	A
C_1-C_5	2.525	2.618	2.462	2.896	2.716	2.843	2.758	2.686
C_1-C_2	1.413	1.452	1.437	1.466	1.456	1.458	1.415	1.408
C_2-C_3	1.402	1.397	1.398	1.398	1.393	1.399	1.400	1.404
C_1-C_2-C_3	121.4	123.8	121.5	124.5	122.6	123.4	121.5	123.2
C_2-C_3-C_4	119.6	120.1	118.6	126.6	123.8	122.8	127.0	119.0
C_1-C_2-C_3-C_4	15.0	0	9.2	0	8.0	16.9	6.5	27.2
X-C_1	1.365	1.354	1.701	1.628	1.605	1.639	1.452	1.459
C_1-X-C_5	135.4	150.5	92.7	125.7	115.6	120.3	145.1	164.6
D_1-C_1-C_2	147.0	123.6	132.2	134.9	130.6	128.3	158.0	151.3
D_1-C_1-C_2-C_3	138.6	180	133.7	180	162.8	146.1	145.7	123.8
X-C_5-C_1-C_2	101.2	180	128.4	180	180	180	172.9	180

[a] Stationary point, see text

Table 3. MINDO/3 geometry of transition states for sigmatropic [1,7] shifts of a group X in 1,3,5-heptatriene, where X=H, CH_3, F



	H		CH_3,S		CH_3,A		F	
	S[a]	A	R	I	R	I[b]	S	A
C_1-C_2	1.432	1.409	1.459	1.451	1.438	1.460	1.400	1.406
C_2-C_3	1.382	1.397	1.382	1.385	1.391	1.379	1.398	1.397
C_3-C_4	1.406	1.403	1.406	1.408	1.404	1.409	1.399	1.405
C_1-C_2-C_3	134.1	130.4	132.0	132.8	130.8	136.5	134.2	130.6
C_2-C_3-C_4	136.2	132.7	137.4	137.0	132.4	139.4	134.1	135.3
C_3-C_4-C_5	132.6	132.1	133.6	137.2	128.7	137.2	131.9	131.4
C_1-C_2-C_3-C_4	0	13.5	11.2	15.6	13.6	0	31.0	13.6
C_2-C_3-C_4-C_5	0	11.8	11.6	13.4	14.0	0	16.6	13.8
X-C_1	1.250	1.329	1.611	1.649	1.682	1.618	1.451	1.450
C_1-X-C_7	184.4	158.3	110.8	124.6	110.6	151.9	144.6	163.3
D_1-C_1-C_2	145.3	145.3	128.1	123.6	126.9	129.5	146.7	152.7
D_1-C_1-C_2-C_3	180	113.5	125.0	127.4	92.4	180	116.8	119.8
X-C_7-C_1-C_2	0	180	116.6	122.2	180	180	90.5	180

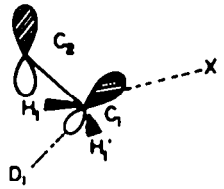
[a] Stationary point, see text

[b] See text

symmetry. In the Tables and text, S and A denote suprafacial and antarafacial shifts, R and I indicate retention and inversion of configuration, respectively.

A full geometry search of the potential energy surface of pentadiene without any restrictions leads to a stationary point for the hydrogen A shift. A similar situation is found for the Me S I shift in pentadiene and the hydrogen S shift in heptatriene. The geometries have been included in the Tables for comparison. The important consequences will be discussed below. We have also calculated the C_{2v} symmetrical states for most systems, the data are omitted from the Tables.

For the transition states of the H and Me shifts in pentadiene and heptatriene, it is found that the C–C distances all have values typical for unsaturated systems. The C_1–C_2 distance is somewhat larger because of the vicinity of the group X. The C_2–C_3 and C_5–C_4 distances in the heptatriene systems are almost equal indicating complete delocalization of the π electrons. The heptatriene dihedral angles are all found to be rather similar, except those in the planar TS found for the Me A I shift (*vide infra*). The angle D_1–C_1–C_2 can vary between 128° (sp^3 hybridization on C_1) and 180° (complete sp^2 hybri-



dization). For the hydrogen shifts an intermediate value of about 146° is found, while for a methyl shift the CH_2 group is almost fully sp^3 hybridized. The dihedral angle D_1–C_1–C_2–C_3 gives an indication for the extent of π-orbital conjugation between C_1 and C_2, its value varies between 90° for maximal overlap and 180° for zero overlap and complete sp^3 hybridization on C_1. It is found that for the predicted allowed transition states there exists much more π-orbital conjugation than for the forbidden TS. For the methyl S shift in heptatriene this dihedral angle has a value of 126° for both R and I, because the developing orbital on C_1 is directed towards the Me carbon atom above the plane (C_1, C_2, C_6, C_7). The X–C_1 distance is somewhat larger than a normal bonding distance: 1.35 Å for X=H and 1.64 Å for X=Me. The MINDO/CI method predicts the H_x–C_1 distance in pentadiene to be 1.297 and 1.267 Å for the S and A TS, respectively.[6] For Me I shifts the Me group is situated much closer to the carbon chain as compared to R states, leading to a larger overlap of its p orbital with the terminal atoms. Simultaneously the distance between the terminal atoms is found to be larger, resulting in decreased nonbonded repulsions. For methyl R shifts the p orbital is directed towards the middle between the terminal atoms.

The hydrogen A shifts in propene can be characterized by the small C_1–C_2–C_3 angle of only 99°. The methylene groups are situated in a position so as to give a rather large overlap of the p-type orbital on C_1 with the shifting hydrogen. Of course a genuine Möbius-type arrangement cannot be reached in a propene system for steric reasons. In the TS for the hydrogen S shift the H atom is situated above the 3-carbon plane having an overlap with C_2 as well. In the suprafacial TS in propene in H_2 out-of-plane bending angle α has also been optimized: α is positive when H_2 is on the same side of the plane as the shifting group X. For the H S shift H_2 is situated slightly below the plane: $\alpha = -3.6°$. It should be noted that the inclusion of this parameter in the geometry optimization is highly important. If α is assumed to be zero the energy minimum found has a heat of formation of 25 kcal/mol above the TS, even though the deviation in α is very small. The C_3H_5 fragment is almost planar. The H_x–C_1 distance of 1.714 Å is notably larger than the value of 1.593 Å found from the MINDO/CI method.[6]

For the Me shifts in propene no TS with a reasonably adequate geometry is found. With inversion of configuration the A state leads over a planar stationary point to the S minimum. In the minimum, however, α is found to be 43°, while the C_1–X–C_3 angle is only 89°. Similarly, the Me R shift leads to a minimum resembling a homocyclopropane system with a C_1–C_2–C_3 angle of only 70°. We conclude that no transition state can be found, because the system collapses to some 4-membered puckered ring system which probably is found as a stationary point only because we have assumed three H atoms to remain bonded at C_x. The geometries found are included in Table 1 for comparison. This complication was not encountered in earlier studies because of the crude geometry models that have been used.[8–10]

Most geometry parameters for the F shift transition states have values similar to those found for the H and Me shifts. The average F–C_1 distance equals 1.455 Å, somewhat larger than the normal MINDO/3 bond length of 1.383 Å.[20]

The angle D_1–C_1–C_2 in the fluorine systems is notably larger than in the hydrocarbon systems, the average value is 153°. The TS for the H and F shifts in heptatriene are almost equal. In the pentadiene S TS the F–C_5–C_1–C_2 dihedral angle has a large value of 173°. In the propene system the equivalent dihedral angle equals 129°, notably differing from the values of 90° assumed by Epiotis[8,9] or 106° found in INDO calculations.[10] However, in the heptatriene TS the value is 90°. In the fluorine S TS in propene the carbon skeleton angle is rather small and α equals 31°. The A shift leads to a stationary point, not a TS.

Ab initio *calculations*. Some sigmatropic reactions have been studied using the STO-3G and 4-31G *ab initio* methods. The ground state of propene has also been calculated by Radom *et al.*[21] The C–H distances found have values of 1.081, 1.085 and 1.088 Å, very close to the value of 1.08 Å assumed throughout this work. For 3-fluoropropene these propene parameters[21] have been taken with a C–F distance of 1.36 Å. This structure is in very good agreement with the experimental data for the *syn* isomer.[22] The perpendicular arrangement has been estimated to be 2.2 kcal/mol higher in energy than the *syn* minimum from *ab initio* calculations.[23] An STO-3G geometry optimization was carried out for the S and A transition states of the hydrogen and fluorine [1,3] shifts in propene by successive optimization of the geometry parameters (8 for a suprafacial TS and 6 for an antarafacial TS). The resulting geometries are given in Table 4. The STO-3G parameters have been used as input to perform one single 4-31G calculation. For the C–F distance in 3-fluoropropene the 4-31G optimum value of 1.412 Å for MeF was taken.[24] More extensive *ab initio* calculations have not been performed because of the amount of computer time necessary.

The STO-3G geometry of the hydrogen S TS in propene is found to be strikingly similar to the MINDO/3

Table 4. STO-3G geometries for transition states of sigmatropic [1,3] shifts of a group X in propene, where X=H, F

	H		F	
	S	A	S	A
C_1-C_3	2.549	2.187	2.122	2.165
C_1-C_2	1.421	1.418	1.397	1.468
X-C_1	1.738	1.393	1.674	1.510
C_1-C_2-C_3	127.6	100.9	98.9	95.0
C_1-X-C_3	94.3	103.4	78.7	91.6
X-C_3-C_1-C_2	72.8	180	143.8	180
D_1-C_1-C_2	169.1	147.7	159.5	158.6
D_1-C_1-C_2-C_3	90.9	135.0	145.2	180[a]
a[b]	-5.0	0	31.5	0
H_1-C_1-D_1	59.5	55.2	53.6[a]	53.2

[a] Value taken from the MINDO/3 geometry
[b] H_2 out of plane bending angle

result. The same resemblance is seen for the A TS, where only the D_1 angles have slightly different values. The fluorine A shift is assumed to proceed via a stationary point as was found with MINDO/3. The geometries from both methods are in fairly good agreement. Only for the fluorine S TS some notable discrepancies are seen. STO-3G calculations predict a large F–C_1 distance of 1.674 Å and a dihedral angle F–C_3–C_1–C_2 of 143.8°. The overall correspondence for geometry parameters between the STO-3G and MINDO/3 methods is rather satisfying for X=H, but less agreement is found for X=F.

Activation energies. The heats of formation calculated from the MINDO/3 method for the ground states (GS) and TS for the sigmatropic reactions are given in Table 5. Values not corresponding to a genuine TS are given between parentheses. From the geometry and energy data we conclude that some of the transition states are only very shallow minima on the potential energy surface. For the Me A R shift in pentadiene, some dihedral angles in the TS differ substantially from those in the planar stationary point, but the heat of formation found is only 0.5 kcal/mol lower. In the TS for the fluorine S shift in pentadiene both the F atom and the C_3–H_3 fragment deviate only little from the plane of the remaining carbon atoms. This probably is only a shallow minimum. For the Me I shift in heptatriene we find equal energies for the S and A TS, the difference being only 0.06 kcal/mol, but the geometries differ considerably because the A TS is planar, while the S system is bent in a boat-type conformation. Since the antarafacial TS is the lower energy state, it cannot be considered to be a "stationary point". Apparently, in the C_s subspace there is a shallow maximum between the planar C_{2v} geometry and the suprafacial TS, which is a local energy minimum.

From the data in Table 5 and from the *ab initio* results the activation energies for the sigmatropic shifts are obtained. Results are collected in Table 6 for those systems for which a real transition state has been found. The selective character of the reactions can be demonstrated using the differences in activation energies for a reaction occurring in the allowed and forbidden modes predicted from qualitative theories. In Table 7 the MINDO/3 energy differences are given between the transition states for the suprafacial and antarafacial modes, and between the TS of a methyl shift occurring with retention and inversion of configuration. STO-3G energy differences are included in Table 6.

From Table 6 it is concluded that MINDO/3 calculations generally predict high activation energies for

Table 5. MINDO/3 heats of formation for sigmatropic [1,j] shifts of the group X=H, CH_3, F. Values between parentheses do not correspond to a real transition state, see text.

		H	F	CH_3,R	CH_3,I
Propene [1,3]					
	GS	7.3	-40.1	6.6	
	TS S	97.5	-59.7	(100.9)	(112.4)
	TS A	83.4	(- 5.8)	-	-
Pentadiene [1,5]					
	GS	22.6	-25.2	19.6	
	TS S	70.7	-12.6	102.9	(123.3)
	TS A	(105.0)	-51.6	123.8	115.5
Heptatriene [1,7]					
	GS	42.9	- 5.0	40.4	
	TS S	(101.9)	-38.4	130.2	129.1
	TS A	68.5	-15.3	117.1	129.0

Table 6. Activation energies for sigmatropic [1,j] shifts

MINDO/3

	H		F		CH_3,R		CH_3,I	
	S	A	S	A	S	A	S	A
Propene [1,3]	90.2	76.1	-19.6	-	-	-	-	-
Pentadiene [1,5]	48.1	-	12.6	-26.4	83.3	104.2	-	95.9
Heptatriene [1,7]	-	25.6	-33.4	-10.3	89.8	76.7	88.7	88.6

Ab initio

Propene [1,3]

	H			F		
	S	A	Δ(S-A)	S	A	Δ(A-S)
STO-3G	159.0	134.8	24.2	112.9	129.2	16.3
4-31G	120.1	112.4	7.7	94.6	138.6	44.0

Table 7. Differences in MINDO/3 activation energies between forbidden and allowed sigmatropic shifts

Suprafacial and antarafacial shifts

	H	F	CH_3	
			R	I
Propene [1,3]	14.1	-	-	-
Pentadiene [1,5]	-	38.9	20.9	-
Heptatriene [1,7]	-	23.0	13.1	-0.1

Methyl shifts with retention and inversion of configuration

	S	A
Pentadiene [1,5]	-	8.3
Heptatriene [1,7]	1.1	11.9

hydrogen and methyl shifts. [1,3] H shifts in propene are not reported to occur.[3] It has been found experimentally that the activation energy for the [1,3] H shift in 2-butene should be higher than 63 kcal/mol, which is the activation energy for the observed *cis-trans* isomerization.[4] The MINDO/3 value of 90.2 kcal/mol thus may constitute an overestimate of maximally 27 kcal/mol. It also is 41.0 kcal/mol higher than the result reported from MINDO/CI calculations.[6] The same method predicts the activation energy for the hydrogen S shift in pentadiene to be 19.8 kcal/mol lower than the MINDO/3 result. From the sparse results reported from MINDO/CI it is not clear whether the A TS is a real transition state (as stated by the authors) or a stationary point (if the geometry would be planar), since insufficient geometry data are available. The MINDO/CI heat of formation for this antarafacial TS is 45.6 kcal/mol lower than the MINDO/3 result.[6] Experimentally an activation energy of 35.4 kcal/mol is found for the hydrogen S shift in pentadiene,[3] while values of 31–36 kcal/mol are reported for shifts in other open diene systems.[3,5] The MINDO/3 result apparently is about 13 kcal/mol too high. A low activation energy of 26 kcal/mol is found for the antarafacial [1,7] H shift in heptatriene, in agreement with experimental values ranging from 15 to 26 kcal/mol.[3]

Resulting activation energies for methyl shifts are all higher than 75 kcal/mol. Alkyl shifts in pentadiene and heptatriene systems are not reported to occur;[3,25] either fragmentation reactions or the much faster hydrogen shifts are found to be favoured. This is in accordance with the high activation energies calculated, which are of the same order as the normal C–C bond energies of 80–85 kcal/mol.[25] It should be noted that the geometry optimization always leads to a bonding transition state. No indication of a dissociative process has been obtained. The high heats of formation found from MINDO/3 could probably be related to the rather small interatomic distances between C_1 and the shifting group as predicted from this method.

For the F shifts the MINDO/3 method remarkably predicts many transition states to have a lower energy than the corresponding ground states. Clearly the parameter set for F in the MINDO/3 program is insufficient. In the set of molecules used to derive these parameters some alkenes have been included with the F atom(s) substituted in α position, not in β position.[20] In another study it has been mentioned that F has the propensity to be bicoordinated in MINDO/3 calculations.[26] This is in full agreement with our findings, which predict the transition states with bicoordinated F to be more favourable than the ground states. However, MINDO/3 results even more intriguingly predict the three "forbidden" transition states to be much lower than the "allowed" modes, the A shift in propene leading to a stationary point. This result will be discussed below.

The predicted activation energies for the H shifts in propene from both *ab initio* methods are much higher than the MINDO/3 values. Since no experimental data are available (*vide supra*), we cannot say which of the

three methods gives more reliable results. For the F shifts also very high activation energies have been found from the *ab initio* methods. It should be noted that the selectivity predictions from the semiempirical and *ab initio* methods are in good agreement, the differences in activation energy all being of the same order. The *ab initio* methods also predict the F [1,3] shift to occur in the suprafacial mode.

For the H and Me shifts the MINDO/3 method always correctly predicts the allowed modes to have the lower activation energies as compared to the forbidden modes. Those systems for which a stationary point has been found (the A [1,5] H shift in pentadiene, the Me S I shift in pentadiene and the S [1,7] H shift in heptatriene) are all predicted to correspond to a forbidden reaction. The shallow energy minimum found for the Me A R shift in pentadiene also corresponds to a forbidden mode. The Me shifts in propene are not considered here, since the calculations lead to structures which cannot represent a genuine TS for a sigmatropic shift, as has been noted before.

For those H or Me shifts where two real transition states can be compared, we see that the MINDO/3 energy differences determining the selectivity in Table 7 all fall in a remarkably narrow range of 8–21 kcal/mol. All stationary points found are at least 8 kcal/mol higher in energy than the TS of the corresponding allowed reactions. Experimentally a lower limit of 8 kcal/mol has been found for the difference between the S and A hydrogen shifts in pentadiene.[27] The only anomaly in Table 7 arises from the Me shift in heptatriene. From the small energy differences found with respect to this system no predictions can be made about the stereochemistry. A clear explanation is not available. Although the absolute activation energies found from MINDO/3 are rather high, the method is quite successful in the predictions on stereoselectivity. This might be due to the cancelling of similar errors in the comparison of two systems that have some resemblance to each other. In both transition states that are to be compared the $X\text{–}C_1$ distance might be too small, leading to a high heat of formation. We think that the selectivity predictions are highly significant and that this method is to a certain extent a useful tool for the study of sigmatropic reactions in linear systems. Similar considerations can be made with respect to the *ab initio* methods. Good correspondence with the semiempirical results was obtained.

Electronic configurations. In Table 8 the difference charge densities are given for the shifting group in the transition state. Values for the stationary points are included for comparison. It is clear that for the allowed modes of the hydrogen and methyl shifts the difference charge density on X always is more negative than for the forbidden modes. Because of the concerted nature of the allowed reactions two partial bonds are connecting the shifting group X: one bond being broken and the other bond being formed. In the allowed reactions these bonds will have more bonding character than in the forbidden modes, where the bonds should be more anti-bonding. This could probably result in a higher electron density on X in the allowed modes.

De Dobbelaere has discussed the concept of aromaticity for the TS of sigmatropic shifts in cyclic systems.[28] The aromaticity model predicts the allowed TS in cyclopentadiene to have 6π electrons in a cyclic conjugated system and a positively charged group X, while a forbidden mode would lead to 4π electrons in the ring and negative charge on X. From our results on linear systems it is clear that here the allowed reactions are not related to an aromatic transition state. The distances between the terminal carbon atoms are larger than 2.3 Å, so the corresponding overlap integrals are almost zero. In most allowed transition states the group X is more negatively charged than in the forbidden modes. So the aromaticity model does not apply to sigmatropic reactions in linear alkene systems.

In Table 8 are also included the MINDO/3 orbital occupancies for the $2p_y$ orbital of the shifting fluorine atom in the TS. Both lobes of this orbital are directed

Table 8. Difference charge densities on the shifting group X in the TS for sigmatropic shifts, and total orbital occupancies in the fluorine $2p_y$ orbital. Values between parentheses do not correspond to a real transition state

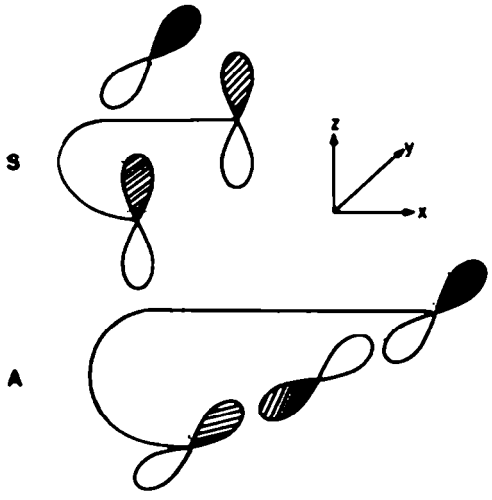
MINDO/3

		Propene	Pentadiene	Heptatriene
H	S	0.218	-0.008	(-0.059)
	A	-0.028	(0.141)	0.000
CH_3,R	S	-	-0.008	0.251
	A	-	0.280	0.001
CH_3,I	S	-	(0.326)	0.079
	A	-	0.058	0.291
F	S	-0.308	-0.336	-0.259
	A	(-0.378)	-0.254	-0.353
F,$2p_y$	S	1.406	1.571	1.397
	A	(1.574)	1.412	1.689

Propene , ab initio

	H		F		
	S	A	GS	TS,S	TS,A
STO-3G	0.217	0.100	-0.154	-0.143	(-0.047)
4-31G	0.336	0.182	-0.455	-0.467	(-0.448)

towards the π lobes of the terminal C atoms as indicated below. The $2p_y$ orbital is antisymmetric with respect to the mirror plane and the twofold rotational axis of the transition states. The $2p_y$ orbital has a large overlap with each of the terminal atoms. The charge in this orbital



clearly parallels the total charge on F. The orbital occupancy of the F 2s orbital is about 1.98, while the $2p_x$ and $2p_z$ orbitals each contain about 1.9 electrons. Apparently, the $2p_y$ orbital is the singly occupied HOMO which determines the behaviour of a shifting fluorine atom, while the 2s, $2p_x$ and $2p_z$ orbitals together can be regarded to constitute the lone pairs. The overlap of the π lobe of the terminal C atoms with the $2p_y$ orbital is much larger than with the $2p_{x,z}$ MO, which is directed towards the centre between the terminal atoms, and which is lying in the x, z plane. From the partial overlap populations given in Table 9 it is also evident that the fluorine $2p_y$ orbital leads to the most effective bonding in the TS for the suprafacial shift in propene.

We conclude that the shift of a F atom proceeds similar to that of a Me group with *inversion* of configuration. The stereochemistry of a F shift is just opposite to that of a H shift.

This mechanism occasionally has been suggested in the literature,[10,29,30] but only a few experiments on halogen shifts are reported.[3] Epiotis assumed the $2p_y$ orbital to contain a fluorine lone pair leading to additional stabilization of the allyl system.[6] He also finds an orbital occupancy of about 1.96 in the F $2p_z$ orbital, which clearly indicates a lone pair. Apparently, his results have been interpreted incorrectly.

From the MINDO/3 calculations it is shown unambiguously that all F sigmatropic shifts proceed with "inversion of configuration". Activation energies calculated from MINDO/3 and the STO-3G and 4-31G *ab initio* methods clearly lead to this conclusion, which is fully supported by the resulting charge densities in the $2p_y$ orbital. Of course for F one cannot really speak of "inversion of configuration". Because of its spherical symmetry the F atom can always obtain the most favourable electronic configuration in the transition state, which leads to the $2p_y$ orbital being involved in the sigmatropic reaction, because it has the largest overlap with the terminal carbon atoms. This conclusion, based on electronic factors, can be extended to all atoms where a p orbital is involved, i.e. all atoms except H. Entirely consistent with this view, the suprafacial [1,3] shifts of alkyl[31] and silyl[25] groups are reported to occur with inversion.

Experimentally, it might be impossible to distinguish between the "retention" and "inversion" modes for a F shift. For every model compound where a shift under "retention" could be proposed, the "inversion" mechanism should always be considered as a serious alternative. When sufficient experimental data on activation energies for F shifts in a large series of molecules should be available, it might be possible to derive a definite conclusion about the reaction mechanism. From a practical point of view it is not really important which mechanism does apply for F.

It should be pointed out that in the calculations on Me shifts the reaction mechanism was imposed by choosing the geometry of the Me group within a certain local symmetry point group, thereby making it possible to calculate the activation energy for both reactions. A similar procedure is impossible for F, because always the most favourable electronic configuration is obtained. When a shifting C atom is substituted with other groups than H, for instance Me or Ph, the inversion mechanism should become more difficult with the increasing bulkiness of the shifting group. Moreover, the larger change in hybridization also disfavours an inversion mechanism. From Table 6 it can be concluded that the activation energies for the allowed Me shifts with retention (83.3 and 76.7 kcal/mol in pentadiene and heptatriene, respectively) are about 12 kcal/mol lower than the values for the corresponding allowed shifts with inversion (95.9 and 88.7 kcal/mol, respectively). Apparently, this effect should be contributed to the unfavourable change in hybridization on the shifting Me carbon atom.

From the total charge densities on the shifting F atom in Table 8 no conclusions can be derived about the selectivity of the reactions. Charge differences between the S and A transition states are only small. The MINDO/3 charge on F is somewhat more positive in the allowed transition states. All charges are similar to the values in the ground state (the MINDO/3 method predicts a charge of −0.347 for F in the ground states). Both *ab initio* methods predict widely differing charges for F, probably as a result of the quality of the basis set.

We have also studied the nature of the various Molecular Orbitals in the transition state, especially the

Table 9. Partial overlap populations between the shifting group and the p_z orbitals of the propene carbon atoms in the transition state; data from the STO-3G and 4-31G calculations, respectively

		C_1 ($2p_z$)		C_2 ($2p_z$)	
H	S	0.0348	0.0414	0.2197	0.2167
F ($2p_y$)	S	0.0248	0.0295	0	0
F ($2p_z$)	S	−0.0005	0.0020	0.0008	0.0035
	A	0	−0.0038	−0.0017	−0.0082

Highest Occupied MO's (HOMO's) which determine the stereochemistry of the reactions. From the MINDO/3 results we see that the allowed transition states can be characterized by the schematic orbital pattern given in Fig. 1.

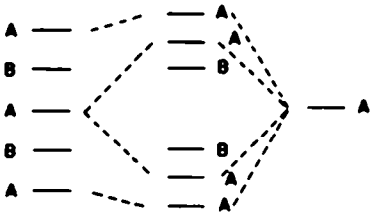


Fig. 1. Molecular orbital diagram for the transition state of allowed sigmatropic shifts in linear alkenes. A and B denote two types of symmetry with respect to the current symmetry element.

At left in the diagram the set of π orbitals of the alkene system is indicated, with alternating symmetry with respect to the crucial symmetry element. At right the determining orbital of the shifting group is indicated, which in an allowed mode has the same symmetry as the (singly occupied) HOMO of the π system. The combination of these two MO's produces two new MO's which in all systems are found to be the second highest occupied and the second lowest virtual MO of the resulting system, as has been noted before by Su[20] and de Dobbelaere.[20] This situation is found to exist in all the allowed modes for both H, Me and F shifts in propene, pentadiene and heptatriene. For fluorine the crucial orbital is seen to be the $2p_y$ orbital, again indicating the "inversion of configuration". For the forbidden modes it is not possible to present a general orbital pattern. In a planar geometry the in-plane orbitals of the shifting group do not combine with the π orbitals, while the terminal C atoms do not participate in the π conjugation.

In the S hydrogen shift in propene, the hydrogen orbital combines with the lowest allyl π orbital. This feature has been described as Subjacent Orbital Control.[22] For the corresponding F shift the orbital diagram is given in Fig. 2. It is clear that the combination of ϕ_2 with $2p_y$ results in a larger splitting of the orbital energy levels than the splitting from the $(\phi_1 + 2p_{x,z})$ combination. A larger splitting is (among other factors) caused by a more effective overlap between the two combining orbitals. The diagram again shows that the F $2p_y$ orbital can be more effective in determining the stereochemistry of the reactions. All MO diagrams from the *ab initio* calculations are in good correspondence with the MINDO/3 results.

From INDO calculations[10] on the suprafacial [1,3] Cl shift in propene an MO diagram was derived similar to Fig. 2. In this case the interactions were studied between a chloride anion and an allyl cation. No difference charge densities were given for the individual chlorine AO's. These results should be considered with caution, since no geometry optimization has been carried out.

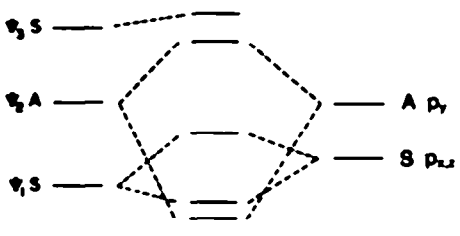


Fig. 2. Molecular orbital diagram for the transition state of the suprafacial [1,3] fluorine shift in propene. S and A denote symmetric and antisymmetric orbitals with respect to the mirror plane.

CONCLUSIONS

The MINDO/3 method is found to be well suited to study the stereoselectivity of sigmatropic reactions. Making use of the *a priori* symmetry of the transition states as predicted from the qualitative theory, the geometry of the transition states can easily be determined. For all the allowed reactions a genuine TS is found, but for some of the forbidden reactions only a secondary stationary point with C_{2v} symmetry results. The MINDO/3 results for propene are supported by the results from *ab initio* calculations. Rather high activation energies have been found from both methods. MINDO/3 activation energies for H shifts are somewhat higher than the experimental values. The MINDO/3 method does not give reliable results for F compounds. F shifts are found to proceed via an inversion-type mechanism, because the $2p_y$ orbital has a much more favourable overlap with the terminal atoms of the alkene system. This result is not influenced by the improvement of the basis set in the *ab initio* calculations or by a better parametrization of the MINDO/3 method. Our calculations give a quantitative support for the predictions of the Woodward–Hoffmann theory. The activation energies for the forbidden reactions are found to be 8–21 kcal/mol higher than the values for the allowed reactions. Methyl shifts with inversion of configuration require an extra activation of 12 kcal/mol as compared to shifts with retention of configuration.

REFERENCES

[1]Part of the thesis of W. A. M. Castenmiller, Eindhoven (1978).
[2]R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Verlag Chemie, Weinheim, Germany (1970).
[3]C. W. Spangler, *Chem. Rev.* **76**, 187 (1976).
[4]J. J. Gajewski, *Mechanisms of Molecular Migrations* (Edited by B. S. Thyagarajan) Vol. 4, p. 1. Wiley, New York (1971).
[5]H. M. Frey and R. Walsh, *Chem. Rev.* **69**, 103 (1969).
[6]R. C. Bingham and M. J. S. Dewar, *Ibid.* **94**, 9107 (1972).
[7]W. W. Schoeller, quoted in Ref. 6.
[8]F. Bernardi, N. D. Epiotis and R. L. Yates, *J. Am. Chem. Soc.* **97**, 1334 (1975).
[9]N. D. Epiotis, R. L. Yates and F. Bernardi, *Ibid.* **97**, 4198 (1975).
[10]T. Minato, S. Inagaki, H. Fujimoto and K. Fukui, *Bull. Chem. Soc. Japan* **50**, 1651 (1977).
[11]R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**, 1285 (1975).
[12]M. J. S. Dewar *et al.*, MINDO/3, Program 279, QCPE, Indiana University, Bloomington, Indiana, U.S.A.
[13]M. J. S. Dewar, *Science* **187**, 1037 (1975); M. J. S. Dewar, *Chem. in Brit.* **11**, 97 (1975); M. J. S. Dewar, *Pure and Appl. Chem.* **44**, 767 (1976); M. J. S. Dewar, *Faraday Discuss. Chem. Soc.* **62**, 197 (1977).
[14]M. C. Flanigan, A. Komornicki and J. W. McIver, Jr., *Modern Theoretical Chemistry*, Vol. 8, (Edited by G. A. Segal) Chap. 1, p. 1. Plenum Press, New York (1977).
[15]W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
[16]R. Ditchfield, W. J. Hehre and J. A. Pople, *Ibid.* **54**, 724 (1971).
[17]W. J. Hehre *et al.*, GAUSSIAN70, Program 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, U.S.A.
[18]J. W. McIver, Jr., *Acc. Chem. Res.* **7**, 72 (1974); R. E. Stanton and J. W. McIver, Jr., *J. Am. Chem. Soc.* **97**, 3632 (1975).
[19]R. C. Bingham, M. J. S. Dewar and D. H. Lo, *Ibid.* **97**, 1294 (1975).

[20]R. C. Bingham, M. J. S. Dewar and D. H. Lo, *Ibid.* 97, 1307 (1975).
[21]L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* 93, 5339 (1971).
[22]E. Hirota, *J. Chem. Phys.* 42, 2071 (1965).
[23]B. Cadioli and U. Pincelli, *J. Chem. Soc.* Faraday II, 68, 991 (1972).
[24]R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* 54, 724 (1971).
[25]J. Slutsky and H. Kwart, *J. Am. Chem. Soc.* 95, 8678 (1973).
[26]W. L. Jorgensen, *Ibid.* 99, 280 (1977).
[27]W. R. Roth, J. König and K. Stein, *Chem. Ber.* 103, 426 (1970).
[28]J. R. de Dobbelaere, J. M. P. van Dijk, J. W. de Haan and H. M. Buck, *J. Am. Chem. Soc.* 99, 392 (1977).
[29]M. J. S. Dewar, *Angew. Chem.* 83, 859 (1971); W. J. Feast and W. E. Preston, *Chem. Commun.* 985 (1974).
[30]C.-C. Su, *J. Am. Chem. Soc.* 93, 5653 (1971).
[31]J. A. Berson and G. L. Nelson, *Ibid.* 89, 5503 (1967); J. A. Berson, *Acc. Chem. Res.* 1, 152 (1968).
[32]J. A. Berson and L. Salem, *J. Am. Chem. Soc.* 94, 8917 (1972); J. A. Berson, *Acc. Chem. Res.* 5, 406 (1972).