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transfer and terminated by reductive elimination.

Experimental Section

The experimental setup has been described in earlier papers.[2] Briefly, Fe$^+$ is generated from Fe(CO)$_5$ by electron impact ionization (100 eV). A VG Instruments ZAB-HF-3F triple-sector mass spectrometer with a B(1)EB(2) configuration was used for the analysis. The machine and its operation have been described elsewhere.[16] In a typical experiment Fe(CO)$_5$ and the nitrile **11** were mixed in a specially designed test tube[17] in an approximate ratio of 2:3. The ions corresponding to RCN/Fe$^+$ having 8-keV kinetic energy are mass selected and focused with B(1)E. Collision gas (He, pressure ca. 5×10^{-6} to 1×10^{-5} Torr) is introduced in the collision chamber located in the third field-free region, and fragment ions are recorded by scanning B(2). In the collision experiment the intensity of the primary ion beam is attenuated to ca. 85%; this corresponds on average to 1.1 collisions.[18] Due to the poor signal-to-noise ratio, signal-averaging techniques were used only in the case of the MI/CA experiment of structure **23** generated from **11**-Fe$^+$ (Scheme IV, and text under heading E); all other spectra were obtained by single scans only.

Compounds **11** and **11a** were synthesized according to Scheme IX by standard laboratory procedures as described in the references given in Scheme IX. For the synthesis of **11c**, the starting *tert*-butyl chloride **29** was replaced by its fully deuteriated isotopomer $(CD_3)_3CCl$, which was synthesized in 82% yield from **29** by either H/D exchange with DCl/D_2O (110° C for 24 h)[19] or reaction of isobutene with DCl/D_2O (room temperature for 24 h). All compounds were fully characterized by spectroscopic methods and purified by various chromatographic means. Full details are reported in ref 17.

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Do Supra–Antara Paths Really Exist for 2 + 2 Cycloaddition Reactions? Analytical Computation of the MC–SCF Hessians for Transition States of C_2H_4 with C_2H_4, Singlet O_2, and Ketene

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Abstract: The "transition structures" for the $2_s + 2_a$ cycloaddition of ethylene with ethylene, with singlet O_2, and with ketene have been determined by MC–SCF gradient methods. The subsequent characterization of these critical points by analytical Hessian computation shows that in each case the critical point is a saddle point of index 2 (i.e., there are two imaginary vibrational frequencies). Thus, the results show that the supra–antara reaction path may not exist at all for 2 + 2 cycloadditions.

One of the novel features of the Woodward–Hoffmann treatment of 2 + 2 cycloadditions[1] was the hypothesis that there are two concerted pathways, a least motion pathway with suprafacial attack on both reactants (supra–supra attack denoted as $2_s + 2_s$) and a non least motion pathway with suprafacial attack on one reactant and antarafacial attack on the other (supra–antara attack denoted as $2_s + 2_a$). Furthermore, while the $2_s + 2_s$ process is supposed to be thermally forbidden, the $2_s + 2_a$ process should be thermally allowed.

In 2 + 2 cycloadditions of normal olefins the $2_s + 2_a$ process is expected to be energetically unfavorable because of steric hindrance and framework distortion. However, this reaction path may become the preferred one in the cycloadditions of olefins with cumulenes, since in the latter species orbitals belonging to two orthogonal planes can be involved, thereby reducing the effects associated with steric hindrance and framework distortion.

This important hypothesis can now be tested rigorously in terms of ab initio computations. In the present paper we present the results obtained on three different cycloaddition reactions for a supra–antara approach: (i) ethylene + ethylene, (ii) ethylene + singlet oxygen, and (iii) ethylene + ketene. The ethylene + ethylene reaction is the textbook example normally used in the discussion of the supra–antara approach. The ethylene + singlet oxygen reaction represents a situation with reduced steric repulsion and framework distorsion. The third reaction, ethylene + ketene,

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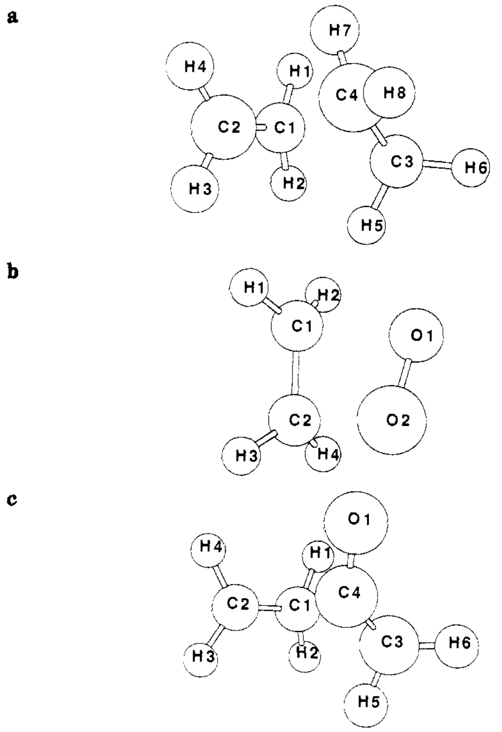

Figure 1. Geometries of supra–antara critical points (numerical values of structural parameters given in Table I): (a) C_2H_4 + C_2H_4, (b) C_2H_4 + O_2, and (c) C_2H_4 + ketene.

represents an example where the supra–antara approach should be favored.

Computational Details

In all cases we have used the CAS (complete active space) MC-SCF method. Integral and derivative calculations have been performed with the GAUSSIAN 82 series of programs,[2] while the MC-SCF gradient computations were carried out with the codes described in ref 3 and 4. The active space was chosen to contain the four π orbitals for the ethylene + ethylene reaction and six π orbitals for the other two systems. In each case, the various critical points have been fully optimized by MC-SCF gradient techniques and characterized by diagonalizing the related Hessian matrices computed analytically at the MC-SCF level.[5]

Of course, the various supra–antara critical points do not have a plane of symmetry, and in each case one of the π bonds is partly broken due to twisting of the ethylenic double bond. Thus, some comment on the choice of the active (or valence) orbital space is necessary. For the STO-3G computations, the active orbitals are unambiguous at infinite interfragment separation. At the interfragment separation of interest, the initial active orbital space can be obtained by orthogonalizing the orbitals obtained at infinite interfragment separation. For the 4-31G computations, the initial orbitals are obtained by projection from the STO-3G optimum orbitals. The nature of the MC-SCF optimized active orbitals is naturally determined by the MC-SCF process itself, and the results are unambiguous provided the occupation numbers of these active orbitals do not approach 2 or 0.

The geometry optimizations have been performed at the STO-3G[6] and 4-31G[7] levels. For reaction i the Hessian matrix has been computed at both the STO-3G and 4-31G levels. Since the two Hessian matrices were very similar and had the same number of directions of negative curvature, the Hessian matrices for reactions ii and iii were computed only at the STO-3G level.

Results and Discussion

In each case we have found the critical point associated with the $2_s + 2_a$ approach. The corresponding geometries are shown in Figure 1 while the geometrical parameters (including the dihedral angle ϑ between the CC bonds of each fragment) have been collected in Table I. In this table we have also given the imaginary frequencies computed for each structure. The STO-3G results for the critical point associated with reaction i have already been reported.[8] It can be seen that in all cases the structure of the transition state is very similar. The transition structure is distinguished by (a) a very long interfragment distance (i.e. greater than 2 Å), (b) a dihedral angle ϑ between the CC bonds of each fragment of 20–40°, and (c) a slightly distorted planar geometry for one ethylene fragment and a distorted geometry for the other

Table I. Relevant Geometrical Parameters (for Notation, See Figure 1) Together with the Values of the Two Imaginary Frequencies Computed for the Supra–Antara Critical Points at the STO-3G and 4-31G Levels

geometrical param	STO-3G	4-31G	geometrical param	STO-3G	4-31G
		Ethylene + Ethylene			
total energy	−154.0230	−155.7562			
imaginary frequencies	−1126 −404	−1072 −327			
ϑ	38.0	40.8			
C2–C1	1.40	1.41	C1–C2–H3	120.0	119.9
H1–C1	1.08	1.07	C1–C2–H4	121.1	121.2
H2–C1	1.08	1.07	C1–C2–C4	87.2	86.2
H3–C2	1.08	1.07	H3–C2–H4	115.7	115.4
H4–C2	1.08	1.07	H3–C2–C4	107.3	107.5
C3–C1	2.30	2.27	H4–C2–C4	93.6	95.6
C4–C2	2.30	2.27	C1–C3–C4	85.2	85.0
C4–C3	1.49	1.46	C1–C3–H5	78.1	76.0
H5–C3	1.08	1.07	C1–C3–H6	146.3	144.1
H6–C3	1.09	1.09	C4–C3–H5	117.8	120.0
H7–C4	1.08	1.07	C4–C3–H6	115.6	116.9
H8–C4	1.09	1.09	H5–C3–H6	110.6	111.0
C2–C1–H1	120.0	119.9	C2–C4–C3	85.2	85.0
C2–C1–H2	121.1	121.2	C2–C4–H7	78.1	76.0
C2–C1–C3	87.2	86.2	C2–C4–H8	146.3	144.1
H1–C1–H2	115.7	115.4	C3–C4–H7	117.8	120.0
H1–C1–C3	107.3	107.5	C3–C4–H8	115.6	116.9
H2–C1–C3	93.6	95.6	H7–C4–H8	110.6	111.0
		Ethylene + O_2			
total energy	−224.6919	−227.2647			
imaginary frequencies	−1516 −565				
ϑ	23.1	26.8	C2–C1–O1	87.2	87.8
C2–C1	1.44	1.42	H1–C1–H2	115.9	117.0
H1–C1	1.08	1.07	H1–C1–O1	106.8	92.7
H2–C1	1.08	1.07	H2–C1–O1	98.0	103.4
H3–C2	1.08	1.07	C1–C2–H3	120.0	120.9
H4–C2	1.08	1.07	C1–C2–H4	119.4	120.2
O1–C1	2.04	2.12	C1–C2–O2	87.2	87.8
O2–C2	2.04	2.12	H3–C2–H4	115.9	117.0
C2–C1–H1	119.4	120.9	H3–C2–O2	98.0	92.7
C2–C1–H2	120.0	120.2	H4–C2–O2	106.8	103.4
		Ketene + Ethylene[a]			
total energy	−226.8320	−229.4089			
imaginary frequencies	−1447 −403				
ϑ	32.0	35.1			
C2–C1	1.40	1.41	H2–C1–C3	94.7	95.7
H1–C1	1.08	1.08	C1–C2–H3	120.4	120.9
H2–C1	1.08	1.08	C1–C2–H4	120.8	121.3
H3–C2	1.08	1.07	C1–C2–C4	81.3	77.2
H4–C2	1.08	1.07	H3–C2–H4	116.5	112.1
C3–C1	2.14	2.09	H3–C2–C4	110.6	112.1
C4–C2	2.29	2.36	H4–C2–C4	93.7	91.0
C4–C3	1.45	1.43	C1–C3–C4	85.6	86.4
H5–C3	1.08	1.07	C1–C3–H5	86.1	89.0
H6–C3	1.09	1.09	C1–C3–H6	138.9	132.8
O1–C4	1.23	1.21	C4–C3–H5	114.3	114.8
C2–C1–H1	119.4	119.0	C4–C3–H6	117.2	117.2
C2–C1–H2	120.5	119.9	H5–C3–H6	111.0	112.7
C2–C1–C3	94.2	97.1	C2–C4–C3	87.0	85.5
H1–C1–H2	115.0	114.7	C2–C4–O1	113.2	114.0
H1–C1–C3	103.8	102.6	C3–C4–O1	135.0	136.0

[a] Due to poor termination of the geometry optimization the 4-31G structure has an rms force of 0.004 rather than the usual 0.0003.

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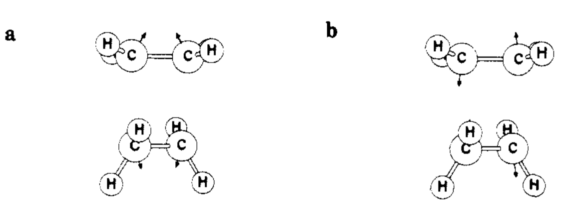

Figure 2. Normal modes corresponding to the two imaginary frequencies for the $2_s + 2_a$ critical point of index 2 for the addition of two ethylene molecules. Only the motion of the carbon atoms is shown: (a) normal mode connecting reactants and products; (b) normal mode connecting two possible gauche transition structures.

fragment (in the case of ethylene, the methylene groups twisted by almost 90°).

The characterization of these critical points by analytical Hessian computation shows that in each case the critical point is a saddle point of index 2. The evolution of the two directions of negative curvature is shown in Figure 2 where we have given the carbon atom components of each normal mode of ethylene + ethylene as an example. Motion along one direction of negative curvature (Figure 2a) leads to the product, while motion along the other direction of negative curvature (Figure 2b) leads to an adjacent gauche transition state, which has been optimized and characterized in all cases. For the ketene + ethylene reaction we have found two different adjacent gauche transition states, one bonded at C1 and the other bonded at C2.

Conclusions

Since each of the supra–antara saddle points is not a true transition structure but rather a local maximum with two directions of negative curvature, the supra–antara reaction pathway does not exist for the examples studied. For the case of ethylene + ethylene and ethylene + oxygen, this might have been expected since the direction of negative curvature that leads to the gauche minimum breaks the symmetry; however, in the case of ketene + ethylene, there is no symmetry. Thus, the results tend to indicate that the supra–antara reaction path may not exist at all for 2 + 2 cycloadditions.

Of course, these computations were carried out with quite modest basis sets. There are numerous examples in the literature where the qualitative nature of a stationary point (see for example ref 9 and 10) was altered by augmenting the basis set with polarization functions. However, for the supra–antara critical points, the second negative direction of curvature (see Figure 2b) connects two gauche fragmentation transition states. A posteriori, it would seem rather unlikely that one could find a maximum (between the supra–antara critical point and the gauche fragmentation transition state) along this coordinate as would be required if the supra–antara critical point were a true transition state.

We do also have some numerical evidence that the qualitative nature of the critical points will not be basis set dependent for these examples. For the ethylene + ethylene example, the very low (>1 kcal/mol) barrier to fragmentation from the trans diradical minimum of tetramethylene appears to be sensitive to the basis set.[8] Doubleday et al.[11] have recently reexamined this problem with a 6-31G* basis. They find that, at the MC-SCF level, the barrier is increased by ca. 1 kcal/mol from the 4-31G [8]/6-31G*[11] result so that the qualitative nature of the critical point does not change in this case.

Registry No. Ethylene, 74-85-1; oxygen, 7782-44-7; ketene, 463-51-4.

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Pseudorotation in Pentacoordinated Phosphorus Compounds. The Influence of the Conformational Transmission Effect on the Barriers to Pseudorotation in Cyclic Alkoxyphosphoranes

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Abstract: A variable-temperature ^{13}C NMR study on a series of monocyclic oxyphosphoranes enabled us to examine the influence of the conformational transmission effect on the barriers to pseudorotation in pentacoordinated phosphorus compounds. It is demonstrated that the pseudorotation rate of monocyclic oxyphosphoranes exhibiting the conformational transmission effect is 2–4 times faster as compared to their counterparts in which the effect is absent. It is shown that the conformational change in the basal ligands of the intermediate SP structures, due to the conformational transmission effect, is responsible for the lowering of the activation barriers by 2–3 kJ·mol^{-1}.

Pseudorotation of stable oxyphosphoranes has been the topic of several studies during the past two decades.[1] The polytopal exchange of ligands around pentacoordinated phosphorus has been extensively studied, both because these compounds are presumed to be intermediates in many biological processes involving phosphate esters[2] and especially because of the growing interest in the stereochemistry of reactions of tri- and tetracoordinated phosphorus compounds. These reactions proceed via pentacoordinated phosphorus intermediates, and therefore, the pseudorotation processes may have a great influence on the structure of the reaction products.[3] In the past few years a lot of information has been obtained concerning the influence of the conformational transmission effect on the structure and dynamics

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