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An *Ab Initio* Molecular Orbital Study on the Ene Reaction of Methyl Acrylate with Propene

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The *exo* and *endo* transition structures for the ene reaction of methyl acrylate with propene have been located with RHF calculations at the 3-21G and 6-31G levels. Energetics have been evaluated with the 6-31G* basis set and MP2 correlation energy correction. The transition-state geometries and the calculated energetics have been compared with those for the parent ene reaction between ethylene and propene. The *exo* and *endo* transition structures resemble rather closely that for the parent ene reaction. Reasonable substituent effects are indicated on activation energies and extents of electron transfer in the transition states. According to the calculated overlap populations, the transition structures for methyl acrylate ene reaction have less asynchronous character in the bond reorganization as compared with the parent ene reaction. The relatively small stability difference between *exo* and *endo* transition structures suggests that intrinsic *exo*/*endo* selectivity in the ene reactions is not so obvious as in the Diels–Alder reactions.

The ene reactions are increasingly powerful tools in the organic synthesis.[1–3] While some thermal ene reactions clearly proceed through a stepwise process with a diradical intermediate, it has been observed that a concerted mechanism is generally preferred.[4,5] Recently, Loncharich and Houk[6] have reported *ab initio* calculations for the parent ene reaction between propene and ethylene. The transition-state geometries for a concerted pathway have been located with RHF calculations at the STO-3G and 3-21G levels. The calculated geometries are useful for understanding and predicting some stereochemical aspects of the ene reactions. From the standpoint of practical utility, however, the ene reactions of enophiles activated with an electron-withdrawing substituent are of great interest. It is quite conceivable that the introduction of an electron-withdrawing substituent on an enophile alters significantly the transition-state geometry. We report here the *ab initio* calculations on the ene reaction of an activated enophile.

The most common electron-withdrawing substituent used for enophile activation is alkoxycarbonyl. We have therefore carried out model calculations on the ene reaction of methyl acrylate with propene. The recent *ab initio*[7,8] and experimental[7] studies on thermal Diels–Alder reactions have revealed that acrylates have an *s-cis* conformation in the transition state. The most likely cause for the preference for the *s-cis* conformation in Diels–Alder transition states originates from the greater electrophilicity of the *s-cis* conformation due to narrower frontier molecular orbital energy gaps than for the *s-trans* conformer.[8] The preference for the *s-cis* conformation in the transition state parallels the ground-state conformational preference observed for the isolated acrylates. In the ground state, the *s-cis* conformer of methyl acrylate has been calculated to be more stable than the *s-trans* conformer by 0.7 kcal mol^{-1} at the RHF/6-31G*//3-21G level.[9] This estimate is in good agreement with the experimental results in the vapor phase.[10] In this context, we have attempted to search for the *exo* and *endo cisoid* transition states.

Computational Details

The *ab initio* calculations were carried out with the GAUSSIAN 86 program.[11] The potential energy surface was explored with MNDO[12] and AM1[13] methods. Transition-state geometry optimizations were carried out starting from the flat region of the MNDO potential energy surface. The transition structures were fully optimized without any constraint by analytical energy gradient techniques[14] at the RHF level of theory. The standard split-valence 3-21G[15] and 6-31G[16] basis sets were utilized in the geometry optimizations. The authenticity of the transition structures was ensured by vibrational frequency calculations. Single-point calculations were then carried out with the 6-31G*[17] basis set at RHF and MP2 levels on the 6-31G optimized geometries for relative energy estimation. And furthermore, in order to make a comparison between the parent and methyl acrylate ene reactions, the calculations at the same computational levels were performed for the parent ene reaction. Starting from the 3-21G geometry presented by Loncharich and Houk,[6] the transition-state geometry for the parent ene reaction was optimized at the 6-31G level and then single-point calculation was carried out with the 6-31G* basis set.

Results and Discussion

Energetics: The calculated energetics are given in Table 1. In ene reactions, it is generally observed that electron-withdrawing substituents on the enophile lower the activation energies. For example, the experimental activation energy for the ene reaction of

Table 1. Energetics of the Ene Reaction of Methyl Acrylate with Propene[a)]

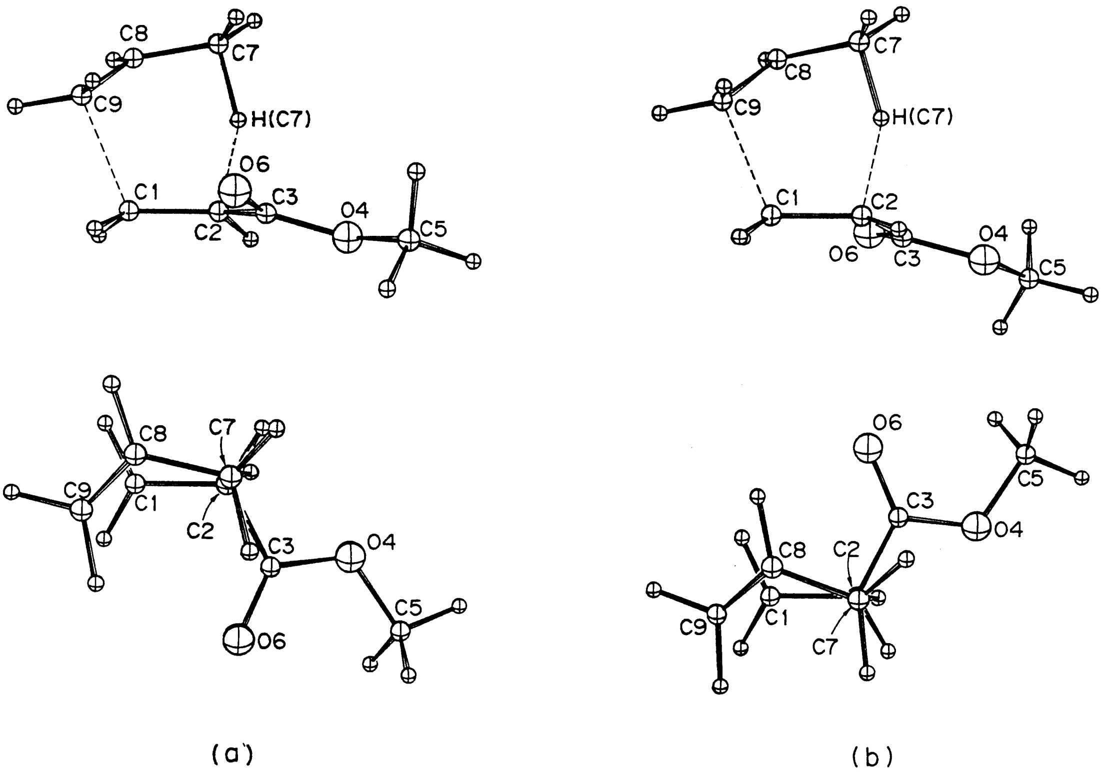
Computational level	Activation energy		Reaction energy
	Exo	*Endo*	
RHF/3-21G	46.4 (45.4)	46.9 (45.9)	−19.2 (−16.4)
RHF/6-31G	53.8 (52.6)	54.1 (52.9)	−15.7 (−12.8)
RHF/6-31G*//RHF/6-31G	56.4	56.6	−19.4
RMP2/6-31G*//RHF/6-31G	24.9	25.3	−25.3
ΔZPE(3-21G)	+0.2	+0.2	+3.3
ΔZPE(6-31G)	0.0	0.0	+3.5
ΔS(3-21G)	−46.5	−45.9	−39.8
ΔS(6-31G)	−46.4	−46.4	−39.8

a) Energies are in kcal mol^{-1}. Entropies are in eu (cal mol^{-1} K^{-1}). kcal=4.184 kJ. Total energies (au) of reactants are as follows; propene −116.42401 (RHF/3-21G), −117.02828 (RHF/6-31G), −117.07142 (RHF/6-31G*//RHF/6-31C), −117.45481 (RMP2/6-31G*//RHF/6-31G); methyl acrylate −302.98202 (RHF/3-21G), −304.53963 (RHF/6-31G), −304.67765 (RHF/6-31G*//RHF/6-31G), −305.53246 (RMP2/6-31G*//RHF/6-31G). Total energies of the *exo* and *endo* transition structures are −419.33207, −419.33127 (RHF/3-21G); −421.48208, −421.48163 (RHF/6-31G); −421.65918, −421.65887 (RHF/6-31G*//RHF/6-31G); −422.94753, −422.94689 (RMP2/6-31G*//RHF/6-31G). Total energies of the product is −419.43667 (RHF/3-21G), −421.59296 (RHF/6-31G), −421.78008 (RHF/6-31G*//RHF/6-31G), −423.02754 (RMP2/6-31G*//RHF/6-31G). The values in parentheses are $\Delta H^{\dagger}$ and ΔH at 298.15 K. The imaginary frequencies computed for the *exo* and *endo* transition structures are 1483i and 1457i cm^{-1} at the 3-21G level and 1519i and 1465i cm^{-1} at the 6-31G level, respectivrly. The motion of atoms in the normal modes corresponding to the imaginary frequencies firmly connect the reactants and the product.

maleic anhydride with terminal alkenes has been measured as 21.5 kcal mol^{-1},[18] as compared to the measured activation energies of 37.5 and 36.5 kcal mol^{-1} for the reactions of ethylene with *trans*- and *cis*-2-butene.[19] The same trend is clearly reproduced with *ab initio* RHF calculations with a split-valence,or better, basis set. With the 3-21G basis set, the activation energy drops from the value of 51.7 kcal mol^{-1}, calculated for the parent ene reaction,[6] to 46.4 and 46.9 kcal mol^{-1} for the *exo* and *endo* transition states, respectively. However, the activation energies calculated with the split-valence 3-21G and 6-31G basis sets are remarkably too large, as compared to the experimental values.[18] The polarization functions cause the energies of the reactants to be lowered more than those of transition structures. The 6-31G* basis set produces even higher activation energy estimates. The RHF activation energies, regardless of the basis sets utilized, are still larger than the activation barrier of 35 kcal mol^{-1} estimated for the parent ene reaction.[6] Overestimation of activation energy with RHF calculations has been also experienced in *ab initio* studies on the parent ene[6] and the related[7,20] reactions. However, the activation energies estimated from the correlation energy correction at MP2 level with the 6-31G* basis set are much closer to the experimental values[18] for the ene reactions of activated enophiles. The activation entropy is estimated to be ca. 46 eu with RHF calculations at the 3-21G and 6-31G levels. The calculated values are rather reasonable, considering that experimental activation entropies for the intermolecular ene reactions of maleic anhydride with various alkenes have been measured as the range from −36 to −46 eu.[18]

Transition-State Geometries: The optimized transition structures are shown in Fig. 1. The *exo* and *endo* transition structures resemble rather closely each other, except for the spatial relationship between the methoxycarbonyl and the propene moieties. The transition-state geometry for the parent ene reaction, which is characterized as an envelope conformation,[6] is almost conserved in the transition states for the methyl acrylate ene reaction. The propene moiety and the C=C double bond moiety of methyl acrylate have pseudo-envelope conformations in the *exo* and *endo* transition structures. However, the forming and cleaving bond lengths in the transition structures are altered significantly upon replacing ethylene with methyl acrylate in the parent ene reaction. According to the 3-21G optimized geometries, the partially formed C–C bond lengths of 1.966 and 1.977 Å for *exo* and *endo* transition structures are shortened somewhat, compared with the value of 2.110 Å for the parent ene transition structure.[6] The transferring hydrogen is located more closely to the original carbon atom in the transition structures for the methyl acrylate ene reaction than for the parent ene reaction. In the 3-21G optimized *exo* transition structure, the partially formed and broken C–H bond lengths are 1.538 and 1.296 Å, respectively. The corresponding values for the *endo* transition structure are 1.533 and 1.295 Å. For the parent ene transition structure, the corresponding C–H bond lengths have been calculated to be 1.477 and 1.394 Å respectively.[6]

The Extents of Bond Reorganization and Electron Transfer in the Transition Structures: The differen-



(a) (b)

Fig. 1. The front and top views of the optimized (a) *exo* and (b) *endo* transition structures for the ene reaction of methyl acrylate with propene. The optimized parameters are given in Å and degrees.

Bond lengths	*Exo*		*Endo*		Bond angles	*Exo*		*Endo*	
	3-21G	6-31G	3-21G	6-31G		3-21G	6-31G	3-21G	6-31G
C1-C2	1.409	1.417	1.409	1.419	C2-C1-C9	111.4	112.6	113.6	114.0
C1-C9	1.966	1.957	1.977	1.948	C1-C2-C3	116.3	118.1	116.2	117.6
C2-C3	1.452	1.452	1.458	1.452	C2-C3-O4	112.7	113.3	112.4	113.4
C3-O4	1.355	1.352	1.356	1.352	C2-C3-O6	125.5	125.4	125.7	125.2
O4-C5	1.449	1.442	1.449	1.442	O4-C3-O6	121.8	113.3	121.9	121.4
C3-O6	1.215	1.226	1.214	1.227	C3-O4-C5	117.7	119.5	117.6	119.4
C7-C8	1.405	1.405	1.404	1.405	C2-H(C7)-C7	153.3	152.4	155.0	153.4
C8-C9	1.384	1.392	1.385	1.394	C8-C7-H(C7)	96.4	96.5	95.6	96.2
C2-H(C7)	1.538	1.554	1.533	1.564	C7-C8-C9	118.5	119.3	118.6	119.0
C7-H(C7)	1.296	1.299	1.295	1.294	C8-C9-C1	101.4	102.2	101.3	102.2
					C1-C2-H(C7)	100.6	101.1	101.0	101.2

Torsional angles	*Exo*		*Endo*	
	3-21G	6-31G	3-21G	6-31G
C1-C2-C3-O4	+166.4	+163.6	−164.9	−162.0
C1-C2-C3-O6	−16.5	−19.0	+17.6	+20.7
C2-C3-O4-C5	+177.7	+178.1	−178.0	−178.0
O6-C3-O4-C5	+0.5	+0.6	−0.5	−0.6
C1-C2-H(C7)-C7	+24.4	+21.2	+2.1	+1.9
C3-C2-H(C7)-C7	−94.5	−100.3	+119.1	+120.6
C2-H(C7)-C7-C8	−34.2	−33.8	−22.1	−21.6
H(C7)-C7-C8-C9	+57.3	+57.9	+59.6	+58.8
C7-C8-C9-C1	−69.2	−67.9	−69.2	−68.8
C2-C1-C9-C8	+49.3	+44.8	+38.1	+37.9

ces in the geometrical features between the parent ene and methyl acrylate ene transition structures suggest that the introduction of methoxycarbonyl group on ethylene alters considerably the extents of bond formation and cleavage in the transition states. In order to evaluate the extents of the bond reorganization in the transition structures from another standpoint, we carried out population analysis, which gives a qualitative indicator of the amount of the electron density shared between two atoms. The overlap populations relevant to the forming and cleaving bonds calculated with the 6-31G* basis set on the 6-31G optimized

Table 2. The Overlap Populations Relevant to the Forming and Cleaving Bonds in the Methyl Acrylate Ene and the Parent Ene Reaction[a)]

Translating bond	Reactant	Product	Transition state	Extent of bond reorganization[b)] (%)
C7-H(C7)		Methyl acrylate ene reaction		
	0.396 (1.083)	0.000 (4.934)	*exo* 0.226 (1.299)	43.0
	0.390 (1.086)			42.2
			endo 0.217 (1.294)	45.3
				44.5
		Parent ene reaction		
		0.000 (5.111)	0.210 (1.375)	47.0
		0.000 (4.955)		46.2
C2-H(C7)		Methyl acrylate ene reaction		
	—	0.383 (1.086)	*exo* 0.176 (1.554)	45.8
			endo 0.187 (1.564)	48.8
		Parent ene reaction		
		0.397 (1.084)	0.193 (1.430)	48.5
		0.392 (1.085)		49.1
C1-C9		Methyl acrylate ene reaction		
	—	0.340 (1.530)	*exo* 0.166 (1.957)	48.8
			endo 0.164 (1.948)	48.2
		Parent ene reaction		
		0.352 (1.531)	0.130 (2.146)	36.9

a) The atom numbering is the same as in Fig. 1. The overlap populations were calculated with the 6-31G* basis set at RHF level on the 6-31G optimized geometries. The values in parentheses are bond lengths in Å. b) Extents of bond reorganization in the transition structures were calculated with the overlap populations, i.e. $(OP_{ts}-OP_{reactant})/(OP_{product}-OP_{reactant})$.

geometries are given in Table 2. In the *exo* and *endo* transition states, C1-C9 overlap populations are 0.166 and 0.164, respectively, while the corresponding overlap population in the parent ene transition state is 0.130. Consequently, as expected from the bond lengths in the transition structures, the overlap populations suggest that there is more C-C single bond formation in the methyl acrylate transition structures, compared with the parent ene transition structure. The evaluation based upon the overlap populations indicates that the extents of the C-C single bond formation and the hydrogen transfer are more equally balanced in the transition structures for the methyl acrylate ene reaction than for the parent ene reaction. The extents of bond formation and cleavage in the transition states were evaluated by comparing the overlap populations for transition structures with those for the reactants and the products. In the parent ene transition structure, the hydrogen is nearly half-transferred, while the C-C single bond is less than 40% formed (Table 2). The hydrogen transfer appears to be somewhat more advanced than the C-C single bond formation in the parent ene reaction. In the transition structures for the methyl acrylate ene reaction, on the other hand, the hydrogen transfer and the C-C single bond formation both proceed slightly less than 50%. It is likely that introduction of methoxycarbonyl group on the enophile reduces the degree of asynchronous character in the bond reorganization.

The electron-withdrawing character of methoxycarbonyl group is clearly recognized in the transition structures. The population analysis with the 6-31G* basis set indicates that there is donation of 0.18 electrons from propene to methyl acrylate both in the *exo* and *endo* transition structures. In the same computational level calculation, only 0.06 electrons is found to be transferred in the parent ene transition structure.

***Exo/Endo* Selectivity:** It is generally accepted that, although *endo* mode of addition in ene reactions is favored by orbital symmetry relationships, the preference is not so marked as in the Diels-Alder reactions. The *exo/endo* selectivity is rather sensitive to the steric effect.[4,21,22)] The calculations that we have carried out, including MNDO calculations, indicate that the *exo* transition state is slightly favored over the *endo* transition state, regardless of the computational levels utilized. The RHF calculations with the 6-31G* basis set give the value of 0.2 kcal mol^{-1} for relative energy difference between the *exo* and *endo* transition states. The correlational energy correction at MP2 level gives somewhat larger (0.4 kcal mol^{-1}) relative energy difference, which is in good agreement with the value provided with MNDO calculations. The relatively small stability difference between the *exo* and *endo* transition structures conceivably reflects subtle *exo/endo* selectivity in ene reactions. The immediate conclusion to be drawn from these calculations is that intrinsic *exo/endo* selectivity in the ene reaction of methyl acrylate is expected to be not so obvious as in the Diels–Alder reactions.

In order to understand the origin of the slight *exo* preference, we carried out some other calculations on the 6-31G optimized transition structures. However, these calculations are not very convincing. First of all we evaluated the distortion energies of the propene and methyl acrylate moieties in the *exo* and *endo* transition-state geometries. We carried out single-point energy calculations on each moiety constrained to the geometries of the transition structures with the 6-31G* basis set at RHF and MP2 levels. The energy of the propene moiety was evaluated by removing the atoms of methyl acrylate followed by the single-point calculations, without altering the transition-state geometries in any way. The energy of the methyl acrylate moiety was evaluated in a similar fashion. The calculated distortion energies of each moiety, in which the influence of electron transfer from propene to methyl acrylate in the transition states is not included, are given in Table 3. The overall distortion energy difference between the *exo* and *endo* transition structures is evaluated to be less than 0.5 kcal mol^{-1} both at RHF and MP2 levels. The propene moiety in the *exo* transition structure is more stable than that in the *endo* transition structure by 0.5 and 0.3 kcal mol^{-1} at RHF and MP2 levels, respectively. The distortion energies of the methyl acrylate moiety in the *exo* and *endo* transition structures are almost the same at RHF level. At MP2 level, the methyl acrylate moiety in the *endo* transition structure is favored by 0.1 kcal mol^{-1}. The differences in interactions between propene and methyl acrylate molecules in the *exo* and *endo* transition structures can be estimated by taking away the differences of the distortion energies of each molecule on the transition-state geometries from the relative energy differences between the *exo* and *endo* transition structures. The remaining energy difference, −0.3 and 0.1 kcal mol^{-1} at RHF and MP2 levels, respectively, might arise from the results of the differences in the several kinds of interactions between propene and methyl acrylate molecules, such as primary and secondary orbital interactions, electrostatic and steric interactions and van der Waals forces. Analysis of transition-state geometries and the overlap populations shows some differences in interactions between propene and methyl acrylate molecules in the transition structures. The forming and cleaving bond lengths and the overlap populations given in Table 2 indicate that the *exo* transition structure is just a little more asynchronous than the *endo* transition structure. The torsional angle C2-Cl-C9-C8 in the *exo* transition structure is slightly larger than in the *endo* transition structure. This might be related to the greater asynchronicity of *exo* transition structure. Part of the differences in interactions between propene and methyl acrylate molecules in the transition structures conceivably comes from the differences in interactions between the propene and methoxycarbonyl moieties. The interatomic distances and the overlap populations between propene moiety and ester carbonyl group are given in Table 4. The ester carbonyl group is closer to the propene moiety in the *endo* transition structure than in the *exo* transition structure. The overlap populations indicate that there are larger interactions between these moieties in the *endo* transition structure. However, the overall effects of interaction between propene moiety and methoxycarbonyl group on *exo/endo* selectivity are not conclusive, since some overlap populations indicate attractive interactions

Table 3. The Distortion Energies of Propene and Methyl Acrylate Molecules in the 6-31G Optimized *Exo* and *Endo* Transition Structures[a)]

Computational level	Propene		Methyl acrylate	
	Exo	*Endo*	*Exo*	*Endo*
RHF/6-31G*	38.4	38.9	22.8	22.8
RMP2/6-31G*	31.9	32.2	16.2	16.1

a) Energies are in kcal mol^{-1}. The distortion energies are the differences between the total energies on the ground-state geometries and those on the transition-state geometries. Total energies (au) of propene on the *exo* and *endo* 6-31G optimized transition-state geometries are −117.01022, −117.00938 (RHF/6-31G*); −117.40400, −117.40339 (RMP2/6-31G*). Total energies of methyl acrylate on the *exo* and *endo* transition-state geometries are −304.64125, −304.64126 (RHF/6-31G*); −305.50658, −305.50684 (RMP2/6-31G*).

Table 4. The Overlap Populations and the Interatomic Distances in the *Exo* and *Endo* Transition Structures[a)]

	C3		O6	
	Exo	*Endo*	*Exo*	*Endo*
H(C7)	−0.017 (2.305)	−0.025 (2.172)	−0.002 (3.038)	−0.003 (2.823)
C7	0.001 (3.387)	−0.005 (3.314)	0.001 (3.823)	0.001 (3.666)
C8	0.001 (3.896)	0.003 (3.527)	0.000 (4.206)	0.003 (3.552)
C9	0.002 (3.597)	0.001 (3.805)	−0.002 (3.616)	−0.001 (3.963)

a) The atom numbering is the same as in Fig. 1. The overlap populations were calculated with the 6-31G* basis set at RHF level on the 6-31G optimized geometries. The interatomic distances (Å) are given in parentheses.

and others are repulsive.

Conclusion

RHF calculations for methyl acrylate ene reaction give reasonable substituent effect on activation energies and extent of electron transfer from ene to enophile in the transition state. MP2 level calculations give quite reasonable activation energy estimates. The parent ene transition-state geometry is almost conserved both in the *exo* and *endo* transition structures. The calculated overlap populations suggest that the extents of the C–C single bond formation and the hydrogen transfer are more equally balanced in the transition structures for methyl acrylate ene reaction than for the parent ene reaction. The relatively small stability difference between the *exo* and *endo* transition structures conceivably reflects subtle *exo/endo* selectivity in ene reactions. Remarkable differences between the *exo* and *endo* transition structures are not seen in the distortion energies of propene and methyl acrylate molecules and in the interaction energies between these two molecules. Consequently, intrinsic *exo/endo* selectivity in the methyl acrylate ene reactions is expected to be not so obvious as in the Diels-Alder reactions.

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