Transition Structures of the Ene Reaction between Methyl Acrylate and Propene

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Searches for the *exo* and *endo* transition states for the ene reaction of methyl acrylate with propene, using split-valence 3-21G and 6-31G basis sets, suggest less asynchronous character in the bond reorganization as compared with the parent ene reaction between propene and ethylene.

The ene reactions of enophiles activated with an electron-withdrawing group are of great interest from the standpoint of practical utility.[1—3] Recently, the STO-3G and 3-21G transition structures of the parent ene reaction between propene and ethylene have been presented by K. N. Houk.[4] The calculated geometries are helpful for predicting some stereochemical aspects of the ene reactions. 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.[5,6] It is quite conceivable, however, that the introduction of an electron-withdrawing group on an enophile alters significantly the transition-state geometry.

The most common electron-withdrawing group 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* and experimental studies[7,8] on thermal Diels–Alder reactions have revealed that acrylates have an s-*cis* conformation in the transition state. The preference for the s-*cis* conformation in the thermal reactions parallels the ground-state conformational preference observed for the isolated acrylates.[9,10] In this context, we have attempted to search for the *exo* and *endo cisoid* transition states.

The transition structures were located with split-valence 3-21G and 6-31G basis sets.† The potential energy surface was explored using MNDO and AM1 methods. The MNDO transition-structure geometries were used as starting points for searches in the *ab initio* calculations. The optimized *exo* and *endo* transition structures are shown in Figure 1. Each was characterized as a transition state by vibrational frequency analysis.‡

The calculated activation energies are presented in Table 1. In ene reactions, it is generally observed that electron-withdrawing groups on the enophile lower the activation energy. The same trend is clearly reproduced in the RHF activation energies. According to 3-21G calculations, the activation energy drops from the value of 51.7 kcal mol^{-1},[4]

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† In the present study, all the calculations were carried out using the GAUSSIAN 86 program (Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA, 1984) on an FACOM M780/MSP computer. The transition-structure geometries were fully optimized using analytical gradient techniques without any constraint.

‡ The imaginary frequencies computed for the *exo* and *endo* transition structures at the 6-31G level are 1519i and 1465i cm^{-1}, respectively. The motion of atoms in the normal modes corresponding to the imaginary frequencies firmly connect the reactants and the products.

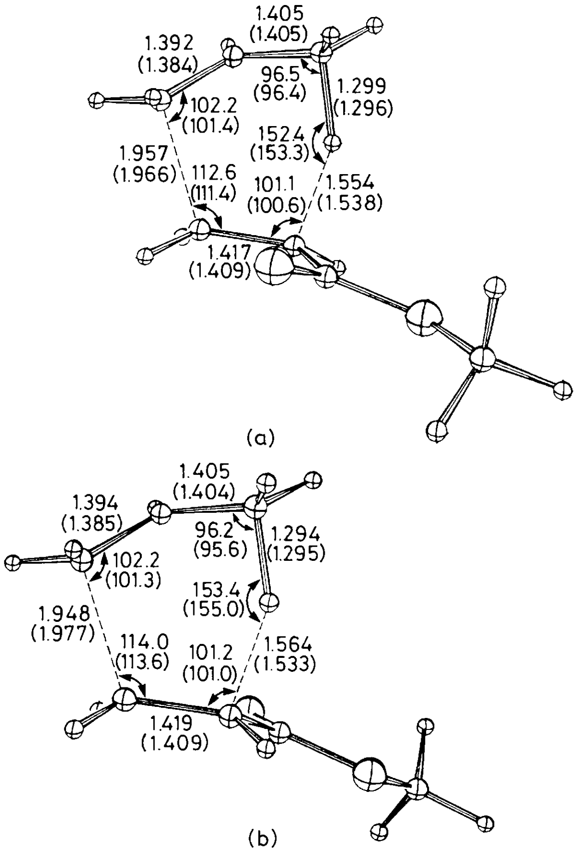

Figure 1. The calculated (a) *exo* and (b) *endo* transition state structures for the ene reaction of methyl acrylate with propene. The 3-21G (in parentheses) and 6-31G optimized parameters are given in Å and degrees.

calculated for the parent ene reaction, to 46.4 and 46.9 kcal mol^{-1} for *exo* and *endo* transition states, respectively. However, compared with experimental activation energies,[11,12] the RHF activation energies are considerably too large regardless of the basis sets utilized. Overestimation of activation energy with RHF calculations has been also experienced in *ab initio* studies on the parent ene[4] and related[7] reactions. The activation energies estimated from the correlation energy correction at the MP2 level with a 6-31G* basis set are much closer to the experimental values[12] for ene reactions of activated enophiles. The *exo* transition state is indicated to be slightly favoured over the *endo* transition state, regardless of the computational level utilized. Conceivably, the relatively small stability difference between *exo* and *endo* transition structures reflects subtle *exo*/*endo* selectivity in ene reaction.[5]

The geometry of transition structure for the parent ene reaction, characterized as an envelope conformation,[4] is almost conserved in 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 partial bond distances in the transition structures are altered significantly upon replacing ethylene with methyl acrylate in the parent ene reaction. According to 3-21G calculations, the forming C–C bond distances 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. The transferring hydrogen is located more closely to the original carbon both in the *exo* and *endo* transition structures.

Table 1. Activation energies for the ene reaction of methyl acrylate with propene.

Computational level	Activation energy[a]/kcal mol^{-1}[b] *exo*	*endo*
RHF/3-21G	46.4	46.9
RHF/6-31G	53.8	54.1
RHF/6-31G*//6-31G	56.4	56.6
RMP2/6-31G*//6-31G	24.9	25.3
ΔZPE(3-21G)	+0.2	+0.2
ΔZPE(6-31G)	0.0	0.0
$\Delta S^{\ddagger}$(3-21G)	−46.5 e.u.	−45.9 e.u.
$\Delta S^{\ddagger}$(6-31G)	−46.4 e.u.	−46.4 e.u.

[a] Total energies (a.u.) of *exo* and *endo* transition structures are −419.33207, −419.33127 (RHF/3-21G); −421.48208, −421.48163 (RHF/6-31G); −421.65198, −421.65887 (RHF/6-31G*//6-31G); −422.94753, −422.94689 (RMP2/6-31G*//6-31G). [b] kcal = 4.184 kJ.

In the *exo* transition structure, values of 1.538 and 1.296 Å are obtained for the partially formed and broken C–H bond distances. The corresponding values for the *endo* transition structure are 1.533 and 1.295 Å, respectively. For the parent ene transition structure, the corresponding partial C–H bond distances are 1.447 and 1.394 Å, respectively.[4] Consequently, the extents of C–C single bond formation and hydrogen transfer are altered considerably in the transition state upon replacing ethylene with methyl acrylate in the parent ene reaction. As compared with the parent ene reaction, there is more C–C single bond formation both in the *exo* and the *endo* transition structures. According to the calculated overlap populations, the extents of C–C bond formation and hydrogen transfer are more equally balanced in the transition structures for the activated reaction than for the parent reaction. It is likely that introduction of an electron-withdrawing group on the enophile reduces the degree of asynchronous character in the bond reorganization.

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