Determination of Reactivity by MO Theory (XXV), Theoretical Studies of ω–Alkenyl Radical Cyclization

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Transition state structures were calculated for A and M routes of ω alkenyl radical cyclization (n=2~4) using MINDO/3–RHF method. Results of our analysis of HOMO level changes indicated that the transition state stability is not controlled by the decoupling effect alone as Bischof suggested, but in greater degree it is determined by through-bond interaction of the HOMOs with the framework $HO-\sigma$ or $LU-\sigma^*$ orbitals. In case of larger n (n>4), the product stability was considered to be the main cause of M route dominance in the cyclization.

Introduction

Reactions between a double bond and a radical center are common in radical chemistry. ω–Alkenyl radicals which contain a terminal double bond and a radical site in the same molecule react via intramolecular cyclization. Two modes of cyclization for ω–alkenyl radicals are known[1a]: (i) Markownikov route, M, (endo cyclization) which produces the thermodynamically more stable product radical, and (ii) Anti–Markownikov route, A, (exo cyclization) which produces the less stable product radical, as shown in Figure 1. In case of a bimolecular radical addition,[2] route M is favored by a lower activation energy and thus leads to the more stable product. However in an ω–alkenyl radical cyclization,[1] the alternative Anti–Markownikov pathway is often favored leading to the thermodynamically less stable product. Recently, theoretical studies on the cyclization of ω–alkenyl radicals have been reported by Bischof using MINDO/3–UHF method of calculation.[1a] The results showed that for small ω–alkenyl radicals, in which the number of methylene group, n, is less than four, route A dominates the cyclization, whereas in case of the ω–hexenyl radical (n=4) route M becomes competative and finally route M controls the cyclization for larger systems. The main cause of the A route predominance in small systems was attributed to a torsional

vibration that decouples the terminal double bond in the M route giving rise to a high activation energy. This decoupling effect in the transition state for M route, nT_M, is due to the geometrical constraint which is relieved as n increases, because the radical gains more dynamic freedom to approach the double bond in a favorable way. Thus any longer ω–alkenyl radical should behave "normal" and cyclize just as in bimolecular radical addition. In order to elucidate further the mechanism of ω–alkenyl radical cyclization, we have performed MINDO/3–RHF computation on the transition states (TS) of ω–alkenyl radical cyclization (n= 2~4) and applied the perturbation molecular orbital (PMO) theory of *n–π* orbital interactions[3] in the analysis of frontier orbital (FMO) splitting effect.

Computation

In this work we used MINDO/3–RHF method[1] throughout in the calculation of TS structures. In order to investigate FMO behaviors in the TS, specifically to examine level changes of the highest occupied (HO) MO, we needed to use RHF instead of UHF calculation. Since the results of our RHF calculations were found very nearly the same as those of the Bischof's UHF results, we have kept his optimized geometries for the TS structures in our RHF calculations (*vide infra*).

Results and Discussion

We first performed a detailed optimization of the TS for butenyl radical cyclization *via* the A route, *i.e.*, for $2T_A{}^5$, as shown in Figure 2. The energy changes accompanied by the movement along the reaction coordinate are shown in Figure 3, and representative geometrical parameters optimized are summarized in Table 1. Both Figure 3 and Table 1 reveal that geometrical parameters and energy changes are continuous with respect to reaction coordinates, satisfying the criterion for a true TS proposed by Lohr and Rothmann.[6] The TS structure obtained in this work by RHF calculation is compared with that obtained by UHF method in Table 2, which clearly demonstrates that the two methods of calculation are comparable. We therefore proceeded with our RHF calculations to other TS structures using optimized geometries of Bischof by UHF.
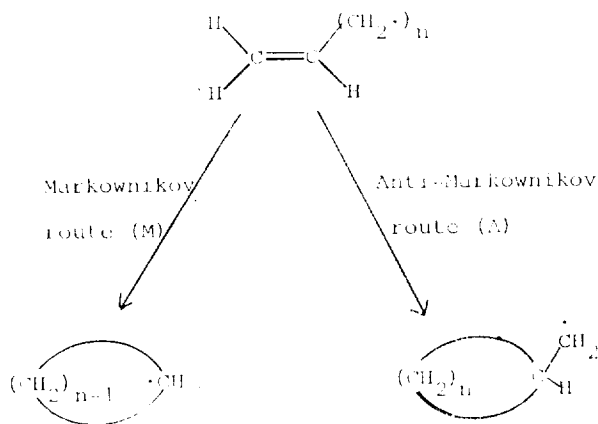

Figure 1. The reactant and product structure for the two reaction modes.

TABLE 1: Changes in Optimized Parameters with respect to Reaction Coordinate for $2T_A$

R. C. (A°) Parameter	2.30	2.10	1.91	1.90	1.89	1.70
$C_1 = C_2$	1.3331	1.3354	1.3515	1.3535	1.3552	1.4033
$C_2 - C_4$	1.4809	1.4858	1.5035	1.5051	1.5035	1.5231
$C_3 - C_4$	1.4414	1.4328	1.4354	1.4326	1.4377	1.4548
$\angle C_2 C_3 C_4$	38.701	44.999	51.037	51.365	51.563	57.100
$\angle C_1 C_2 C_3$	124.61	123.03	121.45	121.17	121.14	122.64

TABLE 2: Comparison of Transition State obtained by UHF and RHF Methods

	UHF	RHF
$C_2 - C_3$ (R. C.)	1.90	1.89
$C_1 = C_2$	1.362	1.355
$C_2 - C_4$	1.492	1.504
$C_3 - C_4$	1.452	1.438
$\angle C_2 C_4 C_3$	81°	80°
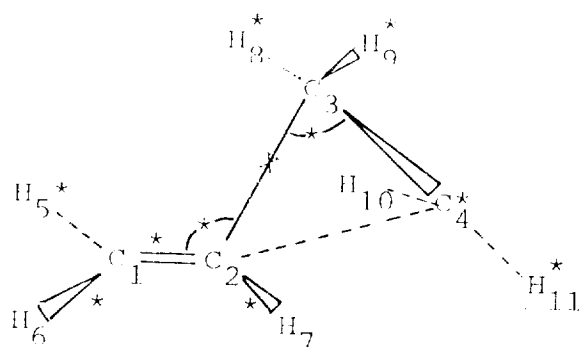
Figure 2. Cyclization *via* A route ($2 T_A$).

—X—: reaction coordinate; ✳ : geometry parameter optimized.
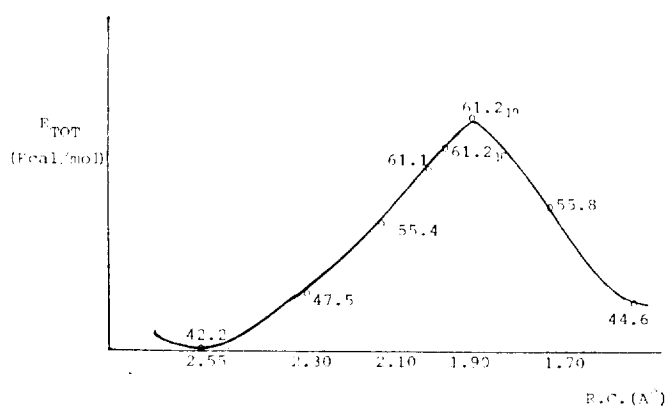
Figure 3. Total energy change diagram for cyclization *via* A route, $2 T_A$. Figures are energies in kcal/mol.

The results obtained for FMO levels and activation energy differences, $\Delta E_a = E_a(nT_M) - E_a(nT_A)$, are summarized in Table 3. Reference to Table 3 reveals that the ΔE_a values are again seen to be comparable to those obtained by the UHF calcula- tions. A system which has an n and a π orbitals separated by a number (N) of intervening C-C σ bonds[7] can interact through space when they are oriented in such a way that the lobes of the two orbitals can overlap. In an ω-alkenyl radical cyclization, the n lobe approaches to one of the two p_π lobes of the two carbon atoms of the π bond, and depending on the carbon atom interacting the pathway of cyclization is determined. In the Anti–Markownikov (exo) route, the TS, nT_A, involves through-space interaction (TSI) of the n with the p_π lobe of the inner carbon, whereas in the Markownikov route, the TS,nT_M, involves TSI of the n with the p_π lobe of the outer carbon atom. As is well known, a result of these TSI between an n and a π orbital is the formation of an allyl type orbital[8]; we were able to identify distinctly the three levels formed, ψ_+, ψ_0 and ψ_- as shown in Figure 4a. The three allyl type MO's obtained for the TS of ω-alkenyl radical cyclization were, in fact, the FMO's of the TS, *i. e.*, ψ_+(HOMO), ψ_0(SOMO)[9] and ψ_- (LUMO),[9] and had general allyl type MO patterns shown in Figure 4b for the two routes of radical cyclization. According to our PMO analysis of orbital interaction,[3] the two AO lobes interacting through space, further interact through (N) CC σ bonds of the framework. However the FMO[8] and "C" approximation[10], coupled with symmetry consideration[11] lead us to a simplified scheme in that the symmetric combination of the two interacting AO lobes, ψ_+, interacts only with the framework HO-σ (LU-σ^*), whereas the antisymmetric combination, ψ_-, interacts only with the framework LU-σ^* (HO-σ) when the number of intervening CC σ bonds N is odd(even). These types of through–bond interaction (TBI) schemes are presented in Figures 4c, 5 and 6. Two consequences of TSI are that ψ_+ is always placed below ψ_- level,[3] and ψ_0 level does not participate in TBI since the

TABLE 3: FMO levels (eV) and Activation Energy Differences, (kcal/mol), $\Delta E_a = E_a(nT_M) - E_a(nT_A)$.

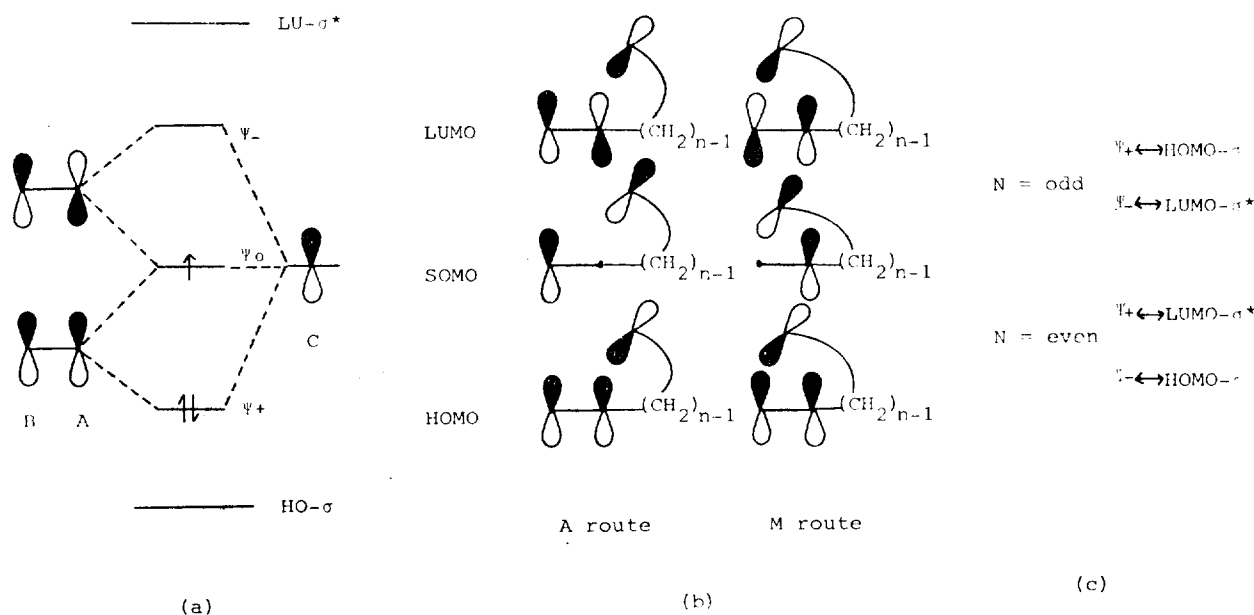|	$2 T_A (e)$	$2 T_M (o)$	$3 T_A (o)$	$3 T_M (e)$	$4 T_A (e)$	$4 T_M (o)$
ψ_+ (HOMO)	−9.89	−9.33	−9.62	−9.63	−9.98	−9.99
ψ_0 (SOMO)	−3.53	−3.47	−3.77	−3.69	−3.75	−3.59
ψ_- (LUMO)	2.27	1.25	2.03	1.58	1.87	1.68
T S I	—	—+	—	—+	—	—+
T B I	—	+	+	—	—	+
ΔE_a UHF	17.0			3.80		0.00
ΔE_a RHF	20.9			2.10		0.70

Figure 4. Orbital interaction patterns (a) allyl type MO levels formed by an ethylenic π and a radical (b) through-space interaction patterns for A and M routes. (c) through-bond interaction schemes of the FMO's ϕ_+ and ϕ_- with the framework HO–σ and LU–σ^* MO's.
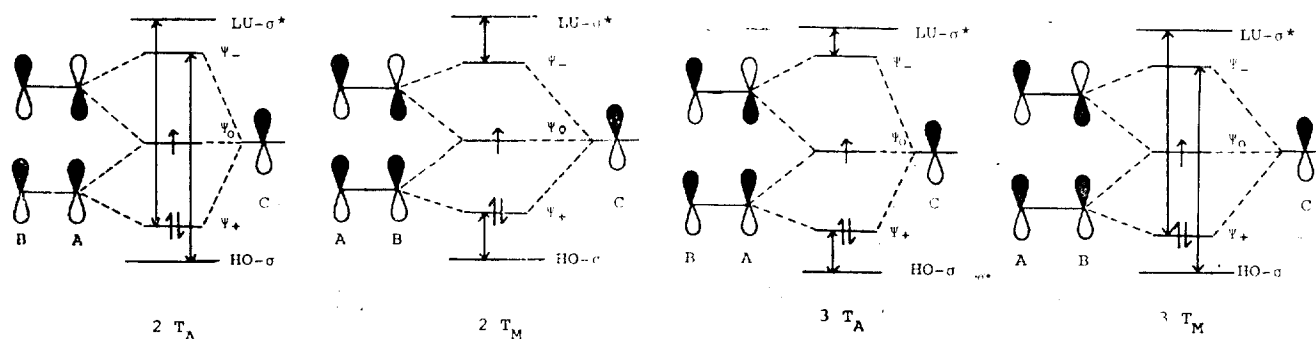

Figure 5. Through-space and through-bond interaction schemes for 2 T_A and 2 T_M structures.
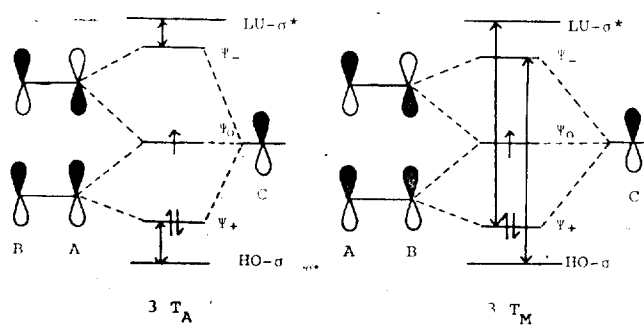

Figure 6. Through-space and through-bond interaction schemes for 3 T_A and 3 T_M structures.

p_π lobe which is to interact with the n lobe disappears due to a node passing through the carbon atom. There are three types of effects to be considered in assessing the changes of the FMOs in the TS of ω-alkenyl radical cyclization:

(i) TSI is stronger and hence the lowering of the HOMO, ϕ_+, is greater in nT_A than that in nT_M, since in the latter decoupling effect interferes with the optimum overlap of the two interacting orbitals.

(ii) As a result of TBI, the HOMO, ϕ_+, level is lowered in the N=even system ($2T_A$, $3T_M$ and $4T_A$), whereas it is raised in the n=odd system[3,12] ($2T_M$, $3T_A$, and $4T_M$); in the former ϕ_+ interacts with the vacant LU–σ^* whereas in the latter it interacts with the occupied HO–σ as shown in Figure 4c, 5 and 6.

(iii) As n (chain length) increases, the M route is favored and hence the HOMO, ϕ_+, will be lowered in nT_M rather than in nT_A due to the larger thermodynamic stability of the product radical in the M pathway.

The FMO levels are summarized in Table 3 together with expected trends of stabilizing (lowering) or destabilizing (raising) effects of HOMO levels by the three major level changes listed above; here (−) sign refers to lowering while

(+) sign to elevating effect. Reference to this table indicates that for butenyl radical cyclization the HOMO of $2T_A$ is lowered, and hence is stabilized, compared to $2T_M$ on account of both TSI and TBI effects. This large difference in the HOMO level is reflected in the large difference in the activation energy causing the route via the $2T_A$ to be favored by as much as 20 kcal/mol. On the other hand, the two. TSI and TBI, have mutually cancelling effects in $3T_A$ and $3T_M$ so that the HOMO levels of the two TS structures are nearly the same resulting in much lower activation energy difference of 2 kcal/mol. For hexenyl radical cyclization the two effects are again operating cooperatively and thus we may expect large HOMO level and activation energy differences. Contrary to this prediction, we however find the HOMO level of $4T_M$ is actually lower than that of $4T_A$ with no activation energy difference. This may well be the manifestation of level changes effected by product stability, *i. e.*, (iii) above. This trend of the M route dominance will be more pronounced as chain length, n, increase as found theoretically as well as experimentally.[13] Bischof's results showed an exception which did not fit into the scheme: the activation enthalpy for the route A cyclization of ω-

pentenyl radical ($3T_A$) was found much larger than expected. In fact, this reaction has not been observed experimentally.[14] In the light of the HOMO level changes effected by TSI and TBI, we can now understand why the $3T_A$ structure gave this unusually high activation energy; inspection of Table 3 shows that this structure being N = odd framework has unfavorable TBI in addition to the probable HOMO elevating effect from the instability of product. We therefore conclude that the TS stability in small ω-alkenyl radical cyclization is not controlled by the decoupling effect (TSI) alone, but in greater degree it is determined by TBI and when n becomes larger (than 4) the product stability dominates the activation energy.

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References

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Molecular Dynamic Study of A Polymeric Solution (II). Solvent Effect

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Molecular dynamic method has been applied to a single polymer chain immersed in a solvent. The interactions for the pairs, of two solvent molecules (SS), of a chain element and a solvent molecules (CS), and of two non-neighbor chain elements (CC) are given by the Lennard-Jones potential, and the interaction between two bonded chain elements is given by a harmonic potential. We changed the CS interaction parameter ε_{CS} to 0.5, 1.0 and 2.0 times of the SS interaction ε_{SS}. We calculated the pair correlation functions for the SS, CS, and CC pairs, end-to-end distance and radius of gyration with the varying ε_{CS} parameters. The results showed that a phase separation occurs between the polymer and solvent in the 0.5 system where $\varepsilon_{CS}=0.5\,\varepsilon_{SS}$. The autocorrelation functions for end-to-end distance and radius of gyration were also calculated.

1. Introduction

Polymeric systems are composed of very large numbers of small molecules, having very complicated intramolecular and intermolecular interactions. Especially, in the solution, these interactions are altered by solvents, and thus the conformation of the polymer chain is also altered by existence of the solvent molecules. The present theories in the literature do not take into account the details of the intramolecular

and intermolecular interactions due to the complication.[1,2]

It is possible to study such complicated systems by a computer simulation. There are three different methods available to study such systems, *i. e.*, molecular dynamics method[3-6], static Monte Carlo method[7-12] and "polymer reptation method"[13-17]. The advantage of a computer simulation is that the shape of the intra-and inter molecular potential functions can be controlled. Among the above three methods of simulation, the molecular dynamics method has some advantage,