A computational study of ene reaction

T.K. Manojkumar *

Center for Computational Chemistry and Center for Computational Biology, Indian Institute of Information Technology and Management-Kerala, Technopark, Trivandrum 695 581, Kerala, India

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ABSTRACT

Computations of ene reactions between propene and different enophiles bearing C=X groups (where X = CH_2, SiH_2, NH, PH, O and S) were carried out at different levels of theory. Relation between the HOMO–LUMO energy gap and electronegativity of heteroatom in X group with the activation energy were computed at CCSD/aVDZ level of theory. Regioselectivity of the reaction at CCSD/aVDZ is also estimated. Nucleus Independent Chemical Shift values of the transition states were computed at B3LYP/aVDZ to estimate the Mobius aromaticity.

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1. Introduction

Ene reaction is widely applied for C—C bond formation reactions [1,2]. Although the mechanism of ene reaction is similar to other pericyclic reactions such as Diels–Alder reaction and sigmatropic reactions, the number of theoretical studies about ene reaction is much less [3]. The increase in the number of articles about ene reaction in recent days mirrors the synthetic utility of the reaction [4–8]. Houk and co-workers have computed the transition state structure of the reactions of propene and formaldehyde [9] and found that regio-selectivity is determined by a stabilizing electrostatic interaction. Uchimaru et al. studied the transition state structure of the ene reaction between methyl acrylate and propene and their studies suggested that there is less asynchronous character in the bond reorganization compared with the parent reaction between ethylene and propene [10]. The product of ene reaction is acyclic compared with that of related Diels–Alder (DA) reaction, that furnishes cyclic adducts. Different types of ene reaction has been reported for the past several years and the diversity is mostly from the enophile used in the reaction. Ene reactions involving alkenes (Alder ene reaction) [11], singlet oxygen [12] azo compounds [13,14], carbonyl functionalities (carbonyl-ene reaction) [15], and nitroso groups [16] have been employed in carbon–carbon/carbon–heteroatom transformations with olefins. It is reported that most of these reactions proceeds through a concerted step involving a cyclic transition state [1]. A recent report indicate that stepwise reaction path is 4 kcal/mol lower than concerted path at CASSCF MO level of theory [17].

It is well known that there can be two possible regioisomers for the ene reaction between propene and a dienophile bearing a heteroatom. The allylic hydrogen may be transferred to "C" of the dienophile or to the heteroatom. In principle, the hetero ene reaction may proceed with C—C bond formation (path I) or C—X bond formation (path II), each passing through a different transition state depending on the regioselectivity of the reactants (Scheme 1) [18]. Because of this property of ene reaction, we selected the same for studying the regioselectivity of CH2=X group in chemical reactions. When X is oxygen, the reaction proceeds exclusively through path I, giving just alcohol and no ether product was observed [18]. On the other hand, most ene reactions of thiocarbonyls proceed preferentially via path II to yield sulfides [16]. Middleton reported the reaction of perfluorothioacetone with propene and β-pinene and in which only sulfide products were isolated [19]. Baldwin reported that thiobenzaldehyde reacts with β-pinene to give a 1:2 ratio of sulphide to thiol, but the yield was much lower than in the other reactions [20].

Carbonyl group is one of the most important reaction center in chemical and biochemical reactions [1,2]. The CO group has a low lying π^* orbital that has a large coefficient on C atom. Although there are many reports about the regioselectivity of CO group in ene reaction and comparisons are available especially related to S atom, a more systematic theoretical study at a higher level of theory is highly desirable to understand the reaction mechanism of similar groups such as CH2=NH, CH2=PH, CH2=SiH2 etc. and the regioselectivity in each case. A concerted reaction mechanism is observed in all cases with a cyclic transition state.

* Tel.: +91 4712527567; fax: +91 4712527568.
  E-mail address: manojtk@iiitmk.ac.in.
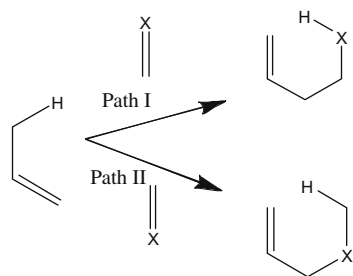
Scheme 1.

2. Computational methods

Geometries were optimized at B3LYP/aVDZ level of theory and frequency computations were performed at the same level. Energies were calculated at MP2/aVDZ and CCSD/aVDZ level of theory. Transition states were located and frequency computations were performed to confirm that the located stationary point is a transition state. Nuclear Independent Chemical Shift (NICS) values were computed at B3LYP/aVDZ using Gauge Independent Atomic Orbital (GIAO) method. All computations were performed using Gaussian-03 suite of programs [21].

3. Results and discussion

Important Geometrical parameters of different structures computed in the present work is given in Table 1 and the corresponding energies are given in Table 2. Structures of the reactants and transition states are shown in Fig. 1.

Transition states of the reaction between propene and ethene has been studied extensively by different computational chemistry research groups. Earlier results predicted an early transition state of H-transfer from propene to ethane [9,18]. Optimizations at B3LYP/aVDZ level of theory also indicate a similar mechanism and the geometry of individual molecules are not much different from those in transition state, except for the breaking C—H bond length. From Table 1, it can be seen that breaking C—H distance is 1.33 Å and bond forming C···H distance is 1.46 Å. The distance between two carbon atom interacting for the C—C bond formation in the TS state is 2.12 Å which is well within the range of C—C bond formation and the corresponding C—C bond length in the product is 1.54 Å. Although C—C bond forming and other bond lengths computed at B3LYP/aVDZ level is matching well with the CASSF results [17], C—H bond making and breaking distances are much shorter at DFT level of theory which is in good agreement with studies performed at MP2 and HF levels of theory [18].

As reported earlier [13,18], ene reaction between formaldehyde and propene prefers the proton transfer to O and alcohol is formed rather than ether. This reaction proceeds through a concerted path and the C—C bond forming distance in TS for alcohol product is 1.96 Å, The C—H bond breaking distance is 1.28 Å, and O—H bond forming distance is 1.38 Å. The activation energy difference between two paths resulting two regioisomers I and II are 15.0 kcal/mol at CCSD/aug-cc-pVDZ level of theory which indicate that alcohol product is highly favored over ether product, and is very much matching with earlier reports [18,22]. The ene reaction between methanethial and propene also may proceed either through path I and path II. The activation energy difference between the two pathways is only in the range of 3 kcal/mol at CCSD level of theory, which is slightly higher than MP2 energies reported earlier [18]. The geometry is also well matching with the earlier reports. The geometry of the constituent reactants are not much different from the isolated one, indicate that the transition state is an early one. The breaking and making C—H bond lengths are 1.19 and 1.99 Å and 1.30 & 1.46 Å, respectively, in path I and path II. From these data it is clear that the reaction may not be having a preferential regioselectivity and both the thiol and sulfide may be formed. Earlier theoretical reports also support these findings [18,23].

Further investigations were carried out on the reaction between propene and methylenimine. In this case, the activation energy difference between the two possible pathways are only in the range of 3 kcal/mol, thereby a mixture of two products is expected. The properties of the TS is similar to that of ethene–propene TS. Here in the TS, the breaking C—H distance of propene is of 1.39 Å (1.20 Å) and methylenimine C—H forming distance is 1.29 Å (1.34 Å) for path I (II). Experimental reports shows that imino ene reaction is highly regioseletive in presence of catalysts [24]. For the ene reaction between phosphaethene and propene, the activation energy difference between two paths are only in the range of 2 kcal/mol. Therefore, this reaction also may not be regioselective and both types of products are expected in the reaction. In both path I and path II the H breaking and making distance are 1.21 and 1.20 Å and 1.21 and 1.50 Å, respectively, for path I and II. Although theoretical reports of Diels–Alder reaction of phosphaethene is available, no results are available to compare ene reaction [25]. Compared to X = S and PH, ene reaction of CH2=SiH2 shows regioselectivity. The activation energy difference between

Table 1a
Important geometrical parameters of transition state structures computed at B3LYP/aug-cc-pVDZ (All bond distances are given in Å, NICS in ppm).

Structure	C1–H1	C1–C2	C2–C3	C3–C4	C4–X1	X1–H5	NICS(0)
TSC	1.33	1.42	1.39	2.12	1.41	1.46	−24.4
TSO	1.28	1.42	1.40	1.96	1.29	1.38	−21.6
TSO′	1.41	1.41	1.40	1.95	1.30	1.33	−24.8
TSN	1.39	1.41	1.39	2.25	1.34	1.29	−22.4
TSN′	1.20	1.45	1.43	1.66	1.34	1.34	−20.9
TSSi	1.27	1.43	1.39	2.18	1.79	1.90	−21.4
TSSi′	1.19	1.44	1.39	2.29	1.77	1.87	−16.0
TSS	1.19	1.44	1.39	1.98	1.71	1.99	−20.6
TSS′	1.30	1.42	1.38	2.42	1.69	1.46	−30.3
TSP	1.21	1.43	1.40	1.98	1.77	2.00	−22.4
TSP′	1.29	1.42	1.38	2.48	1.75	1.50	−22.0

Table 1b
Important geometrical parameters of reactant structures computed at B3LYP/aug-cc-pVDZ (All bond lengths are given in Å and bond angles in °).

Structure	C=X	X—H	XCH
CH2=CH2	1.34	1.09	121.7
CH2=O	1.21		121.8
CH2=NH	1.27	1.03	124.7
CH2=SiH2	1.71	1.48	122.0
CH2=PH	1.68	1.44	97.7
CH2=S	1.62		122.0
CH2=CH—CH3	1.34 (CH2=CH)	1.50 (CH=CH3)	1.10 (C—H)

Table 2a
Activation energy of ene reaction (Energy in kcal/mol).

	B3LYP		MP2		CCSD	
CH2=XHn	TS	TS′	TS	TS′	TS	TS′
CH2=CH2	33.45		23.43		40.72	
CH2=NH	29.69	33.02	22.63	23.26	38.67	41.47
CH2=O	24.14	37.77	19.82	32.66	35.36	50.36
CH2=SiH2	22.27	8.95	14.41	3.41	29.34	15.25
CH2=PH	20.8	18.64	11.46	9	28.33	26.47
CH2=S	13.76	16.56	7.81	6.62	23.11	25.98