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Theoretical studies of the cycloaddition reaction between vinyl sulfene, norbornene and related systems are presented. Since the parameterized AM1 semiempirical method was used, the generated data are only of qualitative value. The vinyl sulfene reactivity was assessed by using frontier molecular orbital (FMO) energy gaps, bond orders, and the charge distribution of the reactants. To obtain more information, as far as the reaction outcome and its feasibility, the transition state structures and activation barriers for competitive pathways are computed.

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Introduction.

Electrophilic sulfines ($R_2C=SO$) are recognized for their ability to react with nucleophiles and their 2π participation in [2+2] and [4+2] cycloaddition reactions [1]. Not as well known is the 4π participation of vinyl sulfenes ($R_2C=CH-CH=SO_2$) in Diels-Alder reactions with select dienophiles. For example, the Diels-Alder adducts of cyclopentadiene and thiocarbonyl compounds are attractive intermediates for the controlled synthesis of polyfunctional cyclopentadiene through sulfur-mediated transformations followed by desulfurization [2]. Vinyl sulfenes ($R_2C=CHCH=SO_2$) have the capability of undergoing [2+2] and [4+2] cycloaddition reactions in which the vinyl sulfene may serve as either a two- or four-electron reactant. The conjugated sulfenes have been proposed as intermediates in the thermal decomposition of thiete 1,1-dioxides [1]. The presence of vinyl sulfene intermediates has been supported by trapping them with phenol [4] and α,β -unsaturated carbonyl compounds [5]. As a source of vinyl sulfene, Dittmer and coworkers [3] used the thermolysis of thiete 1,1-dioxide. Due to its instability, it is trapped with norbornenes through a Diels-Alder cycloadduct. Here, we will present our comparative theoretical study of vinyl sulfene and 1,3-butadiene as dienes for the Diels-Alder reaction. If feasible, this might become a useful route for the preparation of bicyclo-derivatives through sulfur functionalization.

Computational Methodology.

All semiempirical calculations were performed on a DEC 7620 computer. Chem-3D Plus on a Macintosh IIfx was used as a graphical interface for drawing and visualizing all structures and for preparing the input files for MOPAC [6]. The AM1[7] semiempirical methods with the bonds [8] routine was used for optimization of the geometries and to compute the bond orders used. The search for the transition state structures and their verification [9] was performed as described previously [10]. The vibrational and thermal analyses were performed on all optimized structures.

Results and Discussion.

There are advantages and disadvantages of using the AM1 semiempirical methods for the computation of transition state structures. While it is generally accepted that semiempirical methods, such as AM1, give relatively good geometries and energies for non polar, mostly carbon-hydrogen bearing organic molecules [11], the method usually produces poor energies for the transformations that involve bond breaking and bond formation [11]. We have clearly demonstrated this on the example of the cycloaddition of cyanoethene with butadiene and cyclopentadiene [12]. Nevertheless, we have also demonstrated that the transition state structures computed with the AM1 semiempirical method are very close to those obtained with both *ab initio* and density functional methods (DFT) [13]. Although, the activation energies computed with the AM1 method cannot be considered as absolute values, we have demonstrated that they are useful for a qualitative study of the cycloaddition reaction [14]. There has been considerable dispute concerning the mechanism of Diels-Alder reactions [15]; a recent theoretical study at the correlated level supports the concerted mechanism [16]. Here, we have considered only the concerted mechanism of the Diels-Alder reaction. The computational chemist should consider that the AM1 semiempirical method does not include d orbitals in its computation; thus, all structures and energies of the sulfur containing molecules might be misleading. The error might be canceled out for the AM1 computed activation and relative energies of isomers. We implemented Frontier molecular orbital (FMO) theory [17], bond order correlations [18], and activation energies to determine the qualitative reactivity of the reactants presented in Figure 1.

According to FMO theory, the most reactive reagents in a Diels-Alder reaction are those that have the smallest gap in the HOMO energy of one reactant and the LUMO energy of the other. The addition of ethylene to cyclopentadiene has a FMO energy gap of 10.52 and 11.03 eV if the LUMO and HOMO ethylene orbitals are involved.

The FMO energy gap for the norbornene addition to butadiene is interesting in two ways: it selects the HOMO

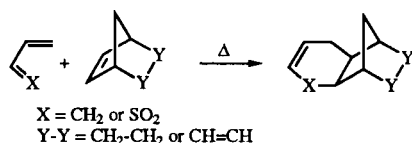


Figure 1. Cycloaddition between norbornenes and vinyl sulfene.

Table 1

LUMO and HOMO Energies (eV) of the Reactants Calculated by AM1 Semiempirical Methods

Compound	HOMO	LUMO
1,3-butadiene	-9.33345	0.48161
vinyl sulfene	-9.45353	-0.91389
norbornene	-9.58299	1.28308
norbornadiene	-9.41122	0.96110
difluoronorbornadiene	-9.25861	0.27992

dienophile and the LUMO diene controlled reaction and it is considerably lower than the ethylene addition to butadiene. The cycloaddition is predicted to have a lower activation barrier and to be an *inverse* Diels-Alder reaction. The FMO energy gap between the vinyl sulfene LUMO and the norbornadiene HOMO is only 8.50 eV (Table 2).

Table 2

Frontier Orbital Energy Gap (eV)

Diene	Dienophile	ΔE_I	ΔE_{II}
1,3-butadiene	norbornene	10.06	10.62
1,3-butadiene	norbornadiene	9.89	10.29
1,3-butadiene	difluoronorbornadiene	9.74	9.61
vinyl sulfene	norbornene	8.67	10.74
vinyl sulfene	norbornadiene	8.50	10.41
vinyl sulfene	difluoronorbornadiene	8.34	9.17

$$\Delta E_I = E_{\text{LUMO(diene)}} - E_{\text{HOMO(dienophile)}}; \Delta E_{II} = E_{\text{LUMO(dienophile)}} - E_{\text{HOMO(diene)}}$$

The synthetic organic chemist could use chemical intuition to explain this reaction with the fact that the norbornene double bond has more energy because the geometry of the sp^2 hybridization cannot be accommodated. According to the AM1 computed structure of norbornadiene, the C=C-C angle deviates by 12.3° from an ideal value of 120° . We have tested the assumption of the more energetic double bond through the computed heat of hydrogenations. Thus, the AM1 computed heat of hydrogenation of ethylene is -28.7 kcal/mol, norbornene is -35.2 and norbornadiene to norbornene is -36.6 kcal/mol. That qualitatively selects the norbornadiene as the most reactive dienophile for the *inverse* Diels-Alder reaction. This difference of reactivity of norbornene and norbornadiene as dienophiles in the

reverse Diels-Alder reaction can also be explained by norbornadiene being slightly higher in HOMO energy (by 0.17 eV) due to its two π -bond interactions (Figure 2).

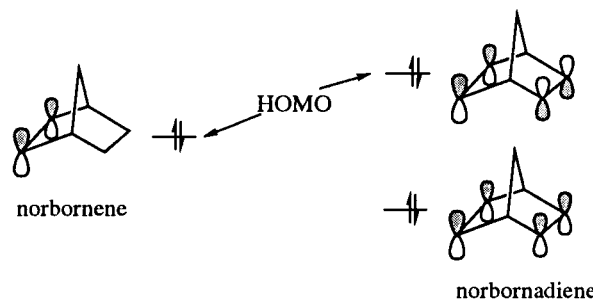


Figure 2. Energy diagram for π occupied molecular orbitals of norbornene and norbornadiene.

Presented above are the qualitative evaluations of vinyl sulfene reactivity regarding its addition to norbornene and norbornadiene. This evaluation will not predict the possibility of *exo-endo* isomer formation. The presence of steric interactions between the *endo* hydrogens of norbornene and butadiene or of the vinyl sulfene in the corresponding transition state structures can be substantial enough to prohibit *endo* isomer formation. Due to favorable FMO interaction in the *endo* transition state with norbornadiene as dienophile it is expected that this transition state would have a lower activation energy than the similar transition state structure with norbornene as a dienophile.

Other qualitative assessments of norbornene and norbornadiene reactivity can be obtained through comparative bond order study. Lendvay [18] demonstrated the usefulness of this method to follow the reaction pathway by following the changes of bond orders from reactants to products. For example, the reactivity of the reactant can be judged on the basis of their bond order values. If the bond order is very low, it can be assumed that the reactivity should be high. Let us examine the reactivity of thiete 1,1-dioxide, norbornene and norbornadiene (Figure 3). It is obvious that the C-S single bond is very weak with bond orders of 0.596 and 0.623, respectively. Consequently in both reactions, the four membered ring opening and the sulfur dioxide elimination, are possible.

Considering the bond order difference for thiete 1,1-dioxide, one would assume ring opening should be pre-

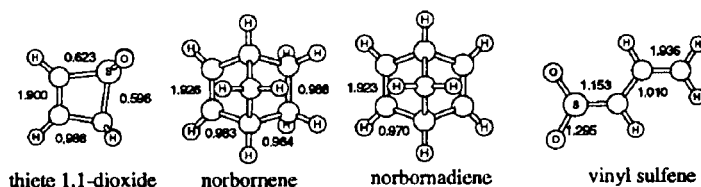


Figure 3. AM1 computed bond orders for the reactants.

ferred. On the other hand, norbornadiene has a slightly lower bond order, suggesting its higher reactivity in comparison to norbornene, as a dienophile in the Diels-Alder reaction. To confirm these findings we estimated the corresponding activation barriers. The ring opening of thiete 1,1-dioxide is estimated to be only 10.3 kcal/mol. If the elimination of sulfur dioxide is to occur, the estimated activation energy is 32.1 kcal/mol; because this process is in competition with ring opening, the reaction should not occur; this was confirmed experimentally. Not even a trace of the cyclopropene or any other products formed by SO_2 elimination were detected [3]. A slight difference in double bond order for norbornene and norbornadiene suggests a very small increase in reactivity for norbornadiene. In the case of vinyl sulfene, the S-C bond order is 1.153 for the single bond. The C-C double bond has a bond order of 1.936 that indicates very low π -bond delocalization and consequently high reactivity as a diene in the Diels-Alder reaction.

To estimate the activation energy for the reaction of vinyl sulfene with norbornene four isomeric transition state structures are computed (Figure 4).

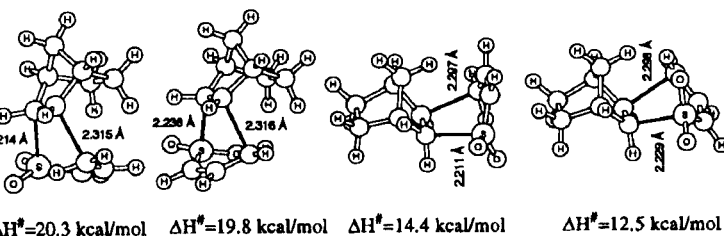


Figure 4. Four isomeric transition structures for vinyl sulfene and norbornene.

As is rare in Diels-Alder reactions, the *endo*-in (first transition structure, Figure 4) is predicted to have the highest reaction barrier. The *exo*-out (last transition state structure, Figure 4) is predicted to be responsible for formation of the cycloadduct. The AM1 computed activation enthalpy is only 12.5 kcal/mol. The experimental results are in agreement with our calculations. When the reaction is carried out only *exo* product was detected [3].

The question of the relative reactivity of vinyl sulfene as a diene for the Diels-Alder reaction is addressed through an evaluation of the activation barrier for the 1,3-butadiene reaction with norbornene (Figure 5). There is

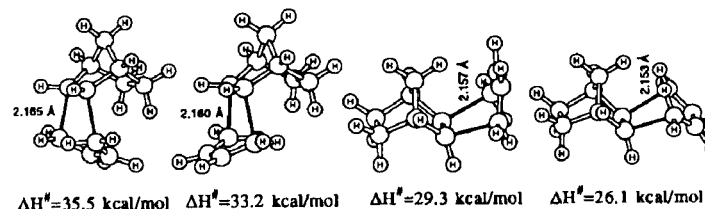


Figure 5. Isomeric transition state structures for 1,3-butadiene addition to norbornene.

little doubt that vinyl sulfene is more reactive than 1,3-butadiene. The computed activation barriers for the isomeric transition state structures between 1,3-butadiene and norbornene are around 15 kcal/mol higher, if compared with similar transition state structures of vinyl sulfene and norbornene (Figures 4 and 5).

In a continuation of our study we investigated the difference in norbornene and norbornadiene reactivity with vinyl sulfene. The computed transition structures with norbornadiene as diene (Figure 6) are very similar to the transition state structures with norbornene (Figure 4). As predicted on the

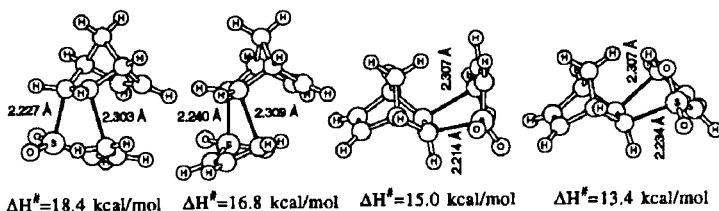


Figure 6. Transition states structures for vinyl sulfene addition to norbornadiene.

basis of qualitative frontier orbital analyses, for an *endo* addition of norbornadiene (first two transition state structures, Figure 6) the activation barrier is slightly lower. The *exo*-in transition state energy difference is 1.9 kcal/mol. This clearly demonstrates the influence of the second double bond. It can be explained in two ways, by molecular orbital interactions in the transition state structure with norbornadiene and by the steric effect of the *endo*-hydrogens of norbornene. These effects are believed incorporated in energy difference of 1.9 kcal/mol. Contrary to the *endo* isomer, the *exo* isomer with norbornene has a lower activation barrier. The HOMO of norbornadiene has a higher energy than the HOMO of norbornene. One explanation could be the inductive effect of the second double bond. If a negative inductive effect is present, electron density on the C-C double bond is lower, and for its HOMO controlled reaction the reactivity will be also lower. The AM1 computed Mulliken's charges [19] at the C-C double bonds are -0.1742 and -0.1722 for norbornene and norbornadiene. Because the nearby environment for the two *exo* transition structures are identical, the difference in charge density might be solely responsible for the lower reactivity.

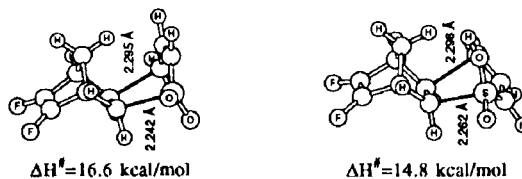


Figure 7. Two *exo* transition state structures for difluorobornadiene addition to vinyl sulfene.

This was further elaborated by the computed *exo* transition structures for difluoronorbomadiene, making the double bonds even more electron demanding. Mulliken's atomic charges on the double bond involved in the Diels-Alder reaction are -0.1668. The estimated activation energy for the *exo* addition is 1.5 kcal/mol higher than of the norbornadiene reaction. One would expect this outcome of the reactivity through FMO evaluation. Actually, FMO energy gap selects difluorobornadiene as the most reactive diene in this study (Table 2). This outcome would be expected if the reaction is LUMO but not a HOMO dienophile controlled reaction. It is also predicted that the difluorobornadiene addition to 1,3-butadiene becomes a normal Diels-Alder reaction. These computational results again demonstrate the weakness of parameterized methods, such as AM1 to properly handle systems that require considerable electron correlation to correctly evaluate energies. Nevertheless we believe the computed relative reactivity based on the activation energies are in qualitative agreement with the experiments.

Conclusion.

The presented results of the semiempirical studies of vinyl sulfene addition to norbornene and related structural models are more qualitative than quantitative in nature. Nevertheless, we can conclude that the ring opening of thiete 1,2-oxide to the corresponding vinyl sulfene is a thermally allowed process with modest (~ 11 kcal/mol) activation energy. The cycloaddition between vinyl sulfene and norbornene is an inverse Diels-Alder (HOMO dienophile or LUMO diene controlled) reaction. Because of high electron demand, addition of vinyl sulfene is predicted to occur with a moderate (~13 kcal/mol) activation barrier with predominant formation of the *exo* cycloadduct. By introducing a second double bond and electron withdrawing substituents, the reactivity is predicted to decline. This conclusion is in full agreement with data obtained when the reaction is carried out experimentally [3].

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