

## Theoretical Study of Ethylene and Vinyl Alcohol Addition to 1,4-Dioxa-1,3-butadiene

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An ab initio theoretical study of the cycloaddition reaction between 1,4-dioxa-1,3-butadiene with ethylene and vinyl alcohol as dienophiles and borane as Lewis catalyst is presented. The geometries of the reactants and transition states were calculated at the RHF/3-21G and RHF/6-31G\* level and the energies were estimated at the RMP2/6-31G\*/RHF/6-31G\* level. The activation energies are compared to the all-carbon cycloaddition reaction. The bond orders of the new forming bonds in the transition state, the charge separation in the transition state, and the energy gap of the frontier orbitals correlate well with the activation barriers for these reactions. The relative reactivity of the reactants is discussed in terms of these parameters.

### Introduction

The Diels–Alder reaction remains one of the most useful approaches to cyclic organic compounds in terms of regio control and simplicity.<sup>1</sup> Furthermore, the introduction of hetero atoms in the dienophile or diene or in both of them presents a powerful tool for the preparation of a wide variety of heterocyclic compounds.<sup>2</sup> The first reported reaction involving an oxabutadiene is the thermal dimerization of acrolein and methyl vinyl ketone giving rise to 3,4-dihydro-2*H*-pyranes.<sup>3</sup> Since then extensive experimental studies of related cycloaddition reactions have been performed.<sup>4</sup> The majority of hetero [4 + 2] photo and thermal cycloaddition reactions that involve the 1,4-dioxa-1,3-butadiene moiety are actually reactions between *o*-quinones and olefinic and acetylenic dienophiles.<sup>5</sup> There are only a few reports of [4 + 2] cycloaddition reactions with 1,4-dioxa-1,3-butadienes.<sup>6</sup>

This reaction can be performed thermally only when strong electron withdrawing groups are attached at the 2,3-position of the diene,<sup>7</sup> or in the presence of Lewis acids (ZnCl<sub>2</sub>) or electron donating dienophiles.<sup>6a</sup>

Extensive theoretical studies have been performed for the all-carbon Diels–Alder reactions.<sup>8</sup> In that respect, the hetero Diels–Alder reactions are considerably underinvestigated,<sup>9</sup> although from a synthetic point of view it is probably the most important method for the preparation of heterocyclic and natural products compounds.<sup>10</sup> There has been a recent semiempirical study of the intramolecular hetero-Diels–Alder reaction of 1-oxa-1,3-butadiene.<sup>11</sup> In this theoretical study the feasibility of the parent reaction between 1,4-dioxa-1,3-butadiene and ethylene was undertaken, and ways to enhance it either

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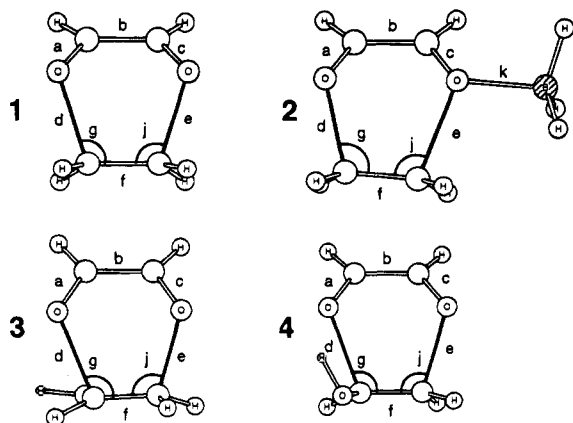


Figure 1. Geometries of the transition structures generated by RHF/6-31G\*.

by introduction of substituents or by the use of catalysts were investigated.

### Computational Methodology

Gas phase geometry optimizations without any restraints were carried out with Gaussian 92<sup>12</sup> at the restricted Hartree-Fock theory<sup>13</sup> level with the 3-21G and 6-31G\* basis sets.<sup>14</sup> All stationary points were identified by performing vibrational analysis with the same basis set used for the optimization. The activation energies were calculated at the RMP2<sup>15</sup>/6-31G\* level on the RHF/6-31G\* optimized geometries.

### Results and Discussion

The differences between 1,4-dioxa-1,3-butadiene and the all-carbon diene in the Diels-Alder reaction originate from the presence of the oxygen atoms that are directly involved in the formation of the two new bonds. The presence of the oxygen lone pairs is expected to push the reactants away due to their repulsion interactions with the  $\pi$  orbitals of the dienophile. The p atomic oxygen orbital overlap with the p carbon orbitals will lower the energy of the HOMO orbital (thus increasing the HOMO-LUMO energy gap). Also, the replacement of two carbonyl bonds with four CO single bonds is thermodynamically unfavorable. Considering all these disadvantages, major changes of the reactants' electronic properties are necessary to facilitate this reaction. This can be accomplished by introducing suitable substituents or by using a catalyst. All of these factors were considered by studying the addition of ethylene without and with  $\text{BH}_3$  as a Lewis acid catalyst, and the addition of vinyl alcohol to 1,4-dioxa-1,3-butadiene.

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Table 1. Selected Geometry Parameters of the Transition State Structures 1-4<sup>a</sup>

TS	a	b	c	d	e	f	g	j	k
1 I	1.276	1.386	1.276	1.962	1.962	1.388	107.6	107.6	
	1.255	1.392	1.255	1.912	1.912	1.400	107.6	107.6	
2 I	1.279	1.384	1.281	1.939	2.081	1.385	106.5	107.0	1.703
	1.262	1.386	1.263	1.854	2.053	1.400	107.4	106.0	1.698
3 I	1.272	1.388	1.280	2.027	1.923	1.377	103.8	107.8	
	1.249	1.392	1.263	2.029	1.844	1.395	102.6	108.7	
4 I	1.271	1.387	1.280	1.995	1.946	1.381	108.0	105.8	
	1.248	1.392	1.263	2.003	1.867	1.397	107.2	105.8	

<sup>a</sup> Denotations a, b, ..., f corresponding to the ones in Figure 1. I: calculated at RHF/3-21G. II: geometries calculated with RHF/6-31G\*.

Table 2. Bond Orders<sup>26</sup> of the New Forming Bonds in Transition Structures 1-4<sup>a</sup>

TS		d	e	d - e	d + e
1	I	0.265	0.265	0	0.530
	II	0.313	0.313	0	0.626
2	I	0.250	0.179	0.071	0.429
	II	0.328	0.221	0.107	0.549
3	I	0.209	0.291	-0.082	0.500
	II	0.224	0.358	-0.134	0.582
4	I	0.218	0.274	-0.056	0.492
	II	0.223	0.339	-0.116	0.562

<sup>a</sup> Bond orders were calculated by AM1 on (I) RHF/3-21G and (II) RHF/6-31G\* optimized geometries. d and e denote the new forming bonds presented in Figure 1.

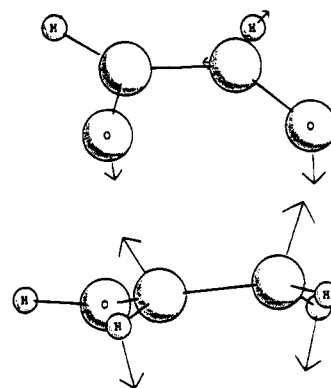


Figure 2. Description of the imaginary frequency for transition structure 3.

**Geometries of the Transition Structures.** The transition state structures generated by RHF/6-31G\* are presented in Figure 1. The corresponding geometry parameters for the transition structures and bond orders<sup>26</sup> for the forming bonds in 1-4 are presented in Tables 1 and 2, respectively. All transition structures had only one imaginary harmonic vibrational frequency, corresponding to the motion for the new forming C-C bonds in the concerted mechanism. As an example, a graphical description of the imaginary vibration of transition structure 3 is presented in Figure 2. The other transition structures have similar atomic motions for the imaginary vibration.

Transition state 1 for the ethylene addition to 1,3-dioxa-1,3-butadiene is fully synchronous and symmetrical. This is not unexpected since both the diene and the dienophile have a plane of symmetry which is retained in the transition structure. The bond order is 0.265 calculated on the RHF/3-21G geometry and 0.313 calculated on the RHF/6-31G\* geometry (Table 2). RHF/3-21G predicts an earlier transition state than RHF/6-31G\* and a considerably lower activation barrier. All other

**Table 3. Differences of Mulliken Charges on Atoms Involved in Bond Formation Calculated by RHF/6-31G\*\*<sup>a</sup>**

TS	$q(\text{dC})$	$q(\text{dO})$	$q(\text{eC})$	$q(\text{eO})$	$q(\text{O})$	CS
1	0.110	-0.068	0.110	-0.068		0.365
2	0.101	-0.044	0.121	-0.113		0.464
3	0.006	-0.140	0.268	-0.069	0.028	0.444
4	0.095	-0.151	0.195	-0.045	0.017	0.435

<sup>a</sup> Key:  $q(\text{dC})$ , charge on carbon of bond d;  $q(\text{dO})$ , charge on oxygen of bond d;  $q(\text{eC})$ , charge on carbon of bond e;  $q(\text{eO})$ , charge on oxygen of bond e;  $q(\text{O})$ , charge on vinyl alcohol carbon; CS, charge separation between the diene and the dienophile.

transition structures are formed from reactants that do not have a plane of symmetry and consequently the transition structures are expected to be asynchronous. The borane catalyzed addition is quite asymmetric. The new C–O forming bond in the vicinity of borane is 0.20 Å longer calculated at the higher level of theory. The corresponding bond orders are 0.328 and 0.221. Asynchronicity is predicted in both isomeric additions of vinyl alcohol. It is more pronounced in the endo isomer **3** than the exo isomer **4** because of steric and electronic interactions between the diene and the OH group of the dienophile. Interestingly, higher asynchronicity was obtained with the 3-21G than with the 6-31G\* basis set. That might be explained by the fact that the 6-31G\* basis set overestimates the electronic interactions in the transition states.

The bond orders give information on the degree of the new bond formation and in a series of similar transition structures can also serve as an indicator of the reactants' reactivity. If the bond order is lower the transition state is formed earlier and is more similar to the reactants than to the product. On the other hand, that will have influence on the activation barrier and the rate of the reaction. In the studied series transition state **2** for the borane catalyzed addition has the lowest bond orders for the two new forming C–O bonds while the addition of ethylene is predicted to have the highest activation barrier (the sum of the two new forming bond orders are 0.549 and 0.626, respectively). This prediction is in agreement with experimental evidence.<sup>6</sup> It should be noted however, that there is a inconsistency between the calculated bond orders and bond lengths for the new forming bond d in **3** and **4** (Tables 1 and 2). While the bond lengths calculated with the two basis sets are almost the same, the bond orders calculated from these geometries instead of slightly decreasing, increase. Presently, we have no explanation for this discrepancy.

**Charge Transfer in Transition States.** The reactivity of reactants in majority of organic reactions can be explained by following the charge transfer in the course of the reaction.<sup>27</sup> It is reasonable to believe that in a series of very similar reactions the ones that have the higher electron transfer are the most reactive. In all cases studied the negative Mulliken charge increases on both oxygens of the diene molecule (Table 3) while the positive Mulliken charge increases on the ethylene carbons. Thus, in the transition states the diene moiety carries considerable negative charge and the dienophile, the same portion of positive charge. The most reactive borane complex has the greatest charge separation in the transition structure **2**, while the least reactive ethylene has the least charge separation in transition structure **1**. The obtained charge separation in the transition states 1–4 confirms that the dienophiles display nucleophilic behavior towards the electrophilic 1,4-dioxo-1,3-butadiene.

**Determination of Reactivity by FMO Theory.** Frontier molecular orbital theory Explains the different reactivity on the basis of the energy levels of the reactants' HOMOs and LUMOs.<sup>16</sup> These energy effects are explained by Klopman<sup>17</sup> and Salem<sup>18</sup> from perturbation theory.<sup>19</sup> The examination of HOMO and LUMO interactions of 1,4-dioxo-1,3-butadiene with ethylene, vinyl alcohol, and 1,4-dioxo-1,3-butadiene-borane complex and ethylene are presented in Figures 3 and 4, respectively. It is well known that the frontier orbital energy levels for the ethylene addition to butadiene are closer for LUMO<sub>ethylene</sub>–HOMO<sub>butadiene</sub> (209.15 kcal/mol) than for LUMO<sub>butadiene</sub>–HOMO<sub>ethylene</sub> (265.65 kcal/mol) and it is called a normal electron demand, LUMO dienophile controlled Diels–Alder reaction.<sup>20</sup> The LUMO<sub>dienophile</sub>–HOMO<sub>diene</sub> energy difference for the ethylene addition to 1,4-dioxo-1,3-butadiene (Figure 3) is 384.65 kcal/mol, which is 175.51 kcal/mol higher than for the ethylene addition to butadiene. The energy gap for the LUMO<sub>diene</sub>–HOMO<sub>dienophile</sub> is only 272.96 kcal/mol but still higher than in the case of the ethylene addition to butadiene, indicating that the reaction is with an inverse electron demand and is LUMO diene<sup>21</sup> and HOMO dienophile controlled.<sup>22</sup> To perform the reaction between inactivated dienes and dienophiles vigorous reaction conditions, such as high pressure and temperature, are required.<sup>23</sup> One way of enhancing the reactivity is by increasing the electron density on the dienophile, as in vinyl alcohol (Figure 3), by increasing its HOMO energy level. Since the LUMO of the diene remains unchanged the energy gap is lowered to 255.39 kcal/mol. Another way of increasing the reactivity is by introducing Lewis acid catalysts that can make complexes with the diene thus lowering its LUMO energy (Figure 4). The LUMO energy is considerably lower than for the uncomplexed diene, and the energy difference is 237.19 kcal/mol.

**Activation Energies.** The total energies of the reactants and transition states are presented in Table 4. The activation energies for the cycloaddition reaction calculated at different theoretical levels are presented in Table 5. Frontier molecular orbital theory predicted that the addition of ethylene to 1,3-dioxo-1,4-butadiene is less favorable than the addition of ethylene to butadiene. Indeed, the activation barriers calculated with three different theoretical models are higher when 1,4-dioxo-1,3-butadiene is involved instead of butadiene. The

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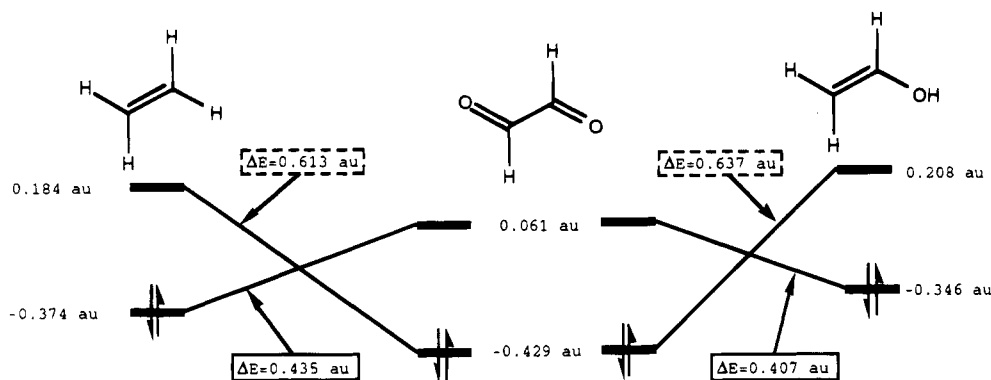
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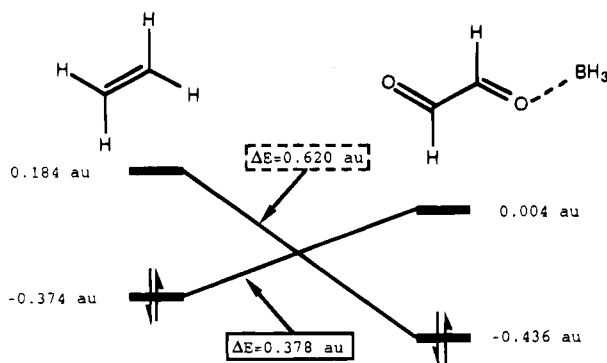
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**Figure 3.** Frontier orbital energy correlation between 1,4-dioxa-1,3-butadiene and ethylene and vinyl alcohol obtained from RHF/6-31G\*.



**Figure 4.** Frontier orbital energies of the diene-borane complex and ethylene.

**Table 4. Energies (au) of the Reactants and the Transition States in the Dienophile Additions to 1,4-Dioxa-1,3-butadiene<sup>a</sup>**

species	E1	E2	E3	E4	E5
C2H2O2	-225.306 96	0.035 93	-226.592 18	0.039 40	-227.183 56
BH <sub>3</sub>	-26.237 30	0.024 52	-26.390 00	0.026 73	-26.464 22
Et	-77.600 99	0.049 02	-78.031 71	0.052 83	-78.284 34
EtOH	-152.041 77	0.053 99	-152.888 89	0.058 91	-153.318 30
1	-302.829 90	0.089 00	-304.509 37	0.096 50	-305.417 31
2	-329.096 12	0.118 77	-330.914 36	0.128 87	-331.914 08
3	-377.274 48	0.093 20	-379.370 98	0.101 92	-380.458 92
4	-377.273 24	0.092 68	-379.369 20	0.101 18	-380.455 30

<sup>a</sup> Key: E1, HF/3-21G; E2, ZPVE HF/3-21G; E3, HF/6-31G\*; E4, ZPVE HF/6-31G\*; E5 MP2/6-31G\*/HF/6-31G\*.

**Table 5. Activation Energies (kcal/mol) for the Dienophile Additions to 1,4-Dioxa-1,3-butadiene<sup>a</sup>**

TS	E1	E2	E3	E4	E5
A <sup>b</sup>	35.90 (0.00)		45.00 (0.00)		16.58 (0.00)
1	48.98 (7.08)	51.52	71.86 (26.86)	74.54	31.75 (15.17)
2	30.83 (-5.03)	36.67	62.46 (17.46)	68.67	11.32 (-5.26)
3	46.59 (10.69)	48.65	69.08 (24.08)	71.35	26.95 (10.37)
4	47.37 (11.47)	49.11	70.20 (25.20)	72.00	29.22 (12.64)

<sup>a</sup> Key: A, ethylene addition to butadiene; E1, HF/3-21G; E2, HF/3-21G + ZPVE correction; E3, HF/6-31G\*; E4, HF/6-31G\* + ZPVE correction; E5, MP2/6-31G\*/HF/6-31G\*. <sup>b</sup> From ref 24.

energy difference is method dependent, thus RHF/3-21G predicts only 7.08 kcal/mol higher energy while the RHF/6-31G\* barrier is considerably higher. It is well known that RHF/6-31G\* usually overestimates the activation energies. Single point energy evaluation at the RMP2/6-31G\* theory level on the RHF/6-31G\* optimized structures predicts that the activation energy for the ethylene addition to 1,4-dioxa-1,3-butadiene is 14.15 kcal/mol higher than ethylene addition to butadiene. Knowing

that ethylene and butadiene do not react under normal experimental conditions, but at rather high temperature and pressure, it is not surprising that there is no experimental evidence for the cycloaddition of ethylene to 1,4-dioxa-1,3-butadiene.

Similar to FMO theory, all ab initio models show considerable decrease of the barrier in the borane catalyzed addition, compared to the uncatalyzed reaction (Table 5). The catalyzed reaction is predicted to have 18.15 kcal/mol (RHF/3-21G), 9.4 kcal/mol (RHF/6-31G\*), and 20.43 kcal/mol (RMP2/6-31G\*/RHF/6-31G\*) lower activation barrier than the uncatalyzed reaction. Moreover, RMP2/6-31G\*/RHF/6-31G\* predicts that the Lewis acid catalyzed reaction has a lower barrier than the corresponding all carbon Diels-Alder reaction. Surprisingly, RHF/6-31G\* still predicts that ethylene addition to butadiene is more reactive. This can be explained by the strong lone pair and  $\pi$  orbital repulsion interactions between the diene and the dienophile,<sup>25</sup> commonly seen in hetero cycloaddition reactions and which are overestimated by the RHF/6-31G\* model chemistry.

As already mentioned, another way to facilitate the inverse Diels-Alder reactions is by introduction of electron donating substituents. Frontier orbital theory predicted that vinyl alcohol should be more reactive than ethylene. However, ab initio calculations at RHF theory level predict that both the exo and endo addition will have higher or similar energy barriers as the addition of ethylene to 1,4-dioxa-1,3-butadiene. Frontier orbital correlations do not include the interactions of the reactants present in the transition state structure which are crucial for the activation energy. There two types of interactions that can be envisaged in these systems. On one hand, the interactions that can increase the energy of the transition states are the  $n-\pi$  repulsions and, on the other, the stabilizing interactions between the hydroxyl hydrogen with the diene p-system and the heteroatom lone pairs. Again Hartree-Fock calculations overestimate the contribution of the destabilizing interactions. MP2 predicts that indeed the addition of vinyl alcohol to 1,4-dioxa-1,3-butadiene should be more feasible

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(27) For the captivity effect, the effect for explaining the radical stabilization with both electron-withdrawing (captor) and electron-releasing (donor) substituent on the radical center see: Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148. Discussion for captadative olefins and dienes in Diels-Alder reactions see: Boucher, J. L.; Stella L. *Tetrahedron* **1988**, *44*, 3595; Boucher, J. L.; Stella L. *Tetrahedron* **1988**, *44*, 3607.

than the addition of ethylene, but still this reaction is less favorable than the ethylene addition to butadiene.

#### Conclusion

Four different approaches for the hetero Diels–Alder addition of 1,4-dioxo-1,3-butadiene as diene were considered: bond order, charge separation in transition structures, frontier orbital energy correlation, and activation energy barriers. All of them are in agreement with

experimental observations and correctly predict that borane catalyzed reaction will have the highest rate of the reaction while the slowest possible addition will be with inactivated ethylene as dienophile. The reactions are with inverse electron demand, and substituents that increase the donor ability of the dienophile and acceptor ability of the diene will facilitate the cycloaddition reaction.