Theoretical Study of the Diels—Alder Reactions of Zirconium Dimer with Ethylene and Butadiene

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A theoretical study of the symmetry concerted Diels—Alder analogue reactions of Zr₂ with ethylene and 1,3-butadiene is carried out. The optimized structures of the complexes indicate breaking of one of the multiple bonds in Zr₂ and 1,3-butadiene and the formation of a six-membered ring in agreement with symmetry concerted models. Thus the reaction of ethylene with Zr₂ is thermally forbidden, while it is allowed for the butadiene case. This is explained based on the natural orbitals picture. The presented potential energy surfaces are useful for the interpretation of possible reactions in both ground and excited states.

1. Introduction

Unsaturated olefins of transition metal complexes are important as starting materials or reactive intermediates in many catalytic processes.¹ In addition, they play an increasingly important role as stoichiometric substrates or reagents in organic synthesis.² Metal complexes undergo a variety of reaction types depending upon the nature of the metal fragment.³ The study of reactions of atoms or small metal clusters with unsaturated hydrocarbons facilitates comprehension of the role of isolated binding size, and in consequence the geometric and electronic structure interplay in the chemistry of transition metal clusters⁴ and metal surfaces. Metal—metal multiple bonds provide versatile templates for the interaction with organic molecules.⁵ The multiple bonds in transition metal dimers offer a variety of low-lying electronic states which can interact with unsaturated organic compounds in a symmetry-concerted fashion. The rich electronic structure of transition metal dimers offers the possibility for organometallic analogues of the Diels—Alder reactions, with more possible templates of orbitals than the classical carbon double bond reactions. The order of the multiple bonds would be a very important factor in such reactions. A recent note⁶ on the reaction of Cu₂ with ethylene in the gas phase raises the question⁷ of a possible organometallic Diels—Alder reaction. The ab initio studies of symmetry based cyclization reactions using transition metal dimers are rare.⁸ We recently studied Mo₂ reaction with olefins.⁹ The Zr₂ dimer with its quadruple bond¹⁰ is a good candidate for the Diels—Alder reactions. Such reactive studies could also be useful in the development of ab initio intermolecular potentials as already demonstrated for the Pt + CO system.¹¹ Extensive ab initio calculations of potential energy curves for symmetry concerted reactions of the Zr₂ dimer with ethylene and butadiene are presented in this work.

2. Method of Calculations

The calculations presented here were performed using the SCF and MCSCF¹² approaches. Geometry optimizations have been done by quasi-Newton—Raphson procedures.¹³,¹⁴ All of the calculations described here were made relativistic effective core potentials (RECPs), which retained the outer 4s4p4d5s subshells of Zr¹⁵ and the 2s2p shells of the carbon atom.¹⁶ The basis set for Zr has been prepared from the LaJohn et al. collection¹⁶ by decontracting the two least diffuse Gaussians in a way which leads to a valence [3s3p3d] basis set. The basis set for carbon was from Pacios and Christiansen,¹⁷ but we leave the most diffuse functions uncontracted. The carbon basis set was supplemented with six-component 3d Gaussian function adopted from Dunning and Hay,¹⁸ leading to a [2s2p1d] basis set. For hydrogen, Van Duijneveldt's²⁰ (4s) basis set, contracted to [2s] was employed. This choice of basis functions leads to 36 orbitals for Et—Zr₂ and 128 orbitals for But—Zr₂ complexes. However, the basis set for the Zr atom in case of CASSCF calculations of But—Zr₂ has been reduced, so that these calculations are feasible. The basis set has been contracted to a [3s2p2d] scheme by contracting the three least diffuse d Gaussians. The 5p Gaussians of the LaJohn et al. basis were split into two segments of three and two Gaussians.

The complete active space self-consistent field (CASSCF) computations were performed for the C₃ᵥ symmetry optimized geometries of Et—Zr₂ complex. Excitations from 13 lowest molecular orbitals were not allowed since these orbitals are not important from the standpoint of valence chemical bonding. However, they were allowed to relax at the CASSCF stage. The active space included nine orbitals among which 10 electrons

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Footnotes:

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TABLE 1: Results of Geometry Optimization of Ground State Structures of Et-ZrZ and But-Zr2 Complexes and Dissociated Fragments at 10.0 Å Separation

<table>
<thead>
<tr>
<th>bond or angle</th>
<th>complex</th>
<th>this work</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>Ethylene–Zr2</td>
<td>1.56</td>
<td>1.35</td>
</tr>
<tr>
<td>Zr–Zr</td>
<td>2.52</td>
<td>2.31</td>
<td>2.34*</td>
</tr>
<tr>
<td>Zr–C</td>
<td>2.91</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>C–H</td>
<td>1.10</td>
<td>1.08</td>
<td>1.084*</td>
</tr>
<tr>
<td>&lt;CCH</td>
<td>111.7</td>
<td>121.8</td>
<td>122.25*</td>
</tr>
<tr>
<td>&lt;HCH</td>
<td>105.4</td>
<td>116.4</td>
<td>115.5*</td>
</tr>
<tr>
<td>&lt;CCH</td>
<td>116.5</td>
<td>126.4</td>
<td>123*</td>
</tr>
<tr>
<td>&lt;HCH</td>
<td>112.3</td>
<td>123.5</td>
<td></td>
</tr>
<tr>
<td>&lt;HCHZr</td>
<td>110.2</td>
<td>116.5</td>
<td>120.1*</td>
</tr>
</tbody>
</table>


The calculations were distributed in all possible ways. The chosen active space allows the realization of any electronic configuration which may prove to be important for equilibrium, transition state, or dissociated geometry of the complex during this reaction process. In the But–Zr2 case (C2v symmetry) 19 orbitals were kept in "core". The active space of eight orbitals was selected, and eight electrons were distributed among them. The calculations were performed using Gamess21 and Gaussian22 packages.

3. Geometry Optimization of Ethylene–Zr2 and Butadiene–Zr2 Complexes

The geometry of the ethylene–Zr2 complex has been optimized assuming C2v symmetry along the reaction pathway (Figure 1). The optimization has been performed at the SCF level, and the results are given in Table 1. The calculated C–C bond distance in the complex corresponds to a C–C single bond.23 The Zr–Zr bond in the complex is 0.2 Å longer than the distance at the dissociation limit and corresponds to a bond elongation after one of the multiple bonds is broken. The HCH angle of 105.4° for the singly-bonded carbons is consistent with the sp3 hybridization on those carbon atoms. The optimized bond distances at the dissociation limit are in excellent agreement with experimental bond lengths in ethylene and with the previously computed Zr–Zr bond distance in Zr2 dimer.11 The geometry at the dissociation limit is suggestive of reasonable geometry reproduction along the whole reaction pathway. The optimized structure of the complex has a dipole moment of 1.48 D. The Mulliken population analysis is consistent with this picture in that the total population of both Zr atoms is reduced by 0.72 electrons in the complex compared to the dissociation limit.

The optimization of the But–Zr2 complex has been performed assuming the C2v symmetry (Table 1). Butadiene and Zr2 lie in two different planes with outer carbons of butadiene lying at the intersection of planes (Figure 2). The optimized angle between the two planes is 96.3°. The Zr–Zr distance in the complex of 2.516 Å is similar to the corresponding bond in the ethylene–Zr2 complex. Bonds in the butadiene skeleton have been relaxed compared to those in a free butadiene and are 1.38 Å for a newly created double bond and 1.48 Å for the new single bonds. The HCH angle of 110° for the singly-bonded carbon atoms in the complex indicates that these carbon atoms exhibit sp3 hybridization, a deep structural change from the sp2 hybridization of carbon atoms of the butadiene. The computed dipole moment of the complex is 1.79 Debye. The Mulliken population indicates transfer of 0.564 electron from the Zr2 dimer to butadiene. Another possible But–Zr2 complex in which both C and Zr atoms lie in one plane has higher energy (12.3 kcal/mol) compared to the structure studied above.

Figure 2. Zr–Zr and C–C bond distance variations for the symmetry concerted reaction of 1,3-butadiene with Zr2.
Figure 3. Orbital energy variation of some of the high lying (occupied) orbitals for different separations of ethylene and Zr₂ for the ground state of the complex (solid lines) and variations of orbital energies corresponding to preserved electronic configuration (dotted line) at equilibrium geometry. Note that the lowest energy configuration changes at 3.0 Å from $a_1[2b_2][2a_2]$ to $a_1[2a_2][2a_1]$. Thus there is a sharp change in the orbital energies of the $b_2$ MO and $a_1$ (III) MO at 3.0 Å.

Figure 4. CASSCF potential surfaces for the $C_2$ concerted reaction of Zr₂ with ethylene.

4. Interaction of Zr₂ with Ethylene and Butadiene in the Ground State

In analogy to the dimerization of ethylene, the ethylene-Zr₂ cyclization can be regarded as a reaction which preserves the $C_2$ symmetry. The optimization of the geometry for the reaction preserving pathway in the $C_2$, symmetry (Figure 1) indicates a sudden change of geometrical parameters of the complex around the ethylene and Zr₂ separation of 3.0 Å. The closed shell wave function of the equilibrium structure is composed as $8a_1^25b_2^23b_1^22a_2^2$. This structure, however, does not dissociate to the energetically lowest fragments. The lowest closed shell electronic structure at the dissociation limit is $9a_1^2$. The most important changes in bond lengths are shown on Figure 1. The dotted line on Figure 1 shows the continuation of the Zr-Zr distance when the ground state configuration is preserved. However, an energetically preferred path leads to a sudden drop in the Zr-Zr distance, for ethylene and Zr₂ separation of 3.0 Å, to values close to the bond in Zr₂. Similarly, the smooth continuation of orbital energies (Figure 3) for the equilibrium configuration is broken by the significant change forced by the energy preferred configuration. The two diabatic curves could be referred to as the dissociation curve and the equilibrium curve. The barrier in the potential energy surface (Figure 4) was constructed by joining the energetically
lower dissociated and equilibrium curves. A similar behavior for the ground state optimization has been observed in the case of Mo₂ interaction with ethylene. This is consistent with the general picture of reaction surfaces between transition metal clusters and hydrocarbons. The transition state for the complex is determined by the crossing of reactant-like surface and the dissociated surface. The single determinantal structure of the wave function (as is shown later in this paper) for BI and B₂ electronic states allows at least qualitative studies of optimized geometries in these states. In both cases the sudden geometrical changes are also observed for particular intermolecular Zr₂ and ethylene separation.

The composition of the closed shell wave function for the butadiene—Zr₂ complex 14a 28a" 2 is the same along the whole reaction pathway, preserving the C₂ symmetry. Consequently, butadiene-Zrz complex 14a 28a" 2 is the same along the whole barrier for the complex formation proceeds smoothly when monitoring the bond distances (Figure 2) and energy changes. No barrier for the complex formation is observed in the case of butadiene + Zr₂.

5. Potential Energy Surfaces for the Low-Lying Electronic States for the Interaction of Zr₂ with Ethylene and 1,3-Butadiene

The low-lying electronic states for the symmetry-concerted reaction (C₂v) of Zr₂ with ethylene are shown in Figure 4. Analogous to those of the diabatic SCF model the changes have their characteristics around Zr—C distance of 3.0 Å from the low energy curve. The CASSCF ground state curve shown in Figure 4 is constructed from the low energy curve along the dissociation pathway with the valence configuration of a₁b₁b₁a₁ for r < 3 Å. For r > 3 Å, the CASSCF curve is from dissociation curve with the leading configuration of a₂b₂a₂b₂. The transition state is the intersection of the two curves. The wave function is influenced by interactions with higher states and has multireference character (Table 2). The ground state dissociates to Zr₂ (1Σᵥ) and the X1 Ag ground state of ethylene. The dissociation energy amounts to only 6 kcal/mol. However, there is a high barrier of 46 kcal/mol for this process. The reaction is thus thermally forbidden.

Low-lying excited states of ethylene—Zr₂ complex dissociate to the ground state of ethylene and low-lying excited states of the Zr₂ dimer. Due to the restricted zeroth-order CASSCF treatment of the electronic states, we do not expect the energy separations of excited electronic states to be reliable. However, the surfaces are expected to provide qualitative trends. The excitation energies at the dissociation limit lie below the lowest excitation energy of ethylene (0.13 Hartree). The energies of vertical excitations are not available for the Zr₂ dimer. However, the order of electronic states agree with the adiabatic excitation energy of ethylene (0.13 Hartree). All excited states studied exhibit energy barriers. These states have distinct multireference character around their respective equilibrium geometries (Table 1). The wave function at the dissociation limit corresponds to low excitations from the wave function of the ground state (a₁b₁a₁b₁a₁), making it very different from the wave function near the equilibrium geometry.

The potential energy curves for the reaction of Zr₂ with 1,3-butadiene are presented on Figure 5. In contrast to low lying states of the ethylene—Zr₂ complex, all curves studied have no barriers. The dissociation energy for the ground state is 47.0 kcal/mol.

6. Discussion of Results and Conclusions

Geometry optimizations of the complexes between Zr₂ and ethylene and 1,3-butadiene lead to structures with elongated Zr—
Diels–Alder Reactions of Zr Dimer


Zr bonds consistent with one bond being broken from the multiple bonds during the formation of the complex. The reactions change ethylene and butadiene double bonds into single bonds which fits very well with the concerted reaction picture. The formation of a new double bond is observed in the reacting butadiene. The closed shell ground state configuration of ethylene–Zr₂ complex is composed of different molecular orbitals at the equilibrium complex and dissociation region. This leads to the ground state energy barrier, even when the reaction is studied at the SCF level. Three molecular orbitals of Zr₂ are involved in reactions proceeding in the low-lying excited states: HOMO $\sigma_2$ (a₁ in the C₂ᵥ symmetry complex) and LUMOs ($\sigma_3(b_2)$ and $\delta_1(b_1)$) (Figure 6). These orbitals face the totally symmetric side of ethylene HOMO(a₁) or unsymmetrical side of butadiene HOMO(a") orbitals (Figure 7). In agreement with the symmetry concerted model, the overlapping orbitals of the same sign leads to the bond formation and ring closure. This is clearly not the case in the ethylene–Zr₂ complex for the B₁ and B₂ states. The ground state complex is formed from the Zr₂ ground state with occupation numbers 1.87 for $\sigma_2$ and 0.12 for $\sigma_4$. The large occupation for natural orbitals in the unsymmetrical $\sigma_2$ orbital leads also to an energy barrier. In the case of butadiene, HOMOs(a") of Zr₂ and butadiene perfectly match and thus smooth curves for the complex formation are observed.

Mulliken population analyses for three electronic states ($^1$A₁, $^3$B₂, and $^1$B₁) of the Et–Zr₂ complex reveals that the breaking of one of the multiple the Zr–Zr) bonds involves d orbitals.

**Figure 6.** The contour plots of three natural orbitals of Zr₂ dimer involved in bonding with olefins. The cutting plane is 0.5 Å above the Zr–Zr bond. Dotted lines signify the negative value of wave function. The increment between successive contours is 0.05 Bohr⁻³⁻. **Figure 7.** The contour plots of ethylene and butadiene highest occupied natural orbitals. The cutting plane is 0.5 Å above the molecular plane. The dotted lines signify the negative value of wave function. The increment between successive contours is 0.05 Bohr⁻³⁻.
The new bond formation leads to the electronic density rearrangement and orbitals overlapping with approaching ethylene gain a significant portion of electronic density coming from the broken bond of zirconium. Again, both p and d orbitals play a significant role in the formation of the Zr–C bonds.

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References and Notes

(22) Gaussian 92, Revision E.2; Frisch, M. H.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1992.

TABLE 3: Structure of Wave Function for Low-Lying Excited States of But–Zr Complex at the Ground State Equilibrium Geometry (Energy in Hartree)

<table>
<thead>
<tr>
<th>state</th>
<th>no. of leading configuration(s)</th>
<th>coeff</th>
<th>corresponding Zr2 state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A'</td>
<td>924</td>
<td>0.887</td>
<td>1Σ+</td>
</tr>
<tr>
<td>1A''</td>
<td>1176</td>
<td>0.555</td>
<td>1Σ−</td>
</tr>
<tr>
<td>3A'</td>
<td>-1176</td>
<td>-0.472</td>
<td>3Σ+</td>
</tr>
<tr>
<td>1A''</td>
<td>840</td>
<td>0.438</td>
<td>1Σ−</td>
</tr>
</tbody>
</table>

The new bond formation leads to the electronic density rearrangement and orbitals overlapping with approaching ethylene gain significant electron population (0.28 for dz2 and 0.18 for px in the ground state). These observations apply to every electronic state studied. The virtual p orbitals of the Zr atom have significant Mulliken population indicating their importance in the bond formation. Similar conclusions are drawn for the butadiene–Zr complex (Table 2). Atomic orbitals of zirconium overlapping with approaching butadiene gain a significant portion of electronic density coming from the broken bond of zirconium. Again, both p and d orbitals play a significant role in the formation of the Zr–C bonds.