Organometallic Analogues of the Diels–Alder Reaction: Molybdenum Dimer + Ethylene; Molybdenum Dimer + Butadiene

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A theoretical study of the symmetry-concerted Diels–Alder analogue reactions of Mo2 with 1,3-butadiene and ethylene is presented. Structure optimizations indicated elongation of the Mo—Mo and C=C bonds in the complexes. The optimized bond distances were found to be close to ones known in organomolybdenum complexes. The presented potential surfaces indicated, in agreement with symmetry-concerted models, that the Mo—C=H complex formation is thermally forbidden, as the reaction has to proceed in the excited state, but the Mo—But complex may be formed in the ground state with addition of thermal energy.

Introduction

Metal–metal multiple bonds provide versatile templates for the interaction with unsaturated organic molecules.1 A rich coordination chemistry of Mo2 and W2 has already been noted with respect to carbon monoxide,2 ethylene,3 allene,4 and butadiene.5 A recent note6 on the reaction of C2H4 with ethylene in the gas phase once again raises the question5 of a possible organometallic analogue of the Diels–Alder reaction:

\[ \text{M} = \text{M} + \quad \text{M} \quad \text{M} \]

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 Mo2 dimer with its sextuple bond7 is a perfect candidate for such a reaction. In this work we study the interactions of low-lying excited states of Mo2 with ethylene and 1,3-butadiene.

Method and Computational Details

The presented calculations were performed using the SCF, CASSCF, and FOCI methods.8 Geometry searches were done by quasi-Newton–Raphson procedures.9,10 All of the calculations described here were made using relativistic effective core potentials (RECPs), which retained the outer 4s4p6d5s shells for Mo11 and 2s2p shells for the carbon atom.12 The basis set for Mo has been prepared from the LaJohn et al. collection11 by decontracting the most diffuse Gaussians in a way which leads to a valence (3s3p2d) basis set. Other basis sets were also used for the test calculations for the Mo2 dimer. The basis set for carbon was from of Pacios and Christiansen,12 but we leave the most diffuse functions uncontracted. The carbon basis set was supplemented with six-component 3d Gaussian functions adopted from Dunning and Hay,13 leading to a (2s2p1d) basis set. For hydrogen, van Duijneveldt’s14 (4s) basis set was employed. The calculations were performed using the Gaussian package of codes.15

Calculations for Mo2 Dimer

The geometry optimizations of ethylene–Mo2 and butadiene–Mo2 complexes depend strongly on the proper description of the Mo—Mo bond. The equilibrium geometry of Mo2 is very sensitive to theoretical methods and basis sets employed. Mo2 calculations serve also as a performance test for relativistic effective core potentials used in the current calculations. Spectroscopic studies16 on the gas phase species lead to the equilibrium distance \( R_e = 1.928 \) Å for Mo2, which is shorter than any other known Mo–Mo quadruple bond.17 The predicted bond order in the Mo2 dimer, based on the overlap population analysis, is \( 6^{18} \) with two \( \sigma \) molecular orbitals and a \( \delta \) orbital supplementing the well-known \( \sigma^* \) and \( \delta^* \) quadruple bond. The available \( \text{ab initio} \) calculations gave bond distances between 1.87 and 2.1 Å, indicating difficulties with the proper reproduction of geometries. We have optimized the geometry of Mo2 by applying the SCF and MCSCF approaches. The calculations were performed with relativistic effective core potentials18 which retained 14 electrons of the molybdenum atom (4s4p4d5s1) in the valence space. Several basis sets were prepared from the ones proposed by LaJohn et al.11 by leaving the most diffuse exponents uncontracted according to the schemes given in Table 1. At both CASSCF
molybdenum. The optimized bond distance in the complex corresponds to a C-C single bond after a single bond is broken. The calculated Mo-C distances are close to the bonds known from organometallic complexes. The Mo-Mo bond in the complex is 0.07 Å in the Mo₂ dimer and corresponds to an average elongation of the Mo-Mo bond. The geometry is the same as the one predicted by other theoretical methods. The SCF bond lengths obtained with the same basis are also in excellent agreement with experimental bond lengths.

Complexes formed due to an avoided crossing at a Mo-C distance of 2.34 Å for the newly created double bond and 1.47 Å for single bonds. The calculated Mo-C bond distance of 2.34 Å compares well with the bonds found in organomolybdenum compounds. The Mo₂-But complex is not as rigid as Mo₂-Eth, and the strain in a newly formed four-member ring is much smaller than that in a four-member ring of the Mo₂-Eth complex. As will be shown later, these geometrical differences affect the energetics of the symmetry-concerted reactions leading to the formation of studied organometallic compounds.

Table 1. Theoretical and Experimental Bond Distances in Mo₂ (Å)

<table>
<thead>
<tr>
<th>basis set</th>
<th>SCF</th>
<th>CASSCF</th>
<th>other theoretical</th>
<th>exp1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5s5p4d)</td>
<td>1.906</td>
<td>1.918</td>
<td>1.929</td>
<td></td>
</tr>
<tr>
<td>(5s5p4d) → [3s3p2d]</td>
<td>1.903</td>
<td>1.923</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reference 16; a Reference 20; SCF with ECP. c Reference 21; SCF.

Geometry Optimization of Mo₂-Ethylene and Mo₂-Butadiene Complexes

The geometry of the Mo₂-Ethylene complex has been optimized assuming C₉ symmetry along the reaction pathway (Figure 1). The optimization has been performed at the SCF level. The C₉ symmetry is preserved along the reaction pathway. The calculated C₉ bond distances at equilibrium are 1.53, 2.00, and 2.16 Å, respectively. The calculated C₉ bond distance in the complex corresponds to a C₉-C single bond. The Mo-Mo bond in the complex is 0.07 Å longer than the one in the Mo₂ dimer and corresponds to an average elongation of the bond after a single bond is broken. The calculated Mo-C distances are close to the bonds known from organometallic compounds containing molybdenum. The optimized bond distances at the dissociation limit (C-C = 1.35 Å, Mo-Mo = 1.93 Å) are in agreement with the bond lengths found in ethylene²² and the Mo₂ dimer.¹⁶ The optimized structure of the Mo₂-Eth complex has a dipole moment of 2.77 D, which is related to a significant charge transfer from the molybdenum atom to the carbon atoms amounting to 0.13 electron.

The optimized angle between the two planes is 79.9°. The Mo-Mo distance in the Mo₂-But complex (2.12 Å) is similar to that of the Mo-Mo quadruple bonds. Bonds in butadiene skeleton have been relaxed compared to those in the free butadiene molecule and are 1.39 Å for the newly created double bond and 1.47 Å for single bonds. The calculated Mo-C bond distance of 2.34 Å compares well with the bonds found in organomolybdenum compounds. The Mo₂-But complex is not as rigid as Mo₂-Eth, and the strain in a newly formed four-member ring is much smaller than that in a four-member ring of the Mo₂-Eth complex. As will be shown later, these geometrical differences affect the energetics of the symmetry-concerted reactions leading to the formation of studied organometallic compounds.

Interactions of Mo₂ with Ethylene

In analogy to the dimerization of ethylene, ethylene-Mo₂ cyclization can be regarded as a reaction which preserves the C₉ symmetry. The Mo₂ dimer has a number of low-lying closed-shell states which may interact with the ground state of ethylene (X1Aₑ). The stable complex is formed by the π₄⁺π₅⁻π₆⁻ valence configuration of Mo₂, which is higher in energy. The ground state SCF potential curve has a significant barrier of 2.7 Å. A simple model such as the closed-shell SCF approach

Figure 2. Optimized structure of the Mo₂-butadiene complex. The Mo-Mo, Mo-C, C-C, and C≡C distances in the complex are 2.12, 2.34, 1.39, and 1.47 Å, respectively. The optimized angle between the two planes is 79.9°. The Mo-Mo, Mo-C, and C-C bond distances of the Mo₂-ethylene complex are 2.00, 2.16, and 1.53 Å, respectively.
shows that potential surfaces between 2.0 and 3.0 Å have very complicated structures with a large number of avoided crossings.

The potential energy surfaces for the interactions of Mo₂ with ethylene and butadiene were studied within the CASSCF formalism. As noted above, the active space is sufficiently flexible to yield reasonable spectroscopic constants near the minima. While the dissociation energies tend to depend more heavily on higher-order correlation effects, qualitative description of such large-scale systems is possible within the CASSCF approach. This was already demonstrated in a recent study on the Pt + CO system. However, in the current study, the more accurate FOCI method, which includes higher-order correlation effects, was used for semiempirical estimation of the dissociation energies. It should also be noted that the computations of the dissociation energies of the Mo₂–Eth and Mo₂–But complexes are easier and less intensive compared to computing the $D_e$ of Mo₂.

The CASSCF computations of the Eth–Mo₂ system were made in $C_{2v}$ symmetry. The active space consisted of six orbitals (three HOMOs and three unoccupied orbitals) which spanned three $a_1$, two $b_1$, and one $b_2$ orbital in the $C_{2v}$ group. Six active electrons were distributed in all possible ways among these orbitals. The FOCI computations included all CASSCF configurations plus those configurations obtained by distributing five electrons in the internal space and one electron in the orthogonal external space in all possible ways.

**Potential Energy Surfaces for the Interactions of Mo₂ with Ethylene and 1,3-Butadiene**

The low-lying electronic states for the symmetry-concerted reaction ($C_{2v}$) of Mo₂ with ethylene are shown in Figure 3. Due to strong interactions between the electronic states, the potential energy surfaces are often irregular. Similar to those of the diatomic SCF model, the curves change their characteristic around a Mo–C distance of 2.7 Å. The CASSCF ground state curve (1A₁) changes its character along the dissociation pathway, and the valence configuration of $\sigma_{2d^2}$ near the equilibrium geometry is replaced by $\alpha_{2d^2}$ near the dissociation limit. The lowest excited state of 1A₂ symmetry also corresponds to a closed-shell configuration. The nature of the state is very similar to that of the ground state; namely, different configurations contribute to it at the equilibrium geometry ($\sigma_{2d^2}^2\sigma_{2b}^2\pi_{2b}$) and the dissociation limit ($\sigma_{2d^2}^2\sigma_{2b}^2\pi_{2b}$) in the CASSCF wave function. The configurations contributing to the ground and lowest excited states are different, however. The complicated structure of both these curves is due to interactions with higher states. The energy barrier for the ground state reaction is 6 kcal/mol when calculated within the CASSCF model. Calculations with the first-order configuration interaction (FOCI) formalism lead to a barrier of 28.6 kcal/mol. The energies of the dissociation products, however, lie much lower than the energy minimum of the complex, and the dissociation energy is -22.97 kcal/mol (CASSCF) or -17.64 kcal/mol (FOCI). The reaction is thermally forbidden. The reaction is photochemically allowed and may proceed in various excited electronic states which lead to the bonding structure. The $3B_1$ state leads to a structure geometrically and energetically very close to the ground state.

The reaction of Mo₂ with 1,3-butadiene has been studied for the ground state only. Since we optimized the geometry for the equilibrium structure only, the complex was dissociated by keeping Mo₂ and butadiene geometries unchanged. In contrast to the ground state potential curve of the Mo₂-Eth complex, the Mo₂ + butadiene complex curve (Figure 4) has a regular shape without any energy barrier. At the CASSCF level, the dissociation energy is 34.9 kcal/mol. The dissociation energy calculated using the FOCI method amounts to 50.3 kcal/mol. Compared to the CASSCF, the FOCI method includes more electron correlation effects. We expect the FOCI $D_e$ to increase further if more electron correlation effects are included. Note that the equilibrium geometry of the complex is fully optimized while the geometries of the dissociated fragments were not fully optimized. Thus, $D_e$ would be overestimated by a few kcal/mol, which however would be offset by the electron correlation effects.

A previous study employed the same basis set for Mo and the CASSCF/CI technique to compute the properties of MoH and MoH⁺. The $D_e$(MoH⁺) obtained using the theoretical method is 41.0 kcal/mol, in almost exact agreement with the $D_e$ value of 41 ± 3 kcal/mol reported by Schilling et al. Due to the similarity of the Mo–H and Mo–C σ bonds, we expect the Mo–C σ bonds in the Mo–butadiene and Mo–Eth complexes to


Figure 3. CASSCF potential surfaces for the $C_{2v}$-concerted reaction of Mo₂ with ethylene. 1 hartree = 27.211 eV = 635.6 kcal/mol.

Figure 4. CASSCF and SCF ground state potential surfaces of the Mo₂ and 1,3-butadiene reaction. 1 hartree = 27.211 eV.
be computed with good accuracies. The complex formation reaction is thermally allowed.

The computed potential energy surfaces reveal significant differences between interactions of Mo$_2$ with ethylene and butadiene. The Mo$_2$-Eth reaction is thermally forbidden and the complex is formed in the excited states, while the formation of Mo$_2$-But proceeds in the ground state potential energy surface spontaneously. These results are in agreement with a simple model of symmetry-concerted reactions based on symmetry considerations of molecular orbitals, in analogy to the Diels-Alder reaction between olefins.

**Conclusion**

Geometry optimizations of complexes between Mo$_2$ and ethylene and 1,3-butadiene lead to structures with elongated Mo—Mo bonds similar to the one found in organometallic compounds containing molybdenum. The C—C bond distances change due to the rearrangement of $\pi$ electrons. Calculated bond distances agree well with chemical intuitions. The C—C bond in the Mo$_2$-Eth complex became close to a C—C single bond. The butadiene ring gains one double bond in the C(2) position.

The predicted Mo—C bond distance agrees with known distances in organometallic compounds composed of Mo.

Potential energy curves for the concerted reactions are very complicated due to many low-lying excited states of Mo$_2$. The formation of the Mo$_2$-Et complex is thermally forbidden in the $^1A_1$ ground state due to a significant barrier found in the potential energy surface. The reaction may however proceed in the excited state and requires irradiation of substrates to access many of the possible excited states leading to a stable complex. The $^1A_1$ ground state curve of Mo$_2$-But has no energy barrier and leads to a stable complex, thus the reaction is thermally allowed. The possible scenario of complex formation reactions deduced from the potential energies agrees with the model of symmetry-concerted reactions in full analogy to the Diels-Alder reaction between olefins.25

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