

ON SYMMETRY-CONCERTED ORGANOMETALLIC ANALOGUES OF THE ETHYLENE DIMERIZATION

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*Dedicated to Professors Krzysztof Pigoń, Józef W. Rohleder
and Zdzisław Ruziewicz on the occasion of their 70th birthday**

A theoretical study of the C_{2v} symmetry-concerted reaction is presented for the addition of ethylene and molybdenum dimer. The potential curves corresponding to different self-consistent field closed shell configurations are studied. A comparison of ethylene dimerization and ethylene-Mo₂ formation reactions indicates close similarities and applicability of the Woodward-Hoffmann model, developed originally for olefins, to organometallics.

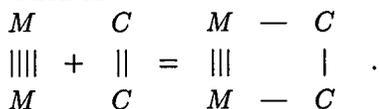
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1. Introduction

Interaction of transition metal dimers which possess multiple bonds with molecules such as ethylene and butadiene could provide a novel insight into organometallic analogues of the Diels-Alder reaction [1-2]. Such reactions can also offer novel models for testing symmetry-concerted organometallic reactions that conform to the Woodward-Hoffmann model of such reactions. Such studies provide

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insight into potential organometallic analogue of the symmetry-concerted ethylene dimerization as



Multiple bonds in transition metal dimers composed of open shell transition metal atoms such as Zr_2 , Mo_2 , W_2 , Cr_2 offer a large number of low-lying electronic states that can interact with unsaturated organic compounds in a symmetry-concerted manner. Such reactions have been studied previously for ethylene with Mo_2 [3], Zr_2 [4] and Cu_2 [5], applying rigorous quantum chemical methods. However, considerations regarding the symmetry-concerted reactions performed by Woodward and Hoffmann [6] lead to successful general rules, even if one applied a much lower level of the theory.

In this work we study the reaction of Mo_2 with ethylene (and the ethylene dimerization for comparison purposes) applying a simple model of self-consistent field (SCF) adiabatic potential curves based on interacting closed shell configurations. The presented approach is equivalent to the one developed by Woodward and Hoffmann [7] for reactions of cyclization of olefins. The above reaction has been studied previously at the advanced *ab initio* level (CASSCF/FOCI) with the inclusion of correlation energy [3], and those results serve as a test for the current qualitative picture. Furthermore, in the current investigation a comparison is made with the analogous 2 ethylene \rightarrow cyclobutane ring closure reaction which is studied here at the same level of the theory.

2. Method and computational details

The presented calculations were performed using the closed-shell SCF method. Potential surfaces were calculated for different configurations assumed for the closed shell wave function. The optimized ground state geometries for the ethylene dimerization and Mo_2 -Eth complex formation reaction pathways at the SCF level have been utilized in the study. All studies performed here were made using relativistic effective core potentials (RECPs), which retained the outer $4s4p4d5s$ shells of Mo [8] and $2s2p$ shells for the carbon atom [9]. The basis set for Mo was prepared from the work of LaJohn et al. [8] by decontracting the most diffuse Gaussians resulting in a valence ($3s3p2d$) basis set. The basis set for carbon was taken from Pacios and Christiansen [9], 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 [10], leading to a ($2s2p1d$) basis set. For hydrogen, Van Duijneveldt's [11] ($4s$) basis set was employed. The calculations were performed using the GAMESS package of codes [12].

The geometry of the Eth_2 complex was optimized assuming the C_{2v} symmetry along the reaction pathway (Fig. 1). The computed cyclobutane geometry (C-C 1.56 Å, C-H 1.09 Å, $\angle HCH$ 107.7 degree) agrees with experimental structure (C-C 1.56 Å, C-H 1.09 Å, $\angle HCH$ 114 ± 8 degree) [13]. The C-C bond distance for ethylene (in the dissociated structure) of 1.35 Å agrees with the corresponding experimental value of 1.322 Å [13]. Values of HCH angles in ethylene and cyclobutane indicate the expected change from sp^2 to sp^3 orbital hybridization on

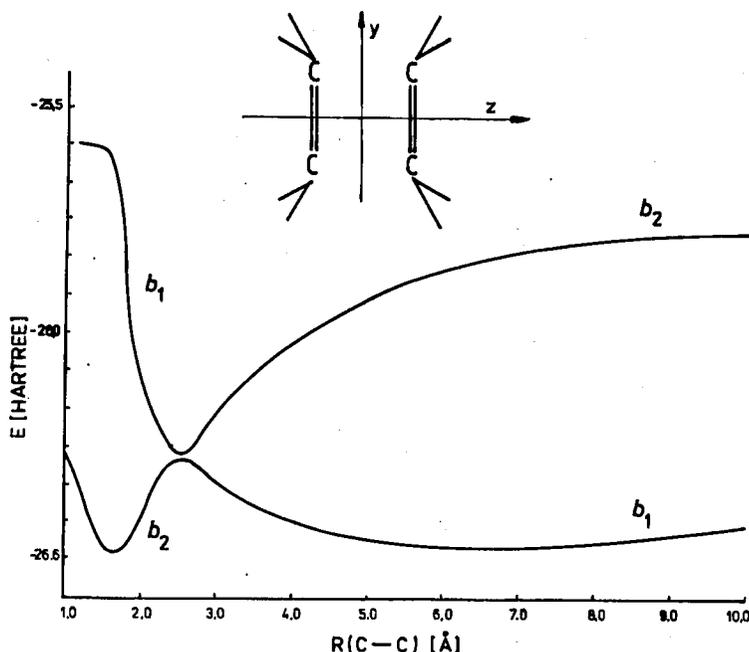


Fig. 1. SCF potential curves for the ethylene dimerization reaction.

carbon corresponding to conversion of the C=C double bond into a single bond. The optimized geometry for the Mo₂-Eth reaction pathway has been adopted from Ref. [3].

The complete active space self-consistent field (CASSCF) calculations performed for the ethylene dimerization included the highest occupied and the lowest unoccupied molecular orbitals in the active space.

3. Results and discussion

The C_{2v} symmetry-concerted reaction (Fig. 1) of the ethylene dimerization leads to cyclobutane. The SCF ground state configuration (1A_1) of cyclobutane is $4a_1^2 2a_2^2 3b_1^2 3b_2^2$. However, the lowest energy for the dissociated cyclobutane to two ethylenes corresponds to a different $4a_1^2 2a_2^2 4b_1^2 2b_2^2$ configuration. The continuation of the cyclobutane equilibrium configuration ((core) b_2^2) along the dissociation pathway leads to the electronic excited state of the dissociated system. The excited state of cyclobutane described by the (core) b_1^2 configuration correlates with the ground state of two separated ethylenes. Such correlations, due to the "non-crossing rule", lead to a potential barrier along the reaction path (Fig. 1). The above behavior of potential curves in a multiconfiguration approach, is predicted more accurately since it allows one to treat both equilibrium and dissociated configurations. The calculation for the ethylene dimerization within the CASSCF formalism, including (core) b_1^2 and (core) b_2^2 configurations in the active space, leads to almost pure single-determinantal configurations for reactants

and product, and gives 44%(core) $b_2^2 + 56%$ (core) b_1^2 wave function at the transition state. Simple HOMO/LUMO CASSCF calculations significantly lower the barrier to 23 kcal/mol, although qualitative conclusions derived from the adiabatic SCF curves are correct.

The question arises about the shapes of the adiabatic SCF curves, when one of the ethylenes is replaced by the metal dimer having a multiple bond. The chosen example of Mo_2 offers a variety of bonds (sixtuple Mo-Mo bond [14]) and a variety of possible configurations. Due to a number of low-lying electronic states of Mo_2 , the reaction arises from the interaction of the ground state of ethylene with different electronic states of Mo_2 . The ground electronic state of the complex has a (core) $b_2^2 b_1^2 a_1^2$ configuration, while for the dissociated structure, the lowest energy corresponds to (core) $b_1^2 a_2^2 a_1^2$. Due to the "non-crossing rule" the ground state potential surface exhibits a potential barrier similar to the dimerization of ethylene. The template of Mo_2 states interacting with ethylene leads to complicated potential surfaces especially in the excited electronic states (Fig. 2). Some low-lying excited states of Mo_2 offer potential barrierless reaction pathways. These observations agree qualitatively with more rigorous CASSCF and FOCI calculations [3].

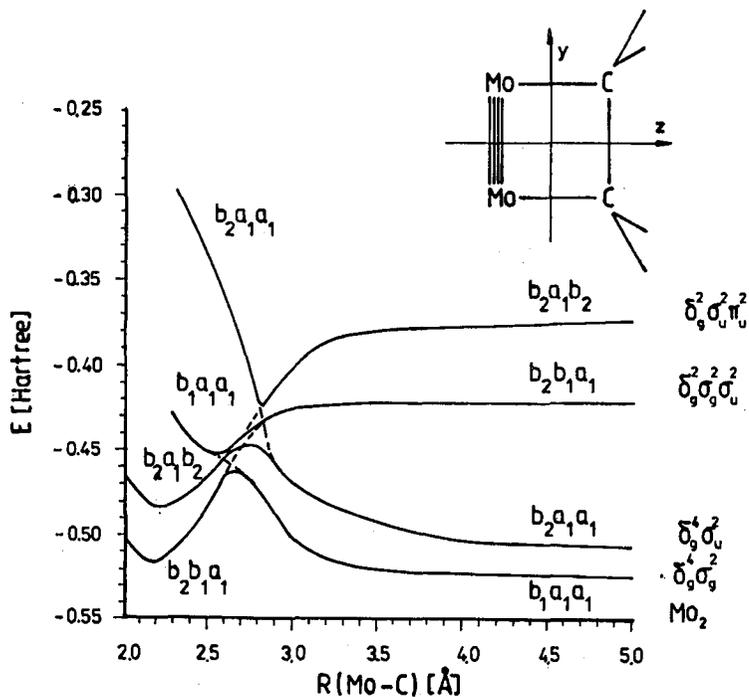


Fig. 2. Closed shell SCF potential curves for the reaction of ethylene with Mo_2 (the calculated values of energy are $-147 + E$).

4. Conclusions

Differences in the composition of the molecular wave function for cyclobutane and the dissociated ethylenes lead to the potential barrier along the reaction pathway. Replacement of one ethylene molecule by the Mo₂ dimer offers a system rich in low-lying electronic states. In the studied test case of Mo₂-Eth, the ground state wave function also changes its character along the reaction pathway (the Slater determinant differs by molecular orbitals carrying different symmetry) in full analogy to the ethylene dimerization. This also leads to an avoided crossing between the ground and excited potential surfaces and in consequence to a potential barrier. However, some low-lying excited states of the Mo₂ dimer, lead to excited state reaction paths without barrier. Both conclusions agree with large scale CASSCF/FOCI calculations including correlation energy [3], indicating the usefulness of the presented approach.

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