

Ring Opening of Methylene-cyclopropane over Lanthanocene Catalyst: A Quantum-Chemical Molecular Dynamics Simulation Study

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Summary: The ring opening of methylenecyclopropane (MCP) catalyzed by lanthanocene (Cp_2LaH) was simulated using a novel tight-binding quantum-chemical molecular dynamics method under reaction temperature. The results indicate the formation of the Cp_2LaH -MCP complex by 1,2-insertion with a subsequent hydrogen transfer followed by the ring opening of the proximal bond.

The subject of metal-assisted ring openings in strained-ring systems is of considerable current interest.^{1–3} The strained methylenecycloalkanes such as methylenecyclopropanes (MCPs) often undergo ring-opening reactions promoted by single-site metallocene-based early-transition-metal or lanthanide catalysts, which have been effectively utilized in organic synthesis,¹ polymerization/copolymerization,² and cycloaddition with alkenes.³ Hence, the study of metallocene catalysts has steadily grown and stimulated numerous experimental^{2,4} and theoretical⁵ investigations. On the other hand, an interesting but often problematic feature of MCPs

is their multiform reactivities that may lead to the formation of a variety of products by the opening of proximal and distal bonds as well as C=C double-bond addition reactions.^{1–5} Furthermore, with the appropriate choice of metals and ligands, the ring-opening polymerization proceeds either by 1,2-insertion^{2b,d} or by 2,1-insertion.^{2e} Moreover, the reactivity of MCP also varies significantly with the size of the lanthanide ion.^{2b,d} Thus, it appears that a certain catalyst selects a particular reaction pathway. Despite the widespread investigation, a full understanding of the reaction mechanism is still far from complete. In addition, much less attention has been paid to the roles of organolanthanide that promote the MCP ring-opening process.^{2b,d,5b} Therefore, the study of MCP ring opening in relation to its reactivity and reaction mechanism is of fundamental importance. Theoretical studies are still relatively few,^{5b} because such studies require huge computational time and, moreover, the systems are highly complicated due to the large relativistic effects.⁶

Although with modern first-principles density functional theory (DFT) methods, total energies of useful accuracy are readily available for given molecular structures of real size systems, optimization of station-

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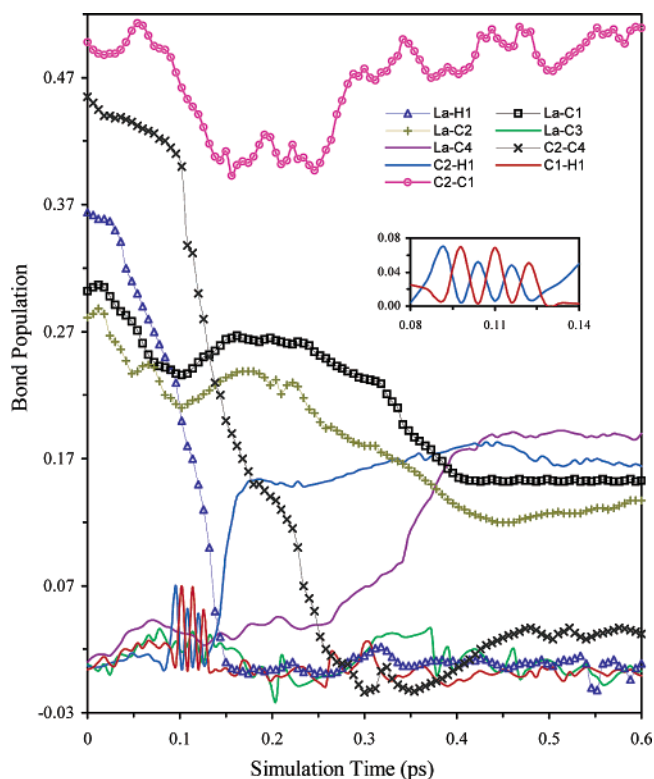


Figure 1. Bond population during the ring opening of MCP over Cp_2LaH with a time interval of 0.2 fs under reaction temperature (298 K). The insert presents the bond population of C1–H1 and C2–H1 bonds from 0.08 to 0.14 ps, respectively.

ary structures and, in particular, transition state structures is still very time-consuming and constitutes a bottleneck in the study of real systems. While the use of modest bases and simplified treatment of electron correlation extend the range of systems that may be studied with a reasonable effort,⁶ the first-principles methods still leave many chemically interesting ligands and substituents out of reach. On the other hand, the tight-binding molecular dynamics method is efficient, and it explicitly incorporates the real electronic structure and bonding of the material obtained from the first-principles results.⁷

In the present investigation, we employed a novel tight-binding quantum chemical molecular dynamics simulation method, Colors, which is over 5000 times faster than the first-principles approach.⁸ This code has been used successfully to investigate several chemical reactions. To realize high accuracy, all the parameters for Colors were determined on the basis of DFT calculations employing the Amsterdam density functional (ADF) program.⁹ The initial structures of Cp_2LaH and MCP were geometrically optimized by both Colors and ADF, and the results are in good agreement with each other as well as with the literature data.^{5j,10} The

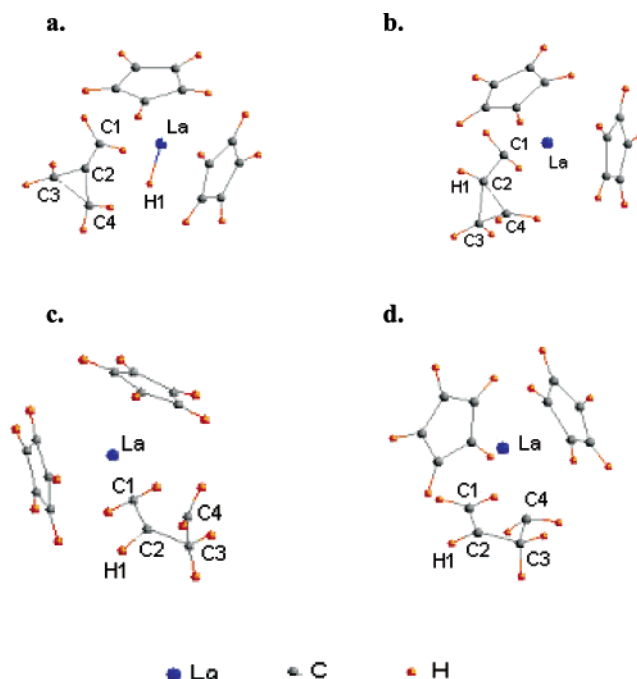


Figure 2. Snapshots of the ring opening of MCP at (a) 0.02 ps, (b) 0.16 ps, (c) 0.28 ps, and (d) 0.41 ps. The C=C double bonds are not shown.

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for the Different Structures Shown in Figure 2

	a	b	c	d
La–H1	2.161	3.401	3.417	3.453
La–C1	2.703	2.673	2.681	3.051
La–C2	2.711	2.697	2.732	3.497
La–C4	3.476	3.317	2.838	2.644
C1–H1	4.359	2.187	2.127	2.101
C2–H1	3.526	1.110	1.107	1.108
C2–C4	1.467	1.591	2.397	2.406
C2C3C4	58.1	63.3	77.5	108.4
C1C3C4–C2C3C4	0.6	27.4	26.3	26.8

dynamic simulation was then performed using Colors. Figure 1 depicts the variation in bond population against the simulation time for the ring-opening process of MCP over lanthanocene catalyst.

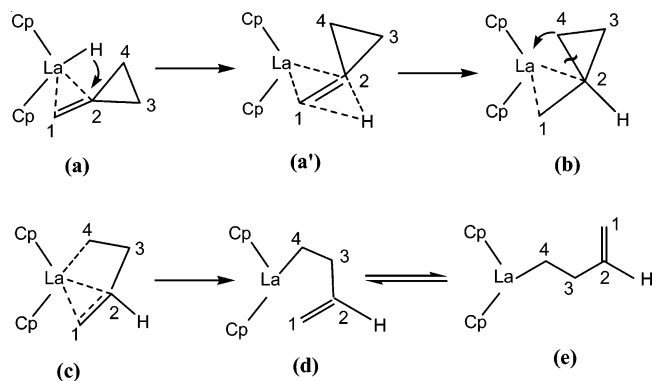
Figure 2 presents the snapshots of the most important steps, and the corresponding structural data are listed in Table 1. It can be deduced from the figure and table that, at first, the ring-opening process of MCP begins with the formation of the Cp_2LaH –MCP complex, in a way similar to the typical polymerization mechanism of oleins.^{5b,i,n} This is exemplified by taking into account the early stages of the reaction (0.02 ps; Figure 2a), where the La–H1 distance (2.161 Å) in the MCP complex is longer as compared to that in Cp_2LaH (2.114 Å). Subsequently, at 0.16 ps (Figure 2b) hydrogen is transferred from La–H to the C1=C2 double bond, which results in the formation of the C2–H1 bond (1.110 Å). This is well supported by the increase in La–H1 distance (3.401 Å). The same is reflected clearly by a sudden decrease and increase in the bond populations of La–H1 and C2–H1, respectively (cf. Figure 1). Furthermore, a change in the C2–C1 single-bond

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Scheme 1. Proposed Ring-Opening Pathways of MCP over Cp_2LaH


population can also be noticed. In addition, the C1C3C4 plane is tilted as compared to its initial position (see Table 1), as a result of the hydrogen transfer from Cp_2LaH . At this juncture, it is also noteworthy here that this hydrogen oscillates for ~ 50 fs between C1 and C2 at ~ 0.1 ps (see inset, Figure 1) before migrating to C2 with a simultaneous widening of the proximal C2–C4 bond along with an increase in the C2C3C4 bond angle (Figure 2b and Table 1). The elongation of the C2–C4 bond as well as an increase in the C2C3C4 bond angle continues, and at 0.28 ps (Figure 2c), the C2–C4 bond breaks and, as a consequence, the formation of new bond (La–C4) occurs (see also Figure 1). Finally, at 0.41 ps or beyond this period, the formation of the La–C4 bond can clearly be noticed with a reversal of the C1=C2 double bond (Figure 2d). Once again, these observations are well supported by the bond population analysis (see Figure 1).

On the basis of the above results, we suggest a plausible mechanism (Scheme 1) for the activation of MCP initiated by lanthanocene catalyst. The proposed intermediate structures are in good correspondence with those shown in Figures 1 and 2 as well as with the data given in Table 1. However, the additional structure (a') presented in Scheme 1 is based on the bond population at time ~ 0.1 ps, where it clearly shows evidence for the oscillation of hydrogen between C1 and C2 (see inset of Figure 1). This intermediate structure obtained by Colors is also compared with that obtained by the DFT

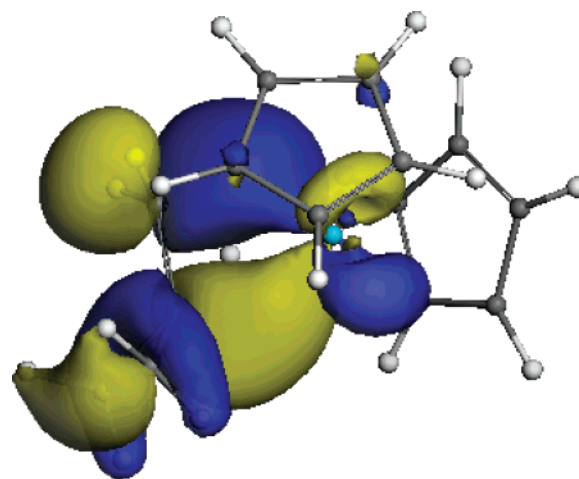


Figure 3. Orbital interaction isosurface of a transition state obtained by the DFT method.

method (see Figure 3),¹¹ and this (transition state) structure is found to be very similar to the intermediate shown in Scheme 1 (a'). Thus, the reaction pathway can be described as follows: the Cp_2LaH –MCP complex is formed initially by 1,2-insertion with a subsequent hydrogen transfer followed by the ring opening of the proximal bond. Therefore, it can also be presumed that the other lanthanide metallocene catalysts may follow a similar ring-opening pathway. However, with additional MCP, either a smooth polymerization or a dimerization may occur.^{2b,d}

Supporting Information Available: Figures and tables giving potential energy curves of various diatomic molecules as well as ionization potential and electron density data for the different elements determined by ADF and Colors and optimized geometry and structural parameters for MCP and Cp_2LaH as well as for the snapshots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) Materials Studio DMol³ version 2.1 (Delley, B. *J. Chem. Phys.* **2000**, 113, 7756) was used for DFT calculation at the level of local density approximation with Perdew–Wang functional correction (Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, B45, 13244). The relativistic effective core potentials and double-numeric quality basis set with polarization functions were considered. This structure shown in Figure 3 is a transition state confirmed by only one imaginary frequency, which shows the overlap between La 5d and C 2p orbitals.