

Fluxional Dynamics of Beryllocene

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Beryllocene is an organometallic in which the bonding between the metal and the cyclopentadienyl (Cp) rings is weak in contrast to analogous molecules containing transition metals in which the interactions are strong. Experimental studies find that beryllocene prefers a so-called "slip-sandwich" conformation of C_s symmetry in the crystal¹ as well as in the gas phase², i.e., Be has one η^1 - and one η^5 -coordinated ring (Figure 1a). Owing to these weak interactions, the molecule undergoes very rapid fluxional processes at elevated temperatures with an estimated rate of $10^{10\pm 1} \text{ s}^{-1}$ at $\approx 300 \text{ K}$ in solution, with an activation barrier of $5.2 \text{ kJ}\cdot\text{mol}^{-1}$ (ref 3). Such ultrafast rearrangements hinder further experimental investigation of molecular properties, although studies via the first-principles molecular dynamics (MD) method of Car and Parrinello⁴ are possible.

We use the scheme of Car and Parrinello as embodied in the projector augmented wave (PAW) code,⁵ employing the gradient-corrected local density approximation (GC-LDA)^{6–10} combined with a supercell approach. We use friction dynamics to find the ground state for electrons and nuclei as well as a Nosé¹¹ thermostat for finite temperature simulations. The usefulness of these techniques has been proven in investigations of organometallic systems.^{12,13} The transition states are determined using floating constraints.¹⁴ Here the atomic structure is optimized under a constraint that defines a reaction coordinate. Global translations and rotations are suppressed with additional constraints. During this optimization process, the reaction coordinate itself "floats" with friction dynamics *against* the force acting on the constraint. For judiciously chosen reaction coordinates and initial states, this dynamics converges to the transition state structure.

In agreement with experiment, our PAW calculation yields the η^1, η^5 -structure (C_s symmetry) as the ground state. The η^2, η^5 -conformations are higher in energy by 9 and $11 \text{ kJ}\cdot\text{mol}^{-1}$ (η^2, η^5 - D_{5h} and η^5, η^5 - D_{5d} , respectively). We investigated the fluxional dynamics of beryllocene at 400 K over several periods totaling $\approx 15 \text{ ps}$ and find that fluxional processes occur via two isomerization mechanisms ("gear wheel" and "molecular inver-

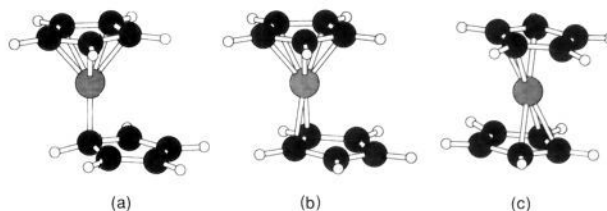


Figure 1. (a) Ground state geometry and (b,c) transition states for the intramolecular transformation of beryllocene. (b) η^2, η^5 -Transition state associated with the gear wheel mechanism. (c) η^3, η^3 -Transition state associated with the molecular inversion mechanism.

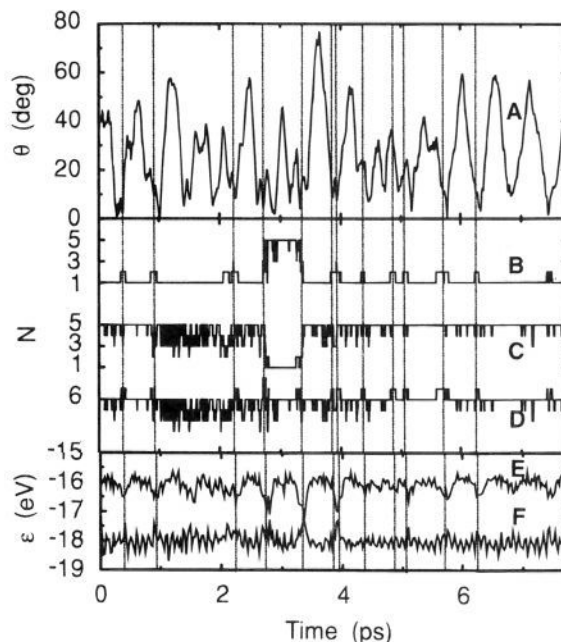


Figure 2. Time evolution of beryllocene at 400 K studied with an MD run. The vertical lines indicate completed rearrangement processes. (A) Tilt angle θ between the two Cp rings. (B, C, and D) Number of bonds (N) from the two rings (B and C) to the Be atom and bonds on the Be atom (D) using a distance criterion for a Be–C bond of 2.1 \AA . (E and F) The two lowest valence band energies (ϵ) with respect to the HOMO. The MO associated with energy level E is localized on the η^1 -ring; the MO corresponding to F is localized on the η^5 -ring.

sion"), with barriers of 5 and $8 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, each characterized by a single transition state.

In the gear wheel mechanism, the bond between Be and the η^1 -ring migrates from one carbon atom to the next, while preserving the interactions with the η^5 -ring. The initial and final states are identical except that the η^1 -ring is rotated 72° about its axis. The transition state (Figure 1b) is η^2, η^5 -coordinated (C_s symmetry) with an activation energy of $5 \text{ kJ}\cdot\text{mol}^{-1}$. The molecular inversion mechanism interchanges the roles of the η^1 - and the η^5 -rings by a motion of the Be atom parallel to the ring planes from the centrally bonded position of one ring to that of the other ring. The transition state for this mechanism (Figure 1c) is an η^3, η^3 -configuration of C_{2h} symmetry with an activation barrier of $8 \text{ kJ}\cdot\text{mol}^{-1}$.

In Figure 2 we present some characteristic results from our MD run showing a time span of $\approx 8 \text{ ps}$. During this time span, 10 gear wheel events and two molecular inversions occur (successful completions are indicated by vertical lines in Figure 2). Taking into account the total of accumulated MD data, the gear wheel and molecular inversion mechanisms have rates of $1\text{--}4$ and $0.3\text{--}1.5 \text{ ps}^{-1}$, respectively. In order to condense the information of the MD runs into concise data, we found that crucial parameters are the tilt angle θ between the Cp rings

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(Figure 2A) and the number of bonds defined by a distance criterion (Figure 2B–D). Most of the time (except around 3 ps), one ring has only one bond to Be (Figure 2B), but occasionally two are formed, corresponding to the transition state of the gear wheel mechanism. Therefore, the η^2, η^5 -coordination signifies attempts (most of which are successful) at such a transition, clearly correlating with a small tilt angle (Figure 2A). Around 3 ps, two molecular inversions take place (Figure 2B and C), which again occur at small tilt angles.

The intramolecular rearrangements also leave their fingerprints in the one-electron energies. The time evolutions of two low-lying, one-electron eigenstates are shown in Figure 2E and F. They lie about 16 and 18 eV below the HOMO and correspond to η^1 - and η^5 -carbon-*s*-skeletal bonding, respectively. As their energy difference is a measure of the electrostatic potential difference between the two rings, it decreases as their respective hapticities approach each other, especially in the η^3, η^3 -conformation, the transition state of the molecular inversion mechanism. The gear wheel mechanism can be associated with a less pronounced reduction of the energy difference, i.e., with a lowering of the upper level, which is localized on the η^1 -ring, while the inversion corresponds to a near degeneracy (Figure 2E and F). Hence these energies can be regarded as indicators of fluxional processes.

A visual analysis of the MD trajectories shows that the Be- η^5 -Cp entity is relatively rigid over longer time spans, while the ring of lower hapticity moves relatively freely, its bonding

sites being “scanned” by the Be atom. Therefore, the dynamics are determined by a slow reorientation of the rings, with the relatively light Be atom following rapidly as a kind of “liquid glue”. The essential steps for the rearrangement processes are clearly subpicosecond events.

Figure 2A shows that the tilt angle θ fluctuates on a time scale of about half a picosecond between 0° and about 50°. Such large tilt angles make both types of rearrangements unfavorable because the corresponding transition states cannot be formed due to large distances to the nonbonded carbon sites. At finite temperature, a large entropy causes an additional stabilization of the η^1, η^5 -configuration over the more symmetric (η^3, η^3 and η^5, η^5) structures. We conclude that the most crucial parameter determining the fluxional processes in beryllocene is the Cp–Cp tilt angle θ , which must be small in order for a rearrangement to occur, but is often large at 400 K for entropic reasons. For small θ angles, it is the lateral arrangement of the Cp rings that determines which of the two mechanisms will take place. For small lateral separations of the rings, the Be atom experiences a large number of potential bonding sites on both Cp rings, so that molecular inversion is facilitated.

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