



Quantum mechanical investigation on acceleration of electrocyclic reactions through transition metal catalysis



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ABSTRACT

Acceleration of the electrocyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene through early transition metal catalysis is investigated through quantum mechanical methods. The reaction proceeds in a non-pericyclic fashion involving two fundamental steps of catalysis (oxidative addition and reductive elimination), and the calculated acceleration effect is very large, up to 24 kcal mol⁻¹. Electrocyclization is highly dependent on the nature, formal oxidation state and coordination number of metal. Ligands are also predicted to show tremendous effect on the activation barrier of a reaction. Lowest activation energy is observed for [Nb(CHD)]⁺ (5.63 kcal mol⁻¹) where Nb is in its highest possible oxidation state i.e. +5.

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1. Introduction

Pericyclic reactions are a class of highly useful organic reactions, and follow concerted mechanism through cyclic aromatic transition state [1,2]. The major classes of pericyclic reactions are: cycloaddition reactions [3], sigmatropic rearrangements [4] and electrocyclic reactions [5]. The less explored classes of pericyclic reaction are dyotropic rearrangements [6–8], hictropic rearrangements [9], cheletropic reactions [10] and group transfer reactions [11]. Pericyclic reactions proceed in the presence of either light or heat [12]. Thermally allowed non-catalyzed pericyclic reactions generally have relatively high activation energies [13]. Extensive research has been carried out [14], and is still continued [15], to accelerate pericyclic reactions by reducing the activation barriers. The acceleration may be achieved with stoichiometric or catalytic amounts of additives [16]. Moreover, pericyclic reactions are also accelerated by microwave [17] and sonication methods [18].

Transition metal catalysis has grown quite rapidly in the recent past [19]. A number of reactions previously difficult or impossible,

can now be easily carried out through transition metal catalysis [20]. Transition metals have been used in the acceleration of pericyclic reactions as well [21]. Cycloaddition reactions and sigmatropic rearrangements are the two most widely studied classes of pericyclic reactions catalyzed by transition metals [21,22]. The transition metal catalyzed cycloaddition reactions are not concerted, rather the processes are multi-steps [23]. Transition metal catalyzed sigmatropic rearrangements, on the other hand, may proceed either in a concerted [24] or multi-step [25] fashion. The mechanism of transition metal catalyzed sigmatropic rearrangements may also change from concerted to multi-step depending on the nature and position of the substituents [22].

The literature also reveals certain examples of metal catalyzed electrocyclization reactions. Wulff-Dötz reaction is a well-known benzannulation reaction involving a crucial metal (Cr, W and related metals) catalyzed electrocyclization reaction [26]. Later, Carpenter and co-workers reported Mo, Cr and W catalyzed 8π electrocyclization reactions [27]. Platinum chloride and gold chloride catalyzed electrocyclization reactions have been used elegantly in the construction of functionalized pyrenes [28]. Moreover, electrocyclization of metal vinylidene complexes (M = Ru, W, Mo) is also reported [29–35]. Schleyer and co-workers have shown theoretically through density functional theory methods (at B3LYP method) that complexation of lithium ion (Li⁺) accelerates the

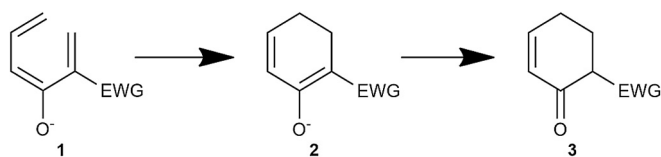
Abbreviations: CHD, Cycloheptadiene.

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electrocyclization of 1,3,5-hexatriene [36].

Among electrocyclic reactions, the most simple, basic and extremely useful reaction in the synthesis of highly demanding organic molecules is the cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene [37]. The reaction has been demonstrated to be involved in the biosynthesis of vitamin D [38], some polycyclic endiandric acids [13], eudesmane sesquiterpene (+)-occidentalol [39], 9,10-deoxytridachione [40], pheromones and some *o*-dialkyl-substituted benzenoids [13]. Electrocyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene can also be used for the construction of functionalized forms of carbocyclic six membered rings [41]. However, the higher activation barrier associated with the electrocyclization of 1,3,5-hexatriene limits its applications in target-oriented synthesis [13]. A non-accelerated thermal 6π electrocyclization generally requires temperatures in the range of 150–200 °C [36]. Jesus Rodriguez-Otero has shown by density functional theory calculations at B3LYP/6-31G** that the activation barrier is 29.8 kcal mol⁻¹ for the electrocyclization of 1,3,5 hexatriene to 1,3-cyclohexadiene [42]. To avoid these harsh reaction conditions, tremendous amount of research has been carried out to effectively decrease the activation energy, and to promote the reaction at room temperature. In this regard, a number of experimental and theoretical studies have also been conducted related to acceleration of certain special groups of 1,3,5-hexatriene [14,15].



Scheme 1. Cyclohexenone formation from Hexenone.

Magomedov et al. have shown that electron-withdrawing groups at position 2 of the 3-oxido hexatrienes (Scheme 1) decrease the activation energy of the 1,3,5-hexatriene electrocyclization [43]. Guner et al. [15] studied the electrocyclization of 1,3,5-hexatriene having 1-dimethyl-amino latent leaving group using the B3LYP/6-31G* level of density functional theory (DFT), and predicted that the activation energy decreases by 18–25 kcal mol⁻¹ in the presence of electron withdrawing substituent such as SO₂Ph and NO₂ at position 2. Jiao and Schleyer [36] investigated the acceleration of electrocyclization through Li⁺ complexation at B3LYP/6-311+G* method of DFT and observed that activation energy decreases by 10.9 kcal mol⁻¹. Recently, Bergman and coworkers [44] demonstrated experimentally and theoretically that 6π electrocyclization can be catalyzed by Lewis acids. The calculations revealed that Lewis acids decreased the activation energy by 2 kcal mol⁻¹. Yao Fu [13], and coworkers have also, previously, shown the promotion of 1,3,5-hexatriene by captodative substitution using a two layer ONIOM method and reported that rapid electrocyclization can be possible for certain specific patterns of captodative substituents on hexatrienes including 3-acceptor-5-donor, 2-acceptor-5-donor, and 2-acceptor-3-donor hexatrienes.

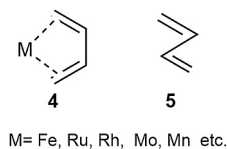
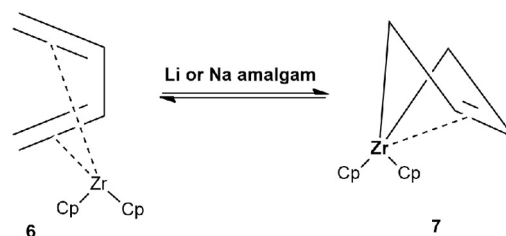


Fig. 1. Coordination of late transition metal with diene.



Scheme 2. Oxidative addition of butadiene to Zr(Cp)₂ complex.

Using the knowledge that Li⁺ can force the 1,3,5-hexatriene in *S-cis*-configuration and can accelerate the electrocyclization reaction, we set out to investigate acceleration of electrocyclic reactions through transition metal catalysis. Complexation of hexatriene with a transition metal may hold the hexatriene in *S-cis* conformation. The mode of interaction of enes with transition metals varies depending on early or late transition metals [45,46] (Fig. 1). The literature reveals that diene can oxidatively add to early transition metals to form metallacycle, (Scheme 2) whereas coordinate covalent bond is observed with the late transition metals (Fig 1) [16]. In the case of middle transition metals catalyzed pericyclic reactions, such as iron, both oxidative addition and coordination have been reported that depends on certain specific conditions such as nature of ligands, substrates and solvents [47].

We became interested in the early transition metals catalysis for the acceleration of electrocyclic reactions. We propose here that electrocyclic reactions may be catalyzed by early transition metals in a fashion similar to the catalysis of sigmatropic and cycloaddition reactions (Schemes 3 and 4). The concerted single step electrocyclic reaction of hexatriene may be split into a two steps process; oxidative addition and reductive elimination (Scheme 5).

Oxidative addition of enes (butadiene or hexatriene) with transition metals will give a metallacycle which upon reductive elimination may deliver a cyclic product (Scheme 5). Oxidative addition of diene to early transition metals is already reported in the literature [46] (vide supra). However, the reductive elimination is not well illustrated for the early transition metals. An early example of a direct reductive elimination of cycloalkanes from metallacycles of group-IV transition metals was reported in 1991 by Mashima and coworkers [48] (Scheme 6) but the yield was only 6%, and the reaction was carried out at very high temperature of 200 °C. Disproportionation product **18** is the main product of the reaction (70% yield, Scheme 6). Although, the reductive elimination product was a minor product but it provides a basis for our concept that if a molecule is judiciously chosen to decelerate the disproportionation then transition metal catalyzed electrocyclic reaction can be envisaged. This reaction further strengthened our

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