



# A comparison of the Simmons-Smith reaction with carbenoids to nitrenoids and oxenoids



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## ABSTRACT

A computational study using both density functional and correlated wavefunction methods on the reaction between ethylene and model zinc carbenoid, nitrenoid and oxenoid complexes ( $L-Zn-E-X$ ,  $E = CH_2$ ,  $NH$  or  $O$ ,  $L = X = I$  or  $Cl$ ) is reported. An investigation at DFT and MP2 levels of theory predicts that the epoxidation of ethylene with  $ClZnOCl$  oxenoid proceeds through a two-step mechanism involving an initial oxometalation and subsequent ring-closure, the latter being the rate determining step (RDS). Among all DFT methods applied in this study, BP86/CEP-31G(d) method produced the most similar geometries and energy barrier for the second step to those derived from MP2 simulations with correlation consistent basis sets. Interestingly, the mechanism of the cyclization reaction of ethylene with  $LZnEX$  is dependent on both  $E$  and  $X$  groups. Cyclopropanation of ethylene with  $IzZnCH_2I$  and aziridination of ethylene with  $IzZnNHI$  proceed via a single-step mechanism with an asynchronous transition state. The reaction barrier for the aziridination with  $IzZnNHI$  is 5.4 kcal/mol lower than that of cyclopropanation. Changing the leaving group of  $IzZnNHI$  from  $I$  to  $Cl$  changes the mechanism of the aziridination reaction to a two-step pathway, with the second step as the RDS. The calculation results from the epoxidation with  $IzZnOI$  and  $ClZnOCl$  oxenoids suggest a two-step mechanism for both oxenoids. The epoxidation reaction barriers for the RDS for both  $IzZnOI$  and  $ClZnOCl$  is  $\sim 15$  kcal/mol, which is  $\sim 6$  kcal/mol less than that calculated for aziridination of ethylene with  $ClZnNHCl$  nitrenoid.

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## 1. Introduction

Cyclopropanes, aziridines and epoxides are three-member ring moieties found in a wide variety of drugs, natural products and other important chemical compounds [1]. For example, cyclopropane containing molecules are used as starting materials and intermediates in organic synthesis due to their inherent ring strain and also have some pharmaceutical applications as general anesthetics [2,3]. Aziridines, the smallest nitrogen-containing heterocycles, are also widely exploited as building blocks for the synthesis of biologically and synthetically important materials [4]. They are bioactive compounds and form key reactive elements in larger, complex molecules, e.g. antitumor agents, taking advantage of their ring strain [4c,5]. Stereospecific ring opening of aziridines can produce several classes of useful molecules such as amines, amino acids, amino alcohols, and other nitrogen-containing compounds [6]. Epoxides such as ethylene oxide and propylene oxide are produced and employed on an industrial scale to form important intermediates for the industrial synthesis of polymers. Moreover, they form building blocks in a variety of bioactive molecules [7].

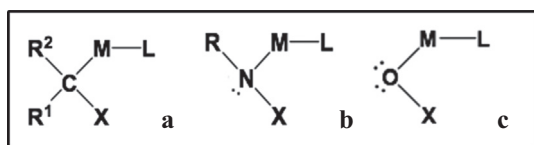
Numerous synthetic routes have been established for cyclopropanation, aziridination and epoxidation of olefins employing transition metal, main group and organic catalysts. Since the reported reaction of zinc carbenoid with olefins to form cyclopropanes by Simmons and Smith [8,9], many studies have been reported on this important organic name reaction, both experimental and theoretical. In 1964, the reaction of a Li carbenoid with olefins to form arylcyclopropanes was first reported by Closs and Moss [10]; theoretical studies suggested that a concerted [1 + 2] addition is more favored versus a stepwise mechanism [11]. In 1987, the reaction of samarium carbenoids with olefins was reported by Molander and coworkers [12,13], while aluminum carbenoid mediated cyclopropanation was first investigated experimentally by Yamamoto and co-workers a couple of years earlier [14].

Traditionally, epoxides and aziridines have been synthesized by the addition of sulfur ylides to the appropriate ketone, aldehyde, imine, or enone (Corey–Chaykovsky aziridination) [15], by the reaction of imines with diazo-containing compounds via the Aza–Darzens reaction [16], or by the cyclization of amino alcohols through the Wenker synthesis [17]. Recently, transition metal-catalyzed synthesis of aziridines with different choice of nitrene/nitrenoid source and metal catalyst has received increasing

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research attention [18]. Evans et al. [19] made a critical discovery with the use of bis (oxazoline) copper (I) complexes for the aziridination of alkenes. In 2013, Cordeiro et al. [20] conducted a DFT study on the mechanism of the copper-catalyzed aziridination of styrene. In 1995, Che et al. developed an efficient ruthenium catalyst to mediate nitrene-transfer reactions to C=C bonds and subsequently, the Rh<sup>II</sup>-catalyzed aziridination of olefins through a concerted mechanism for the transfer of nitrenoid to the olefin was reported by the group of Müller [21]. In 2011, a reusable iron aziridination catalyst, supported by a macrocyclic tetracarbene ligand, with improved atom economy, was developed by Jenkins and co-workers [22]. The following transition metals have been reported for the conversion of olefins into aziridines: Mn, Fe, Co, Cu, Ru, Rh, Pd, Ag and Au [23]. Among these, rhodium-, ruthenium-, and copper-based catalysts generally show better catalytic performance [18b,24].



**Scheme 1.** General structure of (a) carbenoids, (b) nitrenoids, and (c) oxenoids with a metal M and a leaving group X and the supporting ligand L. In this study M = Zn, X = L = I or Cl and R<sup>1</sup> = R<sup>2</sup> = R = H.

**Table 1**  
DFT Gibbs free energy of activation  $\Delta G^\ddagger$  and reaction  $\Delta G_r^\circ$  relative to reactants in kcal/mol for the two-step epoxidation of ethylene by ClZnOCl. Step 1 = oxometalation, step 2 = ring closure (see Scheme 9).

Method	Step1		Step2	
	$\Delta G_1^\ddagger$ (kcal.mol <sup>-1</sup> )	$\Delta G_{r1}^\circ$ (kcal.mol <sup>-1</sup> )	$\Delta G_2^\ddagger$ (kcal.mol <sup>-1</sup> )	$\Delta G_{r2}^\circ$ (kcal.mol <sup>-1</sup> )
BP86/CEP-31G(d)	6.5	-6.0	15.1	-45.4
B97D/CEP-31G(d)	6.8	-3.7	12.1	-52.2
BLYP/CEP-31G(d)	5.6	-4.4	12.4	-44.5
B3P86/CEP-31G(d)	9.6	-5.9	Not found	-50.5
B3LYP/CEP-31G(d)	10.6	-2.6	Not found	-49.9
M06/CEP-31G(d)	10.5	-6.7	25.8	-55.9
( $\langle \Delta G \rangle \pm \sigma$ ) DFT(CEP-31G(d))	8.3 ± 2.2	-4.9 ± 1.6	16.4 ± 6.4	-49.7 ± 4.3
BP86/6-31G(d)	7.8	-3.3	14.0	-43.6
B97D/6-31G(d)	10.0	-1.4	10.7	-48.3
BLYP/6-31G(d)	8.8	-0.2	11.7	-45.0
B3P86/6-31G(d)	11.1	-2.2	20.7	-52.3
B3LYP/6-31G(d)	12.3	1.0	18.5	-51.1
M06/6-31G(d)	12.7	-2.4	24.1	-56.4
( $\langle \Delta G \rangle \pm \sigma$ ) DFT(6-31G(d))	10.5 ± 1.9	-1.4 ± 1.6	16.6 ± 5.3	-49.5 ± 4.8
BP86/6-311+G(d)	7.5	-2.8	12.3	-238.7
B97D/6-311+G(d)	9.8	1.7	9.2	-52.4
( $\langle \Delta G \rangle \pm \sigma$ ) DFT	9.2 ± 2.2	-3.2 ± 2.4	15.6 ± 5.5	-49.6 ± 4.3

Epoxidation is an important process for both industrial and pharmaceutical purposes. Hence, many transition metal catalysts have been successfully developed to make a variety of epoxides from olefins. In addition to well-known epoxidation catalysts based on Ti, V, Mo and W that can facilitate the epoxidation of a variety of alkenes with an alkyl hydroperoxide oxidant, in the last decade several noble metal catalysts utilizing Ru, Pt, Co or Au have been developed for selective epoxidation of alkenes [25]. Epoxidation of propene with dioxygen in the presence of a supported gold catalyst on titania or titanium silicalites was reported by Haruta and co-workers [26] in 1999. They showed that Au/TiO<sub>2</sub> can be used selectively for propene epoxidation in the presence of H<sub>2</sub>. Beller et al. developed a cobalt catalyst, which can be easily recycled, for epoxidation of olefins with high yields [25e].

Carbenoids are putative intermediates in cyclopropanation reactions, and are qualitatively similar to carbenes, but do not necessarily form the free divalent species [10,30]. Experimental and theoretical studies revealed that carbenoid, nitrenoid and oxenoid species have many properties in common, e.g. they are very electrophilic and react easily with nucleophiles through an S<sub>N</sub>2-type mechanism (Scheme 1) [32].

The Simmons-Smith (SS) cyclopropanation is a general and efficient method for the conversion of olefins into cyclopropanes [27]. The utility of the Simmons-Smith reaction compared to other cyclopropanation techniques is due to the stereospecificity and the compatibility of this reagent with different functional groups [28]. The SS reaction is proposed to go through a methylene

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