Evidence for the powerful catalytic ability of imidozirconocene complex from its epoxide ring cleavage reactions – A DFT mechanistic view[#]

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Abstract. Imidozirconocene complex is known for its bifunctional reactivity and catalytic ability and this complex mediates ring cleavage of epoxides. Cyclooctene oxide (**1**) Norbornene oxide (**2**) and 2,5-dimethyl cyclohexene oxide (**3**) undergo ring cleavage in the presence of imidozirconocene complex. Epoxide **1** has accessible β -hydrogens (type I) while epoxide **2** and **3** do not have them (type II). Normally type I epoxides undergo elimination while type II epoxides prefer insertion. All the insertion reactions lead to five-membered metallacycle formation and elimination results in thermodynamically stable allyl-alkoxy product. The insertion is a two-step process following either diradical or zwitterionic pathway, while elimination is a one-step concerted reaction. DFT (density functional theory) modelling of these reactions at B3LYP/LANL2DZ level show that epoxide **1** undergoes elimination in agreement with experiment. However, calculations indicate that epoxide (**2**) proceeds through diradical intermediate in contrast to experimental observations. Surprisingly, epoxide (**3**) that has both the β positions blocked by methyl groups undergoes elimination rather than insertion. AIM and EDA analyses offer further insights on the reaction mechanism and bifunctional reactivity of imidozirconocene complex.

Keywords. Imidozirconocene complex; epoxide ring cleavage reaction; density functional theory; AIM analysis.

1. Introduction

Imidometal complexes attract a lot of interest in recent years due to their potential applications in organic and inorganic transformations.^{1–4} In particular, imidozirconocene complexes (IZC) are known for their high reactivity and wider participation in a variety of reactions.^{5–7} The epoxide ring opening reactions especially the imidozirconocene mediated ring cleavage of epoxides opened up a fascinating field in organic synthesis.^{8–12} Robert G Bergman is a pioneer in this field and has studied several such reactions.^{13,14} Another interesting feature observed in the imidozirconocene epoxide complex is the donation of the lone pair of epoxide oxygen to the metal centre which leads to the formation of a coordinate bond between the oxygen atom and the zirconium metal. In all these epoxide ring cleavage reactions, the IZC shows bifunctional reactivity where the zirconium acts as a Lewis acid and initiates the reaction and in the end, it acts as a Lewis base and completes the reaction.^{15–18} Experimental reports show that epoxides with accessible β -hydrogens (type I) undergo elimination while those without accessible β -hydrogens

(type II) prefer insertion. In general, all the elimination reactions lead to the stable allyl-alkoxy product whereas insertion reactions lead to five-membered metallacycle product. The insertion reaction is a two-step reaction and the reaction is initiated by the cleavage of C_{α} –O bond homolytically or heterolytically leading to diradical or zwitterionic intermediates respectively, whereas elimination is a one-step concerted reaction. Though several experimental reports are available, the mechanistic details of these ring cleavage reactions of epoxides by IZC are scarce. An attempt has been made to understand the mechanism and the role of IZC in these reactions by our group recently.¹⁹ In the present work, the IZC mediated reactions of three epoxides have been modelled and results are compared with available experimental evidences.

2. Computational details

All calculations were performed at B3LYP/LANL2DZ level using Gaussian03 suite of programs.^{20–24} All stationary points on the potential energy surface were characterized by vibrational frequency analysis. All transition states have one imaginary frequency and minima have all real frequencies. In addition to that,

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

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Noodleman's broken symmetry (BS) formalism^{25–27} has been adopted to check the stability of the corresponding diradical species in the diradical pathway using 'STABLE=OPT' keyword implemented in Gaussian03.²⁰

EDA (Energy Decomposition Analysis) has been performed using the Amsterdam Density Functional (ADF 2007) package to analyse the existing bonding interactions between the $\text{Cp}_2\text{Zr}=\text{N}-t\text{-Bu}$ and the epoxide part in the IZC.^{28–37} The interaction energy is given by

$$\Delta E_{\text{int}} = \Delta E_{\text{elestat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}},$$

where $\Delta E_{\text{elestat}}$ is the electrostatic interaction or contribution towards the bonding interactions. ΔE_{Pauli} gives Pauli's repulsion energy between occupied orbitals of the two fragments and ΔE_{orb} furnishes the total orbital contribution or covalent contribution towards the bonding.

Topological analysis has been performed using AIM2000 package³⁸ to obtain further insights into the bonding situations in TS's and intermediates.

Figure 1. The chosen epoxides (1–3) for modelling the ring cleavage mediated by IZC.

The necessary wave functions have been generated at B3LYP/LANL2DZ level using Gaussian03.

3. Results and discussion

Three epoxides have been chosen here and epoxide 1 (cyclooctene oxide) has accessible β hydrogen (type I) and epoxides 2 and 3 (norbornene oxide and 2,5-dimethyl cyclohexene oxide) do not have it (type II) (figure 1). The IZC exists as a coordination complex with tetrahydrofuran (THF) group in THF solution. The greater oxophilicity of epoxides over the THF group leads to the easy replacement of the THF group of IZC by epoxides even at milder condition.¹⁴ Therefore, the calculations were performed by taking imidozirconocene epoxide complex as the reactant. The general mechanism of imidozirconocene mediated epoxide ring cleavage reactions is presented in scheme 1. It can undergo either elimination or insertion. The insertion proceeds either through zwitterionic or radical pathway and forms metallacycle product. Since each epoxide follows different mechanism, epoxides 1, 2 and 3 are discussed one by one in the following section.

3.1 Cyclooctene oxide (1)

The ring cleavage of cyclooctene oxide mediated by IZC is shown in scheme 2. Experiments show that cyclooctene epoxide follow elimination reaction readily¹⁴ and therefore elimination reaction and zwitterionic pathway of the insertion reaction have been modelled at B3LYP/LANL2DZ level and the energy

Scheme 1. General mechanism for both insertion and elimination reactions of epoxide ring cleavage mediated by IZC.

Scheme 2. Mechanism for both insertion and elimination reactions of epoxide ring cleavage of cyclooctene oxide and 2,5-dimethyl cyclohexene oxide mediated by IZC.

profile is given in figure 2. The elimination is found to be both kinetically and thermodynamically more favourable ($\Delta G^\ddagger = 9.32$ kcal/mol) compared to insertion ($\Delta G^\ddagger = 25.64$ kcal/mol). The elimination is a concerted single-step reaction where the breaking of C_α–O bond and the making of N–H bond occurs simultaneously. The acidic nature of the β hydrogen is more readily obstructed by the basic imido nitrogen and thus the reaction leads to the formation of an allyl-alkoxy product.

3.2 Norbornene oxide (2)

Experimental report shows that on ring cleavage, the norbornene epoxide undergoes insertion alone and further, it may proceed *via* either carbon bridged non-classical zwitterionic or through non-bridged classical diradical pathway. In this case, a conclusive evidence towards either of the mechanism from experiments is lacking. While experiments could not trap the zwitterion formed from the rearrangement, only an indirect

Figure 2. Free energy profile for the ring cleavage of cyclooctene oxide mediated by IZC at B3LYP/LANL2DZ.

Scheme 3. The mechanism for both diradical as well as zwitterionic pathways of norbornene oxide ring cleavage reactions of IZC.

evidence through kinetics in favour of zwitterionic pathway was proposed. Hence, both the pathways have been modelled. The overall mechanism for this reaction is described in scheme 3. From the computed energy profile (figure 3), it is clear that epoxide 2 predominantly follows diradical pathway over zwitterionic pathway with a very narrow energy variation which is contradictory to experimentally proposed zwitterionic pathway. Implicit and explicit inclusion of solvent does not stabilize the zwitterionic path as expected. DFT calculations with M06 functional also confirmed the earlier trend that the diradical path is low lying. These things could not clearly resolve the mechanism. Therefore, further

experimental probe or calculations may lead to fruitful conclusions.

3.3 2,5-Dimethyl cyclohexene oxide (3)

In the case of 2,5-dimethyl cyclohexene oxide (3), both elimination as well as insertion have been monitored (figure 4) and for the insertion reaction only the zwitterionic path has been followed. Cleavage of this epoxide has not been experimentally studied yet, but this epoxide has been chosen particularly for the reason that both the β positions were blocked by methyl group. Under

Figure 3. Free energy profile for the ring cleavage of norbornene oxide mediated by IZC at B3LYP/LANL2DZ.

Figure 4. Free energy profile for the ring cleavage of 2,5-dimethyl cyclohexene oxide mediated by IZC at B3LYP/LANL2DZ.

Figure 5. The molecular graph of reactant (RC), insertion transition states ($ITS1_{zw}$ and $ITS2_{zw}$), insertion intermediate (Int_{zw}) and elimination transition states (ETS) for all the epoxides along with its BCPs like bond critical point (red), ring critical point (yellow) and cage critical point (green) are shown.

such conditions normally, the molecule is expected to go insertion. Surprisingly, our calculations reveal that 2,5-dimethyl cyclohexene oxide follow elimination over insertion (figure 4). From the profile, it is clear that elimination is favoured both thermodynamically and kinetically than insertion reaction; the concerted TS is low lying by 28.6 kcal/mol over insertion TS. The main factor that lowers the elimination path is the formation of very stable tertiary carbocation fragment in the 3ETS on the reaction path and the formation is facilitated by the easy removal of acidic β hydrogen. Thus epoxide 3 follows elimination reaction preferably over insertion.

3.4 AIM analysis

The AIM approach is based on the topological properties of the electron density denoted by (ρ) which is used to examine the bonding interactions present in various chemical systems.^{39–42} The topological analysis have been carried out on the optimized geometries of the reactant complexes, transition states and intermediates of all the epoxides studied here, using AIM analysis at B3LYP/LANL2DZ level. According to Bader, the

presence of a (3,–1) bond critical point (BCP) along the bond path is accepted as the standard criterion for the existence of all types of bonding and non-bonding interactions.

In general, the (3,+1) RCP indicates that the existence of a ring structure and the (3,–1) BCP indicates the existence of a bond between two corresponding atoms. Molecular graph of reactant complex (RC), transition states (ITS1_{zw} and ITS2_{zw}) and ETS is presented in figure 5 and the bond critical points (3, –1; BCPs), ring critical points (3, +1; RCPs), and cage critical points (3, +3; CCPs) are represented as small circle of red, yellow and green colour, respectively. The computed topological properties at Zr–O bond critical point are given in table 1.

The presence of (3,+1) RCPs indicated by a dark green circle in reactant, TS2 and ETS indicates the closed ring nature of the species and their absence in TS1 supports the ring cleavage step. Similarly, all TS2 species are confirmed by the presence of (3,–1) BCP between the imido nitrogen and C₂ carbon and moreover, the appearance of (3,+1) RCP confirms the formation of five-membered ring in this mechanism.

Figure 5. (continued).

Figure 5. (continued).

AIM framework further offers excellent evidences for the conversion of Zr–O coordinate bond to Zr–O covalent bond during the course of the reaction. The calculated ρ_{bcp} and $-\nabla^2\rho_{\text{bcp}}$ values at Zr–O BCP (table 1) clearly reveals that the existence of Zr $\leftarrow$ O bond in all the reactant complexes as its $-\nabla^2\rho$ value lies around -0.06 and the domination of eigen values of Hessian λ_3 (0.37) compared to λ_1 (-0.06) and λ_2 (-0.06) at this critical point further support the existence of coordinate bond (O $\leftarrow$ Zr) between O and Zr in all the reactants. At the same time, the same Zr–O BCP in all the intermedi-

ates possess a lower $-\nabla^2\rho$ value compared to that in the reactant complexes suggesting the conversion of coordinate to covalent bond. Similarly, the eigen values of Hessian also reflect the covalent bond conversion trend ($\lambda_1 \approx \lambda_2 > \lambda_3$) in all the intermediates as well as in the ETS's.

The Laplacian of electron density contour maps as well as corresponding gradient vector field trajectories are shown in figure 6 and it clearly explains the ring cleavage step as well as the ring closing process. In the TS1, the charge depletion between the C_α and the

Table 1. Calculated bond critical properties of Zr–O bond in RC, Int and ETS for all the epoxides.

Epoxide	species	ρ	$-\nabla^2\rho$	λ_1	λ_2	λ_3
1	1RC	0.048601	-0.06455	-0.06116	-0.05495	0.37435
	1Int _{ZW}	0.092204	-0.092249	-0.13784	-0.12252	0.62937
	1ETS	0.094906	-0.090118	-0.1452	-0.12316	0.62937
2	2RC	0.047592	-0.064227	-0.0595	-0.05370	0.37020
	2Int _{ZW}	0.106131	-0.137543	-0.1487	-0.14103	0.83998
3	3RC	0.046240	-0.063270	-0.0575	-0.04974	0.36035
	3Int _{ZW}	0.106019	-0.136858	-0.1492	-0.14107	0.83775
	3ETS	0.076137	-0.100410	-0.1032	-0.09243	0.59726

Figure 6. The contour maps of Laplacian of electron density (left) and corresponding gradient vector field of electron density (right) of insertion transition states (ITS1_{zw} and ITS2_{zw}), and elimination transition state (ETS) illustrating the bonding situations.

oxygen atom confirms the ring cleavage step. Moreover, the ring closure nature has been confirmed by the ring critical point in TS2 and ETS as shown in the figure.

3.5 Energy decomposition analysis

In these ring cleavage reactions IZC is known for its bifunctional reactivity. To gain additional insights

into this bifunctional reactivity, EDA has been carried out by considering the $\text{Cp}_2\text{Zr}=\text{N}-t\text{-Bu}$ and epoxide as individual fragments. The computed interaction energies (table 2) ΔE_{int} indicate that the intermediate has greater interaction than that of the reactant complex. The resulting $\Delta E_{\text{elestat}}$ and ΔE_{orb} values reveal that the ionic interactions are predominant in the reactant complex whereas, covalent interactions play a crucial role in the intermediates. On the other hand,

Table 2. Energy decomposition analysis at BP86/TZP of the reactants and intermediates of all the epoxides (**1–3**) and energies in kcal/mol; the value in parentheses gives the percentage contribution to the total attractive interactions ($\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$).

	Epoxide 1		Epoxide 2		Epoxide 3	
	IRC	1Int	2RC	2Int	3RC	3Int
ΔE_{int}	–43.62	–89.32	–18.84	–126.99	–18.00	–127.60
ΔE_{orb}	–23.91 (33.8%)	–129.45 (55.0%)	–20.19 (33.4%)	–156.33 (66.3%)	–22.45 (36.7%)	–176.76 (83.8%)
ΔE_{pauli}	27.15	146.44	41.56	108.89	43.21	83.45
ΔE_{elstat}	–46.86 (66.2%)	–106.31 (45.0%)	–40.21 (66.6%)	–79.55 (33.7%)	–38.75 (63.3%)	–34.29 (16.2%)
$\Delta E_{\text{elstat}} / \Delta E_{\text{orb}}$	1.96	0.82	1.99	0.50	1.73	0.19

Note: RC – Reactant complex and Int– intermediate

$\Delta E_{\text{elstat}} / \Delta E_{\text{orb}} > 1$ implies that the bond is coordinate in nature, whereas $\Delta E_{\text{elstat}} / \Delta E_{\text{orb}} < 1$ implies that the bond is of covalent nature. From the table 1, the $\Delta E_{\text{elstat}} / \Delta E_{\text{orb}}$ values show that in the reactant complex, the lone pair on the oxygen atom is donated to the vacant orbital of zirconium to form the (Zr←O) coordinate bond and this bond is further converted into a full covalent bond in the intermediate. This formation of covalent bond brings the two fragments closer, as a result, ΔE_{Pauli} increases on moving from reactant to the intermediate.

4. Conclusions

The detailed mechanism of ring cleavage reaction of three different epoxides catalysed by imidozirconocene complex have been investigated using DFT calculations. The epoxide **1** follows elimination reaction more readily as observed in experiments. Though epoxide **2** and **3** do not have accessible β -hydrogens, each follows different pathways. Calculations clearly predict that epoxide **2** proceeds via diradical pathway over zwitterionic pathway. The epoxide **3** undergoes elimination than insertion, contrary to expectations, due to acidic nature of β -hydrogen which stabilizes the tertiary carbocation. AIM analysis provides enough evidence for the conversion of the Zr←O bond to Zr–O bond along the reaction path and EDA also confirms the same trend.

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