



Quantum chemical study on anionic polymerization mechanism of propylene oxide^{*}

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Abstract: The quantum chemical method was employed to study the anionic polymerization mechanism of propylene oxide. All the structures are optimized completely at the HF/6-31G+(d) level. The calculated results showed that the ring-opening reaction between the anionic nucleophiles and propylene oxide is feasible, and that the products are mainly secondary alcohols. The anionic ring-opening polymerization of propylene oxide proceeds by nucleophilic attack of the secondary alcohol propagating anion on monomer. The calculated results satisfactorily agree with the experimental facts.

Key words: Propylene oxide, Anionic polymerization, HF, Transition state

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INTRODUCTION

Polyoxypropylene ether is an important industry product widely used in the polyurethane industry and surfactant industry. Over 6.6 million tons of propylene oxide were produced in 2003. About 2/3 of propylene oxide monomers are converted to their respective polymers annually (Xi *et al.*, 2001). It is of significant importance to research the ring-opening polymerization mechanism of propylene oxide for controlling of the polymer's structure and performance.

The ether linkage is characteristically a strong one and is basic in the Lewis sense. The result is that the ring-opening polymerization of cyclic ethers is initiated only by cationic species. The epoxides (the 3-membered oxides) are the exception to this generalization. Epoxides are polymerized by both anionic and cationic initiators due to the high degree of strain

in the small 3-membered ring (Odian, 1991).

Due to the low molecular weight of the product with concomitant complicated byproducts, cationic polymerization of propylene oxide was not industrialized till now. While thanks to the good performance of the product and the accessibility of the anionic catalyst, anionic polymerization of propylene oxide is popular in industry. The propagating anion from the anionic polymerization of propylene oxide is produced by the initiators (e.g. alcohol) reacting with hydroxides, alkoxides, metal oxides, organometallic compounds and other bases, and the propagating anion continuously reacts with monomer to produce the long chain polymers. The reaction is believed to follow the S_N2 mechanism (Odian, 1991; Zhu, 1987).

To the best of our knowledge, investigations on ring-open polymerization of epoxides are mainly focused on kinetics and thermodynamics and rarely on theoretical study (Frimand and Jalkanen, 2002; Pereira *et al.*, 2004; Vila and Mosquera, 2002; Coxon *et al.*, 1997; Liu *et al.*, 2002). By using quantum chemical methods, Wang and Zhang discussed the

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cationic and anionic polymerization mechanism of ethylene oxide, with the calculated results fitting the experimental facts (Zhang *et al.*, 2004; 2005; Wang and Du, 2002). The present work investigated the anionic polymerization mechanism of propylene oxide by using HF/6-31G+(d) method. Without loss of generality, butanol was chosen as initiator for the convenience of calculation.

METHODS AND COMPUTATIONS

The reaction mechanism of anionic polymerization of propylene oxide is the same as that of ethylene oxide. However, the polymerization of an unsymmetrical epoxide such as propylene oxide involves the possibility of two different sites (carbon- α and carbon- β) on the epoxide ring for the nucleophilic ring-opening reaction. Two different propagating species then produce two different products respectively (secondary alcohol and primary alcohol). The two different addition reaction pathways of butanol anion and propylene oxide are shown in Fig.1.

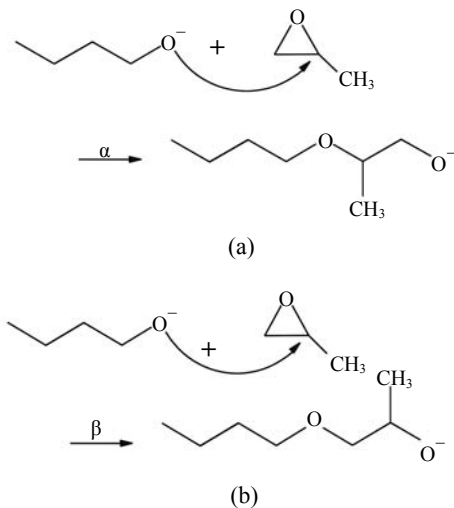


Fig.1 The two different addition reaction pathways of butanol anion and propylene oxide. (a) Carbon- α ; (b) Carbon- β

The modelling molecules above are employed for the optimizations of the structures of the reaction species at the HF/6-31G+(d) level, which is quite reliable in both geometry and energy calculations (Zhang, 2005; Frimand and Jalkanen, 2002). Vibrational analysis for all the optimized structures is performed at the same computational level to obtain

reliable vibrational frequency, zero-point energy and total energy. All the intermediates and transition states are confirmed by the results of vibration analysis and intrinsic reaction coordinate (IRC) calculation. All calculations were performed by the Gaussian 03 (Frisch *et al.*, 2003).

RESULTS AND DISCUSSION

Reaction pathway

In the calculation of the nucleophilic addition reaction between butanol anion and propylene oxide, the optimized structures of reactant and two transition states are shown in Fig.2, in which the two transition states represent two different pathways (butanol anion attack carbon- α or carbon- β). Vibrational analysis on stationary points shows that the vibrational frequency of the reactants and the products are all positive and that the stationary points are stable. The calculated result of the vibrational analysis shows that there is only one strong imaginary frequency in the transition states and that the imaginary frequency of TS1a is -657.4 cm^{-1} , the imaginary frequency of TS1b is -622.08 cm^{-1} . As shown in Figs.2b, 2c, the arrow from the carbon atom in the epoxide ring indicates the

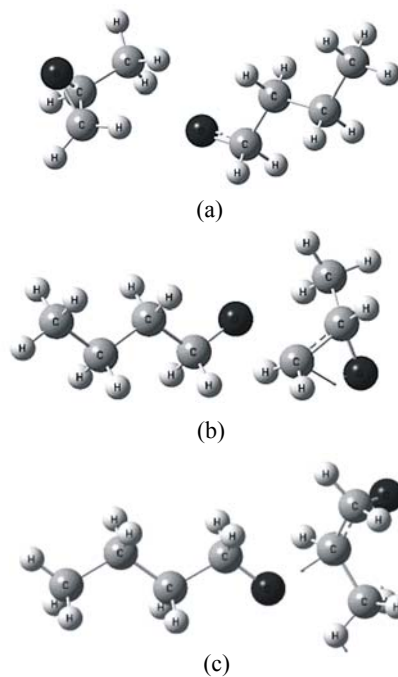


Fig.2 Optimized structures of reactant R1 (a) and transition states TS1a (b) and TS1b (c)

vibration vector direction of corresponding imaginary frequency, which means the vibration represents the bonding between the oxygen atom in the butanol anion and the carbon atom in the epoxide ring. The two transition states are verified by the intrinsic reaction coordinate (IRC) calculations at the HF/6-31G+(d) level.

It was found that in TS1a and TS1b, the bond order between bonding oxygen atom and carbon atom gets larger and that new carbon-oxygen bond tends to form. The bond order of carbon-oxygen bond attacked by butanol anion, regardless of whether it attacks carbon- α or carbon- β , gets smaller and the bond tends to break. All of the facts show that the process of the formation of new bond and the break of the old bond are synchronous, which reveals that the reactions follow the S_N2 mechanism.

The Mulliken electronic charges of oxygen atom in epoxide ring decrease from $-0.486e$ in the reactant R1 to $-0.715e$ (TS1a) and $-0.724e$ (TS1b) in the transition states, and to $-0.845e$ and $-0.907e$ in the respective products. All of these show that electronic charge of butanol anion transfers to propylene oxide and makes it into a new nucleophile.

It is noteworthy to point out that the activation energies of the two reaction pathways with different transition states are not the same. The activation energy of the reaction pathway with transition state TS1a, in which nucleophiles attack carbon- β in the epoxide ring and then produce the secondary alcohol product, is 69.74 kJ/mol and the value is corrected by the zero-point vibrational energies. The activation energy of the reaction pathway with transition state TS1b, in which nucleophiles attack carbon- α in the epoxide ring and then produce the primary alcohol product, which is 80.76 kJ/mol with the value being corrected by zero-point vibrational energies.

Apparently, the above two reactions are parallel reactions. According to transition state theory and kinetics of parallel reaction (Wei and Li, 2004), there are:

$$k_{TS1a} = \frac{k_b T}{h} \exp\left(\frac{-\Delta G_{TS1a}^\ddagger}{RT}\right), \quad (1)$$

$$k_{TS1b} = \frac{k_b T}{h} \exp\left(\frac{-\Delta G_{TS1b}^\ddagger}{RT}\right). \quad (2)$$

And then,

$$\frac{P_{TS1a}}{P_{TS1b}} = \frac{k_{TS1a}}{k_{TS1b}} = \exp\left(\frac{\Delta G_{TS1b}^\ddagger - \Delta G_{TS1a}^\ddagger}{RT}\right) = \exp\left(\frac{\Delta\Delta G^\ddagger}{RT}\right). \quad (3)$$

In the parallel reaction of nucleophiles attacking propylene oxide, the difference between the two activation energies is $(80.76-69.74=11.02$ kJ/mol), suppose $T=300$ K, then

$$\frac{P_{TS1a}}{P_{TS1b}} = \exp\left(\frac{11.02 \times 1000}{8.314 \times 300}\right) = 82.95.$$

The selectivity of the reaction is as high as 98.8% and even when $T=400$ K, the selectivity of the reaction is also 96.5%. Therefore the reaction is under the dynamics control and the main product is secondary alcohols. References on experimental polymerization of propylene oxide, revealed that the product from the initiation step consists of secondary and primary alcohols in the ratio 97:3 (Gee *et al.*, 1959; Odian, 1991; Zhu, 1987). The calculated results are in satisfactory agreement with the experimental facts.

Anionic ring-opening polymerization of propylene oxide

As already discussed above, butanol anion can attack propylene oxide as nucleophile and mainly produces the secondary alcohol propagating anion. Owing to the large net electronic charge of the produced secondary alcohol propagating anion, it can serve as nucleophiles to further attack propylene oxide monomers. In order to investigate the nucleophilic activity of the secondary alcohol propagating anion, the first two reactions of nucleophilic addition between the secondary alcohol propagating anion and propylene oxide are calculated at HF/6-31G+(d) level. The transition states are studied and the activation energy is obtained. Calculation results revealed that the reactions also follow S_N2 mechanism.

In the calculation of the first two reactions of nucleophilic addition between the secondary alcohol propagating anion and propylene oxide, the optimized structures of reactants and two transition states are shown in Fig.3. Vibrational analysis on stationary points shows that the vibrational frequency of the reactants and the products are all positive and that the stationary points are stable. The calculated result of

vibrational analysis shows that there is only one strong imaginary frequency in the transition states and that the imaginary frequency of transition state TS2a is -646.28 cm^{-1} , the imaginary frequency of transition state TS3a is -646.67 cm^{-1} . As shown in Figs.3b, 3d, the arrow from the carbon atom in the epoxide ring indicates the vibration vector direction of corresponding imaginary frequency, which means the vibration represents the bonding between the oxygen atom in the secondary alcohol anion and the carbon atom in the epoxide ring. The two transition states are also verified by the intrinsic reaction coordinate (IRC) calculations.

The total energies and zero-point energies of the different reaction species and every reaction activation energy corrected with zero-point vibrational energies are shown in Table 1.

The calculation shows that the ring-opening of propylene oxide is caused by the attack of the secondary alcohol propagating anion on carbon- β in propylene oxide and that the activation energy is 74.86 kJ/mol . Then, the product anion can further attack carbon- β in propylene oxide to obtain the addition product, with the activation energy being 75.64 kJ/mol . Meanwhile, the Mulliken electronic charges of the oxygen atom in the epoxide ring rapidly decrease due to ring-opening, which indicates that the product

becomes new nucleophiles and further initiates the polymerization of propylene oxide to obtain polymer. In this computational study it was shown that the HF/6-31G+(d) method gives the calculated results of activation energies ($69.74\sim 75.64\text{ kJ/mol}$) in agreement with the experimental results ($65\sim 75\text{ kJ/mol}$) (Gee *et al.*, 1959; Di Serio *et al.*, 2002), which reveals the adequateness of the method employed.

In summary, the anionic polymerization of propylene oxide follows S_N2 mechanism, which proceeds by nucleophilic attack of the secondary alcohol propagating anion on propylene oxide monomer continuously shown in Fig.4.

Table 1 Activation energies at different propylene oxide adduct number

Adduct number	Species	ZPE (Hartree)	Total energies (Hartree)	Activation energies (kJ/mol)
1- α	R1	0.223235	-423.234337	80.76
	TS1b	0.223322	-423.203577	
1- β	R1	0.223235	-423.234337	69.74
	TS1a	0.223228	-423.207773	
2	R2	0.320127	-615.103725	74.86
	TS2a	0.319946	-615.075214	
3	R3	0.416345	-806.965300	75.64
	TS3a	0.416150	-806.936492	

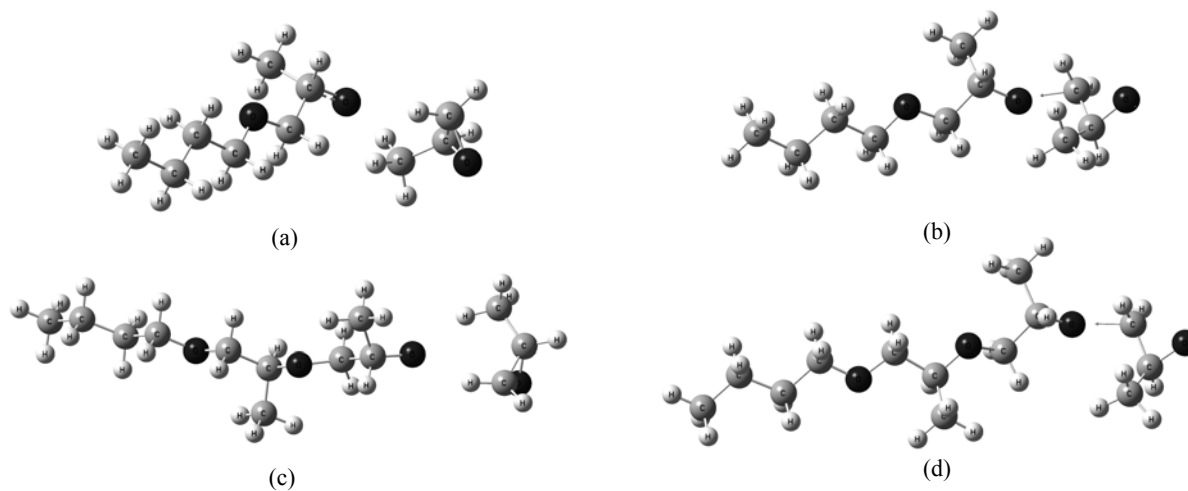


Fig.3 Optimized structure of reactants R2 (a) and R3 (c) and transition states TS2a (b) and TS3a (d)

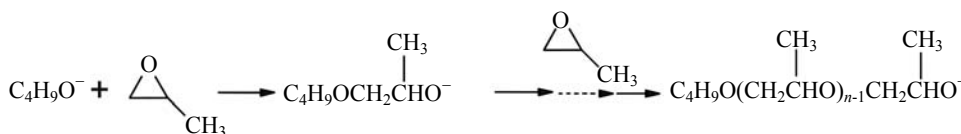


Fig.4 Anionic polymerization mechanism of propylene oxide

CONCLUSION

In the anionic polymerization of propylene oxide, nucleophiles attack carbon- β in the epoxide ring and then produce the secondary alcohol product based on the quantum chemical study. The anionic ring-opening polymerization of propylene oxide proceeds by nucleophilic attack of the secondary alcohol propagating anion on monomer. The agreement of the theoretical study with the experimental results indicates that the application of HF method in anionic polymerization of propylene oxide is feasible.

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