Carbohydrate Polymers 146 (2016) 46–51

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Theoretical study of the reaction of chitosan monomer with 2,3-epoxypropyl-trimethyl quaternary ammonium chloride catalyzed by an imidazolium-based ionic liquid

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ARTICLE INFO

Article history:
Received 16 December 2015
Received in revised form 28 February 2016
Accepted 15 March 2016
Available online 16 March 2016

Keywords:
Imidazolium-based ionic liquid
Chitosan
Catalyze
2,3-Epoxypropyltrimethyl ammonium chloride
DFT

ABSTRACT

The molecular mechanism of the graft reaction of 2,3-epoxypropyl-trimethyl quaternary ammonium chloride with chitosan monomer was investigated by performing density functional theory (DFT) calculations. The calculated results show that the $-NH_2$ group of chitosan monomer is more reactive than its $-OH$ and $-CH_2OH$ groups, and the graft reaction on the $-NH_2$ group is calculated to be exothermic by 20.5 kcal/mol with a free energy barrier of 42.6 kcal/mol. The reaction cannot benefit from the presence of the intruded water molecule, but can be considerably assisted by 1-allyl-3-methylimidazolium chloride ([Amim]Cl) ionic liquid. The reaction catalyzed by the ion-pair is calculated to be exothermic by 36.5 kcal/mol and the barrier is reduced to 29.3 kcal/mol, which are further corrected to 28.0 and 29.1 kcal/mol by considering the solvent effect of [Amim]Cl ionic liquid. Calculated results verified the experimental finding that imidazolium-based ionic liquids can promote the reaction of chitosan with epoxy compounds.

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1. Introduction

With the diminishing of non-renewable resources and increasing concerns about the sustainable development, application of biomass has attracted significant attention (Brandt, Gräsvik, Hallett, & Welton, 2013; Chen, Chew, Kerton, & Yan, 2014; Glisoni et al., 2015; Qian & Zhang, 2010; Shuai et al., 2013). Cellulose, chitin, and chitosan, they have similar structures consisting of several hundreds to more than 10,000 linked D-glucose units or derivative glucose units (Scheme 1) (Simkovitch & Huppert, 2015). Chitin, the second most abundant biorenewable material after cellulose on the earth (Chen et al., 2014) can be easily obtained from the exoskeletons of crustacean, for instance, crab and shrimp, and there is about 12 million tons of natural chitin production each year (Zhou et al., 2013). Chitosan is the *N*-deacetylated derivative of chitin, composed of a repeating unit of β-(1,4)-2-amino-2-deoxy-β-D-glucose, and it is the only alkaline natural biological macromolecule, possessing favorable properties, including good biocompatibility, biodegradability, biological activities, and non-toxicity, etc (Wang et al., 2013). Due to the existence of active groups, hydroxyl group (—OH) and amino group ($—NH_2$), chitosan can evolve into its various graft derivatives, which have a wide utilization in medicine, food, daily chemicals, sewage treatment (Kumar, 2000; Zhou et al., 2013).

Ionic liquids (ILs), in general defined as organic salts, have many excellent physicochemical properties, for example, near-zero vapor pressure, high thermal and chemical stability, strong solubility, good reusability, good designability. As a result, ILs are often referred as the "green solvents" (Endres & Abedin, 2006; Plechkova & Seddon, 2008; Sheldon, 2005). Since the first report of Swatloski et al. (Swatloski, Spear, Holbrey, & Rogers, 2002) that cellulose can be readily dissolved in imidazolium-based ILs without any byproducts, applications of ILs in the biomass field has become a very active hot spot both in academia and industry (Sun, Tian, Xue, Zhang, & Mu, 2014; Wang, Zhu, Wang, Huang, & Wang, 2010). It is found that ILs present not only good solubility ability to biomass materials, but also superior catalytic performance for their degradation and derivation reactions (Ajloo, Sangian, Ghadamgahi, Evini, & Saboury, 2013; Lee et al., 2010; Shi, Zhang, Li, & Deng, 2005; Zhang, 2013).

It is well known that there are many obstacles of modifying chitosan in water, acid, base and other common solvents, including low solubility, difficulty of solvent regain, and severe pollution (Wang et al., 2013; Xie, Zhang, & Li, 2006). Alternatively, the graft reaction of chitosan in ILs has aroused widespread focuses (Wang et al.,

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http://dx.doi.org/10.1016/j.carbpol.2016.03.032
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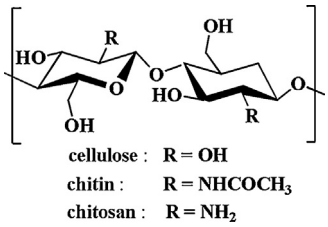


Scheme 1. Structures of cellulose, chitin, and chitosan.

2013). Recently, Yang et al. (2015) reported the reaction of 2,3-epoxypropyl-trimethyl quaternary ammonium chloride (EPTAC) with chitosan in 1-allyl-3-methylimidazolium chloride ([Amim]Cl) IL (Scheme 2). They found that the obtained graft derivatives show improved substitution degree and better regioselectivity compared to these obtained in water, acid, and base, reported by Sajomsang et al. (Jin et al., 2013; Sajomsang, Tantayanon, Tangpasuthadol, & Daly, 2009). This fact indicates that alkyl-imidazolium chloride ILs possess excellent catalytic regioselectivity in the graft reaction of chitosan.

To understand the molecular mechanism of imidazolium-based ILs for catalyzing the graft reaction of epoxy compounds to chitosan, we here present a theoretical study on the reaction of 2,3-epoxypropyl-trimethyl quaternary ammonium chloride and chitosan monomer. By performing density function theory (DFT) calculations (Becke, 1988), we studied the reactivities of different active sites (−OH, $-NH_2$, and $-CH_2OH$) of chitosan monomer towards EPTAC, and the effects of the intruded water molecule, the ion-pair, as well as the IL environment on the reactivity. The calculated results are expected to provide a clear picture of how imidazolium-based ILs promotes the graft reaction of epoxy compounds to chitosan.

2. Model and computational details

As shown in Scheme 3, a chitosan monomer (a basic unit of chitosan) saturated by methyl (to mimic the glycosidic linkage in chitosan) is used as the model compound of chitosan, denoted as R_1. The $-NH_2$, $-CH_2OH$, and −OH groups in R_1 are three potential active sites where the graft reaction of chitosan with EPTAC (R_2) may occur. Depending on the nucleophilic attack position of three active sits on the epoxy propyl group in EPTAC, six different grafted products can be obtained. As shown in Scheme 3, N_1, O_2, or O_3 attack C_4/C_5, the corresponding pathways and products are remarked as I_a/I_b, II_a/II_b, III_a/III_b, and P_{I_a/I_b}, P_{II_a/II_b}, P_{III_a/III_b}, respectively. An ion-pair of [Amim]Cl was used to mimic the catalytic performance of the IL towards the graft reaction.

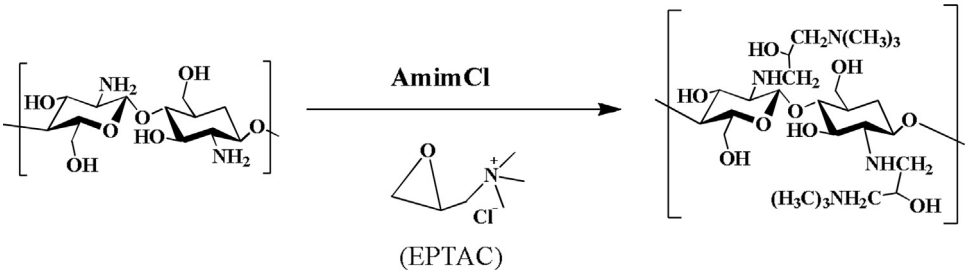
The calculations were carried out by using the B3LYP (Becke, 1988) exchange-correlation functional with the 6–31 g(d,p) basis set. Such a combination of functional and basis set is considered to be an efficient quantum chemistry method for modeling medium-size systems containing *dozens of* atoms, and has been widely used in exploring the mechanism of complex chemical system (Cadierno, García-Garrido, Gimeno, Varela-Álvarez, & Sordo, 2006; Himo, Demko, Noodleman, & Sharpless, 2003; Soriano & Fernandez, 2014). All geometrical configurations for the isolated reactants, intermediates, transition states and products have been fully optimized without any symmetry constraint. The obtained stationary points have been confirmed to be the real local minimum (zero imaginary frequency) or the first-order saddle points (one imaginary frequency) via harmonic vibrational frequency calculations, which also provide free energies at 298.15 K by including entropic contributions. The intrinsic reaction coordinate (IRC) pathways have been traced to ensure that each transition state links two desired minima (Fukui, 1970). To obtain a more accurate result, single-point calculations were carried out at B3LYP/6-311 + g(d,p) level based on the optimized structures at the B3LYP/6-31(d,p) level. The refined single-point energies were then corrected to free energies at 298.15 K and 1 atm using calculated harmonic frequencies. Solvent effect is evaluated by calculating the single point energies of the gas-phase structures at the same level of theory (Brown & Mora-Diez, 2006; Cancès, Mennucci, & Tomasi, 1997; Jena & Mishra, 2005). 1,2-dichloroethane (DCE), whose polarity or dielectric constant (10.125) is comparable to that of ILs (Bini, Chiappe, Pomelli, & Parisi, 2009; Chiappe & Pomelli, 2013) is used as the implicit solvent to simulate the IL environment. The Gibbs free energies are defined as follows:

$$G = E[\text{B3LYP/6-311} + \text{G(d,p)}] + \text{ZPE[B3LYP/6-31G(d,p)}] + H_{298} - TS_{298} \quad (1)$$

The electrostatic potential is computed using the Wave Function Analysis (WFN) program (Bulat, Toro-Labbe, Brinck, Murray, & Politzer, 2010) at the B3LYP/6-311 + g(d,p) level. The molecular surface was defined on the 0.001 au (electrons/bohn^3) contour of its electronic density as proposed by Bader et al. (Bader, Carroll, Cheeseman, & Chang, 1987). Atom charge distribution is obtained by natural bond orbitals (NBO) analyses (Reed, Weinstock, & Weinhold, 1985; Reed, Curtiss, & Weinhold, 1988). All structural optimizations and vibrational frequency calculations were carried out using the Gaussian 09 program package (Frisch et al., 2010). Cartesian coordinates of all optimized structures are given in the Supporting information.

3. Results and discussions

First, we emphasize that Basis Set Superposition Errors (BSSEs) should be considered for the energy barrier calculation of a reaction that involves component change. For the present system, our calculations show that the formations of the initial intermediates between chitosan monomer and EPTAC with and without [Amim]Cl are exothermic processes. The energy barrier of reaction should be calculated to be the energy difference between the transition state and the initial intermediate. So the energy of the intermediate com-



Scheme 2. Reaction of chitosan with 2,3-epoxypropyl-trimethyl quaternary ammonium chloride (EPTAC) in [Amim]Cl ionic liquid.

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