RHODIUM-MEDIATED HYDROGENOLYSIS/ HYDROLYSIS OF THE ARYL ETHER BOND IN SUPERCRITICAL CARBON DIOXIDE/WATER

An Experimental and Theoretical Approach Utilizing BIOVIA Materials Studio

The use of supercritical carbon dioxide ($scCO_2$)/water for the conversion of diphenyl ether was investigated over Rh/C catalysts to achieve the cleavage of C–O bond under mild reaction conditions. In the studied reaction system, ethereal C–O bond was cleaved by hydrogenolysis and hydrolysis, which was strongly hampered if the reaction was conducted individually in CO_2 or in water. There is a combined effect of supercritical carbon dioxide and the solubility of hydrogen at a specific pressure is important for a cleavage and a favorable yield of the desired product. Mechanistic investigations through theoretical calculations together with experimental analysis illustrated that hydrogenolysis and hydrolysis were two reaction paths responsible for the rupture of the C–O bond.

INTRODUCTION

This is a collaborative work between BIOVIA and Dr. M. Chatterjee of the National Institute of Advanced Industrial Science and Technology (AIST); with the purpose of investigating the reaction mechanism responsible for the selectivity of bond breaking in a biomass formation reaction.[1]

Lignin is the most common complex natural polymer, with phenylpropanoid units as the predominant building blocks. It is the third most abundant biomass compound after cellulose and hemicellulose, accounting for 18–40% of dry woods.[2] However, lignin has received less attention because of its resistance to degradation due to the presence of C–O bonds in the phenylpropanoid unit, which is difficult to break down. Hence, lignin depolymerization is a challenging task. Successful cleavage of the C–O bond of DPE would be both an interesting fundamental organic transformation and a significant step towards the depolymerization of lignin into small molecules. In the past few years, several attempts have been made to develop suitable catalysts or processes for the breakdown of the C–O bond. Hydrogenolysis/hydrogenation in supercritical carbon dioxide ($scCO_2$) in the presence of water successfully ruptured the C–O bond of DPE using a commercially available Rh/C catalyst, albeit under mild and simple reaction conditions to achieve high catalytic performance.[2] In this work, our target is to understand the possible reaction path behind the conversion of DPE under the reaction conditions studied. The role of water was significantly critical especially in the presence of CO_2, because CO_2 has a tendency to dissolve in water. Therefore, with the help of theoretical analysis using density functional theory (DFT) along with experimental observation, we attempted a mechanistic investigation to elucidate the actual reaction path of C–O bond cleavage under the working conditions.

FOUNDATION

Scheme 1 represents the conversion of DPE in the presence of hydrogen, which follows (i) hydrogenolysis/hydrogenation, (ii) hydrolysis/hydrogenation and (iii) hydrogenation. Hydrogenolysis of the C–O bond produces equal moles of phenol (PhOH) and benzene (Bz), which were then hydrogenated to cyclohexanol (CHOH)/cyclohexanone (CHO) and cyclohexane (CH), respectively. On the other hand, hydrolysis of DPE forms 2 moles of PhOH that is converted to CHOH via hydrogenation. Hydrogenation of DPE results in a partial aromatic ring hydrogenation product (cyclohexylphenyl ether; CHPE) followed by the formation of dicyclohexyl ether (DCHE), a completely hydrogenated product.
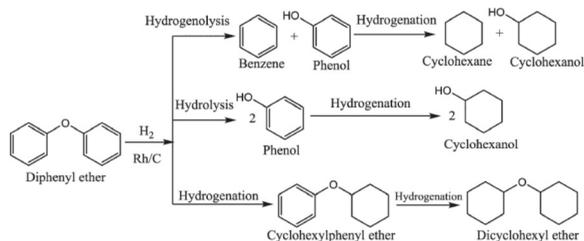
Scheme 1: Reaction scheme for formation of DPE

EXPERIMENTAL

Complete conversion of DPE was observed to be independent of CO_2 pressure, whereas pressure-dependent formation of monocyclic (CHOH and CH) or bicyclic products (CHPE and DCHE) was detected. DPE was completely converted to the corresponding products independent of the CO_2 pressure used.

However, product distribution was strikingly different in comparison with the reaction conducted in the presence of water. An increase in the amount of water from 0.5 to 4 ml increased the selectivity of CHOH from 39.8 to 96%. A negative effect was observed when the amount decreased to 0.2 ml because of the hydrogenation of the aromatic ring.

Addition of more water (16 ml) maintained the conversion, but

Table 1 Conversion of individual intermediates and binary mixtures

Entry	Substrate	Time (min)	Conv. (%)	Product selectivity (%)				
				CHOH	DCHE	CHPE	CHO	CH/Bz
1	PhOH	<5	100	39.8	—	—	60.2	—
2	CHPE	30	100	—	98.2	—	1.2	—
3	DPE + CHPE	30	54.2	15.7	82.0	—	—	2.3
4	DPE + PhOH	30	93.8	24.5	2.1	12.6	54.2	6.6
5	DPE	30	90	28.3	5.4	18.1	41.2	7.0

Reaction conditions: P_{CO_2} = 10 MPa; P_{H_2} = 0.5 MPa; catalyst : substrate = 1 : 5; temp. = 80 °C; water = 4 ml; PhOH = phenol, CHPE = cyclohexylphenyl ether, DPE = diphenyl ether, CHOH = cyclohexanol, CHO = cyclohexanone, CH = cyclohexane, Bz = benzene

Table 1: Conversion of Individual Intermediates and Binary Mixtures

the selectivity of CHOH dropped to 85.8%. As the reaction progressed, product distribution changed and the final product mixture was composed of CHOH (96%) and CH/Bz (4%). Based on the final product composition, hydrolysis was considered as another route contributing to the high selectivity of CHOH in the presence of hydrogen.

Interestingly, a combined effect of water and scCO$_2$ made it possible to break the C−O bond under reasonably mild reaction conditions using Rh/C catalyst. In addition, hydrolysis of DCHE to the generation of CHOH cannot be ignored.

THEORETICAL ANALYSIS

To confirm the possible reaction path of DPE conversion under the working conditions, DFT calculation was performed.

THEORETICAL CALCULATION METHOD

All the calculations related to the transition state were performed with density functional theory (DFT) using DMol3 3-7 and DNP basis set. The transition state (TS) calculations were performed using the synchronous transit methods as included in the DMol3 module of BIOVIA-Dassault Systèmes. Complete Linear Synchronous Transit (LST)/Quadratic Synchronous Transit (QST) begins by performing an LST/Optimization calculation. The TS obtained in that way was used to perform QST maximization. From that point, another conjugate gradient minimization was performed. The cycle was repeated until a stationary point was located or the number of allowed QST steps was exhausted. DMol3 uses the Nudged Elastic Band (NEB) method for minimum energy path calculations. The NEB method introduces a fictitious spring force that connects neighboring points on the path to ensure continuity of the path and projection of the force so that the system converges to the minimum energy path (MEP), which is also called intrinsic reaction co-ordinate if the co-ordinate system is mass weighted. We also calculated the vibration mode to identify the negative frequency to confirm the transition state. To consider the effect of the solvent, we employed the conductor-like screening model (COSMO) solvation method within the DFT formalism as in the BIOVIA-Dassault Systèmes DMol3 program. In this method, the solute molecules form a cavity within the dielectric continuum of permittivity that represents the solvent. The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric medium was described by the generation of screening (or polarization) charges on the cavity surface. The cavity surface is obtained as a superimposition of spheres centered at the atoms, discarding all parts lying on the interior part of the surface. The spheres are represented by a discrete set of points, the so-called basic points; eliminating the parts of the spheres that lie within the interior part of the molecule, BLYP exchanges

correlation functional to eliminate the basic grid points that lie in the interior of the molecule. The radii of the spheres are determined as the sum of the van der Waals radii of the atoms of the molecule and of the probe radius. The surviving basic grid points are then scaled to lie on the surface generated by the spheres of van der Waals radii alone. The basic points are then collected into segments, which are also represented as discrete points on the surface. The screening charges are located at the segment points. We first optimize all the reactants and products in scCO$_2$ medium in the presence of water. We have therefore used a dielectric constant value which reciprocates the value of an ideal mixture of both components, which are 40.15. We performed a TS calculation to find the intermediate and compared the stability of the intermediate. We repeated the calculation with 1 Rh atom. We are not considering the effect of support or specific surface of Rh; the interest was to see the role of Rh in the energy spectrum. A similar approach was also introduced for hydrogenation of nitrobenzene over Pd/MCM-41 in scCO$_2$. The theoretical and experimental results were subsequently used to understand the C−O bond cleavage in the presence of hydrogen in scCO$_2$/water medium. Here, we have considered three key reactions depending on the above experimental results: (i) hydrogenolysis, (ii) hydrolysis and (iii) hydrogenation. Table 2 shows the calculated energy of each possible step of the reaction. The hydrogenolysis of the C−O bond resulted in PhOH and Bz with reaction energy of -14.2 kcal mol^{-1} (Table 2, entry 2). In addition, the calculation also indicated that the hydrolysis of DPE → 2 PhOH and hydrogenation of DPE → CHPE proceeds with the reaction energy change of -7.1 (Table 2, entry 3) and -26.5 kcal mol^{-1} (Table 2, entry 1), respectively. According to the calculated reaction energy, hydrogenation of DPE to CHPE emerged as thermodynamically more favorable than hydrogenolysis.

Hydrolysis of DPE appeared as the energetically least favored reaction path. However, experimental results revealed that monocyclic products obtained via hydrogenolysis and hydrolysis were the major products. To explain this phenomenon, the adsorption energy of DPE and products from hydrogenolysis (PhOH) and hydrogenation (CHPE) was calculated (Table 2; entries 5–8). The mode of adsorption of DPE, PhOH, CHPE and DCHE against a hydrogenated Rh surface is shown in Fig. 1a–d, respectively. Starting with the hydrogenated Rh surface, the calculation shows that the most stable adsorption mode of DPE is angular, with O atom and one of the aromatic rings co-planar to the surface with adsorption energy of -10.87 kcal mol^{-1} (Fig. 1a). On the other hand, PhOH (Fig. 1b) and CHPE (Fig. 1c) are adsorbed via their aromatic ring with adsorption energies of -8.22 and -18.93 kcal mol^{-1}, respectively.

The outcome of the theoretical work clearly shows that the reason for the preferential binding can be explained using the current reaction mechanism study. The preference of binding

is due to the preference of the molecules over the metal surface depending on the environment of the molecule which is replicated using a dielectric constant continuum atmosphere. The selective binding can facilitate the bond breaking; which is otherwise understandable by experiment only. This study is currently extrapolated to monitor the effect more emphatically by explicit use of solvents.

CONCLUSION

In conclusion, we have demonstrated the cleavage of the C–O bond under mild reaction conditions in CO_2/water medium using commercially available Rh/C catalyst. The cleavage of the C–O bond of DPE leads to the formation of CHOH with very high selectivity of 96%. A combined effect of CO and water was clearly evident from the product distribution. The adsorption energy of reactants and products along with the reaction energy of each step revealed that hydrogenolysis and hydrolysis were two key reactions to the cleavage of the C–O bond of DPE. A combination of theoretical methods and experiment is the best way to solve issues like this.

Figure 1: Adsorption geometry of (a) DPE, (b) PhOH, (c) CHPE and (d) DCHE on a hydrogenated Rh surface

Entry	Reaction steps	Reaction energy (kcal mol^{-1})
1	DPE → CHPE	−26.5
2	DPE → PhOH + Bz	−14.2
3	DPE → 2 PhOH	−7.1
4	CHPE → PhOH + CH	−0.92

Entry	Substrate/products	Adsorption energy (kcal mol^{-1})
5	DPE	−10.87
6	PhOH	−8.22
7	CHPE	−18.93
8	DCHE	−24.01

Table 2: Calculated reaction energy of different reaction steps and adsorption energy of substrate and reaction products
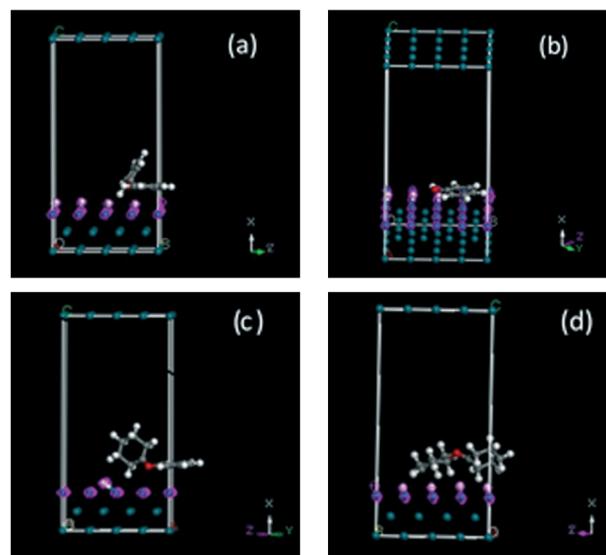
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