

Thermodynamic study and experimental verification on the product distribution of the synthesis of dipropylene glycol from propylene oxide and propylene glycol

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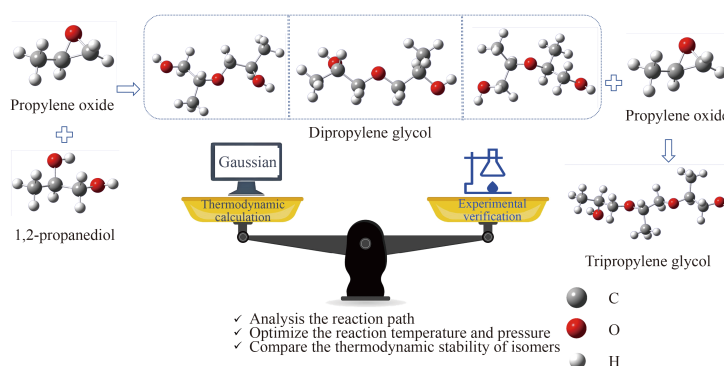
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Abstract: Propylene oxide (PO) is an important petrochemical materials used to produce downstream products such as propylene glycol (PG), polyether polyols, and dipropylene glycol (DPG). Among these, DPG is commonly used as a solvent for fragrances, cosmetics, food additives, and detergents, and can also be served as a moisturizer in cosmetics, showing broad application prospects. The distribution of DPG isomers in the products synthesized from PO and PG has a significant impact

on the quality of the products. Therefore, conducting thermodynamic calculation on the reaction of PO and PG to synthesize DPG can provide a theoretical basis for practical operations and product distribution regulation. So, in this paper, the thermodynamic parameters of PO, 1,2-PG, H₂O, tripropylene glycol (TPG) and three isomers of DPG under different reaction conditions is calculated. Additionally, the $\Delta_r G$, $\Delta_r H$ and $\ln K$ for four potential reactions at various reaction temperatures and pressures are calculated. By designing isodesmic reactions and combining the results of thermodynamic calculations, the $\Delta_r H^\circ$ and $\Delta_r G^\circ$ for the isomers of DPG are obtained, and the relative error is less than 7%. The results show that in the process of preparing DPG by PO and PG, when PO:PG = 1, the reaction temperature ranges from 298.15 to 413.15 K, and the pressure ranges from 101.325 to 506.625 kPa, the reactions of PO + PG $\rightleftharpoons$ DPG and PO + DPG $\rightleftharpoons$ TPG are thermodynamically spontaneous. While the reactions of PG + PG $\rightleftharpoons$ DPG + H₂O and PG + DPG $\rightleftharpoons$ TPG + H₂O are thermodynamically unspontaneous. The optimal reaction temperature and pressure are 413.15 K and 101.325 kPa. The thermodynamic stability of the three isomers is DPG1>DPG2>DPG3 under standard conditions. The accuracy of the computational results is verified through experimental design, and based on this, the factors affecting product distribution are analyzed.

Key words: dipropylene glycol; propylene oxide; 1,2-propylene glycol; thermodynamic



Dipropylene glycol (DPG) is a fine chemical widely used in commercial products^[1]. The LO+ grade DPG is more expensive and serving as high-quality solvent for fragrance, coupling agent and moisturizer in cosmetics^[2–3]. However, industrial grade DPG is cheaper and thus widely used in coatings, plasticizers and polyurethane^[4]. The difference between the two products is mainly in the content of the

isomers^[5]. So, tuning the isomers distribution in the product is very important.

Two methods for producing DPG have been reported: firstly, synthesis of DPG as a byproduct in the hydration of propylene oxide (PO) to produce 1,2-propanediol (PG)^[6–7]. The method is not suitable for industrial production because the difficult in controlling the reaction and the low DPG

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yield. The other method involves the reaction of PO and PG^[8-9] under the action of the acidic^[10-12] or basic catalyst^[13] which is widely employed currently. The product quality under the action of acid catalysts is relatively high with the highest proportion of DPG2, while the product quality under the action of alkaline catalysts is lower with a higher proportion of DPG1. Therefore, the quality of the product is mainly related to the proportion of isomers.

Although there have been some researches on the preparation of DPG from PO and PG, less reported is found on the thermodynamic properties of the reaction and the isomers distribution. The thermodynamic analysis of the reaction can not only serve as an important basis for judging the spontaneity and extent of the reaction, but also provide theoretical guidance for setting reaction conditions and controlling product distribution^[14-16]. It has been reported that the generation ratio of the isomers is well consistent with thermodynamic stability^[5]. As a result, the computational analysis of the thermodynamic parameters of different isomers will be necessary for predicting the ratio of isomers in DPG production.

In this study, the structures of the reactants and products related to the reaction as well as three isomers of DPG are optimized by Gaussian 16 software at the level of B3lyp/6-311+G(d,p) basis set level^[17-20]. The free energy change ($\Delta_r G$), enthalpy ($\Delta_r H$) and equilibrium constant (K) of the reaction under different conditions are calculated. In addition, the isodesmic reaction is designed to obtain the standard enthalpy of formation ($\Delta_f H^\theta$) and standard free energy of formation ($\Delta_f G^\theta$) for each isomer to compare the thermodynamic stability. The yield and product distribution of DPG under different reaction conditions are employed to validate the accuracy of the thermodynamic calculations. This work will provide a theoretical basis for the selection of experimental conditions and the regulation of product distribution.

1 The analysis of the reaction process

1.1 The main reaction pathway

In the presence of acidic or basic catalysts, PO undergoes ring-opening and condenses with PG to form DPG. PO may also react with the produced DPG to form tripropylene glycol (TPG) and other products with higher degrees of

polymerization. The reaction process is shown in Figure 1.

1.2 The related reaction pathway

PG may form DPG via intermolecular dehydration condensation. PG may also react with the produced DPG to form TPG and other polymers. The reaction process is shown in Figure 2.

In short, the following reactions may be involved:



2 Computational methods

The structures of PO, PG, H₂O, DPG and TPG (the structure is in Figure S1) are optimized at B3LYP/6-311+G(d,p) level^[21]. The vibrational frequencies are calculated to characterize the true minima using Gaussian 16 package^[22]. In the temperature range of 373.15 to 433.15 K, and the pressure range of 101.325 to 506.625 kPa, the PG, DPG and TPG are liquid, while H₂O is liquid under some reaction conditions. During optimization of the structure, molecules in the liquid state are calculated using the PCM solvation model^[23-25]. The thermodynamic parameters of each molecule including enthalpy (H), free energy (G) and entropy (S) are obtained under different conditions. Additionally, $\Delta_r H$, $\Delta_r G$ and K of the four possible reactions are calculated.

The structures of the three isomers: 1,1'-oxybis-2-propanol (DPG1), 2,2'-oxybis-1-propanol (DPG2) and 2-(2-hydroxyoxy)-1-propanol (DPG3) are illustrated in Figure 3^[26-27].

The isodesmic reaction method is often used to calculate the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of a compound. In some studies, the results calculated using this method are compared with the experimental values with a maximum deviation of 9.6 kJ/mol^[28-30]. So, $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of DPG1, DPG2 and DPG3 are calculated by using appropriate isodesmic reaction, thermodynamic calculation and relevant empirical values.

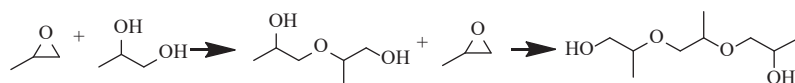


Fig. 1 The reaction process of PO and PG

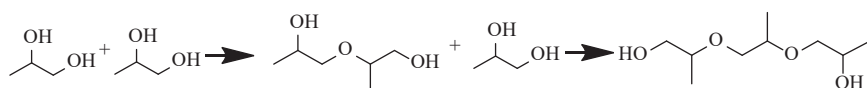


Fig. 2 The reaction process of PG and PG

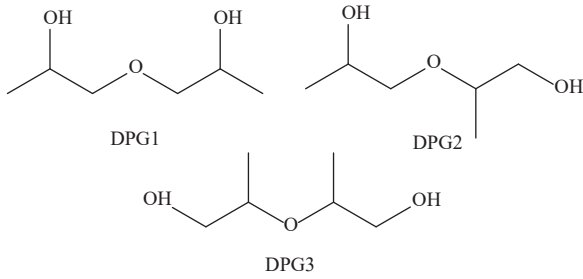


Fig. 3 Structural formulas of isomers of DPG

The isodesmic reaction between PO and PG to form DPG is:



Firstly, the H° of each molecule is calculated at the B3lyp/6-311+G(d,p) basis set level. Then, the reaction enthalpy $\Delta_r H^\circ$ of Eq. (5) is obtained by using the following equations:

$$\Delta_r H^\circ = H^\circ(\text{DPG}) - H^\circ(\text{PO}) - H^\circ(\text{PG}) \quad (6)$$

Additionally, $\Delta_r H^\circ$ of Eq. (5) has the following relationship with $\Delta_r H^\circ$ of reactants and products:

$$\Delta_r H^\circ = \Delta_r H^\circ(\text{DPG}) - \Delta_r H^\circ(\text{PO}) - \Delta_r H^\circ(\text{PG}) \quad (7)$$

According to Eq. (6) and (7), the $\Delta_r H^\circ(\text{DPG})$ is obtained as:

$$\Delta_r H^\circ(\text{DPG}) = [H^\circ(\text{DPG}) - H^\circ(\text{PO}) - H^\circ(\text{PG})] + [\Delta_r H^\circ(\text{PO}) + \Delta_r H^\circ(\text{PG})] \quad (8)$$

In the same way, the formula for calculation of $\Delta_r G^\circ(\text{DPG})$ is as following:

$$\Delta_r G^\circ(\text{DPG}) = [G^\circ(\text{DPG}) - G^\circ(\text{PO}) - G^\circ(\text{PG})] + [\Delta_r G^\circ(\text{PO}) + \Delta_r G^\circ(\text{PG})] \quad (9)$$

In order to calculate the $\Delta_r G^\circ(\text{PG})$, the reaction in Eq. (10) is designed as:



Thus, the Eqs. (11)–(13) can be obtained:

$$\Delta_r S^\circ = S^\circ(\text{PG}) - 3S^\circ(\text{C}) - S^\circ(\text{O}_2) - 4S^\circ(\text{H}_2) \quad (11)$$

$$\Delta_r H^\circ = \Delta_r H^\circ(\text{PG}) - 3\Delta_r H^\circ(\text{C}) - \Delta_r H^\circ(\text{O}_2) - 4\Delta_r H^\circ(\text{H}_2) = \Delta_r H^\circ(\text{PG}) \quad (12)$$

$$\Delta_r G^\circ = \Delta_r G^\circ(\text{PG}) = \Delta_r H^\circ - T\Delta_r S^\circ \quad (13)$$

The T in Eq. (13) is 298.15 K. The calculated values and the experimental values of H° , G° , S° , as well as the experimental values of $\Delta_r H^\circ$, $\Delta_r G^\circ$ of the molecule or atom in Eqs. (6)–(9) and (11)–(13) are listed in Table S1.

3 Experimental

In order to verify the accuracy of the calculation results, the following experiment is designed. The reaction

conditions are: 101.325 kPa, the feed molar ratio is PO: PG=1. The reactants are put into a high-pressure reactor without catalyst, the reaction temperatures are 373.15, 383.15, 393.15, 403.15, 413.15, 423.15 and 433.15 K, respectively. The reactions are also carried out at the optimal temperature for 4, 6, 8, 10 and 16 h, respectively. The products are analyzed on Agilent 8860 Gas Chromatograph equipped with HP-5 column (30 m×250 μm×0.25 μm) and flame ionization detector (FID). The conversion of PO, the selectivity and yield of DPG as well as the selectivity of TPG and the product-distribution are compared.

4 Results and discussion

4.1 Thermodynamic parameters

The thermodynamic parameters including H (Table S2), G (Table S3) and S (Table S4) of the reactants and products involved in reactions (1)–(4) are calculated at different states.

Then, the results are used to obtain the $\Delta_r H$, $\Delta_r G$ and K for the four reactions.

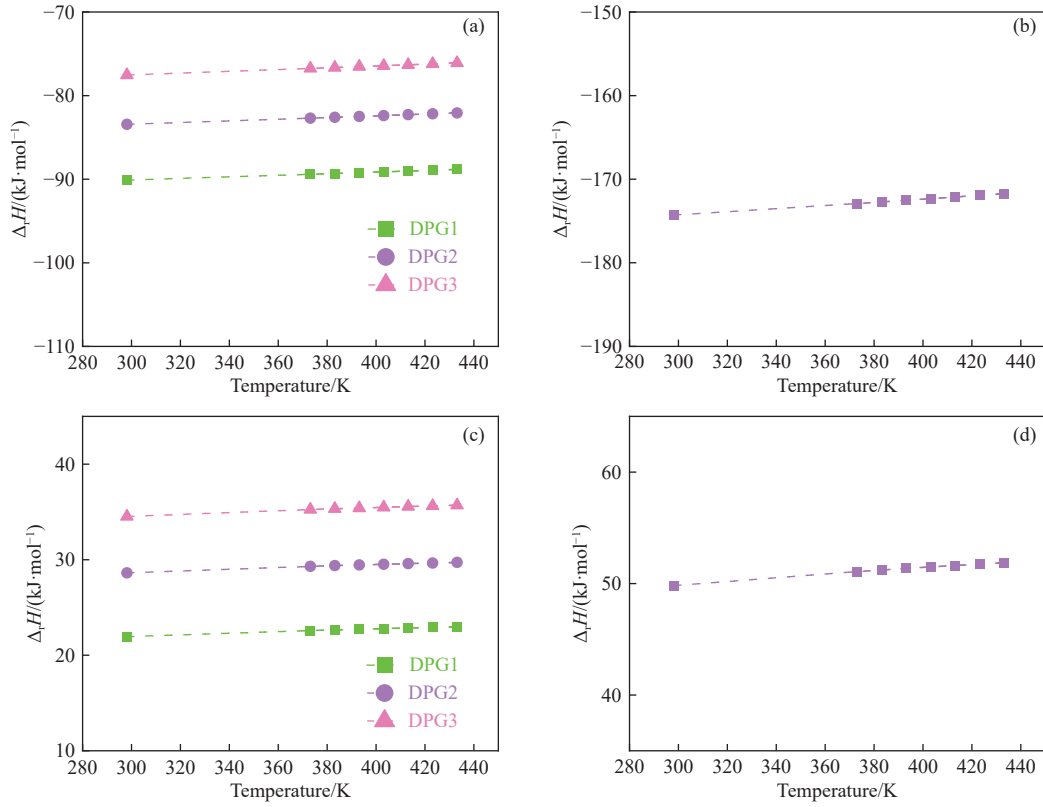
4.2 Calculation of $\Delta_r H$

The effect of temperature on $\Delta_r H$ of the reactions is investigated, and the results are shown in Figure 4. Under standard atmospheric pressure and the temperature ranging from 373.15 to 433.15 K, the $\Delta_r H$ of reactions (1) and (2) are both negative revealing that the reactions are exothermic. While those of reactions (3) and (4) are both positive which mean that the two reactions are endothermic.

4.3 Calculation of $\Delta_r G$

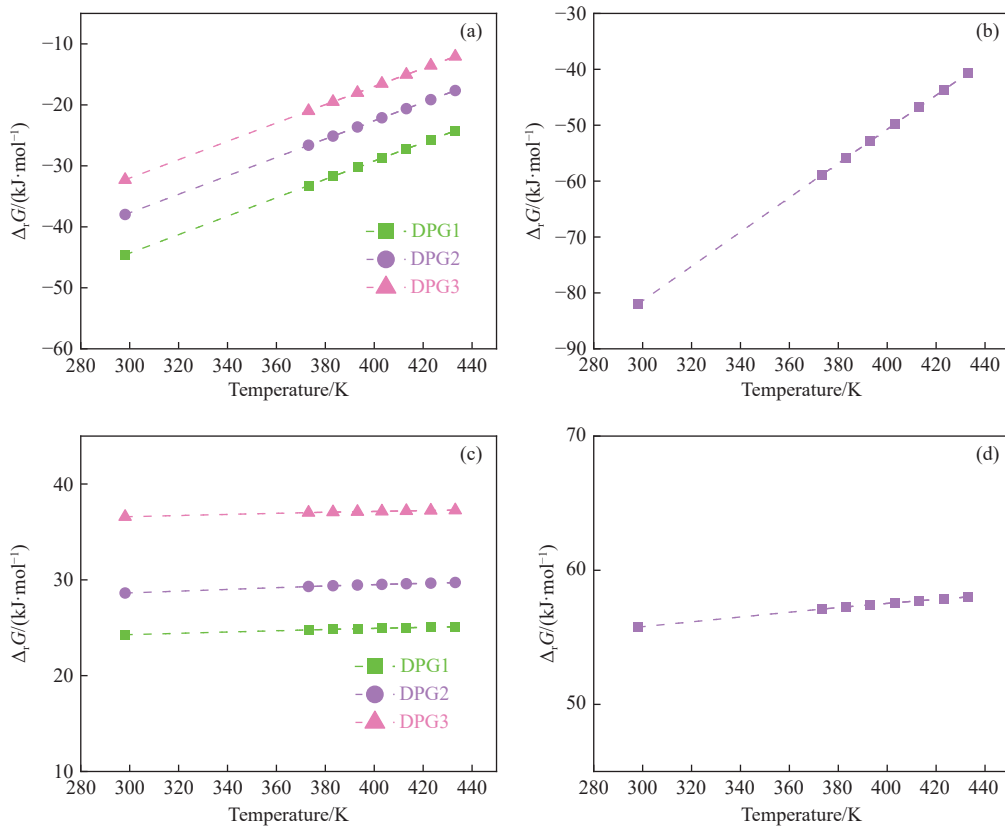
The effect of temperature on $\Delta_r G$ of the reactions is also studied (Figure 5). Under standard atmospheric pressure and the temperature ranging from 373.15 to 433.15 K, $\Delta_r G$ of reactions (1) and (2) are both negative, revealing that the two reactions are spontaneous. Moreover, as the temperature increases, the $\Delta_r G$ becomes larger, i.e., high temperature is unfavorable for the reaction. However, the reactions (3) and (4) cannot occur spontaneously since the $\Delta_r G$ of the reactions are positive.

The effect of pressure on the $\Delta_r G$ of the reactions is illustrated in Figure 6. For the pressure ranging from 101.325 to 506.625 kPa at 298.15, 373.15, 383.15, 393.15, 403.15, 413.15, 423.15, 433.15 K, the $\Delta_r G$ of reactions (1) and (2) are both negative, suggesting that these two reactions can be conducted spontaneously. As the pressure increases, the $\Delta_r G$ decreases, i.e. high pressure is conducive to the reaction. However, the $\Delta_r G$ of reactions (3) and (4) are both positive, illustrating that these two reactions cannot occur spontaneously.



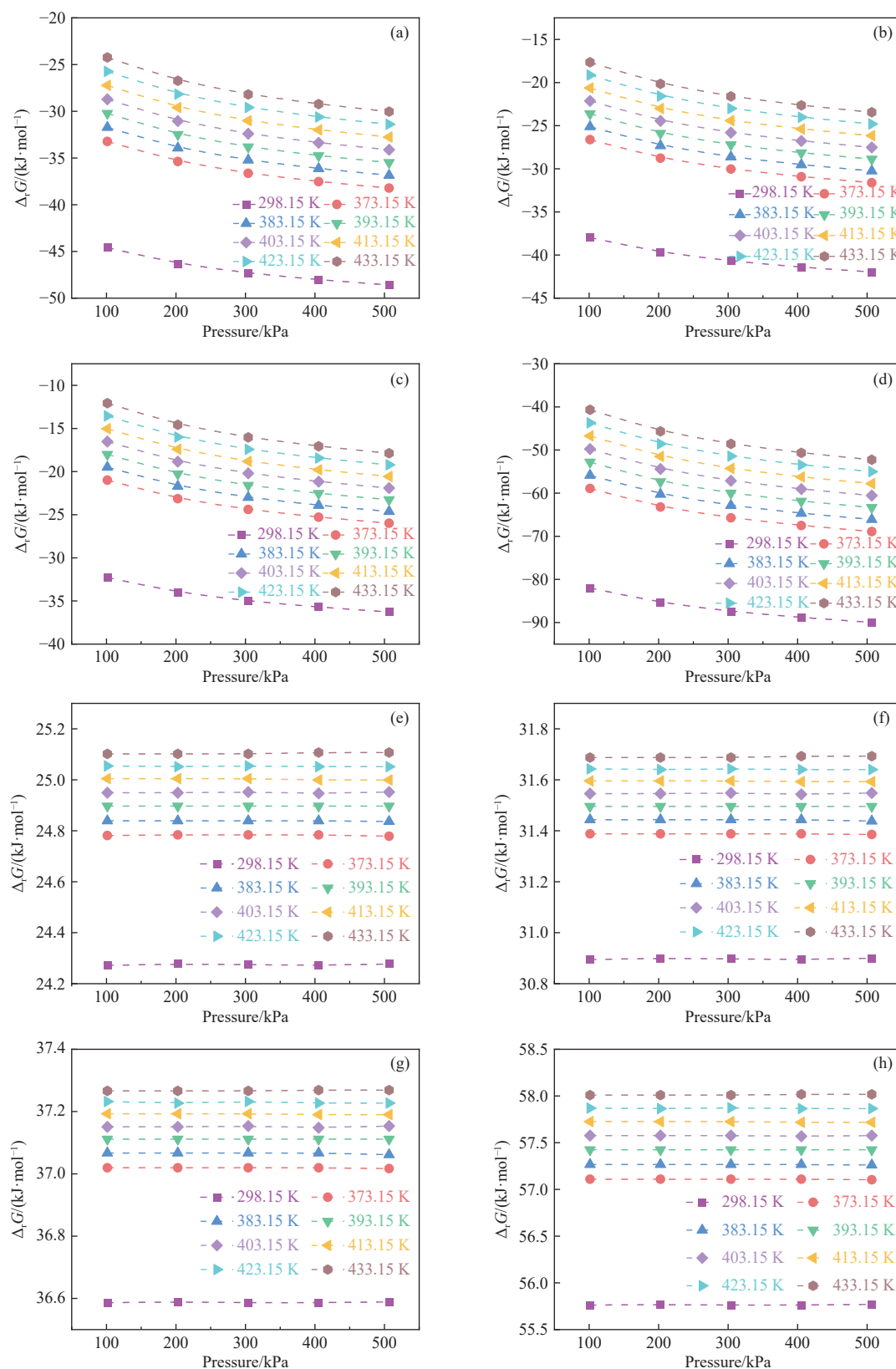
(a): $\text{PO} + \text{PG} \rightleftharpoons \text{DPG}$; (b): $2\text{PO} + \text{PG} \rightleftharpoons \text{TPG}$; (c): $2\text{PG} \rightleftharpoons \text{DPG} + \text{H}_2\text{O}$; (d): $3\text{PG} \rightleftharpoons \text{TPG} + 2\text{H}_2\text{O}$.

Fig. 4 The $\Delta_r H$ of reactions (1)–(4) under different temperatures at 101.325 kPa



(a): $\text{PO} + \text{PG} \rightleftharpoons \text{DPG}$; (b): $2\text{PO} + \text{PG} \rightleftharpoons \text{TPG}$; (c): $2\text{PG} \rightleftharpoons \text{DPG} + \text{H}_2\text{O}$; (d): $3\text{PG} \rightleftharpoons \text{TPG} + 2\text{H}_2\text{O}$.

Fig. 5 The $\Delta_r G$ of reactions (1)–(4) under different temperatures at 101.325 kPa



(a)–(c): $\text{PO}+\text{PG}\rightleftharpoons\text{DPG}$; (d): $2\text{PO}+\text{PG}\rightleftharpoons\text{TPG}$; (e)–(g): $2\text{PG}\rightleftharpoons\text{DPG}+\text{H}_2\text{O}$; (h): $3\text{PG}\rightleftharpoons\text{TPG}+2\text{H}_2\text{O}$.

Fig. 6 The $\Delta_r G$ of reactions (1)–(4) under different pressures at 298.15, 373.15, 383.15, 393.15, 403.15, 413.15, 423.15, 433.15 K respectively

In summary, under the temperature ranging from 373.15 to 433.15 K and the pressure ranging from 101.325 to

506.625 kPa, reactions (1) and (2) are both spontaneous. While reactions (3) and (4) are both non-spontaneous. In the

reaction of preparing DPG from PO and PG, only the following two reactions are included (1), (2).

4.4 Calculation of K

The effect of temperature on K of the reaction is then investigated. As illustrated in Figure 7, under standard atmospheric pressure and the temperature ranging from 373.15 to 433.15 K, the $\ln K$ of reactions (1) and (2) are both positive. As the temperature increases, $\ln K$ decreases, which indicates that high temperatures reduce the extent of the reaction. However, as the temperature increases, the extent of reaction (2) is reduced more than that of reaction (1), revealing that high temperature is conducive to improving the selectivity of DPG. As is well known, increasing the temperature will accelerate the reaction rate. However, when the temperature reaches 403.15 to 413.15 K, $\ln K$ of the preparation of DPG3 will be less than 5, which tends to be reversible. The result shows that the optimal temperature for the reaction is between 403.15 to 413.15 K.

The effect of pressure on the K of the reaction is illustrated in Figure 8. When the pressure is between 101.325 to 506.625 kPa and at 298.15, 373.15, 383.15,

393.15, 403.15, 413.15, 423.15, 433.15 K, the $\ln K$ of reactions (1) and (2) are both positive which increase with the increasing of the pressure. It indicates that high pressure is favorable for the reaction. However, as the pressure increases, the improving extent of reaction (2) is greater than that of reaction (1), suggesting that high pressure is not conducive to promote the selectivity of DPG. So, the suitable reaction pressure is 101.325 kPa (Figure 9).

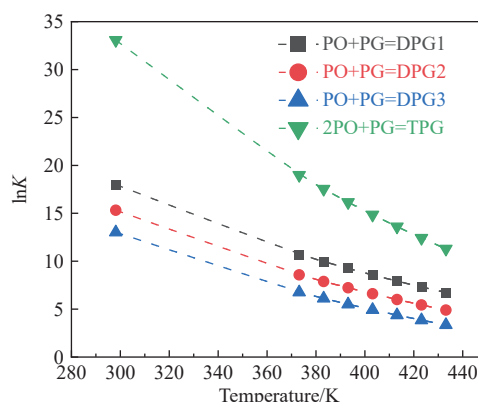
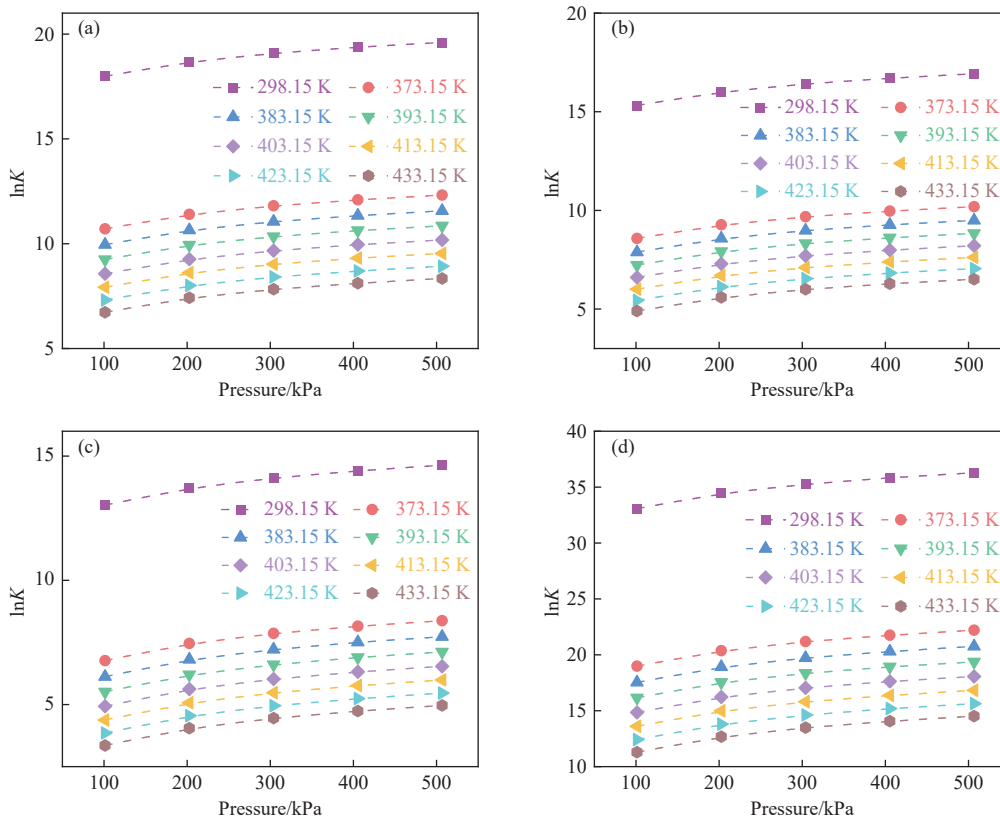


Fig. 7 The $\ln K$ of reactions (1), (2) under different temperatures at 101.325 kPa



(a)–(c): $\text{PO}+\text{PG}=\text{DPG}$; (d): $2\text{PO}+\text{PG}=\text{TPG}$.

Fig. 8 The $\ln K$ of reactions (1), (2) under different pressures at 298.15, 373.15, 383.15, 393.15, 403.15, 413.15, 423.15, 433.15 K respectively

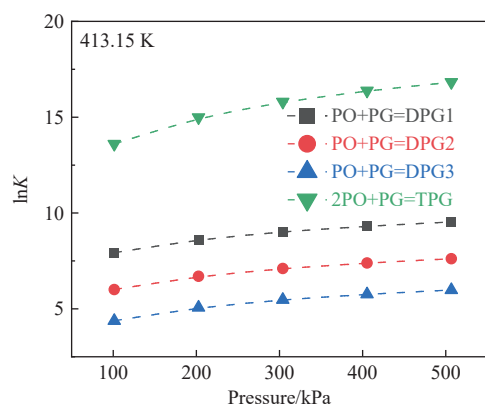


Fig. 9 The $\ln K$ of reactions (1), (2) under different pressures at 413.15 K

4.5 The thermodynamic stability of isomers

Isodesmic reaction 5 is designed to derive the calculation formulas of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ (8), (9). Then, the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of DPG1, DPG2 and DPG3 are obtained respectively, which is compared with the calculation results of the group contribution method^[31] (The calculation data of the group contribution method is in Table S5) with error less than 7%. (Table 1). According to thermodynamic principle, isomer with lower $\Delta_f G^\theta$ will be more stable^[17]. Naturally, it can be found that the thermodynamic stability of the isomers under standard conditions is in the order of: DPG1 > DPG2 > DPG3.

Table 1 Calculated $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of different DPG isomers

the isomers of DPG	$\Delta_f H^\theta / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f G^\theta / (\text{kJ} \cdot \text{mol}^{-1})$
DPG1	-668.58	-430.19
DPG2	-661.79	-423.56
DPG3	-656.01	-417.87
Calculation results of the group contribution method	-624.72* (5.01%–7.02%)	-407.32* (2.38%–5.61%)

*Calculation results of the group contribution method.

4.6 Experimental results

The accuracy of the computational results is thus verified by experiment (Figure 10). The main product of the reaction is DPG, and the by-product is mainly TPG. It can be observed that at 413.15 K, the selectivity of DPG which is the ratio of the amount of substance of DPG produced to the amount of substance of converted PO ($S_{\text{DPG}} = \frac{n_{\text{DPGpro}}}{n_{\text{POcon}}} \times 100\%$) is the highest (Figure 10(a)), demonstrating that the computational results correspond with the experimental results. As shown in (Figure 10(b)), within the first 8 h, the product is primarily DPG. This is because the feed ratio is PG:PO=1, which is beneficial to generate DPG. However, as the amount of DPG increases, it will continue to react with PO to form TPG and the reaction rate of DPG will increase.

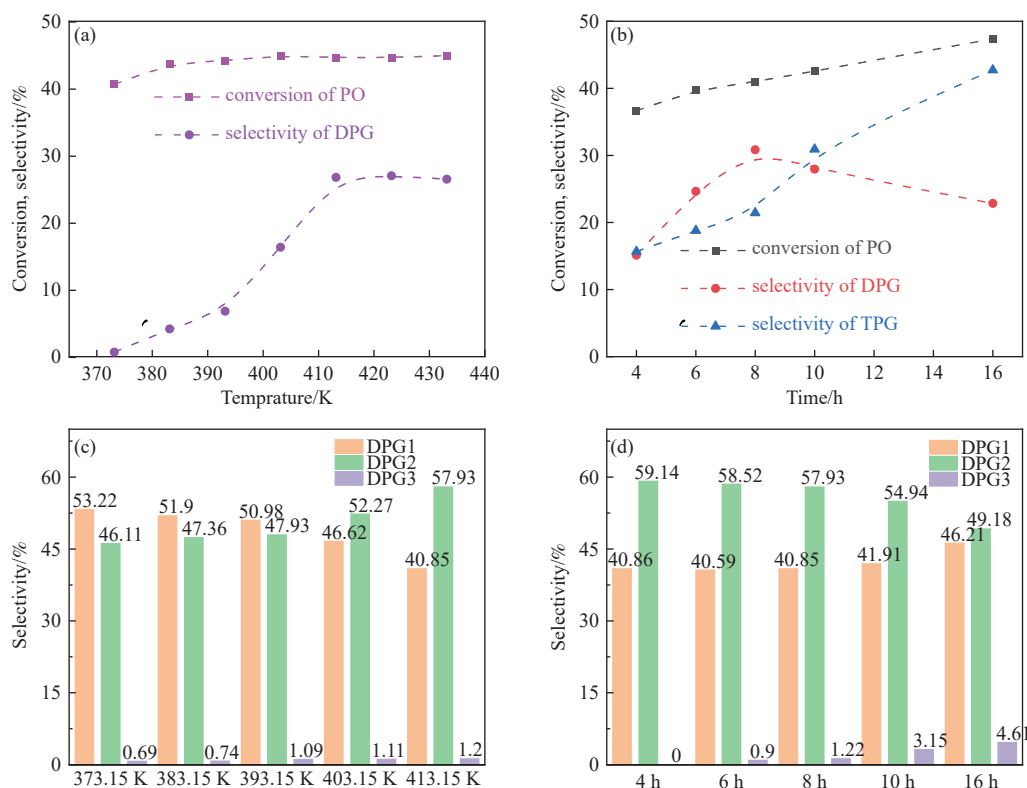


Fig. 10 Experimental results for DPG synthesis from PO and PG under different conditions: (a) Conversion of PO, selectivity of DPG under different temperatures (reaction conditions: 8 h, 101.325 kPa); (b) Conversion of PO, selectivity of DPG and selectivity of TPG under different reaction times (reaction conditions: 413.15 K, 101.325 kPa); (c) Product distribution under different temperatures (reaction conditions: 8 h, 101.325 kPa); (d) Product distribution at different reaction times (reaction conditions: 413.15 K, 101.325 kPa)

When the reaction time reaches 8 h, the selectivity of DPG is maximized at 30.85%. Then the rate of DPG formation is less than the rate of DPG conversion, causing the increasing of TPG selectivity and the decreasing of DPG selectivity. When the reaction time is 16 h, the selectivity of TPG has reached 42.73%, while the selectivity of DPG has fallen to 22.85%. Combined with the results of thermodynamic calculations, when the reaction condition is at 413.15 K and 101.325 kPa, the $\ln K$ of the $2\text{PO} + \text{PG} \rightleftharpoons \text{TPG}$ reaction is 13.60 while that of the $\text{PO} + \text{PG} \rightleftharpoons \text{DPG}$ is 4.38–7.93. This indicates that when the reaction eventually reaches equilibrium, the selectivity of TPG will be significantly higher than that of DPG. The above results show that the thermodynamic calculation results have a certain degree of accuracy and can serve as theoretical references for subsequent research on product distribution.

As shown in Figure 10(c), from 373.15 to 393.15 K, the product ratio is consistent to the thermodynamic stability of the three isomers, which is $\text{DPG1} > \text{DPG2} > \text{DPG3}$. Moreover, the difference between the ratio of DPG1 and DPG2 decreases with the increase of temperature. This is due to the low reaction temperature resulting in a low reaction rate, and the $\ln K$ is higher according to the thermodynamic calculation. So, the reaction is mainly affected by thermodynamics, DPG1 is in high proportion. However, with the increase of temperature, the $\ln K$ decreases, the reaction rate accelerates which will lead to the reduced amount of DPG1 and the increased proportion of DPG2 in the product. When the temperature reaches 403.15 K, the product distribution is influenced by kinetics, with the order of $\text{DPG2} > \text{DPG1} > \text{DPG3}$. The higher the temperature, the larger the proportion of DPG2 is. Since the unreacted PO will further react with DPG to produce TPG, it is difficult to find a equilibrium state of the target reaction. So, we predict the final state by studying the changes of DPG isomers in the reaction process. The product distribution at 413.15 K for different reaction durations are also compared (Figure 10(d)). The formation rates of the three isomers are $\text{DPG2} > \text{DPG1} > \text{DPG3}$, so the content of DPG2 is the highest, and the content of DPG3 is the lowest. As the reaction progresses, DPG will further react with PO to form TPG. The thermodynamic calculation results show that the thermodynamic stability of the three isomers is different. Thus, DPG2 and DPG3 are easier to react with PO. So, with the extension of the reaction time, it can be clearly seen that the content of DPG2 in the isomers is decreasing, and the proportion of DPG1 is increasing, which is also consistent with the thermodynamic calculation results. In summary, the yield of DPG can be improved by optimizing the reaction time and the PG/PO ratio. For the regulation of product distribution, thermodynamic factors and kinetic factors need to be considered at the same time. Low temperature is beneficial to generate DPG1 while high temperature is conducive to the formation of DPG2. The formation rate of different isomers can also be controlled by using different catalysts by tuning the activation path of the reactants.

5 Conclusion

The thermodynamic parameters of PO, PG, TPG and different isomers of the product DPG are calculated at the B3lyp/6-311+G(d,p) basis set level. By calculating the $\Delta_r G$ and $\Delta_r H$ of each reaction under different conditions, it is concluded that only reactions (1) and (2) are spontaneous, while the reactions (3) and (4) are thermodynamically non-spontaneous when $\text{PO}:\text{PG} = 1$, the reaction temperature ranges from 298.15 to 413.15 K, and the pressure ranges from 101.325 to 506.625 kPa. By comparing the $\Delta_r G$, $\Delta_r H$ and $\ln K$ of the reactions (1) and (2) under different conditions, the optimal reaction temperature and pressure is determined to be 413.15 K and 101.325 kPa. By designing the isodesmic reaction, the $\Delta_r G^\circ$ and $\Delta_r H^\circ$ of three isomers are calculated, and the thermodynamic stability under standard conditions is obtained as following: $\text{DPG1} > \text{DPG2} > \text{DPG3}$. The experimental results show that the results of theoretical calculation are relatively accurate. By combining the results of thermodynamic calculations with experimental verification, a certain reference direction is proposed to enhance the yield of DPG and regulate the distribution of products.

Supporting Information

The Supporting Information is available free of charge to the readers.

Data availability

The data measured in this study are available within the article. Other data used in this work will be made available on request.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] HOOTH M J, HERBERT R A, HASEMAN J K, et al. Toxicology and carcinogenesis studies of dipropylene glycol in rats and mice[J]. Toxicology, 2004, 204(2/3): 123–140.
- [2] LEVENE P A, WALT A. On condensation products of propylene oxide and of glycidol[J]. J Biol Chem, 1927, 75(1): 325–336.
- [3] DI MAURO C, TRAN T-N, MIJA A. One-pot terpolymerization synthesis of high carbon biocontent recyclable epoxy thermosets and their composites with flax woven fibers[J]. ACS Sustainable Chem Eng, 2021, 9(25): 8526–8538.
- [4] WANG B, DUAN C, ZHANG Z, et al. Research on the catalytic synthesis of dipropylene glycol and tripropylene glycol by solid acid[J]. Chem Ind Eng, 2024, 41(4): 45–54.

- [5] SONG S, WEI J, FANG X, et al. Experimental study on the synthesis of dipropylene glycol by acidic ionic liquid catalyst[J]. Shandong Chem Ind, 2018, 47(16): 42–3+9.
- [6] LI X. A new process for direct hydration to propylene glycol[J]. Chem Eng Desn, 1999, (3): 35–6+4.
- [7] HORBATENKO Y, PÉREZ J P, HERNÁNDEZ P, et al. Reaction mechanisms for the formation of mono- and dipropylene glycol from the propylene oxide hydrolysis over ZSM-5 zeolite[J]. J Phys Chem C, 2014, 118(38): 21952–21962.
- [8] BENHAM A L, KURATA F. Kinetics of the catalyzed and uncatalyzed liquid-phase hydration of propylene oxide[J]. AIChE J, 1955, 1(1): 118–24.
- [9] HUANG Y, QI G, QIAN J, et al. Fe-Zn bimetallic cyanide catalyzed ring-opening polymerization of propylene oxide[J]. Acta Polym Sin, 2001, (2): 210–214.
- [10] ATEŞ A. The modification of aluminium content of natural zeolites with different composition[J]. Powder Technology, 2019, 344: 199–207.
- [11] GACKOWSKI M, DATKA J. Acid properties of hierarchical zeolites Y[J]. Molecules, 2020, 25(5): 1–24.
- [12] JIANG H, WANG H, WANG H, et al. Rich-O-vacancy WO_3/ZrO_2 with high Lewis/Brønsted ratio: An efficient catalyst for the highly selective synthesis of dipropylene glycol[J]. Ind Eng Chem Res, 2020, 25(5): 1–24.
- [13] LU L, XIANG Y, XIA D, et al. Research on the synthesis process of organic amine catalytic dipropylene glycol[J]. Chem Ind (Xi'an, China), 2009, 38(3): 359–362.
- [14] CHANDLER W D, JOHNSON K E. Thermodynamic calculations for reactions involving hydrogen halide polymers, ions, and lewis acid adducts. 3. systems constituted from Al^{3+} , H^+ , and Cl^- [J]. Inorg Chem, 1999, 38(9): 2050–2056.
- [15] ZHANG X-Y, BIAN S, TIAN H-F, et al. Thermodynamic possibility analysis of CH_3COOH synthesis from CH_4 and CO_2 [J]. Mol Catal, 2024, 559: 114090.
- [16] SI D, SONG X, LI H, et al. Study of the mechanisms of dialkyl carbonates directly formed from carbon dioxide and alcohols: New insights from kinetic and thermodynamic processes[J]. Mol Catal, 2020, 482: 110699.
- [17] WANG F, CHEN J, LI D. Density functional theory study on stability and thermodynamic properties of polybrominated phenothiazine compounds[J]. Acta Chim Sin (Chin Ed.), 2009, 67(14): 1650–1658.
- [18] WANG L, LIU Y, JING S, et al. Molecular design and performance prediction of pyrimidine energetic compounds[J]. New Chem Mater, 2021, 49(9): 179–187.
- [19] ZHANG Y, MA W, LIN M, et al. Thermodynamic calculation of diazotization and coupling reaction of p-aminobenzene sulfonic acid[J]. Energy Chem Ind, 2023, 44(6): 24–31.
- [20] ZHU W, CHEN S, WANG Y, et al. Investigation into the quantitative structure-biototoxicity relationship of antibiotics and their estrogenic receptor disruption effects[J]. Chem Biodiversity, 2024, 22(3): e202401843.
- [21] LEE C, YANG W, PARR R G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density[J]. Phys Rev B, 1988, 37(2): 785–789.
- [22] FRISCH M J, TRUCKS G W, et al. Gaussian 16 Revision A. 03[CP]. 2016.
- [23] LALEVÉE J, ALLONAS X, JACQUES P. Electronic distribution and solvatochromism investigation of a model radical (2, 2, 6, 6-tetramethylpiperidine N-oxyl: tempo) through TD-DFT calculations including PCM solvation[J]. J Mol Struct: Theochem, 2006, 767(1): 143–147.
- [24] LOPEZ S A, MUNK M E, HOUK K N. Mechanisms and transition states of 1, 3-dipolar cycloadditions of phenyl azide with enamines: A computational analysis[J]. J Org Chem, 2013, 78(4): 1576–1582.
- [25] TOMASI J, CAMMI R, MENNUCCI B, et al. Molecular properties in solution described with a continuum solvation model[J]. Phys Chem Chem Phys, 2002, 4(23): 5697–5712.
- [26] HAVLIK A J, HILDEBRANDT A F. Hildebrandt. Structures of dipropylene glycols from nuclear magnetic resonance spectroscopy[J]. J Polym Sci Part A: Polym Chem, 1959, 41(138): 533–535.
- [27] SEXTON A R, BRITTON E C. Synthesis and identification of dipropylene glycol isomers[J]. J Am Chem Soc, 1953, 75(17): 4357–4358.
- [28] DOROFEEVA O V, FILIMONOVA M A. Self-consistent enthalpies of formation of adamantanes by isodesmic reaction network[J]. Chem Thermodyn, 2018, 126: 31–37.
- [29] ZVENTURA O N, SEGOVIA M. Density functional computational thermochemistry: Accurate determination of the enthalpy of formation of perfluoropropane from DFT and ab initio calculations on isodesmic reactions[J]. Chem Phys Lett, 2005, 403(4): 378–384.
- [30] DOROFEEVA O V, SUNTSOVA M A. Enthalpy of formation of Cl-20[J]. Comput Theor Chem, 2015, 1057: 54–59.
- [31] PU Y L. The Benson group contribution method was used to estimate the thermodynamic properties of the synthesis of diethylhexyl sebacate[J]. Technol Dev Chem Ind, 2016, 45(9): 53–55.

环氧丙烷和 1,2-丙二醇合成二丙二醇的产物分布的热力学研究及实验验证

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摘要: 环氧丙烷 (PO) 是一种重要的石油化工原料, 可用于生产丙二醇 (PG)、聚醚多元醇和二丙二醇 (DPG) 等下游产品。其中, 二丙二醇可用作香精香料、化妆品、食品添加剂和洗涤剂等的常用溶剂, 还可作为化妆品的保湿剂, 应用前景较广。而 PO 和 1,2-丙二醇 (PG) 合成 DPG 产物中异构体的分布对于产品的品质有很大的影响。因此, 对 PO 和 PG 合成 DPG 的反应进行热力学研究能够对实际操作和产物分布调控提供理论依据。本研究计算了 PO、1,2-PG、水、二缩三丙二醇 (TPG) 以及 DPG 的三种同分异构体的热力学参数。计算了在不同反应条件下生成不同 DPG 异构体反应的 $\Delta_f G$, $\Delta_f H$ 和 $\ln K$ 。通过设计等键反应, 并结合热力学计算结果得出 DPG 的三种同分异构体的 $\Delta_f H^0$ 和 $\Delta_f G^0$, 相对误差小于 7%。结果表明, 对于 PO 与 PG 制备 DPG 反应, 当 PO:PG=1, 反应温度在 298.15–413.15 K, 压力在 101.325–506.625 kPa 下, $PO + PG \rightleftharpoons DPG$ 和 $PO + DPG \rightleftharpoons TPG$ 两个反应在热力学上是可以自发进行的, $PG + PG \rightleftharpoons DPG + H_2O$ 和 $PG + DPG \rightleftharpoons TPG + H_2O$ 两个反应在热力学上是不可能自发进行的; 最优反应温度和压力为 413.15 K 和 101.325 kPa; 在标况下, 三种异构体的热力学稳定性为 $DPG1 > DPG2 > DPG3$ 。通过设计实验验证了计算结果的准确性, 并在此基础上, 分析了影响产物分布的因素。

关键词: 二丙二醇; 环氧丙烷; 1,2-丙二醇; 热力学

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