


 Cite this: *RSC Adv.*, 2022, 12, 12152

# Theoretical analysis and evaluation of reaction routes by “three-parameter difference” †

 Yu-Cong Song,  Xiao-Shu Ding,\* Chang-Cheng Wu and Yan-Ji Wang \*

How to choose a high-efficiency, green and inherent safety synthetic route is an important issue for the development of the chemical industry. “Three-parameter difference” is a complex parameter with the calculation of Gibbs free energy, atom utilization and inherent safety index, and can be used to comprehensively evaluate the thermodynamic feasibility, greenness and safety of chemical reactions. This parameter has been proposed and established, but the reliability has not been determined. In this study, the parameter has been corrected to make it more universal. It was calculated and studied in the synthesis of dimethyl carbonate and toluene diisocyanate, separately. The results showed that the reaction pathways for synthesizing dimethyl carbonate from the gas-phase oxidative carbonylation of methanol by a one-step process, and toluene diisocyanate from dimethyl carbonate-ionic liquid hydroxylamine have obvious advantages and future research prospects. They are consistent with the existing actual research, which can prove the reliability of the “three-parameter difference”. More importantly, the parameter provides a theoretical basis and has an adequate practical guidance significance to design and evaluate a new synthesis route.

Received 27th February 2022

Accepted 4th April 2022

DOI: 10.1039/d2ra01320g

[rsc.li/rsc-advances](https://rsc.li/rsc-advances)

## 1. Introduction

At present, the chemical industry is developing from the early single technical and economic index to the goal of paying equal attention to the triple indexes of engineering economy, environment-friendly and process safety.<sup>1</sup> The “three-parameter difference” parameter has been proposed and defined by our research group based on Gibbs free energy, atom utilization and inherent safety index as the theoretical basis for evaluating the thermodynamic feasibility, greenness and safety of chemical reactions.<sup>2</sup> However, there is a little introduction on the use of this parameter. In this study, the synthesis pathways of dimethyl carbonate and toluene diisocyanate, covering various of phase states and types of reaction routes, were comprehensively analyzed by using this parameter, and hence the optimal reaction route was designed. By comparing with the existing research results, the reliability of the “three-parameter difference” was verified, which provides examples for the synthesis of the chemical products, particularly the proposal of new processes.

## 2. Definition and correction of “three-parameter difference”

We defined the difference  $\Delta R_i$  between the three parameters ( $x_{\Delta G_i^0}$ ,  $y_{\text{AU}i}$ ,  $z_{\text{OSI}'_i}$ ) of the chemical reaction  $i$  and the three

parameters  $(-1, 1, 0)$  of the ideal chemical reaction as the “three-parameter difference”, as shown in the following formula. That is, the degree of proximity to the ideal reaction was used to characterize the comprehensive performance of the reaction, and this was used as a criterion to provide a basis for the selection of the chemical reaction path. The smaller the  $\Delta R_i$  value is, the closer to the ideal chemical reaction;  $\Delta R_i = 0$ , which represents the ideal chemical reaction.

$$\Delta R_i = \left[ \left( x_{\Delta G_i^0} + 1 \right)^2 + \left( y_{\text{AU}i} - 1 \right)^2 + z_{\text{OSI}'_i}^2 \right]^{1/2}$$

$$(i = 1, 2, \dots, R)$$

where  $x_{\Delta G_i^0}$  is the ratio of the Gibbs free energy of reaction  $i$  to the absolute value of the minimum Gibbs free energy for all reactions,  $x_{\Delta G_i^0} = \Delta G_i^0 / |\min(\Delta G_i^0)|$ ;  $y_{\text{AU}i}$  is the atom utilization of reaction  $i$ ;  $z_{\text{OSI}'_i}$  is the ratio of the inherent safety index of reaction  $i$  to the maximum inherent safety index of all reactions,  $z_{\text{OSI}'_i} = \text{OSI}'_i / \max(\text{OSI}'_i)$ .

Detailed calculations of Gibbs free energy, atomic utilization and inherent safety index mentioned above are provided in the ESI.†

On this basis, the following provisions are recommended.

(1) The selection rules of reaction conditions are as follows: the reaction conditions of the industrialized process are actual reaction conditions. Due to the uncertainty and research goal for each reaction condition in the basic research, the reaction temperature was selected as 70–150 °C; the reaction pressure as 5–25 bar; the reaction yield as 90–99%.

Tianjin Key Laboratory of Inherent Safety Chemical Process, School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China. E-mail: [yjwang@hebut.edu.cn](mailto:yjwang@hebut.edu.cn); [dxshu@hebut.edu.cn](mailto:dxshu@hebut.edu.cn)

† Electronic supplementary information (ESI) available. See <https://doi.org/10.1039/d2ra01320g>

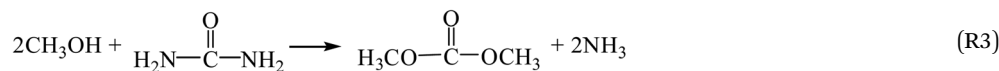
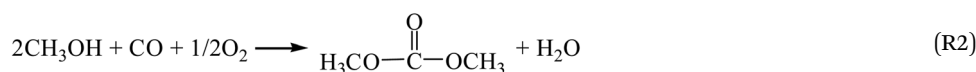
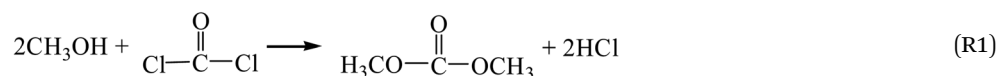


(2) For a multi-step reaction system, the  $\Delta R_i$  of the total reaction is the average value of the steps. However, the reactions with smaller or larger of  $\Delta R_i$  should be paid more attention.

evaluate the advantages and disadvantages. The material safety index (Table S1†) and the process safety index (Table S2†) of each reaction for the synthesis of DMC are shown in the ESI.†

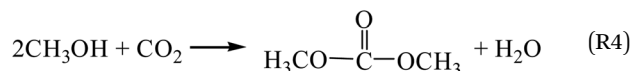
### 3.1. Reaction route for DMC synthesis from methanol as the initial raw material

The reaction equations are as follows:

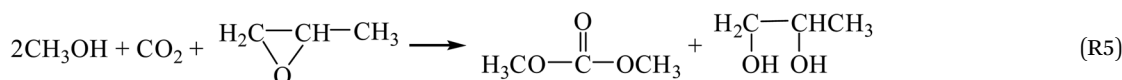


## 3. Analysis of the reaction route for the synthesis of dimethyl carbonate

Dimethyl carbonate (DMC) has excellent reactivity because there are various functional groups in the molecule, such as methyl, methoxy, and carbonyl group. Therefore, it can replace highly toxic phosgene and dimethyl sulphate as the carbonylation or methylation agent. At present, with the rapid development of the electric vehicle industry, the market demand of DMC in electrolytes is huge. Since the 1980s, numerous synthetic routes of DMC have been developed, mainly including phosgene process,<sup>3</sup> transesterification method,<sup>4-6</sup> gas-phase oxidative carbonylation of methanol (one-step process,<sup>7,8</sup> two-step process<sup>9</sup>), methanol-urea alcoholysis method,<sup>10,11</sup> methanol-CO<sub>2</sub> method<sup>12</sup> and methanol-propylene oxide-CO<sub>2</sub> method.<sup>13,14</sup> In this section, the “three-parameter difference” was first applied to the analysis and comparison of the reaction route for the “synthesis of DMC with methanol as the initial raw material”, and then, the similar reaction paths with different raw materials were analyzed and compared to predict and



According to the Gibbs free energy, atom utilization and inherent safety index (Table S3†) of each reaction for the DMC synthesis obtained above,  $\Delta R_i$  was calculated, and the results are shown in Table 1. It can be seen that the order of the OSI is  $R_2 > R_1 = R_5 > R_3 > R_4$ , indicating that the methanol-CO<sub>2</sub> method (R4) is the safest with the lowest inherent safety index. However, the Gibbs free energy of this method is greater than 0 (Fig. S1†) in the temperature range (298–1000 K), that is, it cannot proceed spontaneously in thermodynamics, so  $\Delta R_4$  is relatively large. The gas-phase oxidative carbonylation of methanol by the one-step process (R2) is less than 0, and the atom utilization rate is high, and  $\Delta R_2$  (1.014) is the minimum, indicating that it is the most favorable. Moreover, this method has certain advantages, such as easily available raw materials, low toxicity, simple process and low cost. It is a promising method, which is consistent with the existing research status.<sup>7,8</sup>

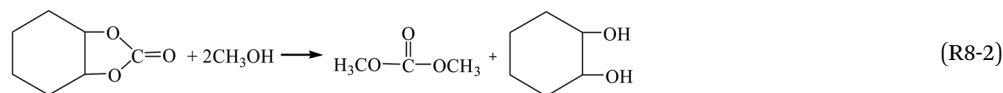
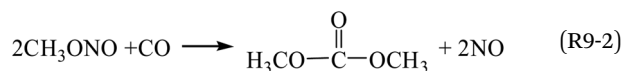
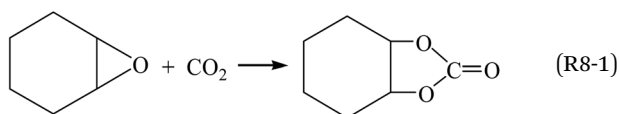
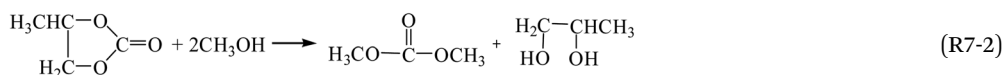
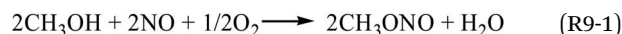
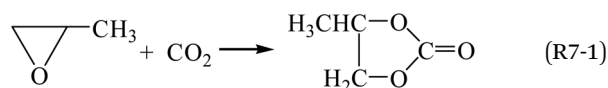
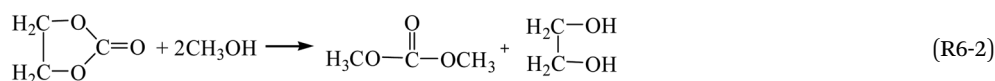
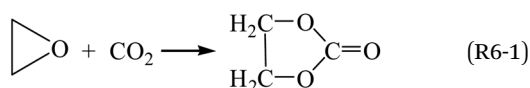


**Table 1** “Three parameter difference” of reactions for DMC synthesis from methanol as the initial raw material

Reactions	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$	Atom utilization	OSI'	$\Delta R_i$
R1	-113.57	0.553	16	1.105
R2	-219.17	0.833	18	1.014
R3	-2.36	0.726	13	1.255
R4	38.04	0.833	11	1.334
R5	0.41	0.542	16	1.415

### 3.2. Implementation path analysis

**3.2.1. Comparison of transesterification with different epoxides as raw materials.** Dimethyl carbonate was synthesized by the transesterification of ethylene oxide,<sup>13</sup> propylene oxide<sup>15,16</sup> and cyclohexane oxide<sup>17</sup> as raw materials, respectively. The reaction equations are as follows:



The Gibbs free energy, atom utilization and inherent safety index (Table S4†) of the above-mentioned reactions were calculated, and the “three-parameter difference”  $\Delta R_i$  of each reaction are shown in Table 2. It can be seen that the transesterification (cyclohexenyl carbonate) (R8-2) is the most prone to occur thermodynamically, and the  $\Delta R_{8-2}$  (0.860) is the smallest. However, the Gibbs free energy of cyclohexene oxide-CO<sub>2</sub> (R8-1) is greater than 0 (Fig. S2†) within the temperature range, and the  $\Delta R_{8-1}$  (3.639) is the largest. The average of the three-parameter difference of the two-step reaction is significantly larger than the other two reaction paths. The intrinsic safety index OSI' of transesterification (propylene carbonate) (R7-2) is the lowest and the intrinsic safety is the highest. Considering comprehensively, the  $\Delta R_7$  (1.303) of transesterification (propylene oxide) is relatively small, which indicates that the reaction route for synthesizing DMC from propylene oxide as the raw material is the most favorable.

**3.2.2. Comparison of the two-step process and the one-step process for the gas-phase oxidative carbonylation of methanol.** The reaction equations for the synthesis of DMC by the gas-phase oxidative carbonylation of methanol are as follows:



Table 2 "Three-parameter difference" of transesterification with different epoxides as raw materials<sup>a</sup>

Reactions	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$	Atom utilization	OSI'	$\Delta R_i$	$\overline{\Delta R_i}$
R6 R6-1	-2.40	1	20	1.405	1.387
R6 R6-2	-19.56	0.592	19	1.368	
R7 R7-1	-34.33	1	20	1.291	1.303
R7 R7-2	23.74	0.542	10	1.315	
R8 R8-1	484.63	1	13	3.639	2.250
R8 R8-2	-187.82	0.437	13	0.860	

<sup>a</sup>  $\overline{\Delta R_i}$  is the average value of stepwise reaction  $\Delta R_i$ . The same as below.



According to the Gibbs free energy, atom utilization and inherent safety index (Table S5<sup>†</sup>) of the above-mentioned reactions,  $\Delta R_i$  was calculated, and the results are shown in Table 3. It can be seen that the  $\Delta R_2$  (0.962) of the gas-phase oxidative carbonylation of methanol by the one-step process is smaller than that of two-step process  $\Delta R_9$  (1.160), and the Gibbs free energy is lower in the investigated temperature range, making it easier to proceed thermodynamically (Fig. S3<sup>†</sup>). The  $\Delta R_i$  of the multi-step reaction is positively correlated with the number of reaction steps, that is, the more reaction steps, the greater is the mean value. Integrating multiple reactions can reduce the reaction steps, thereby decreasing the  $\Delta R_i$ , which is the target direction of developing the reaction path.

**3.2.3. Comparison of the two-step method with propylene glycol as a recycling agent and methanol-urea alcoholysis.** The reaction equations for the synthesis of DMC by the two-step method with propylene glycol as the circulating agent<sup>18</sup> and the methanol-urea alcoholysis method are as follows:

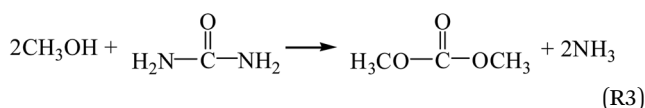
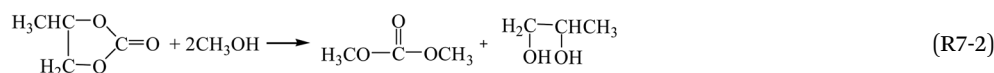
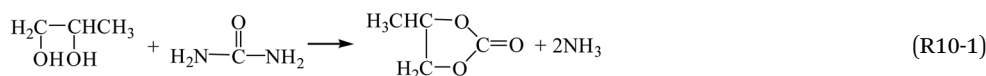


Table 3 "Three-parameter difference" of the gas-phase oxidative carbonylation of methanol to DMC

Reactions	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$	Atom utilization	OSI'	$\Delta R_i$	$\overline{\Delta R_i}$
R9 R9-1	-90.94	0.872	19	1.166	1.160
R9 R9-2	-128.24	0.600	19	1.154	
R2 R2	-219.17	0.833	18	0.962	0.962

Table 4 "Three-parameter difference" of reactions for DMC synthesis

Reactions	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$	Atom utilization	OSI'	$\Delta R_i$	$\overline{\Delta R_i}$
R10 R10-1	-26.10	0.750	12	0.956	1.533
R7 R7-2	23.74	0.542	10	2.109	
R3 R3	-2.36	0.726	13	1.379	1.379

The Gibbs free energy, atom utilization and inherent safety index (Table S6<sup>†</sup>) of the above-mentioned reactions were calculated, and the "three-parameter difference"  $\Delta R_i$  of each reaction are shown in Table 4. It can be seen that the methanol-urea alcoholysis method  $\Delta R_3$  (1.379) is smaller than the two-step method with propylene glycol as the circulating agent. It is verified again that the  $\Delta R_i$  of the multi-step reaction is positively correlated with the number of reaction steps. Transesterification (propylene carbonate) (R7-2) has the lowest OSI' and the highest intrinsic safety, but it is not feasible in thermodynamics within the temperature range investigated (Fig. S4<sup>†</sup>), that is why  $\Delta R_{7-2}$  (2.109) is larger.

## 4. Analysis of the reaction route for the synthesis of toluene diisocyanate from toluene as the initial raw material

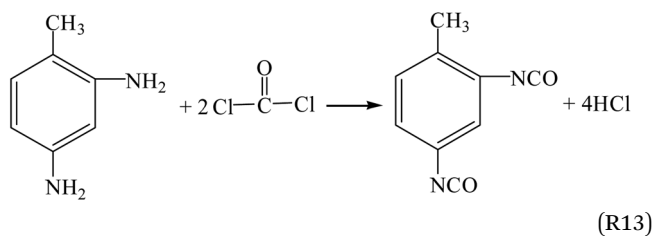
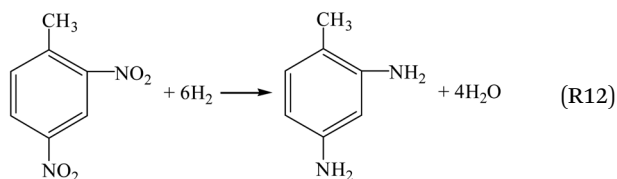
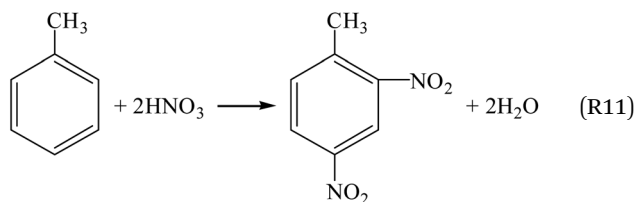
Toluene diisocyanate (TDI) is an important organic intermediate used in the manufacturing of polyurethane foams. Polyurethane

produced by TDI has excellent properties, such as wear resistance, low temperature resistance, oil resistance and ozone resistance, and is widely used in foam plastics, elastomer wear-resistant materials and coatings.<sup>19,20</sup> The industrial production methods of TDI mainly include: phosgene process,<sup>21</sup> reduction carbonylation method,<sup>22</sup> oxidative carbonylation method,<sup>23</sup> carbon dioxide



method,<sup>24</sup> dimethyl carbonate method<sup>25–27</sup> and urea method.<sup>28</sup> On this basis, we proposed the dimethyl carbonate-ionic liquid hydroxylamine method. The specific reaction equations are as follows. The material safety index (Table S7†) and the process safety index (Table S8†) are shown in the ESI.†

(1) Phosgene process (R11–R13).



(2) Reductive carbonylation one-step method (R11, R14).

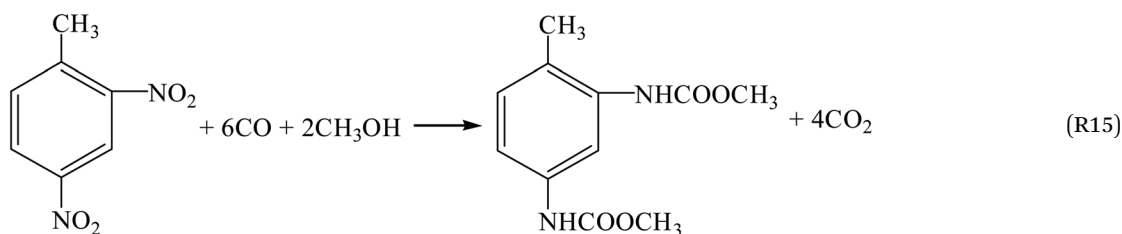
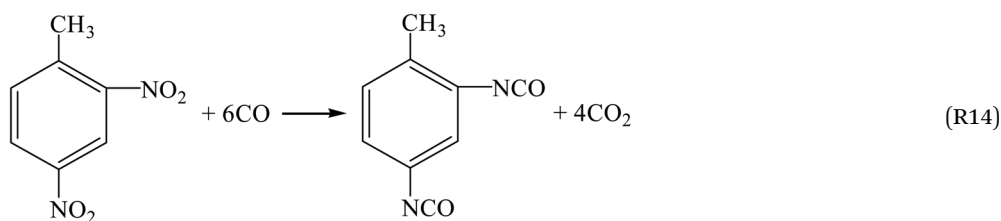


Table 5 "Three-parameter difference" of reactions for the TDI synthesis<sup>a</sup>

Reactions	$\Delta G_{298}^0/(\text{kJ mol}^{-1})$	Atom utilization	OSI'	$\Delta R_i$	$\overline{\Delta R}_i$	
$R_{\text{I}}$	R11	-213.32	0.835	14	1.004	1.015
	R12	-928.75	0.629	20	0.947	
	R13	-176.11	0.544	13	1.095	
$R_{\text{II}}$	R11	-213.32	0.835	14	1.004	1.062
	R14	-973.53	0.497	23	1.119	
$R_{\text{III}}$	R11	-213.32	0.835	14	1.004	1.076
	R15	-954.97	0.575	20	0.968	
	R16	-18.56	0.732	17	1.257	
$R_{\text{IV}}$	R11	-213.32	0.835	14	1.004	1.054
	R12	-928.75	0.629	20	0.947	
	R17	-368.76	0.868	18	1.008	
$R_{\text{V}}$	R16	-18.56	0.732	17	1.257	
	R11	-213.32	0.835	14	1.004	1.119
	R12	-928.75	0.629	20	0.947	
$R_{\text{VI}}$	R18	145.66	0.868	12	1.269	
	R16	-18.56	0.732	17	1.257	
	R11	-213.32	0.835	14	1.004	1.105
$R_{\text{VII}}$	R12	-928.75	0.629	20	0.947	
	R19	69.59	0.787	12	1.211	
	R16	-18.56	0.732	17	1.257	
$R_{\text{VIII}}$	R11	-213.32	0.835	14	1.004	1.114
	R12	-928.75	0.629	20	0.947	
	R20	64.87	0.777	14	1.248	
	R16	-18.56	0.732	17	1.257	
	R21	-370.38	0.773	14	0.898	1.122
	R19	69.59	0.787	12	1.211	
	R16	-18.56	0.732	17	1.257	

<sup>a</sup>  $R_{\text{I}}$ : phosgene process;  $R_{\text{II}}$ : reductive carbonylation one-step method;  $R_{\text{III}}$ : reductive carbonylation two-step method;  $R_{\text{IV}}$ : oxidative carbonylation method;  $R_{\text{V}}$ : carbon dioxide method;  $R_{\text{VI}}$ : dimethyl carbonate method;  $R_{\text{VII}}$ : urea method;  $R_{\text{VIII}}$ : Dimethyl carbonate-ionic liquid hydroxylamine method.



(3) Reductive carbonylation two-step method (R11, R15, R16).

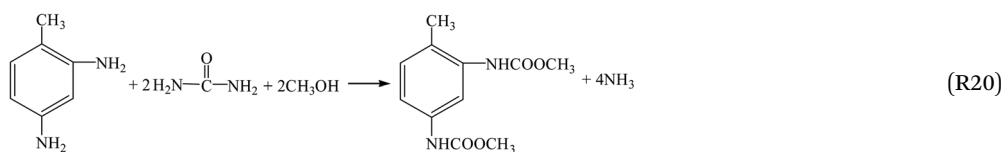
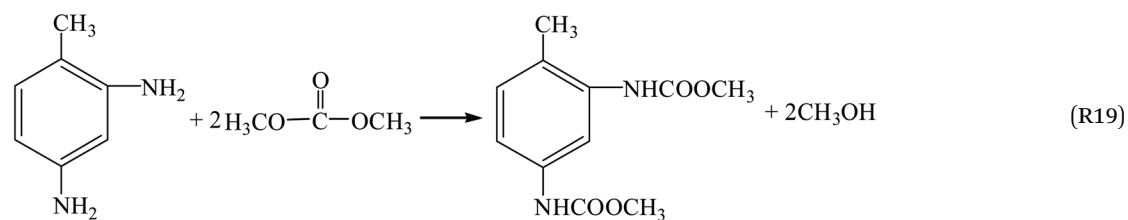
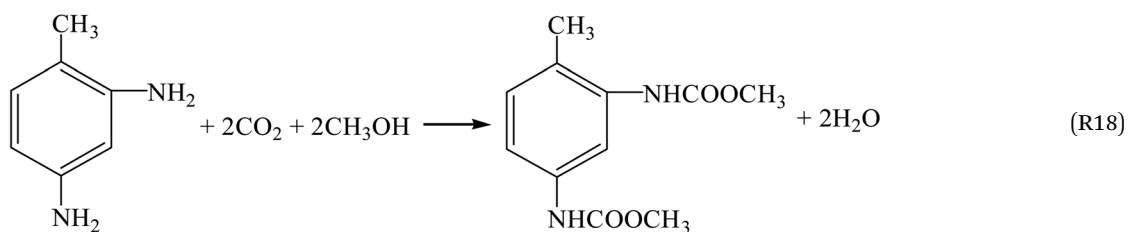
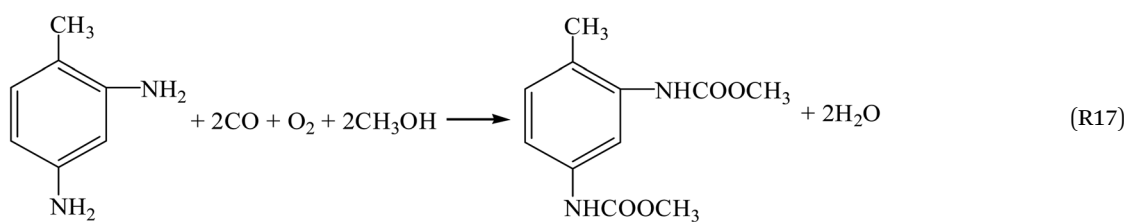
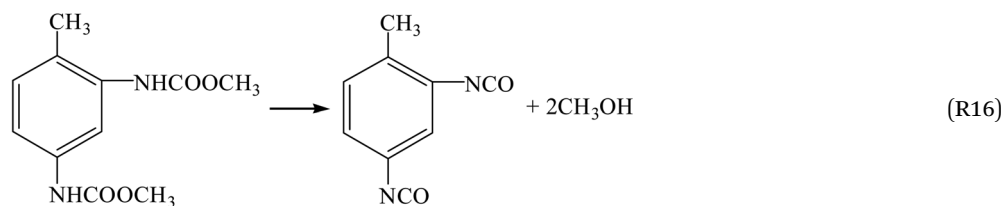
(4) Oxidative carbonylation method (R11, R12, R17, R16).

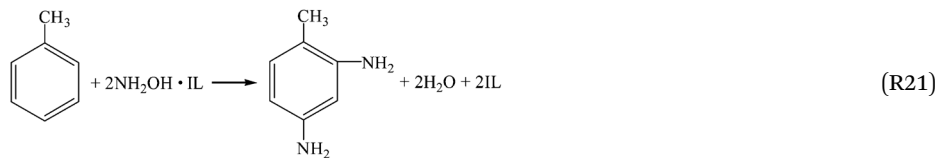
(5) Carbon dioxide method (R11, R12, R18, R16).

(6) Dimethyl carbonate method (R11, R12, R19, R16).

(7) Urea method (R11, R12, R20, R16).

(8) Dimethyl carbonate-ionic liquid hydroxylamine method (R21, R19, R16).





According to the Gibbs free energy, atom utilization and inherent safety index (Table S9†) of each reaction for TDI synthesis obtained above,  $\Delta R_i$  was calculated, and the results are shown in Table 5. It can be seen that the order of the OSI' is  $R_{14} > R_{12} = R_{15} > R_{17} > R_{16} > R_{11} > R_{20} = R_{21} > R_{13} > R_{18} = R_{19}$ , which indicates that the synthesis of TDI by the carbon dioxide method (R18) or dimethyl carbonate method (R19) is the safest and has the highest inherent safety. However, these two reactions cannot occur spontaneously in thermodynamics (Fig. S5†), which is the reason for the larger  $\Delta R_{18}$  and  $\Delta R_{19}$ . Considering the overall reaction safety, the order of the OSI is  $R_{IV} > R_V = R_{VI} = R_{VII} > R_{III} > R_I = R_{II} > R_{VIII}$ , which indicates that the synthesis of TDI by the dimethyl carbonate-ionic liquid hydroxylamine method has the highest inherent safety. And  $\Delta R_{21}$  (0.898) is the minimum, which shows that it is the most advantageous (pre-development process) and lays a theoretical foundation for the development of a new process. The order of the  $\Delta R_i$  mean value is  $\Delta R_{VIII} > \Delta R_V > \Delta R_{VII} > \Delta R_{VI} > \Delta R_{III} > \Delta R_{II} > \Delta R_{IV} > \Delta R_I$ , basically positively correlated with the number of the reaction steps. That is, by integrating multiple reactions and reducing reaction steps, the value of  $\Delta R_i$  can be obviously decreased, making it closer to the ideal chemical reaction. That is to say, one-step reaction not only simplifies the reaction steps, but also breaks the thermodynamic limitation, removes the safety hazards from the source, and improves the atomic economy.

## 5. Conclusion

The “three-parameter difference” based on Gibbs free energy, atom utilization and inherent safety index can evaluate the thermodynamic feasibility, atomic economy and inherent safety of chemical reactions comprehensively. The smaller the “three-parameter difference” is, the closer it is to the ideal reaction. In this study, the synthesis of DMC and TDI were taken as examples, and the  $\Delta R_i$  of each reaction was calculated and analyzed. The synthesis of DMC by the gas-phase oxidative carbonylation of methanol by a one-step process ( $\Delta R_2 = 1.104$ ) and the synthesis of TDI by the dimethyl carbonate-ionic liquid hydroxylamine method ( $\Delta R_{VIII} = 1.122$ ) had more potential. The results were consistent with the existing actual research, which proves the reliability of the “three-parameter difference”. The model has an adequate practical guidance significance to evaluate new synthesis routes.

## Symbol description

Nr	NFPA reactivity rating
Nf	Flammability

Nt	Toxicity
Ne	Explosiveness
Rt	Temperature subindex
Rp	Pressure subindex
Ry	Yield subindex
Rh	Heat of reaction subindex
ICI	Individual chemical index
IRI	Individual reaction index
OSI'	Individual safety index
OCI	Overall chemical index
ORI	Overall reaction index
OSI	Overall safety index

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (U20A20152, 21878069) and the Central Government Guide the Development of Local Science and Technology Special Fund (206Z4002G).

## References

- 1 Y. Wang, Z. Li and S. Wang, *Intrinsic Safety Catalytic Process*, Chemical Industry Press, Beijing, 2018.
- 2 X. Ding, C. Wu and Y. Wang, *Chin. Sci. Bull.*, 2020, **65**, 401–409.
- 3 Y. Ono, *Pure Appl. Chem.*, 1996, **68**, 367–375.
- 4 W. Hui, M. Wang, W. Zhang, Z. Ning, W. Wei and Y. Sun, *Catal. Today*, 2006, **115**, 107–110.
- 5 D. W. Kim, C. W. Kim, J. C. Koh and D. W. Park, *J. Ind. Eng. Chem.*, 2010, **16**, 474–478.
- 6 Y. Watanabe and T. Tatsumi, *Microporous Mesoporous Mater.*, 1998, **22**, 399–407.
- 7 X. Ding, X. Dong, D. Kuang, S. Wang, X. Zhao and Y. Wang, *Chem. Eng. J.*, 2014, **240**, 221–227.
- 8 Y. Song, X. Ding, Y. Yan, S. Wang and Y. Wang, *CIESC J.*, 2019, **70**, 1401–1408.
- 9 K. Nishihira, S. Yoshida and S. Tanaka, *J. Clean. Prod.*, 1997, **5**, 312.
- 10 D. Lakshmi, B. Rao and L. Nakka, *Catal. Commun.*, 2019, **122**, 1–4.
- 11 M. Wang, Z. Ning, W. Wei and Y. Sun, *Stud. Surf. Sci. Catal.*, 2004, **153**, 197–200.





## Paper

- 12 A. A. Marciniak, O. C. Alves, L. G. Appel and C. Mota, *J. Catal.*, 2019, **371**, 88–95.
- 13 Y. Chang, J. Tao, B. Han, Z. Liu, W. Wu, L. Gao, J. Li, H. Gao, G. Zhao and J. Huang, *Appl. Catal. Gen.*, 2004, **263**, 179–186.
- 14 L. A. Ming, A. Mk, C. Lnb and C. Mga, *Chem. Eng. Sci.*, 2020, **231**, 116267.
- 15 B. M. Bhanage, S. I. Fujita, Y. Ikushima, K. Torii and M. Arai, *Green Chem.*, 2003, **5**, 71–75.
- 16 T. Wei, M. Wang, W. Wei, Y. Sun and B. Zhong, *Fuel Process. Technol.*, 2003, **83**, 175–182.
- 17 Q. Yang, H. Wang, X. Ding, X. Yang and Y. Wang, *Res. Chem. Intermed.*, 2015, **41**, 4101–4111.
- 18 T. Zhang, B. Zhang, L. Li, N. Zhao and F. Xiao, *Catal. Commun.*, 2015, **66**, 38–41.
- 19 A. Hassan, E. Bagherzadeh, R. G. Anthony, G. Borsinger and A. Hassan, *US Pat.* 0005589A1, 2009.
- 20 X. Zhao, Y. Wang, F. Li, S. Wang and J. Cong, *Petrochem. Technol.*, 1999, **9**, 611–614.
- 21 S. Ozaki, *J. Syn. Org. Chem. Jpn.*, 1972, **28**, 285–295.
- 22 Y. Watanabe, Y. Tsuji, R. Takeuchi and N. Suzuki, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3343–3348.
- 23 F. Shi, T. L. Sima and Y. Deng, *Chem. Res. Chin. Univ.*, 2000, **21**, 1566–1568.
- 24 A. Ion, C. V. Doorslaer, V. Parvulescu, P. Jacobs and D. Vos, *Green Chem.*, 2008, **10**, 111–116.
- 25 G. Wang, D. Ma, X. Jia, X. Cui, X. Zhao and Y. Wang, *Ind. Eng. Chem. Res.*, 2016, **55**, 8011–8017.
- 26 S. Wang, G. Zhang, X. Ma and J. Gong, *Ind. Eng. Chem. Res.*, 2007, **46**, 6858–6864.
- 27 Y. Wang, X. Zhao, F. Li, S. Wang and J. Zhang, *J. Chem. Technol. Biotechnol.*, 2010, **76**, 857–861.
- 28 X. Zhao, N. Wang, Y. Geng, H. An and Y. Wang, *Ind. Eng. Chem. Res.*, 2011, **50**, 13636–13641.

