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Influence of reaction conditions on product distribution in the green oxidation of cyclohexene to adipic acid with hydrogen peroxide

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ABSTRACT

The effect of reaction conditions (such as the amount of sulfuric acid, reaction temperature and feeding style of reactants) on the product distribution in the green oxidation of cyclohexene to adipic acid was investigated. This reaction, with 30% hydrogen peroxide as oxidant in the presence of a homogeneous peroxy tungstate catalyst, is of great industrial interest for not using of organic solvent and phase-transfer catalyst. The synthesis we investigated produces adipic acid as the product, glutaric acid and succinic acid as main byproducts, and cyclohexanediol is an intermediate. Using this green method, a 94.5% yield of adipic acid has been achieved while byproducts and intermediates could be reduced. Finally, a proposed mechanism for the formation of glutaric acid was suggested, it was also supported by density functional theory calculations.

1. Introduction

The green synthesis of adipic acid (ADA) is extremely urgent and desirable for many reasons [1–8]. As the main precursor for nylon 6,6 and polyurethane plastics, ADA is of great importance to industry [9]. It is commonly prepared in industrial process by oxidizing cyclohexanol or cyclohexanone using nitric acid, which results in the formation of environmentally unfriendly nitrous oxide (N_2O) [10]. Organic solvents, which are also harmful to the environment and difficult to be disposed of, are also used in current industrial processes as phase-transfer agents to increase reaction rates [11]. Moreover, tungstates have received extensive attention for cleavage of alkenes in organic solvents [12,13].

The formation of N_2O can be avoided using H_2O_2 to oxidize cyclohexene directly in the presence of a tungsten containing catalyst (Fig. 1(a)). Using tungstic acid and 61% H_2O_2, Fujitani and Nakazawa achieved a 61% yield of ADA, with a 5.0% yield of byproduct glutaric acid (GA), and a 3.0% yield of intermediate cyclohexanediol (Diol) [14]. Oguchi et al. used 35% H_2O_2 to oxidize C_6H_{10} to ADA in tert-butanol in the presence of a tungstic acid catalyst to obtain a 62% yield of ADA and 18% yield of Diol [15]. Sato et al. [16] used 30% H_2O_2 with $Na_2WO_4{\cdot}2H_2O$ as catalyst and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as phase-transfer agent without organic solvent in the oxidation of C_6H_{10} to ADA resulting in a 93% yield of ADA, and they proposed the reaction pathway (Fig. 1(b)).

It is also desirable to eliminate organic solvents and phase-transfer catalysts from the synthesis of ADA due to their economic and ecological disadvantages, which have been widely researched [17–19]. Deng and his colleagues used tungstate as a catalyst to investigate the influence of an organic ligand and the amount of catalyst on the yield of ADA. Their excellent result was a 96% yield of ADA [20]. Wang et al. used tungstate catalyst with sulfuric acid and a small amount of ligand which resulted in a 90% yield of ADA [21]. In addition, Gong et al. [22] discovered that the acidity of additive had a major effect on tungstate catalyst.

Although the green synthesis of ADA has been extensively demonstrated [8,23–28], the technology has not been applied in industrialization, because many practical problems are still unsolved. How to obtain high quality of ADA and keep the recyclability of the catalyst system normal are two significant technical problems, which are associated with the economic and clean production of ADA. In addition, little work has been reported to investigate the influence of reaction conditions on product distribution in the green oxidation of cyclohexene to adipic acid. In order to promote our proceeding pilot test, further provide the scientific basis for the industrialization of the green synthesis of ADA in the near future and obtain a more thorough understanding of this reaction, in this paper, we used high performance liquid chromatography (HPLC) to investigate how reaction conditions changed product distribution in this reaction in detail. Furthermore, we proposed a possible mechanism for the generation of the main

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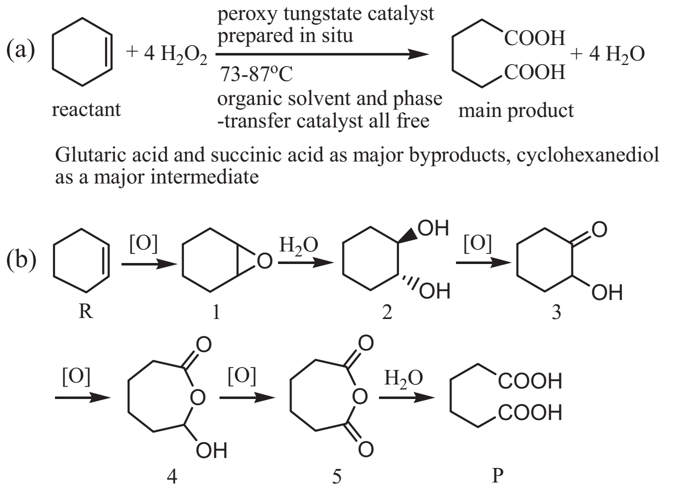

Fig. 1. (a) Our experiment for the green oxidation of cyclohexene to adipic acid. (b) The possible reaction pathway proposed by [16].

byproduct GA, and it is supported by density functional theory calculations.

2. Experimental

2.1. Reaction and determination

Reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. HPLC analyses were carried out using Agilent 1100 HPLC system with a quaternary pump, a UV detector and a RID detector. HPLC separations were carried out on an Agilent TC-C18 reversed phase column (25 cm × 4.6 mm, 5 μm particle size) using a 30% methanol in 5 mM ammonium acetate buffer at pH 3.3 and 30 °C. UV data was collected at 225 nm.

Under the condition of organic solvent and phase-transfer catalyst all free, $Na_2WO_4 \cdot 2H_2O$, sulfuric acid and 30% H_2O_2 (molar ratio was 1:3.26:218, H_2O_2 was added in one time or batches) were introduced in a 500 mL round-bottomed flask. The mixtures were stirred 30 min to prepare in situ the peroxy tungstate catalyst, then cyclohexene (the total molar ratio to H_2O_2 was 1:4.36, added in one time or batches) was added and the system was heated to reflux. After reflux, the reaction was stirred for 6 h at 80–95 °C. The resulting hot solution was used for yield determination by HPLC.

2.2. Computational methods

The geometries of the reactant, intermediates and product in reaction were optimized at the B3LYP/6-31G (d, p) level [29–31] via density functional theory (DFT) method, which has been widely used in explaining many chemical problems [32]. All stationary points have been characterized with a full vibrational analysis, and all reported energy differences include zero point energy corrections. The corresponding vibrational frequencies were calculated at the same level to take account of the zero-point vibrational energy (ZPVE). All theoretical calculations were performed using the GAUSSIAN03 [33] suite of software.

3. Results and discussion

3.1. Influence of the amount of sulfuric acid on product distribution

According to our experiments, acid is necessary for green synthesis of ADA. An appropriate acidic system can keep H_2O_2 stable, as well as enhance the oxidative ability of H_2O_2, which is consistent with acid-catalyzed steps from intermediate 1 to intermediate 2 and from intermediate 5 to product in Fig. 1. However, the suitable amount of acid, which is critical to the selectivity of this reaction, has not been investigated completely yet. Hence, in this work, the influence of the amount of sulfuric acid on the product distribution of this reaction was studied and the results are shown in Table 1.

Table 1
The influence of the amount of sulfuric acid on product distribution.

n (sulfuric acid)/n (C_6H_{10})	Yield (%)			
	ADA	GA	SA	Diol
0.028	80.4	4.63	0.800	0.050
0.047	84.4	5.21	0.970	0.080
0.065	88.1	5.35	1.12	0.090
0.083	87.3	5.49	1.08	0.13
0.10	87.1	5.27	1.12	0.14

SA: succinic acid. Reaction temperature in stage A was 73 °C, in stage B was 91 °C; reactants were one-time fed in stage A.

As shown in Table 1, increasing the molar ratio of sulfuric acid-to-C_6H_{10} from 0.028:1 to 0.065:1 caused a corresponding increase in ADA yield from 80.4% to 88.2%. Further increasing the molar ratio of sulfuric acid-to-C_6H_{10} from 0.065:1 to 0.10:1 led to the ADA yield decreasing slightly. A similar effect was found on the yield of byproducts GA and SA. The yield of intermediate Diol gradually increased with the increase of the molar ratio of sulfuric acid-to-C_6H_{10}, and it almost unchanged when this ratio was higher than 0.065:1. The experimental results indicate that this route is not only an oxidation reaction, but also an acid-catalyzed reaction; meanwhile, it reflects that this reaction should have the multi-step reaction mechanism. And the information is consistent with the reaction pathway proposed by Sato et al. (Fig. 1(b)). Moreover, the yield of byproducts GA and SA increased obviously when the molar ratio of sulfuric acid-to-C_6H_{10} was more than 0.028:1, it may be that acid could promote the cleavage of C–C bond (shown in Fig. 4). So improving the selectivity of this reaction should not only depend on increasing the amount of sulfuric acid. Thus the sulfuric acid-to-C_6H_{10} molar ratio of 0.065:1 was selected in subsequent experiments.

3.2. Influence of reaction temperature on product distribution

This work first reports that the temperature of this reaction could be controlled at two stages under organic solvent- and phase-transfer catalyst-free conditions. According to our extensive experiments, this reaction should include the reflux stage (stage A in Fig. 2) and the constant temperature stage after reflux (stage B in Fig. 2). In stage A, since the reaction temperature gets close to the boiling point of water–C_6H_{10} mixture (70.9 °C), C_6H_{10} will be consumed completely during this stage, and the two-phase system can be converted to homogeneous phase at the end of stage A. Based on the literature [16], epoxidation of C_6H_{10} and hydration of epoxide to Diol (Fig. 1) mainly occur in stage A, and at the end of stage A, a lot of Diol has been detected in our experiment by HPLC. In stage B, Diol is further oxidized to ADA (Fig. 1) through some reaction steps similar to the literature [16].

At the beginning of stage A, the system contains hydrophobic phase (C_6H_{10}) and hydrophilic phase (aqueous H_2O_2 and catalyst), and the system is converted to homogeneous phase (hydrophilic phase) in stage B. In our opinion, the two stages should need different reaction temperatures, so the reaction temperatures of two stages which are essential for optimizing product distributions have been investigated and the results are given in the following parts.

Table 2
Influence of reaction temperature in stage A on product distribution.

Reaction temperature in stage A (°C)	Reaction time in stage A (h)	Yield (%)			
		ADA	GA	SA	Diol
60	5	87.3	5.16	1.18	0.16
65	4	87.0	5.72	1.21	0.12
73	2	86.5	5.47	1.08	0.090

Reaction temperature in stage B was 91 °C; molar ratio of sulfuric acid-to-C_6H_{10} was 0.065:1; reactants were one-time fed in stage A.

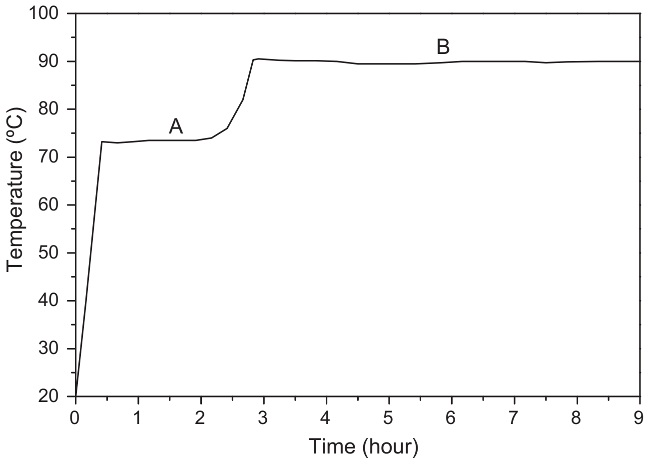

Fig. 2. Typical temperature–time curves for the direct oxidation of C_6H_{10} to ADA with aqueous H_2O_2.

3.2.1. Reaction temperature in stage A

In reaction stage A, the effect of temperature (from 60 °C to 73 °C) on product distribution was studied. The highest temperature, 73 °C, gets close to the boiling point of water–C_6H_{10} mixture (70.9 °C). 60 °C was chosen as the lowest temperature to make the reaction proceed normally. The results are listed in Table 2.

As shown in Table 2, with the increase of reaction temperature in stage A, the reaction time and the yield of intermediate Diol decreased remarkably, which indicated that higher temperature in stage A accelerated the reaction rate. However, the yield of product ADA decreased slightly and the yields of byproducts GA and SA showed light fluctuation. At 73 °C, the total amount of byproducts did not observably increase and the reaction was completed in a shorter time, thereby 73 °C was selected as the experimental temperature of stage A in subsequent experiments.

3.2.2. Reaction temperature in stage B

The effect of temperature in stage B on product distribution is presented in Table 3.

In stage B, the highest yield of ADA (90.7%) was obtained at 87 °C (Table 3). As temperature increased, the yield of SA changed lightly, but the yield of GA increased substantially from 4.32% to 5.47%, and the yield of Diol decreased constantly at higher temperature. The result indicated that with the increase of reaction temperature in stage B, some intermediates were gradually converted to ADA. At higher temperature, the oxidation rates of Diol and other intermediates increased to produce more byproducts. At lower temperature, provided energy was insufficient for the reaction resulting in incomplete oxidation of Diol and therefore low ADA yield. The reaction temperature of 87 °C was proved to be the optimal temperature for reducing side reactions and allowing the highest ADA yield.

Table 3
Influence of reaction temperature in stage B on product distribution.

Temperature in stage B (°C)	Yield (%)			
	ADA	GA	SA	Diol
80	87.8	4.32	1.08	0.35
83	88.5	4.17	0.950	0.25
87	90.7	4.33	1.02	0.13
91	88.1	5.35	1.12	0.090
95	86.5	5.47	1.11	0.060

Reaction temperature in stage A was 73 °C; molar ratio of sulfuric acid-to-C_6H_{10} was 0.065:1; reactants were one-time fed in stage A.

3.3. Influence of feeding style in stage A on product distribution

In order to further increase the yield and quality of ADA, the feeding style of reactants in stage A was investigated under optimum reaction conditions (the amount of sulfuric acid and reaction temperature). The results are shown in Fig. 3. In experiments **a–e**, half of the overall C_6H_{10} was initially added simultaneously with the corresponding equivalent of H_2O_2 (3.16, 3.56, 3.96, 4.36 and 4.76 equiv.). The other half of C_6H_{10} and the corresponding amount of H_2O_2 were added in five equal batches as the reaction proceeded in stage A. The final molar ratio of H_2O_2-to-C_6H_{10} was adjusted to 436:100 in experiment **a–d**. For experiment **e**, much more H_2O_2 was added to make a final H_2O_2-to-C_6H_{10} molar ratio of 476:100. In experiment **a–c**, H_2O_2 was residual when all of C_6H_{10} has been added, and the residual H_2O_2 was added as the reaction proceeded in stage A.

With the increase of the H_2O_2-to-C_6H_{10} molar ratio in each feeding in stage A, the yield of ADA reached a maximum value with 94.5% under the molar feeding ratio of 4.36:1 (experiment

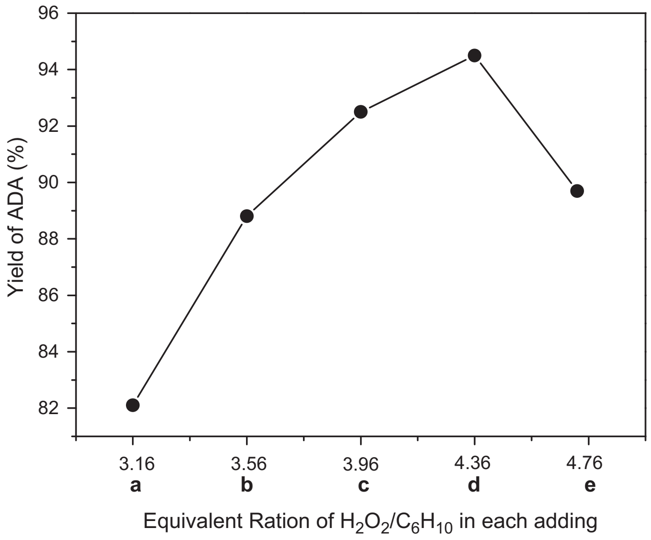

Fig. 3. The yield of ADA is influenced by the feeding ratio of H_2O_2-to-C_6H_{10} in stage A. In the first four experiments (**a–d**), the final molar ratio of H_2O_2-to-C_6H_{10} was held at 436:100. In experiment **e**, more H_2O_2 was added to extend the experiment range, and the final molar ratio of H_2O_2-to-C_6H_{10} was 476:100. Reaction temperature in stage A was 73 °C, in stage B was 87 °C; molar ratio of sulfuric acid-to-C_6H_{10} was 0.065:1.

Table 4
Each adding ratio of H_2O_2-to-C_6H_{10} in stage A on main byproducts and intermediate.

$n\,(H_2O_2)/n\,(C_6H_{10})$	Yield (%)		
	GA	SA	Diol
3.16:1	7.04	1.38	0.18
3.56:1	5.40	0.980	0.15
3.96:1	5.68	1.06	0.14
4.36:1	4.42	0.820	0.12
4.76:1	4.26	0.710	0.080

Reaction temperature in stage A was 73 °C, in stage B was 87 °C; molar ratio of sulfuric acid-to-C_6H_{10} was 0.065:1.

d) (Fig. 3). In different feedings, lower equivalent ratio of H_2O_2-to-C_6H_{10} diminished the oxidation capacity of the reaction, which resulted in intermediates being converted to byproducts instead of being oxidized to ADA. When the molar ratio of H_2O_2-to-C_6H_{10} in each adding increased, the oxidation capacity of the system enhanced, allowing intermediates to be fully oxidized to ADA. However, excessive H_2O_2 results in decreasing the yield of ADA (experiment **e**), due to over-oxidation of C_6H_{10}.

The influence of each adding ratio of H_2O_2-to-C_6H_{10} in stage A on major byproducts and intermediate was also investigated (Table 4). It could be found that increasing the molar ratio of H_2O_2-to-C_6H_{10} for each feeding, the yield of GA and SA significantly decreased, and the yield of Diol reduced gradually. Hence our experiments indicate that moderate feeding of the H_2O_2-to-C_6H_{10} molar ratio of 4.36:1 is the optimized feeding style for producing ADA and suppressing the formation of byproducts.

3.4. Proposed mechanism for the formation of primary byproduct GA

The main byproduct impacts not only the quality of ADA but also the recyclability of the catalyst system, thus it is necessary to investigate its generation mechanism for reducing its formation in follow-up study. Based on our experimental results, as well as the oxidation pathway from C_6H_{10} to ADA advanced by Sato et al. [16], we have illustrated a proposed mechanism for the generation of primary byproduct GA, shown as follows.

As shown in Fig. 4, there should be at least ten reaction steps from Diol to byproduct GA in our opinion. First, **Diol** can obtain a proton from H_3O^+ via transition state **TS1**. Second, the newly generated intermediate **M1** will lose a water molecule to form intermediate **M2** via transition state **TS2**. Third, the proton leaves from **M2** to a water molecule, and intermediate **M3** can be formed via transition state **TS3**. Fourth, H_2O_2 provides oxygen and there is an oxygen insertion reaction via transition state **TS4**. Fifth, the intermediate **M4** is hydrolyzed into **M5** (formic acid) and **M6** (cyclopentanol) by water via transition state **TS5**. Sixth, **M6** is oxidized by H_2O_2 into intermediate **M7** (cyclopentanone) via transition state **TS6**. Seventh, there is also an oxygen insertion reaction to generate **M8** via transition state **TS7**, and the oxygen is still provided by H_2O_2. Eighth, **M8** is hydrolyzed into **M9** by water via transition state **TS8** under acidic condition. Ninth, **M9** reacts with a H_2O_2 to form **M10** via transition state **TS9**. At last, the intermediate **M10** also reacts with a H_2O_2 to form the byproduct **GA** via transition state **TS10**.

For preliminary evaluating the possibility of the proposed mechanism, the geometry structures of all the reactant, stable intermediates and product in the proposed mechanism have been optimized at the B3LYP/6-31G (d, p) level and the calculated Gibbs free energies are outlined in Fig. 5.

This calculated free energy result of the proposed mechanism mainly contains four processes. (1) Protonation of one hydroxyl in **Diol** to form **M1**, followed by the removal of one molecule of H_2O to generate the five-membered ring **M2**. This is a spontaneous process. (2) **M2** is deprotonated to form **M3**, which has the highest positive ΔG in the pathway. Although ΔG of this step is 27.74 kcal/mol, the most negative ΔG (−71.57 kcal/mol) in the next step should be helpful to drive the reaction forward. (3) The five-membered ring **M3** is converted to cyclic ester **M8** with a six-membered ring via **M4**, **M6** and **M7**. The overall ΔG is favorable for the formation of **M8**. (4) Esterlysis of cyclic ester **M8**, followed by oxidation of hydroxyl group of **M9** and aldehyde group of **M10** to finally form byproduct **GA**, is also an energetically favorable reaction.

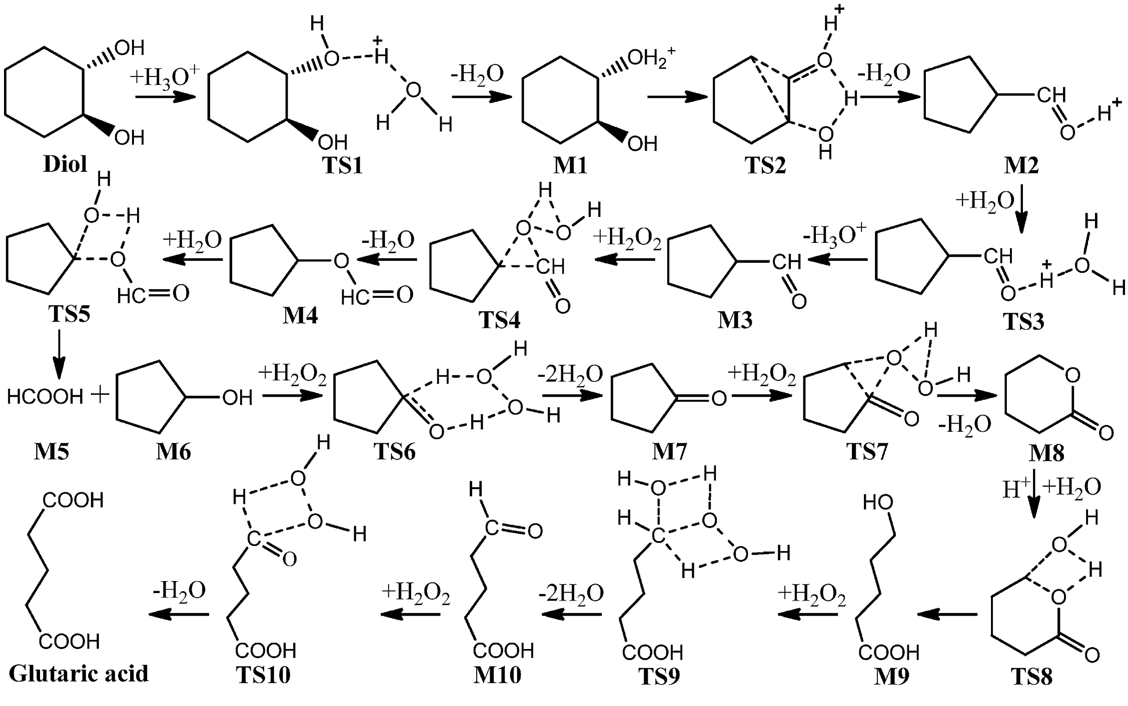

Fig. 4. A proposed mechanism for the formation of byproduct GA in green synthesis of ADA.

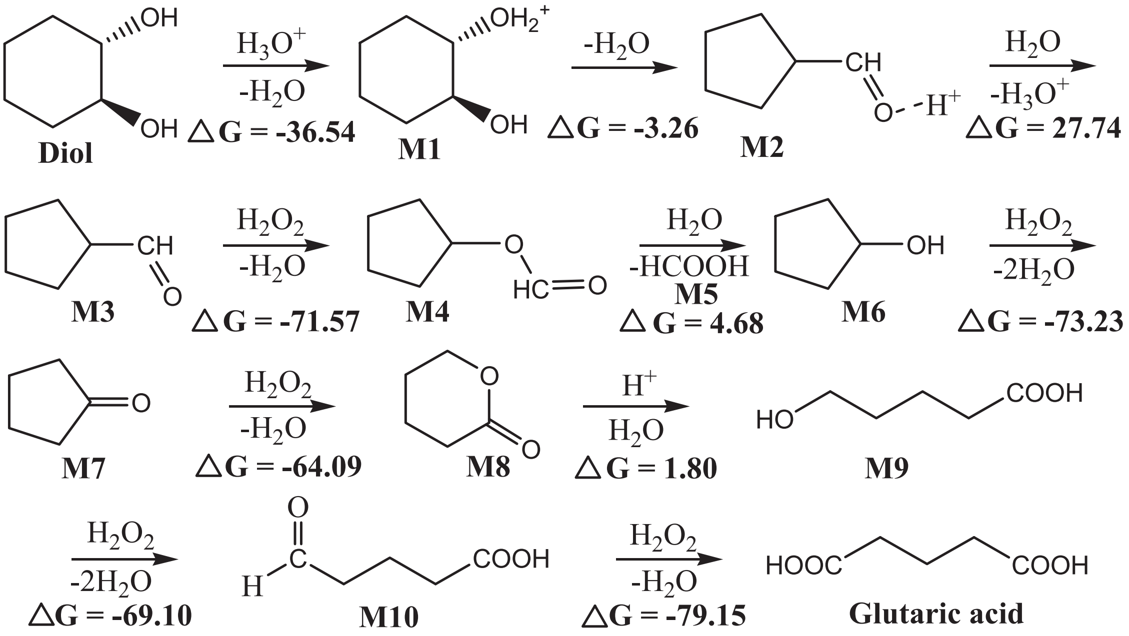

Fig. 5. Gibbs free energy based on DFT (B3LYP/6-31G (d, p)) calculation result of the proposed mechanism for the formation of GA in green synthesis of ADA (*G*: Gibbs free energy, unit: kcal/mol).

The calculated results indicate that acid is necessary in some steps of proposed mechanism above and the amount of the acid is one of the critical factors for the generation of GA. Although acid is essential for green synthesis of ADA, excess acid will promote the further cleavage of C–C bond obviously to form byproducts such as GA. Thus, appropriate acidic system is very important for optimizing product distribution, and this is consistent with the experimental result (Section 3.1). In addition, the calculation result indicates that the molar ratio of H_2O_2 to reactant needed in the formation of GA is higher than that of ADA, so much higher molar ratio of H_2O_2 to reactant will decrease the selectivity of main reaction and accelerate the generation of GA and other byproducts, which is corresponding to the experimental result (Section 3.3). In our recent experiment, a small quantity of formic acid (**M5**) has been detected in reaction system by ion chromatography. As mentioned above, the suggested formation mechanism of byproduct GA should be reasonable to exist under the experimental conditions. The intermediate species in Fig. 5, which are generated in side reactions, may be some of the other intermediates or other byproducts.

4. Conclusions

Under the condition of organic solvents and phase-transfer catalysts all free, we studied the influence of reaction conditions on product distribution in the green oxidation of cyclohexene to adipic acid with 30% hydrogen peroxide in the presence of peroxy tungstate catalyst. The results indicate that the amount of sulfuric acid, the reaction temperature in stage B and the feeding style of reactants are main influence factors on this oxidation reaction. The optimized reaction conditions are obtained as follows: the molar ratio of sulfuric acid to C_6H_{10}, 0.065:1; reaction temperature at 73 °C in stage A and 87 °C in stage B; initially adding half of the overall C_6H_{10} simultaneously with the 4.36 (molar ratio) equivalent H_2O_2, and then adding the other half of C_6H_{10} and the corresponding 4.36 (molar ratio) equivalent H_2O_2 in five equal batches as the reaction proceeded in stage A. Under the optimized reaction condition, a 94.5% yield of adipic acid is obtained, meanwhile, byproducts and intermediates are reduced. Moreover, a proposed mechanism for the generation of the main byproduct (GA) in this reaction has been suggested and studied using Gaussian 03 programme. This work improves the yield and quality of ADA, provides the scientific basis for the industrialization of the green synthesis of ADA and offers some important information for a more thorough understanding of this reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.04.041.

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