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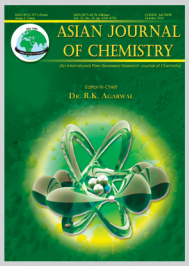

# Aldol Condensations of Aldehydes and Ketones Catalyzed by Primary Amine on Water

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Potassium glycinate-catalyzed aldol condensation reactions of aromatic aldehydes and ketones on water at room temperature have been developed. Under optimal conditions, various condensation adducts are furnished in up to 63 % yield. By simple separation of the oil phase, potassium glycinate-containing water is reused to catalyze aldol condensation for six runs without loss of catalytic activity. Theoretical investigation reveals correlation between the yields and dehydroxylation energy barriers of aldol products, reasonably low activation energy of 11.9 kcal/mol for transition state formation in condensation of benzaldehyde and acetone, vibrations between aldol donor and acceptor, which correspond to the only imaginary frequency (-179.8i).

**Key Words: Aldol condensations, Glycine, Heterogeneous catalysis, Primary amine, α,β-Unsaturated ketones.**

## INTRODUCTION

The aldol condensation reaction has been applied to C-C bond formation in synthetic organic chemistry and is recognized as a classical method to prepare α, β-unsaturated ketones from aromatic aldehydes and ketones. Some of which are key substructures in naturally occurring products, such as chalcones[1,2]. Recently, an alternative protocol has been reported that α,β-unsaturated ketones are synthesized in good yields through reactions of alkenyl trichloroacetates and aldehydes, using mild dibutyltin dimethoxide as catalyst[3].

Aldol condensation reactions of aromatic aldehydes and aliphatic ketones are often performed in the presence of inorganic acids and bases, such as sulfuric acid[4], nafion-H, amberlite IR-120[5], hydrotalcite[6], NaOH and KOH[7,8]. However, these catalysts have numerous disadvantages such as difficulties in catalyst recovery, corrosion problems to reaction equipment and large amounts of residues to environment. With environmentally benign considerations for aldol condensation reactions, Lewis acids $RuCl_3$[9], $RE(OPf)_3$ (RE = rare earth metal)[10] and Fe(BTC) (BTC = 1,3,5-benzenetricarboxylic acid)[11] are employed as effective catalysts. Other attempts have also been paid to metal(II) complex catalyzed aldol condensations, in which Co(II), Ni(II), Cu(II) and Zn(II) are involved[12].

Organocatalysis continues to represent a major topic and a competitive area of research in the arena of organic chemistry. Bicyclic amidine DBU (Diazabicyclo [5.4.0] undec-7-ene) is found to be an effective organic base catalyst for aldol condensation reactions with equimolar water as cocatalyst[13]. Proline-derived organocatalysts are also presented to facilitate aldol condensations, in which secondary amine readily forming corresponding active enamines are underlined[14-17]. However, weaker basicity of primary amine, disfavourable to the imine formation, is more difficult to accelerate aldol condensations. These results suggest to find primary amine catalyst able to perform condensation reactions with good activities and selectivities. Meanwhile, from view point of green chemistry, aqueous reaction is called up nowadays[18]. In this article, we report novel, simple and robust potassium glycinate (gly-k) catalyzed aldol condensation reactions of aromatic aldehydes and ketones on water and put forward to primary amine catalyzed reaction mechanism, assisted with the method of quantum chemistry.

## EXPERIMENTAL

The $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance 500 MHz spectrometer at 20-25 ºC. $^1H$ NMR spectra were reported in parts per million using TMS (δ = 0.00 ppm) as an internal standard. $^{13}C$ NMR spectra were reported in parts per million using solvent $CDCl_3$ (δ = 77.2 ppm) as an internal standard.

The end point of the reactions were monitored by thin layer chromatography (TLC). Thin layer chromatographys were prepared on glass plates (75 × 25 mm) coated with silica gel (about 0.5 mm thick). Column chromatography was performed on silica gel and concentration of organic solution

was usually achieved on a rotary evaporator with a vacuum pump. All analytical grade reagents were purchased locally. Starting materials were used without any further purification.

**General procedure**

**Preparations of amino acid salts:** The amino acid salts **1b-d** and **2b-d** were prepared according to following steps: alkali metal hydroxide was added into a flask. An amount of methanol was put into the flask. Then corresponding amino acid was added to this mixture. After stirred for 0.5 h at room temperature, the resulting solution was concentrated to a sugar paste state by a rotary evaporator and dried in vacuo to give a white solid.

**Condensations of aldehydes with ketones:** To a solution of potassium glycinate (20 mol %) and $H_2O$ (1.5 mL) in a glass test tube were added aldehyde (2 mmol) and acetone or cyclohexanone (0.5 mL). The mixture was stirred at room temperature for 19-35 h until no further transformation was observed by thin layer chromatography. The crude mixture was diluted by $H_2O$ (20 mL) and extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with saturated sodium chloride, dried over anhydrous $MgSO_4$ and filtered. Solvents were removed under vacuum by a rotary evaporator to obtain yellow liquid and pure α, β-unsaturated ketone product was isolated from yellow liquid by column chromatography on silica gel using ethyl acetate and petroleum ether (1:10 to 1:50, v/v) as eluent.

**Detection method**

**(E)-4-phenylbut-3-en-2-one (Table-4, entry 1):** Reaction time = 19 h; a yellow oil; 146.4 mg, 58 % yield; eluent: ethyl acetate/petroleum ether = 1:50; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.71 (d, *J* = 16.5 Hz, 1H), 7.39-7.42 (m, 3H), 7.51 (d, *J* = 16.5 Hz, 1H), 7.53-7.55 (m, 2H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 27.61, 127.25, 128.36, 129.08, 130.63, 134.52, 143.56, 198.52.

**(E)-2-benzylidenecyclohexanone (Table-4, entry 2):** Reaction time = 19 h; a yellow waxy oil; 107.6 mg, 29 % yield; eluent: ethyl acetate/petroleum ether = 1:50; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.74-1.79 (m, 2H), 1.90-1.95 (m, 2H), 2.54 (t, *J* = 7.0 Hz, 2H), 2.82-2.85 (m, 2H), 7.31-7.34 (m, 1H), 7.37-7.41 (m, 4H), 7.49-7.51 (m, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 23.53, 24.03, 29.09, 40.49, 128.48, 128.67, 130.45, 135.73, 135.76, 136.83, 201.94.

**(E)-4-(4-methoxyphenyl)but-3-en-2-one (Table-4, entry 3)**: Reaction time = 24 h; a yellow solid; 177.3 mg, 50 % yield; eluent: ethyl acetate/petroleum ether = 1:40; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.87 (s, 3H), 6.63 (d, *J* = 16.5 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 27.57, 55.56, 114.61, 125.20, 127.23, 130.13, 143.41, 161.78, 198.56.

**(E)-2-(4-methoxybenzylidene)cyclohexanone (Table-4, entry 4)**: Reaction time = 24 h; a yellow solid; 167.8 mg, 39 % yield; eluent: ethyl acetate/petroleum ether = 1:40; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.76-1.80 (m, 2H), 1.89-1.93 (m, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.83-2.86 (m, 2H), 3.89 (s, 3H), 7.01 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 2H).

**(E)-4-(4-nitrophenyl)but-3-en-2-one (Table-4, entry 5):** Reaction time = 22 h; a yellow solid; 17.9 mg, 5 % yield; eluent: ethyl acetate/petroleum ether = 1:10; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 6.83 (d, *J* = 16.5 Hz, 1H), 7.54 (d, *J* = 16.0 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 28.20, 124.37, 128.97, 130.55, 137.58, 140.23, 148.77, 197.70.

**(E)-2-(4-nitrobenzylidene)cyclohexanone (Table-4, entry 6):** Reaction time = 22 h; a yellow solid; 47.2 mg, 10 % yield; eluent: ethyl acetate/petroleum ether = 1:10; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.63-1.84 (m, 2H), 1.85 (d, *J* = 14.5 Hz, 2H), 2.10-2.14 (m, 2H), 2.40-2.44 (m, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 2H).

**(E)-4-(furan-2-yl)but-3-en-2-one (Table-4, entry 7):** Reaction time = 31 h; a bronzing waxy oil; 115.2 mg, 42 % yield; eluent: ethyl acetate/petroleum ether = 1:50; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 3H), 6.49-6.50 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.67 (d, *J* = 3.5 Hz, 1H), 7.28 (d, *J* = 16.0 Hz, 1H), 7.51 (s, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 27.98, 112.68, 115.79, 124.44, 129.58, 145.16, 151.04, 198.00.

**(E)-2-(furan-2-ylmethylene)cyclohexanone (Table-4, entry 8):** Reaction time = 35 h; a bronzing waxy oil; 221.9 mg, 63 % yield; eluent: ethyl acetate/petroleum ether = 1:50; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.79-1.84 (m, 2H), 1.87-1.92 (m, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.90-2.92 (m, 2H), 6.50-6.51 (m, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 7.38-7.39 (m, 1H), 7.55 (s, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 23.08, 23.32, 28.51, 40.03, 112.40, 116.18, 123.11, 132.64, 144.67, 152.51, 200.53.

**(3E,5E)-6-phenylhexa-3,5-dien-2-one (Table-4, entry 9):** Reaction time = 27 h; a pale yellow solid; 110.1 mg, 32 % yield; eluent: ethyl acetate/petroleum ether = 1:50; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 3H), 6.26 (d, *J* = 15.5 Hz, 1H), 6.85-6.97 (m, 2H), 7.26-7.38 (m, 4H), 7.46 (s, 1H), 7.48 (s, 1H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 27.51, 126.80, 127.40, 129.00, 129.37, 130.64, 136.11, 141.41, 143.57, 198.55.

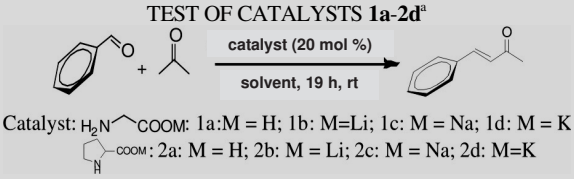
**(E)-2-((E)-3-phenylallylidene)cyclohexanone (Table-4, entry 10)**: Reaction time = 35 h; a yellow solid; 52.7 mg, 12 % yield; eluent: ethyl acetate/petroleum ether = 1:50; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.79-1.84 (m, 2H), 1.86-1.92 (m, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.73-2.76 (m, 2H), 6.92-7.04 (m, 2H), 7.24-7.31 (m, 2H), 7.34-7.37 (m, 2H), 7.47-7.49 (m, 2H); $^{13}$C NMR (500 MHz, $CDCl_3$): δ 23.23, 23.51, 27.09, 40.16, 123.28, 127.30, 128.95, 129.02, 135.18, 135.60, 136.83, 141.08, 200.93.

## RESULTS AND DISCUSSION

Our initial study focused on investigation of the catalytic efficiencies of catalysts **1a-2d** and aldol condensation of benzaldehyde and acetone was chosen as model reaction. The reactions were conducted in acetone at room temperature for 19 h and the results were summarized in Table-1. No product was observed when catalytic amount of glycine **1a** was used (Table-1, entry 1). Potassium salt catalyst **1d** exhibited improved catalytic activity and α, β-unsaturated ketones were obtained in 29 % yield (Table-1, entry 4). Lithium or sodium glycinate gave the yield of 8 % (Table-1, entries 2 and 3). Under the same conditions, both proline **2a** and its derivative

**2d** also demonstrated moderate activities and selectivities (Table-1, entries 5 and 8). With considerations of atom economy, reaction simplicity and interest of primary amine catalysis, potassium glycinate was utilized to further investigate solvent effects.

TABLE-1
TEST OF CATALYSTS **1a**-**2d**[a]




Catalyst: $H_2N$ COOM: 1a:M = H; 1b: M=Li; 1c: M = Na; 1d: M = K
COOM: 2a: M = H; 2b: M = Li; 2c: M = Na; 2d: M=K

| Entry | Catalyst | Yield (%)[b] |
|---|---|---|
| 1 | **1a** | 0 |
| 2 | **1b** | 8 |
| 3 | **1c** | 8 |
| 4 | **1d** | 29 |
| 5 | **2a** | 32[c] |
| 6 | **2b** | 0 |
| 7 | **2c** | 7 |
| 8 | **2d** | 35 |

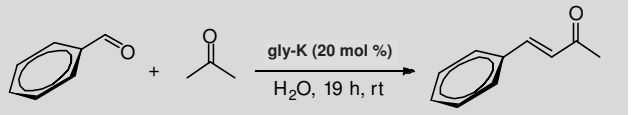
a. Conditions: A mixture of 2 mmol benzaldehyde and 20 mol % catalyst in 2 mL acetone was stirred at room temperature for 19 h; b. Isolated yields; c. Condensation product was confirmed by $^1$H NMR spectrum.

We explored several solvents to condensation reaction catalyzed by potassium glycinate, such as dichloromethane, $CHCl_3$, toluene, THF, ethyl ether, ethyl acetate, DMSO and DMF (Table -2). The dehydration products were produced in polar or less polar solvents and no significant solvent effects were observed (Table-2, entries 1-8). The properties of ion pair hydrophilicity and alkane hydrophobicity inspired us to perform water phase reaction. The product was formed in 61 % yield on $H_2O$ (Table-2, entry 9). Subsequently, effect of $H_2O$/acetone volume ratio on the reaction efficiency was evaluated in the aldol condensation reaction of benzaldehyde and acetone. The yields decreased gradually with increase of water content or with dilution of potassium glycinate concentration (Table-2, entries 9-13). Preferential $H_2O$/acetone proportion was established to be 1:0.33 (v/v) and afforded the condensation product in 58 % yield (Table-2, entry 11).

As can be seen from Table-3, the yields of α, β-unsaturated ketones improved initially and then decreased with catalyst loading increasing from 10 to 30 mol%. 20 mol % Catalyst **1d** was appropriate for the reaction and provided (E)-4-phenylbut-3-en-2-one in 58 % yield (Table-3, entry 3).

After optimal conditions were established, this method was extended to aldol condensations of other aromatic aldehydes, heteroaromatic aldehydes and enal with acetone and cyclohexanone. As shown in Table-4, aldol condensations of benzaldehyde and substituted benzaldehyde proceeded smoothly at room temperature for 19 to 35 h, yielding condensation adducts in yields of 5 to 58 %. Non-substituted benzaldehyde provided the condensation product in 58 % yield. Electron-donating methoxyl substituted benzaldehyde afforded α, β-unsaturated ketones in 50 % yield for acetone and 18 % yield for cyclohexanone (Table-4, entries 3 and 4). Surprisingly, when electron-withdrawing nitro substituted benzaldehyde

TABLE-2
TEST OF SOLVENT EFFECTS[a]

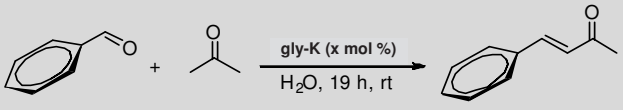



| Entry | Solvent | Yield (%)[b] |
|---|---|---|
| 1 | DCM/acetone (1:1) | 41 |
| 2 | $CHCl_3$/acetone (1:1) | 36 |
| 3 | $C_7H_8$/acetone (1:1) | 35 |
| 4 | THF/acetone (1:1) | 35 |
| 5 | $Et_2O$/acetone (1:1) | 33 |
| 6 | EtOAc/acetone (1:1) | 35 |
| 7 | DMSO/acetone (1:1) | 30 |
| 8 | DMF/acetone (1:1) | 28 |
| 9 | $H_2O$/acetone (1:1) | 61 |
| 10 | $H_2O$/acetone (1:0.6) | 56 |
| 11 | $H_2O$/acetone (1:0.33) | 58 |
| 12 | $H_2O$/acetone (1:0.14) | 49 |
| 13 | $H_2O$/acetone (1:0.08) | 36 |

a. Conditions: A mixture of 2 mmol benaldehyde and 20 mol % catalyst **1d** in 2 mL specified solvents was stirred at room temperature for 19 h, the volume ratios of acetone and solvent were shown; b. Isolated yields.

reacted with acetone, dehydrated product was in 5 % yield along with aldol product in 49 % yield (Table-4, entry 5). Nitrobenzaldehyde with cyclohexanone produced the corresponding dehydrated adduct only in 10 % yield (Table-4, entry 6). Based on these observations, we envisioned that the yields were affected by substituents on aromatic ring, reactant with electron-withdrawing substituent probably led to higher energy barrier ΔE for carbonium formation *via* dehydroxylation of aldol product (**Scheme-I**, ΔE values at the B3LYP/6-31G* level[19] listed in Table-4), which gave lower yield for condensation product and electron-donating group had no significant effects on reactivity and selectivity. In the reaction of heteroaromatic furane and ketones, we obtained the unsaturated product in 42 % yield for acetone and in 63 % yield for cyclohexanone (Table-4, entries 7 and 8). Interestingly, using enal as a substrate, diene products were furnished in 32 and 12% yields, respectively for two aldol donors (Table-4, entries 9 and 10).

TABLE-3
OPTIMIZATION OF CATALYST LOADING[a]

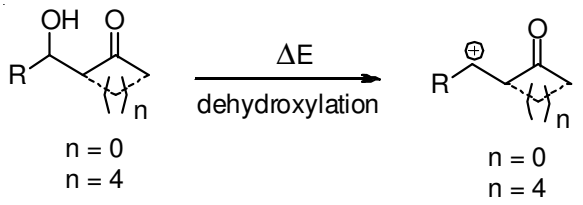



| Entry | *x* | Yield (%)[b] |
|---|---|---|
| 1 | 10 | 18 |
| 2 | 15 | 40 |
| 3 | 20 | 58 |
| 4 | 25 | 48 |
| 5 | 30 | 48 |

a. Conditions: A mixture of 2 mmol benaldehyde and *x* mol % catalyst **1d** in 2 mL solvent (1:0.33, water/acetone) was stirred at room temperature for 19 h; b. Isolated yields.

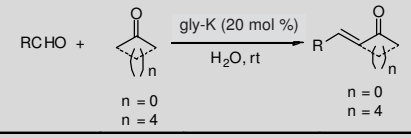
From above experimental analysis, successive carbonium formation from aldol adduct was regarded as a vital process for the aldol condensation. The yields exhibited partially relationship with calculated energy barriers. Aldol product

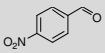
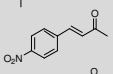
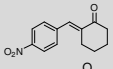
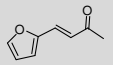
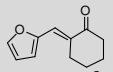
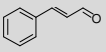
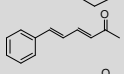
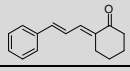
β-hydroxy ketones, precursors of condensation adducts, 4-hydroxy-4-(4-nitrophenyl)butan-2-one and 2-[hydroxy(4-nitrophenyl) -methyl]cyclohexanone from nitrobenzaldehyde were transformed to their corresponding carbonium intermediates with highest energy barriers (247.1 kcal/mol for acetone and 234.1 kcal/mol for cyclohexanoe, respectively), which exactly led to condensation products in lowest yields of 5 and 10 % and reversely aldol products were major in these two reactions (Table-4, entries 5 and 6). Other energy barriers were distributed in the range of 201.8-232.2 kcal/mol, which corresponded to 12-63 % yields.




**Scheme-I** Schematic of aldol product dehydroxylation.

TABLE-4
REACTIONS OF VARIOUS ALDEHYDES AND KETONES[a]




| Entry | Aldehyde | | Product | Yield (%)[b] | ΔE (kcal/mol) |
|---|---|---|---|---|---|
| 1 |  | n = 0 |  | 58 | 232.2 |
| 2 | | n = 4 |  | 29 | 218.3 |
| 3 |  | n = 0 |  | 50 | 218.3 |
| 4 | | n = 4 |  | 18[c] | 210.2 |
| 5 |  | n = 0 |  | 5 | 247.1 |
| 6 | | n = 4 |  | 10 | 234.1 |
| 7 |  | n = 0 |  | 42 | 224.0 |
| 8 | | n = 4 |  | 63 | 213.3 |
| 9 |  | n = 0 |  | 32 | 220.7 |
| 10 | | n = 4 |  | 12 | 201.8 |

a. Conditions: A mixture of 2 mmol aldehyde and 20 mol% catalyst **1d** in 2 mL solvent (1:0.33, water/ketone) was stirred at room temperature; b. Isolated yields; c. Yield was determined by $^1$H NMR spectrum.

In order to check the reusability of potassium glycinate, condensation reaction of benzaldehyde and acetone was investigated. The reaction mixture was formed by two phases: an oil phase containing reactants and an aqueous phase containing the catalyst. After the reaction was completed, ethyl ether extract was injected subsequently to stirred reaction mixture and after a while, ethereal layer containing the product (α, β-unsaturated ketone) was pumped out from the aqueous phase by syringe. The aqueous solution was used directly for the next run by adding starting materials. The results were listed in Table-5. After five consecutive reuses, the yield of the product did not obviously decrease. It indicates that water used as solvent makes the separation of oil phase easier and more importantly, potassium glycine salt can be recycled easily due to its solubility in the aqueous phase.

TABLE-5
RECYCLING OF AQUEOUS SOLUTION OF CATALYST **1d** FOR ALDOL CONDENSATION BETWEEN BENZALDEHYDE AND ACETONE[a]

| Run | Time (h) | Yield (%)[b] |
|---|---|---|
| 1 | 19 | 58 |
| 2 | 21 | 52 |
| 3 | 24 | 58 |
| 4 | 23 | 52 |
| 5 | 23 | 52 |
| 6 | 22 | 48 |

a. Conditions: A mixture of 2 mmol benzaldehyde and 20 mol % catalyst **1d** in 2 mL solvent (1:0.33, water/acetone) was stirred at room temperature; b. Isolated yields.

In our endeavor to depict mechanistic information typically for model reaction, we performed quantum chemical calculations on the transition state (TS) and intermediate **A** (Fig. 1). Our proposal is founded on bifunctional aminocatalysis and equilibrium shift from imine to active enamine[20]. It is well know that due to weaker basicity of primary amine than secondary and tertiary amines, primary amine is of less nucleophilic ability to form imine, which is disfavourable to reaction forwards. In this catalytic cycle, the benzaldehyde is initially activated through oxygen atom binding to $K^+$ by electrostatic interaction and acetone condenses with the primary amine group of catalyst through carbonyl addition and water elimination steps to form imine intermediate **A**. Rearrangement of imine **A** leads to the formation of active enamine, which can react with activated benzaldehyde *via* conjugation addition in transition state **B** to give an imine **C**. After imine **C** hydrolyzes to give aldol addition adduct **D** in the presence of water and elimination of water generates aldol condensation adduct **P**. Alternatively, imine **C** dehydrates to α, β-unsaturated imine **D'** and subsequently imine **D'** hydrolyzes to aldol condensation adduct **P**. Two pathways produce one additional water molecule, respectively. In contrast to secondary amine-catalyzed aldol condensation of aldehyde and ketone, which proceeds through iminium ion, enamine to iminium ion in tandem, the primary amine-catalyzed reaction proceeds *via* imine **A**, enamine **B** and imine **C**[21]. It appears that this catalyst is generally efficient for aldol condensation reaction.

The key transition state **B** and its relative complexes **A** were optimized at the B3LYP/6-31G* level. The corresponding activation energy was calculated to be 11.9 kcal/mol, which indicated that the activation barrier for the formation of transition state **B** was reasonably low. The only imaginary frequency of the transition state was -179.8 i, which corresponded to the vibration between the aldol donor and acceptor. The electrostatic potential (ESP) on the surface of transition state was negative in the vicinity of carbon terminal of enamine and confirmed the electron-rich nature of the enamine (Fig. 2).

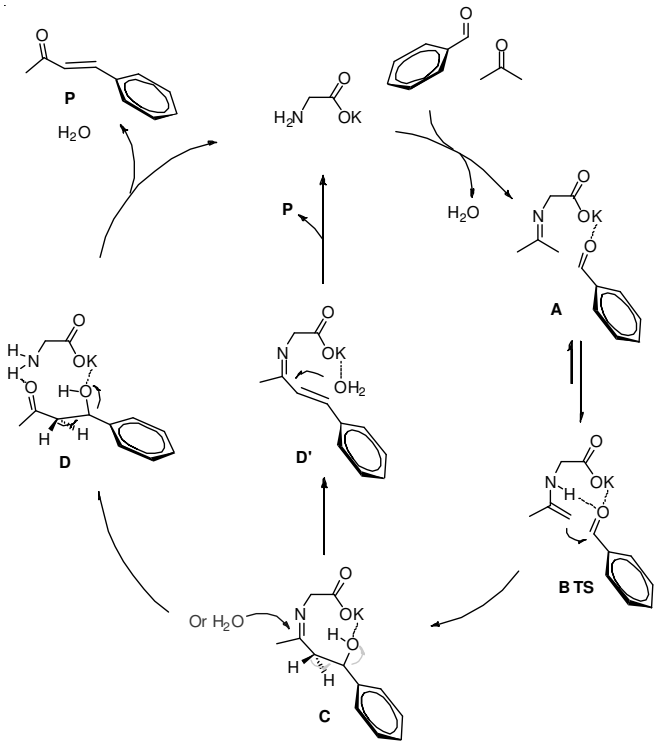



Fig. 1. Proposed potassium glycinate-catalyzed reaction mechanism for model reaction

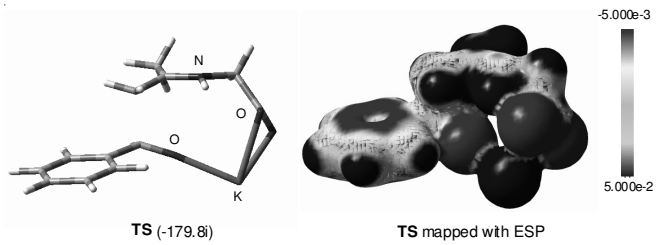



Fig. 2. Transition state B (left) and side view (right) showing the electrostatic potential mapped

## Conclusion

In conclusion, we have developed novel and effective potassium glycinate-catalyzed aldol condensations of aldehyhes and ketones on water. Various α,β-unsaturated ketones are furnished in up to 63 % yield. In experiment, by simple separation of the aqueous phase from reaction mixture, potassium glycinate-containing water can be reused several times without loss of catalytic activity. The simple procedures are expected to contribute to industrial application. Theoretical investigation shows that at the B3LYP/6-31G* level, reasonable activation energy is calculated for formation of transition state and the only imaginary frequency (-179.8i) corresponds to key vibration between aldol donor and acceptor.

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