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## Article

# Proton-gradient-transfer acid complexes and their catalytic performance for the synthesis of geranyl acetate



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## ABSTRACT

Special proton-gradient-transfer acid complexes (PGTACs) in which the bonded protons are not equivalent and have gradients in transfer ability, acidity, and reactivity were reported. The acidity gradient of the protons gave the PGTACs excellent catalytic activity and selectivity in the esterification of terpenols. These PGTACs are “reaction-induced self-separation catalysts” and can be easily reused. The kinetics with PGTACs as catalyst in the esterification of geraniol were also studied for use in engineering design.

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## 1. Introduction

Esters are important chemical intermediates and products in the food, cosmetic and pharmaceutical industries. Acid-catalyzed esterification reactions are the most prevailing methods to produce esters in both industry and academia [1–4]. Strong inorganic and organic acids, such as  $\text{H}_2\text{SO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$ , are well-known catalysts for esterification. These catalysts have good catalytic activity but suffer from the problems of causing equipment corrosion, being difficult to separate from the solution, have low selectivity, give side reactions, and cause environment pollution [5]. To overcome these drawbacks, many novel homogeneous and heterogeneous acid catalysts have been developed, such as special Lewis acid catalysts [6], heteropolyacids [7,8], ionic liquid catalysts [9–15], acidic zeolites [16–18], macroporous polymeric acids [19], sulphated

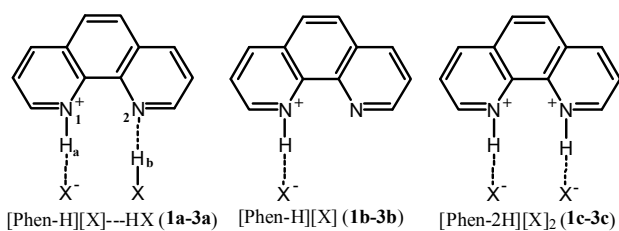
complexes [20–23], acidic resins [24,25], and other solid acids [26,27]. Among these catalysts, the acidic complexes formed by the neutralization reaction between Brønsted acids and bases are receiving more attention for their low cost, low corrosiveness and reasonable catalytic activity [2,9,10–12,28–30]. Protonic ionic liquids (PILs) are typical examples of such complexes [2,9–12].

Because there is a lone electron pair on the N atom of the Brønsted base, the proton of the acid transfers to the N atom with a large Gibbs free energy change [31,32] during the formation of the PILs cations. As a result, the proton bonds tightly to the Brønsted base and the acid strength is reduced compared to the free acid [33]. However, the catalytic activity of PILs is related to their acid strength [9]. Hence, compared to the free acid used to produce the PILs, the catalytic activity of these PILs in acid-catalyzed reactions are usually weaker.

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**Scheme 1.** Structure of [Phen-H][X]...HX, [Phen-H][X] and [Phen-2H][X]<sub>2</sub>. X<sup>-</sup> = CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> (**1**), HSO<sub>4</sub><sup>-</sup> (**2**), and CH<sub>3</sub>PhSO<sub>3</sub><sup>-</sup> (**3**).

In contrast to these widely known PILs, we reported here a new bonding mode between the Brønsted acid and base. They are called proton gradient transfer acid complexes (PGTACs). The PGTACs were generated by a reaction between phenanthroline (Phen) and acid in 1:2 mole ratio ([Phen-H][X]...HX, **1a-3a** in Scheme 1). These complexes are interesting because only one proton (H<sub>a</sub>) formed a covalent bond with the N atom of Phen, and another proton (H<sub>b</sub>) formed a hydrogen bond with another N atom. Furthermore, H<sub>b</sub> can transfer between the N atom and X anion with a low barrier. That is, the transfer abilities of the H<sub>a</sub> and H<sub>b</sub> protons are different. The PGTACs are a good compromise between the free acid (HX) and [Phen-H][X] when both catalytic activity and selectivity are taken into consideration. In particular, these PGTACs can be easily separated and reused because of the nature of the salts, so a green reaction separation integration is enabled.

## 2. Experimental

### 2.1. Materials

All chemicals were analytical grade and used without any purification. 1,10-Phenanthroline (Phen) was purchased from Sun Chemical Technology (Shanghai) Co. Ltd. Geraniol, acetic anhydride, methylsulfonic acid (MSA), H<sub>2</sub>SO<sub>4</sub>, *p*-toluenesulfonic acid (PTS), and D72 resin were obtained from Jintan Huagong Chemical Research Institute (Jiangsu, China). Lewatit® K 2620 resin was purchased from Aladdin Industrial Corporation (Shanghai, China). The other alcohols were obtained from Energy Chemical (China) Co. Ltd.

### 2.2. Methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on an Agilent DD2 400MR equipment operating at 400 and 100 MHz, respectively. The elemental analysis (EA) was obtained using a Heraeus-CHN-O-Rapid analyzer. The ESI MS spectra were determined with a LCQ-fleet ESI Mass Spectrometer. The FTIR spectra of the samples were recorded on a PerkinElmer Spectrum 100 Series FTIR spectrometer with a universal ATR accessory. Thermogravimetry characterization for these PGTACs was carried out on a PerkinElmer Diamond TG/DTA from room temperature to 800 °C with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. An Agilent 8453 UV-visible spectrometer was used to determinate the Hammett functions (*H*<sub>0</sub>) of the PGTACs. The experiments were carried out in methanol solution (2

mmol/L) of PGTACs and other catalysts at room temperature (25 °C). Dimethyl yellow (p*K*<sub>a</sub>(I)<sub>aq</sub> = 3.3) was used as the indicator (0.085 mmol/L), and the UV-visible determination was carried out in the range of 200–700 nm.

### 2.3. Synthesis and characterization of PGTACs

To a vigorously stirred ethanol solution (100 mL) of 1,10-phenanthroline (18.02 g, 0.1 mol), ethanol solution (50 mL) of sulfuric acid (19.60 g, 0.2 mol) was added at 0 °C. The mixture was stirred for a further 12 h at reflux temperature. The ethanol was removed by evaporation to give a reddish liquid. Then, the colored residue was washed with benzene three times and dried in vacuum to give the purified PGTACs **1a**. This catalyst was solidified on cooling (yield: 99%). PGTACs **2a** to **3b** were synthesized similarly to the preparation of PGTACs **1a**. The yields of these PGTACs were all above 99%. The structural maps of **1a-3b** are shown in Figure 1.

PGTACs **1a**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 9.34 (1 H, d), 9.33 (1 H, d), 9.13 (1 H, d), 9.10 (1 H, d), 8.39 (2 H, s), 8.27 (1 H, d), 8.25 (1 H, d), 2.44 (6 H, s). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 148.22, 141.98, 138.03, 129.77, 127.82, 126.03, 40.37. MS (ESI): *m/z* = 181.08 [M + H]<sup>+</sup>. Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C 45.16, H 4.30, N 7.53; Found: C 45.14, H 4.31, N 7.55.

PGTACs **3a**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 9.33 (1 H, d), 9.32 (1 H, d), 9.12 (1 H, d), 9.10 (1 H, d), 8.38 (2 H, s), 8.26 (1 H, d), 8.25 (1 H, d), 7.49 (4 H, d), 7.13 (4 H, t), 2.29 (6 H, s). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 147.62, 145.29, 142.03, 137.82, 137.30, 129.58, 128.10, 127.54, 125.77, 125.46, 20.75. MS (ESI): *m/z* = 181.08 [M + H]<sup>+</sup>. Anal. Calcd. for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C 59.54, H 4.58, N 5.34; Found: C 59.50, H 4.63, N 5.30.

PGTACs **1b**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 9.31 (1 H, d), 9.30 (1 H, d), 9.06 (1 H, d), 9.04 (1 H, d), 8.35 (2 H, s), 8.21 (1 H, d), 8.19 (1 H, d), 2.31 (3 H, s). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 148.09, 142.44, 137.59, 129.94, 127.95, 126.23, 40.18. MS (ESI): *m/z* = 181.08 [M + H]<sup>+</sup>. Anal. Calcd. for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S: C 56.52, H 4.35, N 10.14; Found: C 56.55, H 4.35, N 10.13.

PGTACs **3b**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 9.32 (1 H, d), 9.31 (1 H, d), 9.09 (1 H, d), 9.07 (1 H, d), 8.37 (2 H, s), 8.24 (1 H, d), 8.23 (1 H, d), 2.28 (3 H, s). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ = 148.14, 146.14, 142.30, 138.13, 137.85, 129.94, 128.54, 127.94, 126.17, 125.99, 21.24. MS (ESI): *m/z* = 181.08 [M + H]<sup>+</sup>. Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S: C 64.77, H 4.55, N 7.95; Found: C 64.70, H 4.57, N 8.04. Data for PGTACs **2a** and **2b** have been reported in other being published articles.



**Fig. 1.** Prepared PGTACs samples **1a**, **2a**, **3a**, **1b**, **2b** and **3b**.

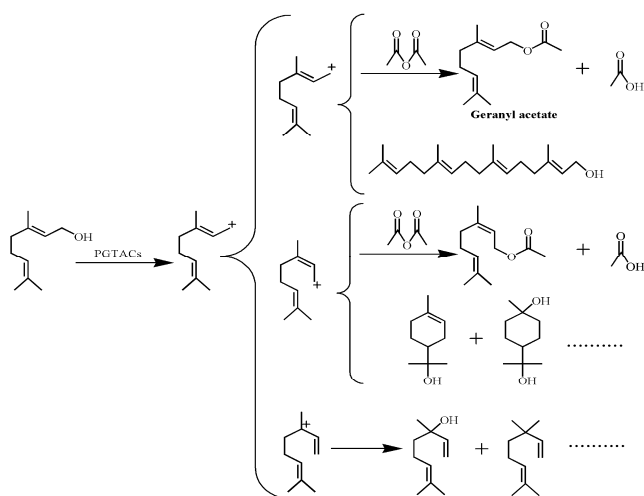
## 2.4. Esterification of geraniol

Geraniol (1.54 g, 0.01 mol) and acetic anhydride (1.02 g, 0.01 mol) were added to a 100 mL three neck round bottom flask and heated to a designed temperature. Then **1a** (0.074 g, 0.2 mmol) was added to the mixture and stirred at 50 °C for 2 h. **1a** was separated from the reaction system by easy decantation. The yield of geranyl acetate was determined by GC-MS with an internal standard (*n*-butyl acetate). The proposed mechanism for the reaction of geraniol with acetic anhydride with the use of PGTACs as catalyst is shown in Scheme 2.

## 3. Results and discussion

### 3.1. Structure analysis

In this paper, we focused on the exploration of the novel protonic catalysts. The reaction between Phen and HX 1:1 can generate [Phen-H][X] compounds (**1b–3b**) that are in fact analogues of PILs, even though the melting points of [Phen-H][X] were a bit high (Table 1). There is still one N atom with a lone electron pair in [Phen-H][X]. It was a surprise to find that one more HX can react with [Phen-H][X] to produce the dicationic compounds [Phen-2H][X]<sub>2</sub> (Scheme 1, **1c–3c**). All the experimental characterization of the 2:1 (acid:Phen) reaction products suggested the formation of complexes (**1a–3a**) between



**Scheme 2.** Suggested mechanism for the reaction of geraniol with acetic anhydride with the use of PGTACs as catalyst.

**Table 1**  
Physical and chemical properties of the catalysts.

Catalyst	$T_m^a / ^\circ\text{C}$	$T_d^b / ^\circ\text{C}$	$H_0^c$
<b>1a</b>	62.2	300.1	2.86
<b>2a</b>	180.6	298.3	2.81
<b>3a</b>	110.3	286.1	2.60
<b>1b</b>	103.2	299.5	4.59
<b>2b</b>	198.6	331.9	4.23
<b>3b</b>	157.2	332.2	4.35
MSA	—	—	2.62
H <sub>2</sub> SO <sub>4</sub>	—	—	2.58
PTS	—	—	2.60

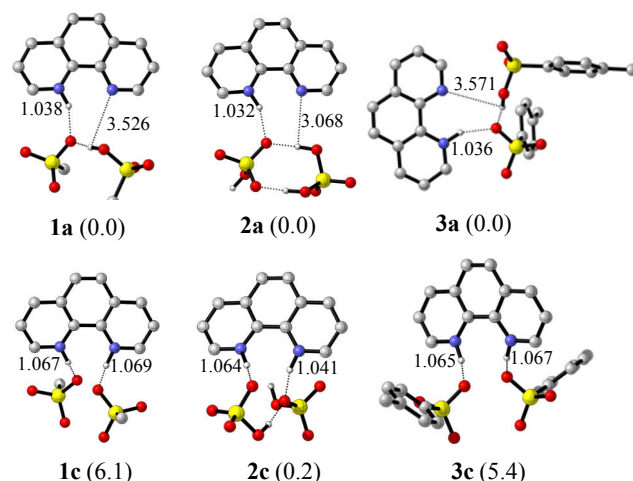
<sup>a</sup> Melting point; <sup>b</sup> Decomposition temperature; <sup>c</sup> Hammett acidity.

[Phen-H][X] and HX. Both the <sup>1</sup>H NMR and elemental analysis clearly showed that the complexes were composed of Phen and acid in 1:2 mole ratio. However, the ESI MS analysis for all the products gave  $[M + H]^+ = 181.1$ , revealing that the complexes contain only a single cation ([Phen-H]<sup>+</sup>) rather than the di-cation ([Phen-2H]<sup>2+</sup>). Furthermore, the acid strength of **1a–3a** was about two orders of magnitude larger than that of **1b–3b** (Table 1), also indicating that the two protons in **1a–3a** were not equivalent. That is, the 2:1 (acid:Phen) reaction products were not [Phen-2H][X]<sub>2</sub>. The melting points of the 2:1 products (**1a–3a**) were close to those of some PILs [9], but obviously lower than those of the corresponding 1:1 products (**1b–3b**).

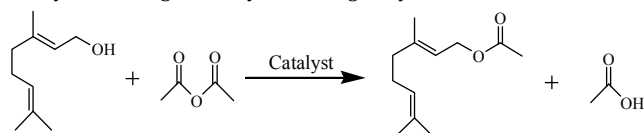
To understand why the two protons are not equivalent and explore the structures of **1a–3a**, the optimization of the 2:1 (acid:Phen) complexes were performed at the B3LYP/6–31++G\*\* level using methanol as solvent. The calculations further confirmed the experimental results that only H<sub>a</sub> formed a covalent bond with the N atom and H<sub>b</sub> only formed a hydrogen bond with another N atom. The N–H<sub>a</sub> and N–H<sub>b</sub> distances ranged from 1.032 to 1.036 Å and 3.068 to 3.571 Å, respectively (Fig. 2).

### 3.2. Catalytic performance of the PGTACs

Geranyl acetate is known as terpenol [34]. The olefin functional groups in terpenols are susceptible to the acids used in the esterification reaction [35]. Strong acids give total conversion but much byproducts, while weak acids exhibit excellent selectivity but poor catalytic activity. In this paper, the two protons in PGTACs gave it an appropriate acidity (**1a**,  $H_0 = 2.86$ , Table 2) between a strong acid (MSA,  $H_0 = 2.62$ , Table 2) and weak acid (**1b**,  $H_0 = 4.59$ , Table 2). The PGTACs have both the advantages of strong and weak acids, and gave excellent catalytic activity and selectivity for the esterification of geraniol (Entries 1 and 2, Table 2). Although the reactions catalyzed by



**Fig. 2.** Optimized structure of [Phen-H][CH<sub>3</sub>SO<sub>3</sub>]...CH<sub>3</sub>SO<sub>3</sub>H (**1a**), [Phen-H][HSO<sub>4</sub>]...H<sub>2</sub>SO<sub>4</sub> (**2a**), and Phen-H][CH<sub>3</sub>-Ph-SO<sub>3</sub>]...CH<sub>3</sub>-Ph-SO<sub>3</sub>H (**3a**). All H atoms of C–H are omitted for clarity. The values shown are N–H distance in Å. Values in parentheses are relative energy in kcal/mol.

**Table 2**Catalyst screening for the synthesis of geranyl acetate<sup>a</sup>.

Entry	Catalyst	Time (min)	Conversion <sup>a</sup> (%)	Selectivity (%)
1	<b>1a</b>	120	99.5	96.9
2	<b>2a</b>	120	100	90.7
3	<b>1b</b>	120	45.3	95.7
4	<b>2b</b>	120	59.3	98.6
5 <sup>b</sup>	CH <sub>3</sub> SO <sub>3</sub> H	10	100	65.0
6 <sup>c</sup>	H <sub>2</sub> SO <sub>4</sub>	1	100	57.1
7 <sup>d</sup>	D72	120	72.3	83.3
8 <sup>d</sup>	Lewatit®K 620	120	83.2	77.4

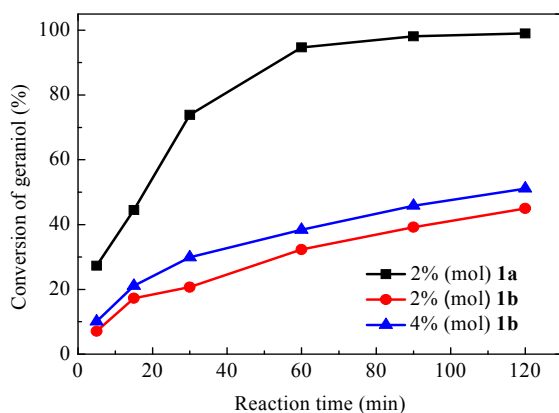
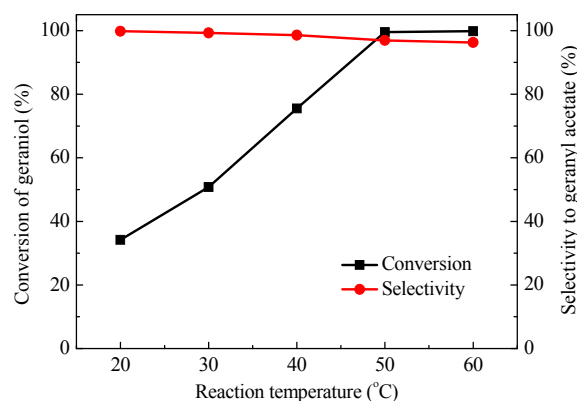
Reaction condition: geraniol (0.02 mol), acetic anhydride (0.02 mol), 2% (mol) catalyst, temperature = 50 °C.

<sup>a</sup> Conversion of geraniol determined by GC with *n*-butyl acetate as the internal standard. <sup>b</sup> 20 °C. <sup>c</sup> 0.2% (mol) catalyst and 20 °C. <sup>d</sup> The dosage of the two resins is equal to the amount of 2% (mol) **1a**.

the PILs analogues (**1b** and **2b**) gave good selectivity, their catalytic activities were low due to their weak acidity (Entries 3 and 4) [9]. On the contrary, the free acids (MSA and H<sub>2</sub>SO<sub>4</sub>) were too active and gave low selectivity even when the reaction temperature was reduced to 20 °C (Entries 5 and 6). Hence, the PGTACs were good compromises between the free acid HX (strong acid) and the PILs analogues [Phen-H][X] (weak acid).

The widely used homogeneous inorganic and organic acids are very difficult to separate and reuse. Resins have been widely used for many esterification reaction because they are easily separated [24,25]. We tested two resins (D72 and Lewatit®K 620) in the esterification of geraniol and found that these resins were of lower reactivity and poorer selectivity (Entries 7 and 8, Table 2) than that of **1a** with the same catalyst dosage.

To optimize the reaction conditions of PGTACs **1a** in the catalytic reaction of geraniol, the effects of reaction time, temperature and catalyst dosage on the conversion of geraniol and selectivity to geranyl acetate were explored systematically. In Fig. 3, it is shown that the conversion of geraniol increased dramatically in the first 1 h (to 94.7%) and was nearly complete at 2 h (99.6%) in the presence of **1a**. It is worthwhile to

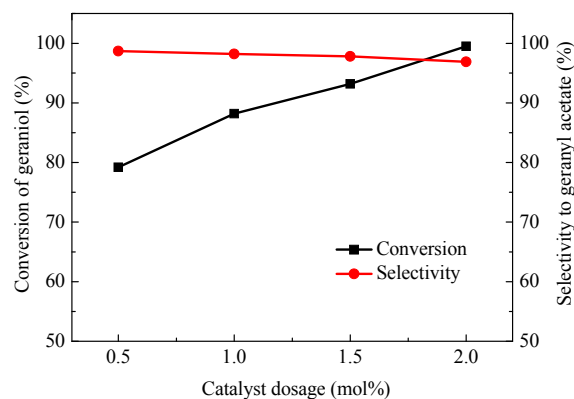
**Fig. 3.** Conversion versus time for the esterification of geraniol with different catalysts.**Fig. 4.** Effect of reaction temperature on the conversion of geraniol and selectivity to geranyl acetate.

note that the reaction catalyzed by 4% (mol) **1b** was far slower than that using 2% (mol) **1a**. This reaction data further proved that the two protons in **1a** are not equivalent.

The effect of reaction temperature was examined from 20 °C to 60 °C with a 1:1 molar ratio of geraniol and acetic anhydride to the catalyst dosage of 2% (mol) at 2 h. The results are shown in Fig. 4. It was found that the conversion of geraniol increased from 35.2% to 100% with increased reaction temperature from 20 to 60 °C, while the selectivity was only slightly decreased (from 99.5% to 95.7%). In addition, the 96.4% yield of geranyl acetate at 50 °C, 0.7% more than that at 60 °C, illustrated that the optimal reaction temperature was 50 °C.

The effect of catalyst dosage on the conversion of geraniol and selectivity to geranyl acetate was also investigated. The results are illustrated in Fig. 5. The conversion of geraniol increased with the increase of catalyst dosage from 0.5% (mol) to 2% (mol), while the selectivity to geranyl acetate remained almost unchanged (98.7% to 96.9%). Therefore, an appropriately increased dosage of catalyst **1a** was beneficial to the production of geranyl acetate, and the suggested catalyst dosage is 2% (mol).

Using **1a** as catalyst, we explored the scope of this highly effective reaction for the esterification of different terpenols under the standard conditions (Table 3). Good to excellent yields

**Fig. 5.** Effect of catalyst dosage on the conversion of geraniol and selectivity to geranyl acetate.

of esters were obtained for all the reactions investigated. For easily oxidizable terpenols, such as **6a**, **10a** and **11a**, the yields ranged from 85% to 89%. It is beneficial that the reasonable acidity and excellent selectivity of PGTACs could decrease the shedding of OH groups. As we know, the shedding of OH groups is the main process to produce water in the esterification of terpenols and acetic anhydride. The hydration products can be easily generated between terpenols and water with the acid as catalyst. Therefore, the PGTACs were appropriate catalysts in the esterification of terpenols and acetic anhydride. The esterification yields of all the other alcohols investigated here were >95%. PGTAC **1a** was super effective for the esterification of aromatic alcohols and the reactions were completed in 2 h with almost 99% yield. All the esters produced can be easily separated due to their immiscibility with the catalyst. It is worthwhile to note that all the materials used for the production of PGTAC **1a** are very cheap, which would make these esterification reactions of high yield very competitive.

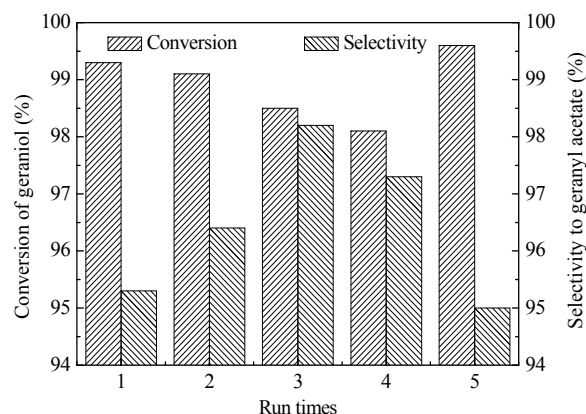
### 3.3. The recycle of PGTACs

It was exciting to find that the PGTACs are “reaction-induced self-separation catalysts” [3]. PGTAC **1a** has good solubility in alcohols whereas it is insoluble in esters. Hence, at the end of

**Table 3**  
Esterification of different terpenols catalyzed by **1a**.

Entry	Reactant	Temperature (°C)	Time (h)	Yield <sup>b</sup> (%)
1		50	3	95
2		50	6	85
3		50	4	>99
4		60	3	>99
5		50	3	>99
6		40	4	89
7		40	5	89
8		30	2	98
9		50	2	>99
10		50	2	>99
11		50	2	>99
12		50	2	98

Reaction conditions: alcohol (0.02 mol), acetic anhydride (0.02 mol), **1a** (0.4 mmol). <sup>a</sup> Determined by GC with *n*-butyl acetate as the internal standard.

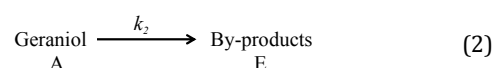
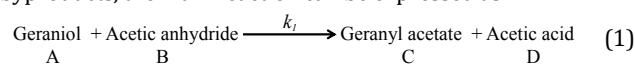


**Fig. 6.** Recycling of catalyst **1a** in the esterification of geraniol.

the reaction, a liquid-liquid biphasic system was formed and the heavy phase contained catalyst **1a**. The heavy phase can be used as catalyst directly without any treatment. The <sup>1</sup>H NMR of recycled **1a** showed that there was little anionic loss. After regeneration of **1a** by reacting with a small amount of acid at the fourth cycle, catalyst **1a** can be regenerated and reused for at least 5 cycles without significant loss of catalytic activity (Fig. 6).

### 3.4. Kinetics study of the esterification of geraniol with the use of PGTACs as catalyst

For future process design, the kinetics with PGTACs in the esterification of geraniol was also investigated. The kinetic study was carried out under the above conditions with the use of **1a** as catalyst. From the consideration of the generation of byproducts, the main reaction can be expressed as:



Here, a widely used pseudohomogeneous (PH) model [36,37] was used to describe the kinetics of the esterification of geraniol catalyzed by PGTACs **1a**. Combining reactions (1) and (2), we can express the rate equation of geranyl acetate, by-products and geraniol as:

$$\frac{dC_C}{dt} = k_1 C_A C_B \quad (3)$$

$$\frac{dC_E}{dt} = k_2 C_A \quad (4)$$

$$-dC_A/dt = k_1 C_A C_B + k_2 C_A \quad (5)$$

Using Eqs. (3)–(5), the reaction rate constants  $k_1$  and  $k_2$  can be estimated from the experiment data. The results are listed in Table 4. The values of  $k_1$  and  $k_2$  increased notably with the increasing temperature. In addition, the comparison of the experimental and calculated conversion of geraniol was also studied (Fig. 7). It illustrated that the PH model is a good kinetic model for the esterification of geraniol with PGTACs **1a** as catalyst.

The activation energy ( $E_a$ ) is also an important factor that determines the catalytic ability of the catalyst in the esterification of geraniol. From the reaction rate constants  $k_1$  and  $k_2$  at different temperatures,  $E_a$  and the pre-exponential factors can

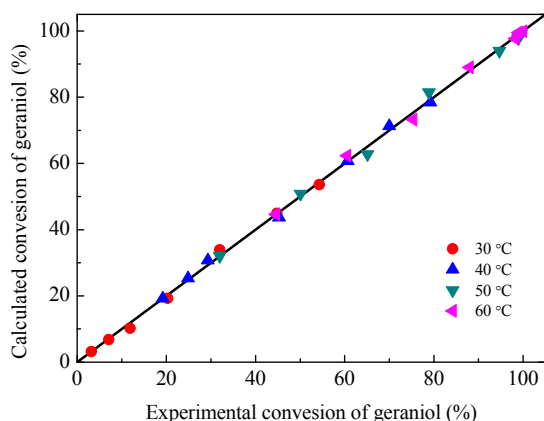


**Table 4**

Reaction rate constants at different temperatures.

Temperature (°C)	$k_1$ ( $10^3$ kL/(mol·min))	$k_2$ ( $10^3$ min $^{-1}$ )
30	68.7	3.5
40	197.9	6.1
50	986.4	29.0
60	1041.1	46.2

Reaction conditions: Catalyst used for the kinetic study was **1a**, catalyst loading was 2% (mol), molar ratio of geraniol to acetic anhydride was 1:1, and reaction time was 2 h.



**Fig. 7.** Comparison of the experimental and calculated conversion of geraniol at different temperatures.

be calculated using the Arrhenius law (Eq. (6)), written as Eq. (7). The linear fit between  $\ln k$  and  $1/T$  is shown in Fig. 8.

$$k = Ae^{-E_a/RT} \quad (6)$$

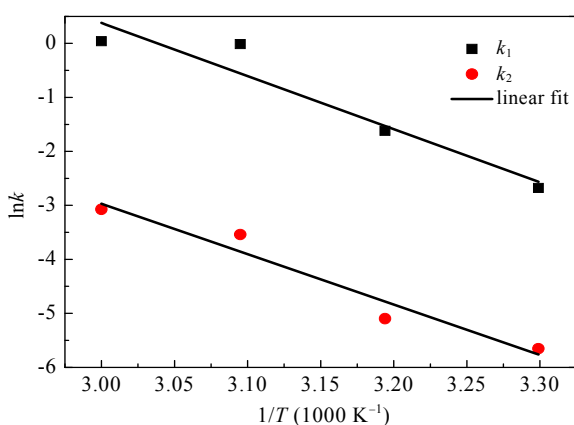
$$\ln k = \ln A - E_a/RT \quad (7)$$

The activation energies  $E_{a1}$  and  $E_{a2}$  and pre-exponential factors  $A_1$  and  $A_2$  were 72.36 and 79.68 kJ/mol, and  $2.23 \times 10^{11}$  and  $1.60 \times 10^{11}$ , respectively. The rate constants were written as:

$$k_1 = 2.23 \times 10^{11} \exp(-72.36 \times 10^3/RT) \quad (8)$$

$$k_2 = 1.60 \times 10^{11} \exp(-79.68 \times 10^3/RT) \quad (9)$$

The lower activation energy of the side reaction (Eq. (2)) than that of the primary reaction (Eq. (1)) implied that a low temperature is beneficial for the synthesis of geranyl acetate, while an elevated temperature can generate more byproducts.



**Fig. 8.** Arrhenius plots for the esterification of geraniol with acetic anhydride.

## 4. Conclusions

Reactions between acid and Phen in the mole ratio of 2:1 generated special proton-gradient-transfer acid complexes (PGTACs) where the two protons are not equivalent and have gradients in transfer ability, acidity, and reactivity. The PGTACs gave excellent catalytic activity and selectivity for esterification with a series of terpenols as substrate. The PGTACs are a good compromise between strong and weak acids from the aspect of activity. These PGTACs are “reaction-induced self-separation catalysts” and can be easily reused. The advantages of the PGTACs in catalytic activity, selectivity, separation, and price are attractive for use in the esterification reactions in industry.

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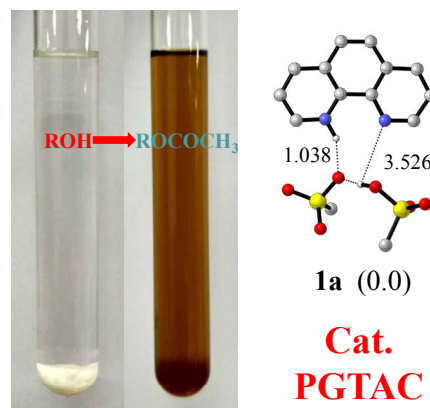
## Graphical Abstract

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**Proton-gradient-transfer acid complexes and their catalytic performance for the synthesis of geranyl acetate**

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The esterification of geraniol was catalyzed by PGTACs with nonequivalent protons. The PGTACs exhibited excellent catalytic activity and selectivity in the synthesis of geranyl acetate and were characterized as “reaction-induced self-separation catalysts”.



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