Mechanism of Friedel−Crafts Acylation Using Metal Triflate in Deep Eutectic Solvents: An Experimental and Computational Study

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ABSTRACT: In this paper, we develop a method for Friedel−Crafts acylation using metal triflate in deep eutectic solvents. Various metal triflates were tested and provided good to excellent yields of corresponding ketone products. The density functional theory calculation revealed the metal effects on the formation of active intermediate acylium triflate as well as the acidic condition. The metal triflate in the deep eutectic solvent can be recovered and reused with a little loss in the catalytic activity.

Rare-earth metal triflate catalyst

M: Ga, Tb, Nd, Eu, Ce, La, Pr, La, Dy, In, Ho
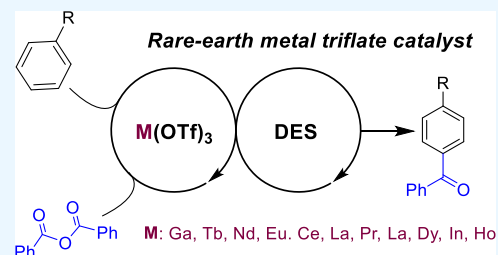
INTRODUCTION

Friedel−Crafts acylation reaction is one of the important reactions of synthetic aromatic ketones.[1,2] The common acylation reaction employs acyl chlorides, acid anhydrides, or carboxylic acids as acylating reagents in the presence of traditional catalysts including Lewis acids[3−6] (anhydrous $ZnCl_2$, $AlCl_3$, $FeCl_3$) or Brønsted acids[6−8] (concentrated sulfuric acid, hydrochloric acid), nanoparticles,[9−11] ionic liquids,[12−14] metal triflates,[15,16] mesoporous zeolite,[17] nitrogen-doped carbon,[18,19] metal oxides,[20] heteropoly acids,[21,22] and solid superacids.[23] Besides, several effective methods were applied to the Friedel−Crafts acylation reaction, including flow chemistry,[24] ultrasound activation,[15] and microwave irradiation.[25]

Metal triflates, water-compatible Lewis acids, have increased interest in organic synthesis.[26−30] Metal triflates are considered green catalysts for alternative traditional Lewis acids due to their strong Lewis acidity and high tolerance toward water.[31−35] Metal triflates can be used with organic solvents or water, and they are easily recycled without a decrease in catalytic activity.[36−38] Metal triflate has been known as an effective catalyst for Friedel−Craft transformation in the past 2 decades.[36,39−41] While there is the conventional understanding that Lewis acid is a stoichiometric requirement for the reaction and metal cation can fill this role, triflate anion also is crucial.[42−44] Currently, our theory study highlights that triflate helps stabilize the acylium and accommodate kinetic accessible pathways in the C−C bond formation process.[45] However, the details of how this species is formed under the support of Lewis acid are still unexplored, especially when extending the list to rare-earth metals. To get more insights into the chemical transformation, a density functional theory (DFT) calculation also is performed.

Deep eutectic solvents (DESs) have received attention in various applications due to their distinctive properties.[46−48] DESs have been designed by a suitable combination of quaternary ammonium salts (*e.g.,* choline chloride, imidazolium chloride) with hydrogen bond donors (HBDs).[49−51] Choline chloride has widely been used as an organic salt to produce eutectic mixtures due to its low cost, biodegradability, and low toxicity.[52] HBDs are urea, ethylene glycol, glycerol, carbohydrates, carboxylic acids, and amino acids.[53] Owing to their low cost and low toxicity, DESs have been prepared and employed as green reaction media for organic synthesis.[54−56]

As part of our ongoing interest in applying green chemistry in organic synthesis, we disclose here the Friedel−Crafts acylation reaction using metal triflates in a DES. The method provided a powerful tool for the synthesis of aromatic ketones with high yields and short reaction times. The metal triflate in DES can be recovered and reused with a little loss of catalytic activity. The mechanism was proposed by combining experiments with DFT calculations.

RESULTS AND DISCUSSION

Synthesis of DES. DESs were synthesized according to previously reported literature.[57−59] In this paper, DESs were synthesized by heating a mixture of choline chloride and HBDs (3-phenylpropionic acid, urea, pyrrole, imidazole, or indole) at 100 °C for a short reaction time (Table 1). DESs were
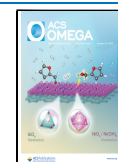
Table 1. Preparation of DESs from Choline Chloride and Various HBDs at 100 °C

entry	HBDs	time (min)	yield (%)
DES I	3-phenylpropionic acid	25	95
DES II	urea	30	97
DES III	pyrrole	30	98
DES IV	imidazole	25	96
DES V	indole	25	97
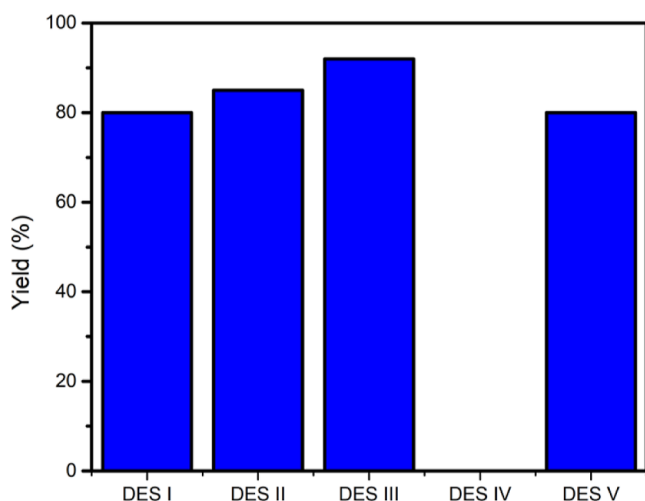
**Figure 1.** Effect of DESs in the acylation of anisole.

prepared in high yields and used for the reaction without further purification.

Optimization of Reaction Conditions. The influence of DESs on the yield of the Friedel−Crafts benzoylation was tested by the reaction of anisole and benzoic anhydride at 100 °C for 10 min under microwave irradiation. Among these DESs, DES III provided the highest yield and was chosen as a reaction medium to optimize Friedel−Crafts benzoylation (Figure 1).

The benzoylation of anisole and benzoic anhydride (Bz_2O) was chosen as a model reaction with 0.1 g of DES III and 5 mol % metal triflates (Table 2). The influence of metal triflate (5 mol %) catalyst was studied under microwave irradiation at 100 °C for 10 min. All of them gave good yields (>75%) with high regioselectivity in the para position (Table 2, entries 1−10). The best result was obtained with $Pr(OTf)_3$. The reaction did not occur when the reaction was carried out in the absence of the catalyst (entry 11, Table 2). Next, the amount of $Pr(OTf)_3$ (from 1 to 10 mol %) was also investigated under the same reaction conditions (Table 2, entries 7 and 12−15), and 5 mol % of $Pr(OTf)_3$ was chosen for further studies. Similarly, the reaction temperature was tested with high yield and conversion (Table 2, entries 7 and 16−18). Besides, conventional heating and ultrasound irradiation were also tested in the present method and provided lower yields and longer reaction times than microwave irradiation (Table 2, entries 19 and 20).

Next, we investigated the effect of anhydride reagents in the Friedel−Crafts acylation under optimized conditions. All the tested acid anhydrides, including acetic anhydride, propionic anhydride, and butyric anhydride, afforded the desired products in high yields under microwave irradiation at 100 °C for 10 min (Scheme 1). The C3-acylation of indole and anhydride was carried out under similar conditions. Different anhydride acids were investigated, and the desired products were obtained in good yield with high selectivity to C3-position (Scheme 2).
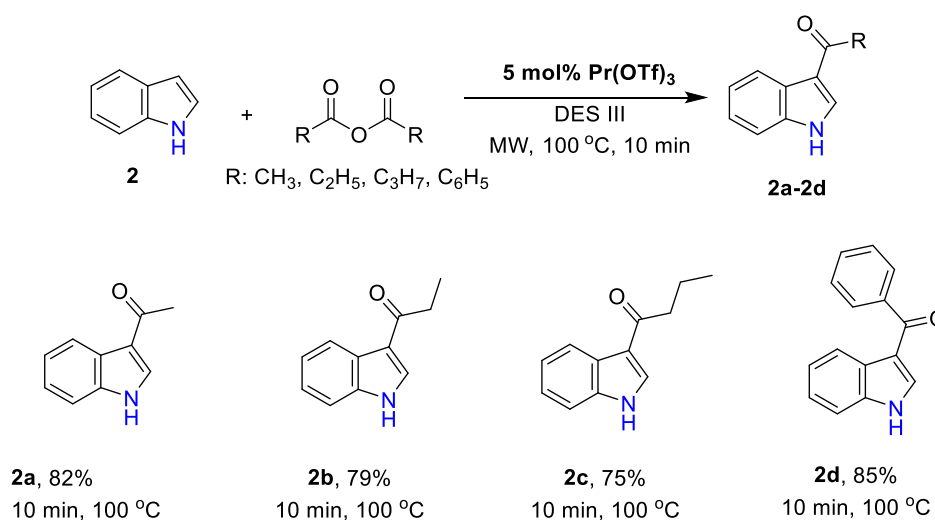
Table 2. Optimization of Reaction Conditions
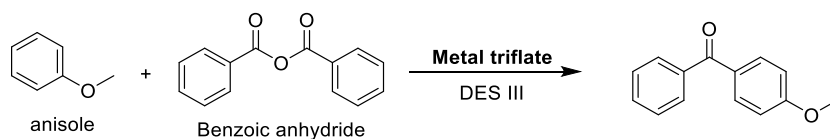
entry	catalyst (mol %)	temperature (°C)	time (min)	method	yield (%)
1	Ga(OTf)₃ (5)	100	10	MW	80
2	Nd(OTf)₃ (5)	100	10	MW	78
3	Eu(OTf)₃ (5)	100	10	MW	81
4	Ce(OTf)₃ (5)	100	10	MW	78
5	Tb(OTf)₃ (5)	100	10	MW	80
6	La(OTf)₃ (5)	100	10	MW	79
7	**Pr(OTf)₃ (5)**	**100**	**10**	**MW**	**92**
8	Dy(OTf)₃ (5)	100	10	MW	77
9	In(OTf)₃ (5)	100	10	MW	84
10	Ho(OTf)₃ (5)	100	10	MW	75
11	no catalyst	100	10	MW	0
12	Pr(OTf)₃ (1)	100	10	MW	70
13	Pr(OTf)₃ (3)	100	10	MW	80
14	Pr(OTf)₃ (7)	100	10	MW	92
15	Pr(OTf)₃ (10)	100	10	MW	93
16	Pr(OTf)₃ (5)	60	10	MW	79
17	Pr(OTf)₃ (5)	80	10	MW	82
18	Pr(OTf)₃ (5)	120	10	MW	85
19	Pr(OTf)₃ (5)	100	240	heating	85
20	Pr(OTf)₃ (5)	80	120	ultrasound	89

Scheme 1. Effect of Anhydride Acids in the Acylation of Anisole

1a, 80%
10 min, 100 °C

1b, 85%
10 min, 100 °C

1c, 92%
10 min, 100 °C

1d, 92%
10 min, 100 °C
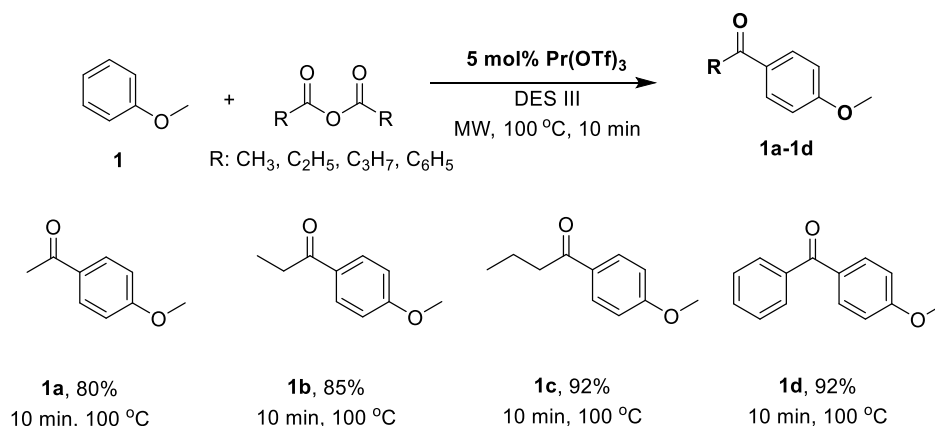
Scheme 2. Effect of Anhydride Reagents in Indole Acylation

2a, 82%
10 min, 100 °C

2b, 79%
10 min, 100 °C

2c, 75%
10 min, 100 °C

2d, 85%
10 min, 100 °C

Scheme 3. Synthesis of Some Aromatic Ketones under the Current Method

3d, 87%
10 min, 100 °C

4d, 73%
20 min, 100 °C

5d, 85%
15 min, 120 °C

6d, 89%
15 min, 120 °C

7d, 92%
20 min, 140 °C
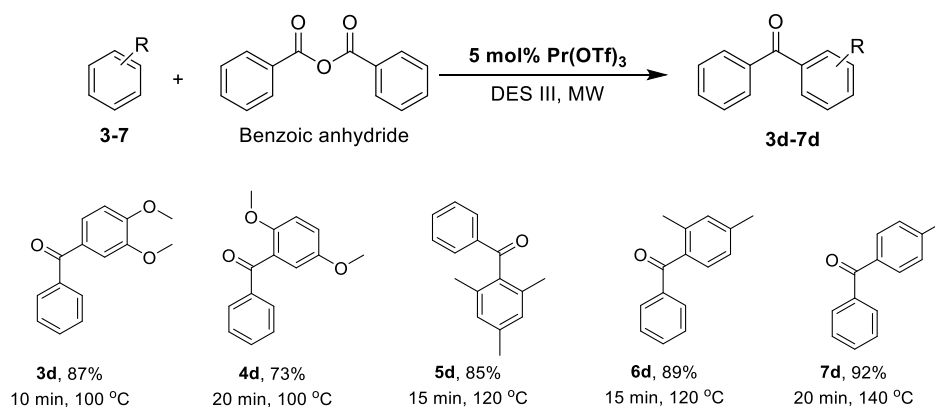
In addition, the effects of different arenes with electron-donating groups were tested with benzoic anhydride as the benzoylation agent (Scheme 3). 1,2-Dimethoxybenzene, 1,4-dimethoxybenzene, mesitylene, 1,3-dimethylbenzene, and toluene were reactive under the current method, and the desired products were obtained in good yields. 1,4-Dimethoxybenzene provided the desired product in a lower yield than the others, presumably due to the steric effect.

The recyclability of $Pr(OTf)_3$ in DES III was tested in the acylation of anisole and indole under microwave irradiation. Remarkably, after recycling for three cycles, yields of desired products were obtained with a slight decrease in yields after each cycle (Figure 2), presumably due to the loss of the catalyst in the recovery procedure.

It is important to compare the current work with the previous literature in the acylation of anisole using acidic catalysis. A comparative study of the present method with the
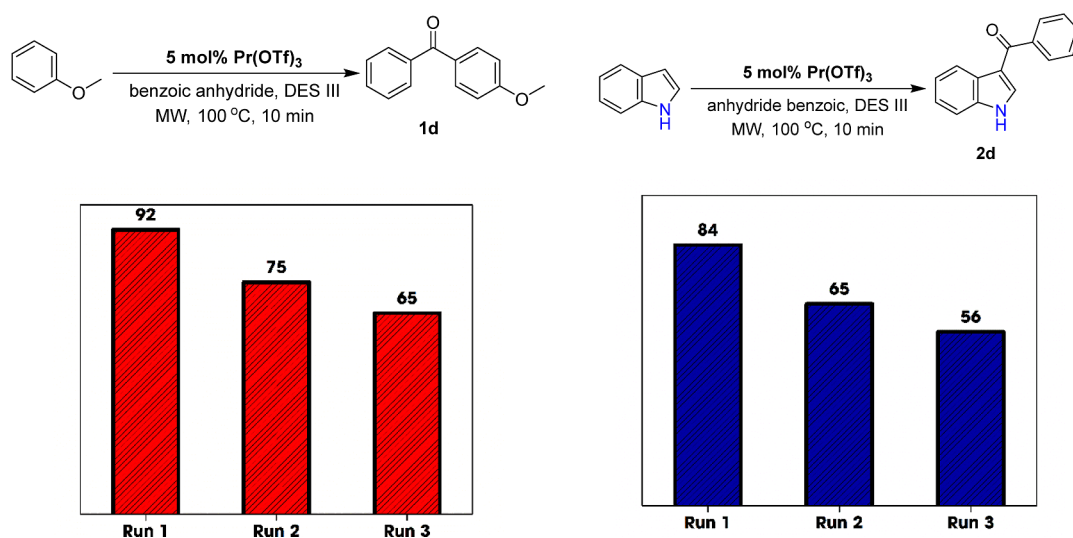
Figure 2. Recycling of Pr(OTf)$_3$ in DES III.

Table 3. Comparison of Current Work with the Previous Literature

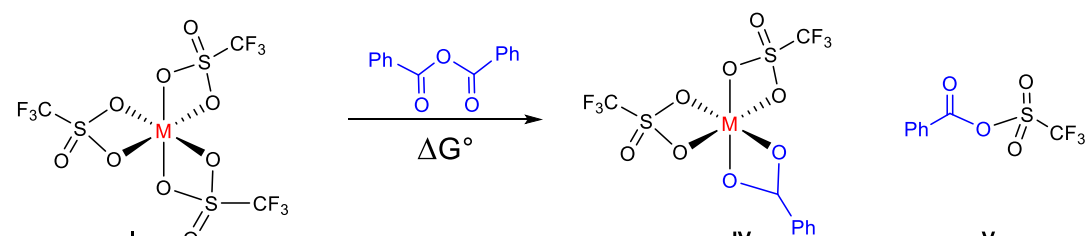| entry	substrate	reactant	catalyst/solvent	temp/time	yields (%)
1	anisole	(PhCO)$_2$O	Cu(OTf)$_2$/[bmim]BF$_4$	80 °C/overnight	46[16]
2	anisole	Ac$_2$O	Cu(OTf)$_2$/[bmim]BF$_4$	80 °C/overnight	48[16]
3	anisole	(C$_2$H$_5$CO)$_2$O	Cu(OTf)$_2$/[bmim]BF$_4$	80 °C/overnight	55[16]
4	anisole	(PhCO)$_2$O	H-USY-29/[C$_2$mim][NTf$_2$]	80 °C/120 min	<60[60]
5	anisole	Ac$_2$O	20% IL/MIL-101 (5 mol %)	80 °C/1 h	78.9[61]
6	anisole	Ac$_2$O	Pr(OTf)$_3$/[cholineCl][pyrrole]	100 °C/10 min	80 (this work)
7	anisole	(PhCO)$_2$O	Pr(OTf)$_3$/[cholineCl]$_3$[pyrrole]$_7$	100 °C/10 min	80 (this work)
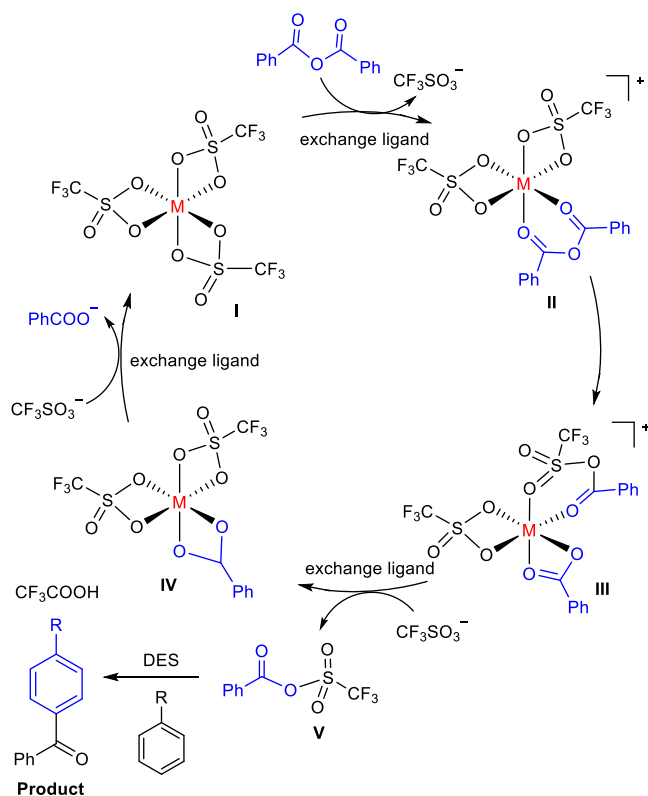
Figure 3. Proposed acylation mechanism by rare-earth triflate catalysts.

previous literature is shown in Table 3. The present catalytic system was found to be useful for the acylation of anisole, affording the corresponding products with shorter reaction times and higher yields.

Mechanistic Discussion: A Computational Study. The proposed mechanism undergoes two main processes: generation of electrophile intermediate **V** catalyzed by metal triflate complexes (from **I** to **V**) and the electrophilic substituent S$_E$Ar (from **V** to the final product) (Figure 3).

Only the former pathway shows the influences of different metals and will be focused on. On the proposed catalytic cycle, **I** to **IV**, first, the octahedral catalyst **I** undergoes the ligand-exchange process with acid anhydride reagent and produces complex **II**. Connecting to the same center with triflate allows anhydride and triflate ligands have proper proximity to proceed with the C−O bond formation. This step generates the key intermediate **V** but at this time is still bound to the metal center. An equivalent of triflate anion occupies the same position as **V** in the next step (**III** to **IV**), and as a result, the electrophile is released. Table 4 shows that with all metals, there is the exothermic process of the first part mechanism. However, directly comparing the energy value could be problematic because of the difference in spin states of the metallic series.

In the second part, the Friedel−Craft reaction catalyzed by DES can occur following the reported mechanism.[45] Complex **IV** undergoes another ligand-exchange process with one more equivalent of triflate to regenerate the catalyst. Due to the exchange ligand steps being mainly contributed by dynamic behavior,[62] the kinetics of the reaction is not determined. On the other hand, the rate-determining step is expected to locate

Table 4. Thermodynamics of the Catalytic Process Generating Active Species V[a]

metal triflate	Eu(OTf)$_3$	Ce(OTf)$_3$	Dy(OTf)$_3$	In(OTf)$_3$	La(OTf)$_3$	Nd(OTf)$_3$	Tb(OTf)$_3$	Pr(OTf)$_3$
ΔG°	−38.4	−28.1	−16.6	−30.5	−21.7	−24.1	−23.9	−23.7

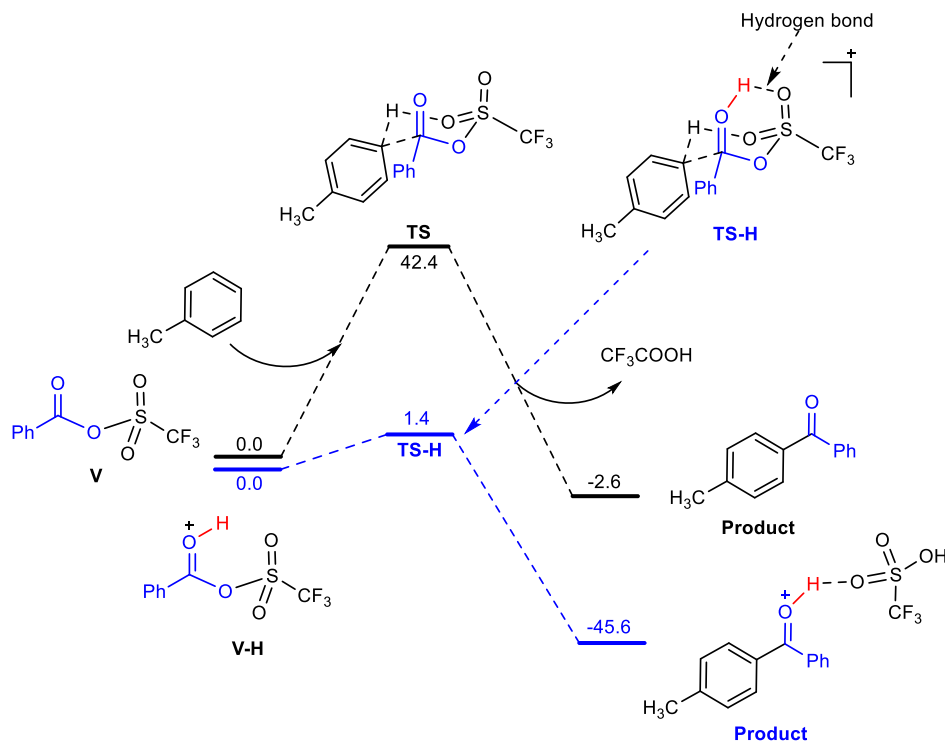[a]Gibbs free energies are in kcal/mol.

Figure 4. Potential energy surface for acylation. Gibbs free energies are given in kcal/mol.

in the chemical transformation from **V** to the product. The potential energy surface of this transformation reveals the important role of the acid environment in reaction kinetics. The energy demand for the C−C bond formation step connected directly from compound **V** is very high 42.4 kcal/mol. However, while protonated, not only does the electrophile of the carbonyl increase but also the transition state at this time **TS-H** is also stabilized by the intramolecular hydrogen bond (Figure 4). As a result, the energy barrier of the protonated pathway is brought down to only 1.4 kcal/mol, leading to the reaction occurring much easier.

■ EXPERIMENTAL SECTION

Synthesis of DES. A round-bottomed flask (5 mL volume) was charged with choline chloride (6.0 mmol, 0.834 g) and 3-phenylpropionic acid (6.0 mmol, 0.900 g); then it was placed in an oil bath and heated at 100 °C in a magnetic stirrer until forming a homogeneous liquid. After finishing, the reaction mixture was cooled down to room temperature and then washed with diethyl ether (3 × 5 mL) to give the purified DESs. Similar procedures were carried out for the preparation

of the choline chloride−urea (DES II), choline chloride−pyrrole (DES III), choline chloride−imidazole (DES IV), and choline chloride−indole (DES V) at the molar ratios of 1:2, 3:7, 3:7, and 3:7, respectively.

General Procedures for Friedel−Crafts Acylation. Anisole (1 mmol, 0.108 g), benzoic anhydride (1 mmol, 0.226 g), metal triflates (0.01 equiv), and DESs (0.1 g) were added into a 10 mL pressurized glass tube with a Teflon-coated septum equipped with a magnetic stirrer. The tube was capped and placed into a CEM microwave at 100 °C for 10 min. After cooling, the mixture was extracted with diethyl ether (3 × 15 mL). The organic layer was then decanted, washed with aqueous NaHCO$_3$ (2 × 10 mL) and water (10 mL), and dried with anhydrous Na$_2$SO$_4$. The diethyl ether solvent was then recovered using a rotary evaporator. The yield and selectivity of products were determined by gas chromatography using naphthalene as an internal standard. All products were known compounds and were identified by comparing their mass spectra with the GC−MS spectral library (NIST14.L library).

General Procedure for the Recovery of DES. After completion of the reaction, DES was washed with diethyl ether

(10 × 5 mL) to extract both the starting materials and products completely. DES was then dried in ovens at 80 °C for 1 h and was reused for the next run.

Computational Study. All reported geometries were fully optimized utilizing the Gaussian 16[63] implementation of the B3LYP[64,65] functional with def-SVP basis set.[66,67] TSs were located by a combination of direct TS and quadratic synchronous transit QST3 techniques, followed by confirmation of minimums which along with atomic displacements along the imaginary modes ensure that located TSs connect to corresponding minima.

CONCLUSIONS

In conclusion, we have improved the Friedel−Crafts acylation of aromatic compounds with acid anhydrides under microwave irradiation. The metal triflates in DESs were found to enhance the yields of desired products. The catalytic system could be recycled in three cycles with a little loss of activity promising for large-scale applications. The prominent feature of the current work is the combination of experimental and computational studies. This research has provided a proposed mechanism for Friedel−Crafts acylation through two main processes, including electrophile generation and S_EAr reaction. The most energetic demand is C−C bond formation, and acidic conditions accommodate the accessible kinetic barrier *via* hydrogen bonds.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03944.

Optimized geometries, electronic energies, ^1H and ^{13}C NMR, and HRMS of products (PDF)

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Author Contributions

M.-T.T.N., N.L., and H.T.N. contributed equally. M.-T.T.N. and H.T.N. carried out the experiments. N.L., N.-N.P.-T., T.D.V.L., V.K.T.N., and Y.K. calculated the reaction mechanism and analyzed the data. P.H.T., N.L., H.T.N., and N.-N.P.-T. prepared the figures and wrote the paper. All authors have seen the manuscript and approved the submission.

Notes

The authors declare no competing financial interest.

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