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The immobilized $NaHSO_4 \cdot H_2O$ on activated charcoal: a highly efficient promoter system for *N*-formylation of amines with ethyl formate

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The immobilized $NaHSO_4 \cdot H_2O$ on activated charcoal was used as a highly efficient promoter system for facile *N*-formylation of amines with ethyl formate. All reactions were carried out in refluxing ethyl formate (54 ºC) under mild conditions within 10-100 min to afford the product formamides in high to excellent yields (80-94%).

1. Introduction

The protection of amines by the formation of formamides is one of the most important and widely used transformations in organic chemistry.[1] Formamides as important class of amine derivatives have been used widely in the synthesis of pharmaceutically valuable compounds such as fluoroquinolines,[2] 1-arylimidazole-5-carboxylates,[3] 1-formyl-1,2-dihydroquinolines[4] nitrogen bridged heterocyles,[5] oxazilidones,[6] cancer chemotherapeutic agents,[7] fungicides,[3,8] preparation of isocyanates,[9] foramidines,[10] and nitriles,[11] the Vilsmeier-Haake formylation reaction,[12] allylation[13] and hydrosilylation[14] of carbonyl compounds. Due to wide synthetic and biological applications of formamides, a number of methods and reagents such as Cl_3CCHO,[15] $CH(OEt)_3$,[16] $NaOEt/CHCl_3$,[17] HCO_2NH_4,[18] HCO_2NH_4/nano Fe_3O_4/PEG-400,[19] 2,2,2-trifluoroethyl formate,[20] phenyl formate,[21] pentafluorophenyl formate,[22] acetic formic anhydride,[23] and $KF\text{-}Al_2O_3/CHCl_3$,[24] formic acid in the presence of HCO_2Na,[25] $NH_2OH \cdot HCl$,[26] I_2,[27] DCC,[28] EDCI,[29] $ZnCl_2$,[30] In,[31] ZnO,[32] TiO_2-P25 (TiO_2-SO_4^{2-})[33] nanoceria,[34] Zr-MCM-41,[35] $NiFe_2O_4$@SiO_2-PPA,[36] γ-Fe_2O_3@HAp-SO_3H,[37] $WO_4(SO_3H)_2$,[38] Fe(III)-exchanged sepiolite,[39] 2-chloro-4,6-dimethoxy-1,3,5-triazine,[40] melamine trisulfonic acid,[41] thiamine hydrochloride,[42] TBD-based ionic liquids,[43] Brønsted acidic ionic liquid (RHA-

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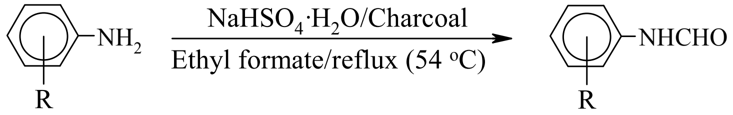
[pmim]HSO_4)[44] PEG-400,[45] $HClO_4/SiO_2$,[46] silica sulfuric acid,[47] hafnium(IV) bis(perfluorooctane-sulfonyl)imide complex supported on fluorous silica gel,[48] ultrasound,[49] ultrasound/[bmim]BF_4,[50] and ultrasound/nano CeO_2,[51] ethyl formate in the presence of 2-(sulfooxy)propane-1,2,3-tricarboxylic acid/SiO_2,[52] silphos [$PCl_{3-n}(SiO_2)_n$],[53] and microwave/disulfonamides polymers[54] have been reported for the formylation of various primary and secondary aromatic/aliphatic amines. In this context, some protocols did not use any catalysts/promoters, and the formylation reactions were carried out under particular conditions.[55,56] Recently, *N*-formylation of amines has been extensively reviewed by Gerack *et al.*[57]

Many of these methods suffer from various drawbacks such as using expensive or toxic formylating reagents/catalysts, acidic reaction conditions, organic solvents, the excess amounts of formic acid, high reaction temperature, prolonged reaction times and removal of by-products. Therefore, there is a need to develop a better catalyst or conditions for synthesis of formamides in terms of operational simplicity and economical viability. Herein, we wish to introduce the immobilized $NaHSO_4 \cdot H_2O$ on activated charcoal as an efficient promoter system for facile *N*-formylation of various amines in refluxing ethyl formate (54 °C) under net conditions (Scheme 1).



Scheme 1. *N*-formylation of amines with $NaHSO_4 \cdot H_2O$/activated charcoal system

2. Results and Discussion

Hydrated sodium hydrogen sulfate, $NaHSO_4 \cdot H_2O$, as a cheap and mineral weak acidic reagent, has been found to have some useful applications in organic synthesis.[58] In this context, using $NaHSO_4 \cdot H_2O$ as an efficient promoter has been successfully used by our research group for the Biginelli synthesis of 3,4-dihydropyrimidin-2(*1H*)-ones[59,60] and facile reduction of carbonyl compounds with $NaBH_4$.[61] In line with the outlined strategies for *N*-formylation of amines, we found that this transformation in the presence of hydrated sodium hydrogen sulfate has not been investigated yet. Therefore, this subject and our research interest to prepare formamides as a key intermediate, encouraged us to investigate the influence of $NaHSO_4 \cdot H_2O$ on the titled transforma-tions.

N-formylation of amines was primarily examined by the reaction of aniline with ethyl formate as a non-acidic formylating agent in the absence and presence of $NaHSO_4 \cdot H_2O$. The results of this investigation are summarized in Table 1. Entries 1 and 2 show that the formylation of aniline in the absence of hydrated sodium hydrogen sulfate did not any take place, and the reaction with a molar ratio of aniline:$NaHSO_4 \cdot H_2O$ (1:0.1) in refluxing ethyl formate (2 mL) encountered with low efficiency (40%). This result exhibited that though hydrated sodium hydrogen sulfate affected the rate of formylation reaction, however, the influence was not sufficient and therefore completion of the reaction required to an additional co-catalyst.

Nowadays, activated charcoal, because of its high degree of micro-porosity (just one gram of activated carbon has a surface area in excess of 500-1500 m^2 being readily achievable) provides a high surface area and this situation makes it more desirable for academic and industrial applications.[62-64] In this context, we decided to incorporate the weak acidic character of $NaHSO_4 \cdot H_2O$ and micro-porosity of activated charcoal with together, and so using them as an efficient promoter system in *N*-formylation of aniline by ethyl formate. The incorporation of hydrated sodium hydrogen sulfate with activated charcoal was carried out by mixing some mass ratio of $NaHSO_4 \cdot H_2O$ and activated charcoal in water and then evaporation of the solvent in a microwave oven to afford different composition percentage of the immobilized $NaHSO_4 \cdot H_2O$ on activated charcoal. The influence of the obtained immobilized systems was then studied in *N*- formylation of aniline (1 mmol) with ethyl formate (2 mL) (entries 4-7). Among the examined systems, the immobilization of 0.2 g $NaHSO_4 \cdot H_2O$ on 0.1 g activated charcoal shows a dramatic acceleration leading to complete the reaction within 25 min. Therefore, the conditions mentioned in entry 7 were selected as the optimum conditions.

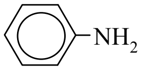
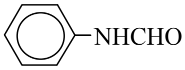
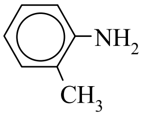
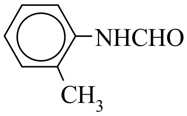
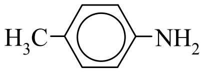
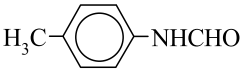
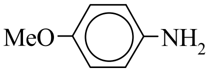
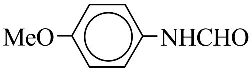
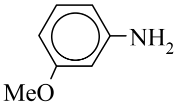
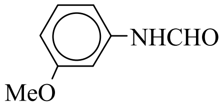
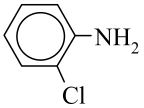
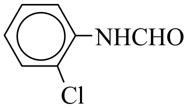
Table 1. Optimization experiments for *N*-formylation of aniline with ethyl formate in the presence of $NaHSO_4 \cdot H_2O$/activated charcoal system[a]

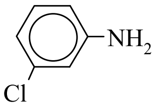
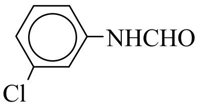
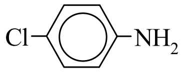
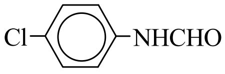
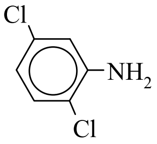
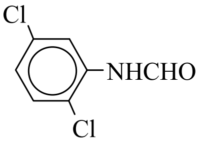
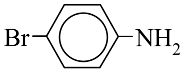
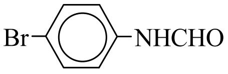
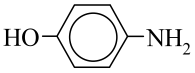
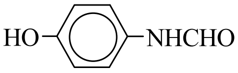
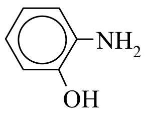
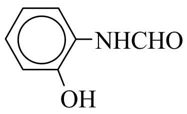
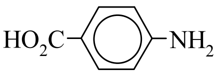
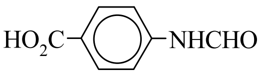
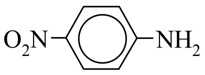
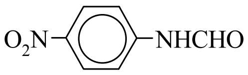
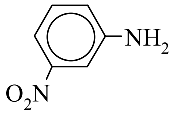
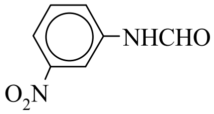
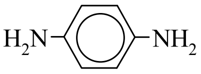
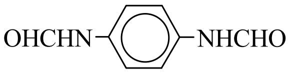
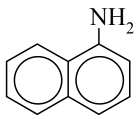
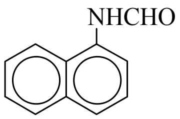
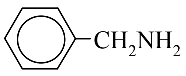
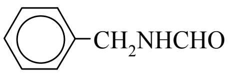
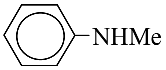
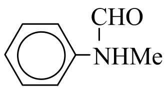
Entry	Charcoal (g)	$NaHSO_4 \cdot H_2O$ (g)	Condition	Time (min)	Conv. (%)
1	-	-	reflux	360	0
2	-	0.1	reflux	360	40
3	0.1	-	reflux	360	30
4	0.05	0.05	reflux	120	70
5	0.1	0.05	reflux	120	75
6	0.1	0.1	reflux	30	85
7	0.1	0.2	reflux	25	100

[a] All reactions were carried out with 1 mmol of aniline in ethyl formate (2 mL).

Encouraged by the result, the capability of this synthetic protocol was more studied with the reaction of various aromatic primary amines containing electron-releasing or withdrawing groups with ethyl formate at the optimized reactions conditions. Table 2 shows the general trend and versatility of this synthetic method. As seen, all reactions were carried out successfully in the presence of the immobilized $NaHSO_4 \cdot H_2O$ (0.2 g) on activated charcoal (0.1 g) within 10-55 min to afford the products formamides in high yields (80-94%). The table also shows that the effect of substitutions on aromatic rings is noteworthy. Electron-releasing groups accelerated the rate of formylation reaction and in contrast withdrawing substitutions prolonged the reaction times through the deactivation of aromatic rings. Entries 11 and 12 also show that the current protocol is only useful for *N*-formylation of aromatic primary amines, and in the case of 2- and 4-aminophenols, *O*-formylation of phenolic substitution did not any take place. This means that the chemoselective *N*-formylation of aromatic primary amines can be successfully carried out in the presence of phenolic substitutions. More examination also resulted that in the case of aromatic secondary and aliphatic amines such as *N*-methylaniline and benzylamine, this protocol was also efficient and produced the corresponding formamides in 85-91% yields (Table 2, entries 18 and 19).

Table 2. *N*-formylation of amines with ethyl formate in the presence of $NaHSO_4 \cdot H_2O$/activated charcoal system[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]	m.p. (°C)	ref.
1			25	92	46-48	48
2			19	88	60-62	48
3			18	91	52-54	48
4			12	90	81-82	19
5			10	93	55-57	65
6			32	92	77-80	48

7			35	94	56-57	65
8			40	92	100-102	48
9			45	90	149-151	48
10			33	89	118-120	48
11			37	87	135-137	19
12			30	91	129-131	19
13			55	90	256-258	44
14			50	93	194-195	48
15			45	90	134-135	65
16			30	80	210-212	44
17			31	94	136-138	44
18			45	91	60-62	48
19			100	85	123-124	19

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[a] All reactions were carried out with 1 mmol of amines in the presence of $NaHSO_4 \cdot H_2O$/activated charcoal (0.2 g : 0.1 g) system in refluxing ethyl formate (2 mL). [b] Yields refer to isolated pure products.

The usefulness and capability of $NaHSO_4 \cdot H_2O$/activated charcoal system in *N*-formylation of amines was highlighted by a comparison of the obtained results for aniline with other reported reagents (Table 3). A case study shows that in viewpoints of availability and cheapness of the reagents, non-acidic character of formylating agent, mild reaction conditions and easy work-up procedure, the current protocol shows a more or comparable efficiency towards the other reagents. Although the exact mechanism of this synthetic method is not clear, however, we think that the weak acidic character of $NaHSO_4 \cdot H_2O$ activates the ethyl formate for nucleophilic attack of amines. In addition, the microporosity of activated charcoal provides the excess and more efficient pores or surfaces for better interaction of amines, ethyl formate and $NaHSO_4 \cdot H_2O$.

Table 3. Comparison of *N*-formylation of aniline with $NaHSO_4\cdot H_2O$/activated charcoal system and other reported reagents

Entry	Catalyst	Mol%	Conditions	Time (min)	Yield (%)	ref.
1	$NaHSO_4\cdot H_2O$/activated charcoal	0.014	C_2H_5OCHO/reflux (54 ºC)	25	92	a
2	$ZnCl_2$	10	HCO_2H/70 ºC	10	96	30
3	TiO_2-P25	0.1 g	HCO_2H/r.t.	45	99	33
4	γ-Fe_2O_3@ Hap-SO_3H	0.9	HCO_2H/r.t.	20	97	37
5	SiO_2-$HClO_4$	2.5	HCO_2H/r.t.	15	96	46
6	2-(sulfooxy)propane-1,2,3-tricarboxylic acid/SiO_2	0.13 g	C_2H_5OCHO/r.t.	7.5 h	90	52
7	Silphos $[PCl_{3-n}(SiO_2)_n]$	1 g	C_2H_5OCHO/r.t	75	92	53

[a]Current protocol.

3. Conclusions

In summary, we have shown that $NaHSO_4\cdot H_2O$/activated charcoal system can be used as an efficient promoter system for *N*-formylation of various amines with ethyl formate. All reactions were carried out successfully using the immobilized $NaHSO_4\cdot H_2O$ (0.2 g) on activated charcoal (0.1 g) per 1 mmol of amines within 10-100 min. The product formamides were obtained in 80-94% yields. The cheapness and availability of the reagents, high yields and easy work-up procedure as well as the benefits of neat reaction conditions are the advantages which make this protocol a synthetically useful addition to the present methodologies.

Acknowledgements

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Experimental

General

All reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. Activated charcoal was obtained from Merck Company (Art No 102186). ^1H and ^{13}C NMR spectra were recorded on 300 MHz Bruker spectrometer. All chemical shifts were measured with reference to TMS ($\delta = 0.00$ ppm). FT-IR spectra were recorded on Thermo Nicolet Nexus 670 spectrophotometer using the KBr-pellet technique. All products are known and were characterized by their ^1H, ^{13}C NMR and FT-IR spectra followed by comparison with authentic data. TLC was applied for the purity determination of the substrates, products and the reaction monitoring over silica gel 60 F254 aluminum sheet.

Preparation of the immobilized $NaHSO_4\cdot H_2O$ on activated charcoal

In a round-bottomed flask, a solution of $NaHSO_4\cdot H_2O$ (0.2 g) in distilled water (2 mL) was prepared. Next, activated charcoal (0.1 g) was added and the mixture was stirred vigorously for 15 min at room temperature. The solvent was then evaporated by microwave irradiation (500 W) to afford the immobilized $NaHSO_4\cdot H_2O$ on activated charcoal (0.3 g).

A typical procedure for *N*-formylation of amines with ethyl formate in the presence of $NaHSO_4\cdot H_2O$/activated charcoal system

In a round-bottomed flask (5 mL) equipped with a magnetic stirrer and condenser, a solution of aniline (1 mmol, 0.093 g) in ethyl formate (2 mL, 0.025 mol) was prepared. $NaHSO_4\cdot H_2O$/activated charcoal (0.3 g) was then added and the reaction mixture was stirred under reflux conditions (54 ºC) for 25 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was passed through a short column of silica gel (200-400 mesh) and the eluted solvent was then evaporated under reduced pressure to afford the pure *N*-phenyl formamide in 92% yield (0.111 g, Table 2, entry 1).

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