Activated charcoal: a highly efficient promoter for selective oxidation of alcohols to aldehydes and ketones by K$_2$S$_2$O$_8$ at solvent–free conditions

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C H R O N I C L E	A B S T R A C T
	Selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones was achieved efficiently using K$_2$S$_2$O$_8$/activated charcoal system. All reactions were carried out at solvent–free conditions (40–45 ºC) within 15–60 min to give the products in high to excellent yields.

1. Introduction

The selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is an important and pivotal reaction in organic synthesis [1-4]. Pyridinium chlorochromate [5], Pr$_4$NRuO$_4$[6], BaMnO$_4$[7,8], KMnO$_4$/kieselguhr[9], MnO$_2$[10-12], MnO$_2$/kieselguhr[13], DMSO/CO$_2$Cl$_2$[14], DMSO/DCC[15], DMSO·SO$_3$·Pyr [16], Ag$_2$CO$_3$/celite[17,18], Dess–Martin periodinate[19], *o*-iodobenzoic acid (IBX) [20,21], I$_2$/Li$_2$CO$_3$/[bmim]BF$_4$[22], TsNBr$_2$[23], CeO$_2$/RuCl$_3$·H$_2$O[24], H$_2$O$_2$/hexamolybdochromate(III)[25], air/ruthenium cluster[26], air/copper–bisisoquinoline[27], air/ruthenium/TEMPO[28], and polymer–bound Co–oxidants in the presence of TEMPO catalyst [29] are some of the oxidants which have been utilized for such transformation. However, most of the mentioned protocols suffer from several drawbacks in terms of harsh reaction conditions, use of expensive volatile organic solvents, high cost, instability, high toxicity and operational difficulty.
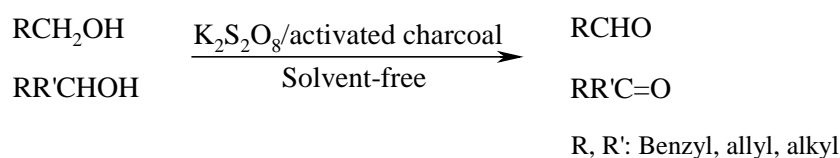
Recently, persulfate (S$_2$O$_8$$^{2-}$) as an alternative oxidant has achieved increasing attention in the oxidation of environmental contaminants [30-40]. Use of persulfate has several advantages. It is a strong

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oxidizing agent and stable at room temperature. Heat, transition metal ions and UV radiation can excite persulfate to sulfate anion−radical ($SO_4^{-\bullet}$) and this species significantly enhances the oxidation potential of persulfate [41-43]. In spite of this potentiality, the capability of persulfate for oxidation of alcohols is low. Therefore, such transformation with persulfate was rarely documented. The literature review shows that selective oxidation of alcohols to carbonyl compounds has been achieved by $K_2S_2O_8$ in a Brönsted ionic liquid ([Hmim]−CH_3SO_3)[44]. Though the method produces aldehydes and ketones selectively in moderate to high yields, however, using expensive ionic liquid as a solvent puts some restrictions to use this protocol for any practical applications.

In line of the outlined strategies and our ongoing attention to explore the synthetic applications of persulfate, herein, we wish to introduce activated charcoal as a highly efficient promoter for selective and efficient oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones with $K_2S_2O_8$ at solvent−free conditions (Scheme 1).

$$RCH_2OH \qquad \xrightarrow[\text{Solvent-free}]{K_2S_2O_8/\text{activated charcoal}} \qquad RCHO$$

$$RR'CHOH \qquad\qquad\qquad\qquad\qquad\qquad RR'C=O$$

R, R': Benzyl, allyl, alkyl

Scheme 1. Selective oxidation of alcohols by $K_2S_2O_8$/activated charcoal system

2. Results and Discussion

Activated charcoal possesses quite a few unique characteristics. High degree and tunable micro porosity (just one gram of activated charcoal has a surface area of 500–1500 m^2), high stability in caustic and acidic media and rich surface chemistry (due to ability to form surface−oxygen complexes) make this material very valuable as a promoter or solid bed for immobilization of other reagents [45]. Recently, we reported some useful applications of activated charcoal in organic synthesis [46-48].

Unique characteristics of activated charcoal and our goal to introduce a green and practical protocol for oxidation of alcohols by persulfate encouraged us to enhance the oxidative potential of $K_2S_2O_8$ by its incorporation with high surface area and micro porosity of activated charcoal. We also interested to perform the reactions at solvent−free conditions. Since, solvent−free reactions are desirable from ecological point of view and in many cases offer considerable synthetic advantages in terms of yield, selectivity and simplicity of the reaction procedures.

The influence of micro porose activated charcoal was studied by performing the solvent−free oxidation of benzyl alcohol with $K_2S_2O_8$ (Table 1). The results showed that oxidation of benzyl alcohol with the alone $K_2S_2O_8$ did not have a proper efficiency at room or elevated temperature (Table 1, entries 1 and 2) (Scheme 2, path a). By addition a small amount of micro porose activated charcoal to the mixture of $PhCH_2OH$ and $K_2S_2O_8$, the rate of oxidation reaction was dramatically accelerated and benzaldehyde was obtained as the sole product. More examinations revealed that the complete oxidation of benzyl alcohol into benzaldehyde required a molar equivalent of $PhCH_2OH$:$K_2S_2O_8$ (1:3) and activated charcoal (0.05 g) at solvent−free conditions (45–50 °C) (Table 1, entry 5) (Scheme 2, path b). Although, using the excess amounts of $K_2S_2O_8$ (4 mmol) (entry 6) or activated charcoal (0.1 g) (entry 9) per 1 mmol of benzyl alcohol accelerated progress of the reaction, however, their results in decreasing the reaction time were not remarkable. So, the conditions mentioned in entry 5 were selected as the optimal.
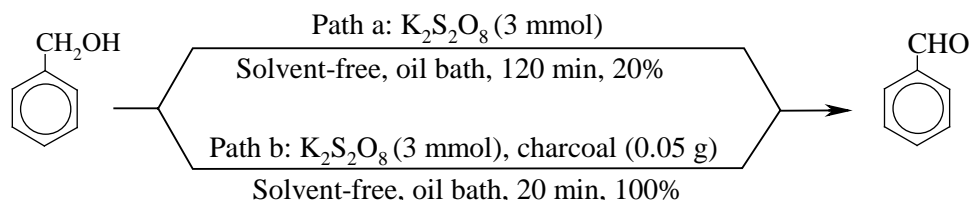
Scheme 2. Selective oxidation of benzyl alcohol by $K_2S_2O_8$ in the absence (path a) and presence of activated charcoal (Path b)

The studies also showed that $K_2S_2O_8$/activated charcoal system has two distinguished characteristics: i) prolonging the reaction time (240 min) and using the excess amounts of $K_2S_2O_8$ (4 mmol) did not carry out the over oxidation of benzaldehyde into benzoic acid (Table 1, entry 7), and ii) $(NH_4)_2S_2O_8$ as $K_2S_2O_8$ exhibited the same reactivity and selectivity in oxidation of benzyl alcohol to benzaldehyde (Table 1, entry 10). This means that changing the counter ion of persulfate did not affect the behavior of oxidation reaction.
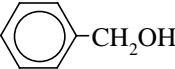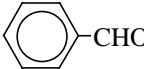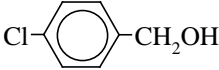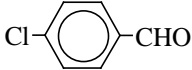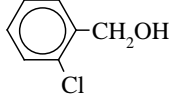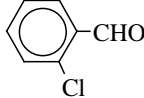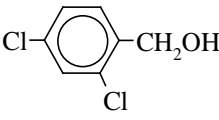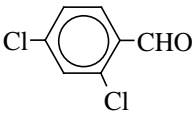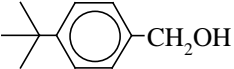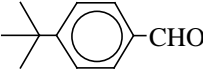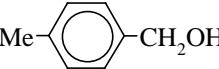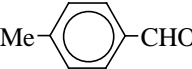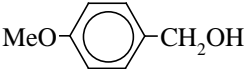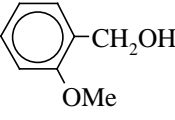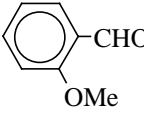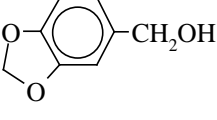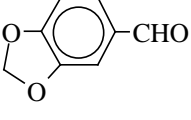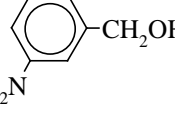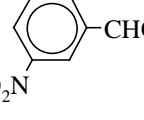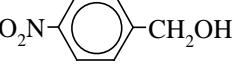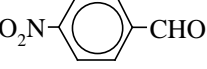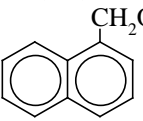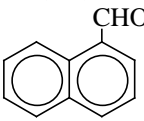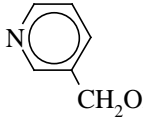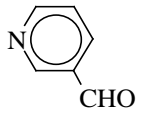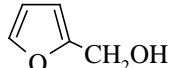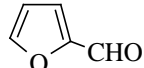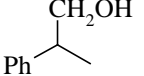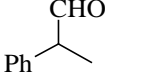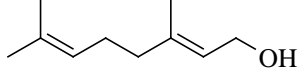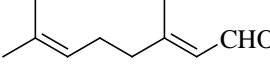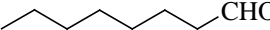
Table 1. Optimization experiments for selective oxidation of benzyl alcohol to benzaldehyde by $K_2S_2O_8$/activated charcoal system.[a]

Entry	Charcoal (g)	$K_2S_2O_8$ (mmol)	Condition[b]	Time (min)	PhCHO (%)	PhCH$_2$OH (%)	PhCO$_2$H (%)
1	–	3	rt	120	–	–	–
2	–	3	oil bath	120	20	80	–
3	0.05	1	oil bath	120	45	55	–
4	0.05	2	oil bath	120	70	30	–
5	0.05	3	oil bath	20	100	–	–
6	0.05	4	oil bath	17	100	–	–
7[c]	0.05	4	oil bath	240	100	–	–
8	0.1	2	oil bath	120	75	25	–
9	0.1	3	oil bath	18	100	–	–
10[d]	0.05	3	oil bath	20	100	–	–

[a]All reactions were carried out with 1 mmol of benzyl alcohol at solvent–free conditions. [b]Temperature of oil bath was 45−50 ℃. [c]The reaction was completed within 17 min, however, prolonging the reaction time (240 min) did not produce benzoic acid as an over oxidation product. [d]The reaction was carried out by $(NH_4)_2S_2O_8$.

The selectivity and oxidative potential of $K_2S_2O_8$/activated charcoal system was further studied by examination of a broad range of primary and secondary alcohols at the optimized reaction conditions. Table 2 shows that structurally different benzylic, heteroaryl, allylic and aliphatic primary alcohols were efficiently and selectively oxidized to the corresponding aldehydes using 3 molar equivalents of $K_2S_2O_8$ and 0.05 g activated charcoal at solvent–free conditions (40−45 ℃). All reactions were completed during 15−60 min without any over oxidation to produce carboxylic acid compounds. Investigation of the results reveals that electron donating substituents on aromatic rings generally activated benzylic alcohols leading to accelerate progress of the reaction, whereas, electron withdrawing groups prolonged the reaction time through the deactivation of benzylic alcohols. We also found that during the oxidation reaction with $K_2S_2O_8$/activated charcoal system, the C=C moiety was remained intact. So, geraniol as an allylic primary alcohol was successfully converted to the corresponding α,β−unsaturated aldehyde (citral) without any side product formation (Table 2, entry 16).

Table 2. Oxidation of primary alcohols to aldehydes by $K_2S_2O_8$/activated charcoal system.[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)[c]
1	Ph–CH₂OH	Ph–CHO	20	95
2	4-Cl-C₆H₄–CH₂OH	4-Cl-C₆H₄–CHO	55	98
3	3-Cl-C₆H₄–CH₂OH	3-Cl-C₆H₄–CHO	60	98
4	2,4-Cl₂-C₆H₃–CH₂OH	2,4-Cl₂-C₆H₃–CHO	50	96
5	4-tBu-C₆H₄–CH₂OH	4-tBu-C₆H₄–CHO	18	97
6	4-Me-C₆H₄–CH₂OH	4-Me-C₆H₄–CHO	20	98
7	4-MeO-C₆H₄–CH₂OH	4-MeO-C₆H₄–CHO	15	95
8	2-OMe-C₆H₄–CH₂OH	2-OMe-C₆H₄–CHO	35	94
9	3,4-methylenedioxybenzyl alcohol	3,4-methylenedioxybenzaldehyde	60	96
10	3-O₂N-C₆H₄–CH₂OH	3-O₂N-C₆H₄–CHO	55	98
11	4-O₂N-C₆H₄–CH₂OH	4-O₂N-C₆H₄–CHO	60	96
12	1-naphthyl-CH₂OH	1-naphthyl-CHO	40	94
13	pyridin-3-yl-CH₂OH	pyridin-3-yl-CHO	30	92
14	furan-2-yl-CH₂OH	furan-2-yl-CHO	50	85
15	Ph-CH(CH₃)-CH₂OH	Ph-CH(CH₃)-CHO	60	93
16	geranyl type alcohol–OH	geranyl type–CHO	45	90
17	CH₃(CH₂)₆CH₂OH	CH₃(CH₂)₆CHO	50	88

[a]All reactions were carried out with the molar ratio of substrate/$K_2S_2O_8$ (1:3) in the presence of activated charcoal (0.05 g) at solvent–free conditions (45–50 ℃) [b]All starting materials were completely converted to the corresponding products. [c]Yields refer to isolated pure products.

The summarized results in Table 3 show that the oxidation of various aliphatic and benzylic secondary alcohols with $K_2S_2O_8$/activated charcoal system was also accessible. As it's seen, using 3 molar equivalents of $K_2S_2O_8$ and 0.05 g activated charcoal at solvent-free conditions (40–45 °C) efficiently oxidized secondary alcohols to the corresponding ketones. All reactions were completed within 20–55 min to afford the products in 92–98% yields. In the case of secondary allylic alcohols, the oxidation of β-ionol with $K_2S_2O_8$/activated charcoal system was also carried out selectively without the further oxidation of double bond (Table 3, entry 6). In addition, the successful conversion of (−)-borneol to camphore (entry 7), shows that the present protocol can be used easily for the oxidation of more hindered secondary alcohols.

Table 3. Oxidation of secondary alcohols to ketones by $K_2S_2O_8$/activated charcoal system.[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)[c]
1			20	97
2			35	98
3			40	98
4			40	92
5			50	89
6			30	93
7			55	95

[a]All reactions were carried out with the molar ratio of Subs./$K_2S_2O_8$ (1:3) in the presence of activated charcoal (0.05 g) at solvent−free conditions (45–50 °C). [b]All starting materials were completely converted to the corresponding products. [c]Yields refer to isolated pure products.

The influence of activated charcoal on reactivity of $K_2S_2O_8$ is not clear, however, we think that high surface area and micro porosity of activated charcoal maybe play roles through a widespread interaction of $K_2S_2O_8$ with the alcohol, and excitation of persulfate to more powerful sulfate anion−radical ($SO_4^{-\bullet}$) that accelerates the oxidation process.

3. Conclusions

In this investigation, we have shown that activated charcoal dramatically promotes the oxidative potential of $K_2S_2O_8$ towards alcohols. $K_2S_2O_8$/activated charcoal system exclusively oxidizes various primary alcohols to the corresponding aldehydes and secondary alcohols to the ketones. All reactions were carried out at solvent−free conditions (40−45 °C) (15−60 min) to afford the products in high to excellent yields. Versatility of this synthetic method for a broad range of alcohols, perfect selectivity and high efficiency as well as the benefits of solvent−free conditions are the advantages which make this protocol a useful addition to the present methodologies.

4. Experimental

4.1 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). ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra (in CDCl$_3$, Aldrich 99.8%) were recorded on 300 MHz Bruker Avance spectrometer. All chemical shifts were measured with reference to TMS (δ = 0.00 ppm). FT−IR spectra were recorded on Thermo Nicolet Nexus 670 spectrophotometer using the KBr pressed pellet technique. All products are known and were characterized by their ^{1}H, ^{13}C NMR and FT−IR spectra followed by a comparison with authentic samples [49,50].

4.2 A typical procedure for selective oxidation of 4−chlorobenzyl alcohol to 4−chlorobenzaldehyde by K$_2$S$_2$O$_8$/activated charcoal system

A mixture of 4−chlorobenzyl alcohol (0.143 g, 1 mmol), K$_2$S$_2$O$_8$ (0.810 g, 3 mmol) and activated charcoal (0.05 g) was ground in a mortar for 55 min at 45−50 ℃. The progress of the reaction was monitored by TLC (*n*−hexane/EtOAc: 8/2). After completion of the reaction, the mixture was washed with EtOAc (6 mL) and then filtered. Evaporation of the solvent affords pure 4−chlorobenzaldehyde in 98% yield (0.138 g, Table 2, entry 2).

Acknowledgments

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