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Response to the Reviewers' comments

Referee: 5

Comment 1:

The authors describe a method offering a mild entry into the class of nitroaromatics building on a rather similar literature precedence published a few years ago (ref #16), albeit the current work is conducted in an entirely water-based medium instead of in an organic solvent (acetonitrile). An adequate question to ask concerns the regioselectivity of this protocol and the authors claim they cannot identify any other isomer than the main product. This obviously depends on how intense and how deep one is looking and not finding the minor isomer in the final product is by no means a guarantee that it might not be formed during the reaction. Thus, a very important issue to address is whether the crude process solution, i.e. the reaction mixture after completed reaction but before start of work up, contains anything else but the documented product? As the yield is hovering <90%, it could be suspected that some starting materal as well as small amounts of other regioisomers might be present. This has to be clarified!

Response:

According to our typical procedure (page 11), we did the HPLC of the crude products before start of work up. From the HPLC traces we could detect only one isomer. The reported yield is the isolated yield which has been indicated in Table 1 as a footnote. Since no trace of starting material or other isomeric product was found in the HPLC trace we concluded regioselectivity of this protocol. Since we report isolated yield, there is a likelihood of some loss of product during work up (extraction and recrystallization). We hope that this clarifies the point raised by the reviewer.

Comment 2:

Another key aspect of this transformation is to establish whether it is conducted in an entirely homogenous phase or rather displays heterogeneity in some form (pseudoheterogenous). The latter seems quite likely given the composition of the system and, therefore, an investigation on the effects of stirring speed should render some valuable insights into these aspects. Currently, the experimental procedure just makes the simply statement that "the mixture was stirred", which poses questions like what type of stirrer, what stirring speed (rpm), presence of any device (e.g. typ of baffle) that could break the laminar flow pattern and ensure better mixing behaviour (vertical movement and not only horizontal flow). Hence, this lack of understanding calls for a series of experiments where the reaction outcome is studied as a function of the mixing regime in the flask!

Response:

Micellar solutions are not macroscopically heterogeneous. However, micellar solutions are considered to be microscopically heterogeneous due to the presence of micelles which are typically of about 2 to 3 nm radius.

We used a magnetic stirrer for stirring (this is now mentioned in the typical procedure, p. 11). We repeated the reactions by changing the speed of stirring, but found no change in the reaction rate. Stirring only helped in the initial solubilization of the substrate in the aqueous micellar solution.

Comment 3:

On p. 4, it is unclear why the same reference (#14) is mentioned twice in the same sentence.

Response:

This has been corrected now.

Comment 4:

Throughout the paper, change table 1 to Table 1

Response:

As suggested 'table 1' is now written as 'Table 1'.

Comment 5:

On p. 10, final sentence before acknowledgements - what does the statement "...the agreement was better." mean? In what way were spectral data and melting points better than the ones documented in the literature?

Response:

We have now corrected the sentence by deleting "the agreement was better".

Comment 6:

As the actual identity of the nitration species is highly unclear, it can be seen as misleading if, as is done in Figure 1 (p. 22), this species nitronium ion) is highlighted as the reactive component formed under the current condition and acting as the reaction partner with the aromatic substrate. The authors should either continue their investigations into the true nature of the nitrating species or present their assumption of the reaction mechanism in a less ambiguous way.

Response:

To ascertain the formation of nitronium ion in the reaction mixture, we recorded the Raman spectra. Accordingly, on pages 8 and 9 of the revised manuscript we added the following text:

Formation of nitronium ion through hydrolysis of the SDS monomers may be shown as

 $C_{12}H_{25}SO_{4}^{-} + H_{2}O \xrightarrow{H^{+}} C_{12}H_{25}OH + HSO_{4}^{-}$ $HSO_{4}^{-} \rightleftharpoons H^{+} + SO_{4}^{-}$ $HNO_{3} + H^{+} \rightleftharpoons NO_{2}^{+} + H_{2}O$

To confirm the generation of nitronium ion, we recorded the Raman spectra of aqueous 0.05 M SDS and 0.05 M SDS + 1.0 M HNO₃ solutions. The Raman spectrum of the latter after subtracting the contribution from the aqueous 0.05 M SDS solution is shown in Fig. 1A. The spectrum showed an intense peak at 1047 cm⁻¹, which can be attributed to nitrate and bisulfate (produced from the hydrolysis of SDS) ions as both these ions are reported³²⁻³⁶ to show Raman line in the range of 1040 – 1050 cm⁻¹. In view of the

reported³²⁻³⁴ Raman line of nitronium ion at 1400 cm⁻¹, the Raman line at 1418 cm⁻¹ in Fig. 1B is indicative of the presence of nitronium ion in the solution.



Fig. 1. Raman spectra of (A) aqueous $0.05 \text{ M SDS} + 1.0 \text{ M HNO}_3$ solution after subtracting the contribution from aqueous 0.05 M SDS solution and (B) the enlarged view of the spectra in the range from 1175 to 1750 cm⁻¹.

In the experimental section on page 11 we have given the details of Raman spectral measurement.

The earlier Fig. 1 which was a schematic and presumptive representation of the presence of nitronium ion in the reaction mixture has now been replaced by the new Fig. 1 which shows the Raman spectra as shown above.

We thank the Referee and hope that our response and clarifications would satisfy the Referee.

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Regioselective nitration of aromatic compounds in an aqueous sodium dodecylsulfate and nitric acid medium⁺

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† Electronic supplementary information available: Scanned NMR and HPLC spectra

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Abstract

An aqueous solution of sodium dodecylsulfate in the presence of dilute nitric acid at room temperature works as a mild medium for the nitration of aromatic compounds with high regioselectivity.

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Introduction

Nitration of aromatic compounds is a fundamental reaction of great industrial importance and the nitro aromatic compounds are key organic intermediates in various important functional group transformations. A mixture of concentrated or fuming nitric acid with sulfuric acid has been used as the most common nitrating reagent for the nitration of benzene, alkyl benzene and less reactive aromatic compounds,¹ but highly reactive aromatic compounds such as phenols and anilines get oxidized in the nitric acid and sulfuric acid mixture rather than undergoing nitration. A wide variety of nitrating reagents have been developed including the use of Fe (III)² or Cu (II),³ montmorillonite clay,⁴ zeolites,⁵ bismuth (III) salts,⁶ group IV and VI metal salts,⁷ lanthanide (III) salts,⁸ indium salts⁹ and so on. Selective nitration of aromatic compounds has been reported with solid acid catalysts as well.¹⁰ Nitration of aromatic compounds such as phenol and salicylic acid has also been carried out photochemically.¹¹ Most recently, even ionic liquids (ILs) have been employed as nitrating systems.¹²⁻¹³ However, majority of the reported nitration methods suffer from disadvantages such as highly acidic media, excess nitration (di- or tri-nitro products instead of mononitration), tedious work-up, and problems associated with use of organic solvents. Another notable disadvantage of the conventional methods of nitration is the formation of more than one isomer, which is a problem even in case of ILs.¹² These disadvantages associated with the known nitration methods have led researchers to develop from time to time newer methods by using better nitrating mixtures.

The use of surfactants for nitration reactions of aromatic compounds has gathered a lot of attention over the years. Surfactant molecules bearing both hydrophilicity and hydrophobicity characters aggregate to form microstructures known as micelles. The surfactant concentration at which microstructures begin to form in a solvent is referred to as the critical micelle concentration (cmc). Chhatre et al.¹⁴ carried out selective nitration of phenol to *ortho*-nitro phenol in nitric acid/sodium dioctylsulfosuccinate (AOT)/benzene microemulsion medium. The concentration of nitric acid used in this microemulsion varied from 5 to 10 M (M = mol dm⁻³). Selective nitration of phenols and anisole has also been reported in nitric acid (8M)/cationic surfactant/isooctane microemulsions.¹⁵ The cationic surfactants used dodecyltrimethylammonium bromide and are didodecyldimethylammonium bromide.¹⁵ Sana et al.¹⁶ reported nitration of a series of aromatic compounds in acetonitrile medium using HNO₃ (1 mM) in the presence of anionic, cationic or nonionic surfactants. Surfactants have also been used as phase transfer catalysts during nitration of aromatics in two-phase system by Wang et al.¹⁷ resulting in high regioselectivity. These methods of nitration involving surfactants also suffer from the disadvantage of using organic solvents.

Sodium dodecyl sulfate (SDS), an anionic surfactant, is known to undergo hydrolysis.¹⁸ In a recent study¹⁹ on the aggregation behavior of SDS in aqueous nitric acid, we detected from conductivity data hydrolysis of the surfactant when the concentration of HNO₃ was about 0.02 M or more. Visualizing that hydrolysis of SDS monomers might facilitate formation of nitronium ions,¹⁹ it occurred to us that an aqueous solution of SDS + HNO₃ (with concentration > 0.02 M) may act

as a nitrating mixture. Accordingly, we report in this paper a simple methodology for the nitration of aromatic compounds that offers a mild route to the synthesis of mono-substituted products in aqueous medium at room temperature. The nitrated products have been successfully isolated using a novel method.

Results and discussion

Nitration of a number of aromatic compounds listed in Table 1 was carried out in aqueous medium. In the nitration reactions, the concentrations of HNO₃ and SDS were kept as 1.0 M and 0.05 M, respectively. The concentration of SDS was chosen such that it is well above the cmc (0.008 M) of SDS. Micelles formed above cmc are known to solubilize organic compounds and this has enabled us to carry out all the nitration reactions in water (Scheme 1).



Scheme 1

The nitrating mixture was first tested for nitrating phenol and we obtained only *para*-isomer in excellent yield (Table 1), thus exhibiting high selectivity. Formation of only the *para*-isomer was confirmed by HPLC. Presence of phenol at the micellar interface without penetrating into the core has been reported²⁰ in the case of CTAB (cetyltrimethylammonium bromide), a cationic surfactant, on

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the basis of ¹H-NMR. Similarly, in the present nitrating mixture probably the presence of phenol at the micellar interface and a favorable orientation of phenol are responsible for the *para*-selectivity.

Another interesting highlight of the present study is the direct nitration of aniline without protecting the amino group to yield 4-nitroaniline. Similar nitration of aniline without any protecting agent has been recently reported by Zolfigol et al.¹³ using an ionic liquid and by Sana et al.¹⁶ using surfactants and dilute HNO₃ (1 mM), but in both the reports^{13,16} reactions have been carried out in organic solvents.

The present protocol in aqueous medium can be successfully used to carry out nitration of aromatic compounds even in the presence of strong electron withdrawing groups such as the nitro, carboxylic acid, keto, etc. The nitration of p-nitrophenol afforded 2,4-dinitrophenol in good yield. Here, again the alignment of p-nitrophenol at the SDS micelle can be compared to that of p-cresol at the TX-100 micelles,²¹ where the –OH group is pointed towards the bulk phase. Metadirecting aromatic compounds such as benzoic acid, acetophenone furnished the expected products with good yields (Table 1). All the compounds were confirmed from the analytical and spectroscopic data.

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Sl. No.	Substrate	Product	Time (min)	Yield (%) ^b	Melting Point (°C)	
					Found	Reported
1	но-	HO-NO2	20	89	111-113	114 ^c
2	H ₂ N	H ₂ N-NO ₂	20	86	147-149	148 ^c
3	HO-NO2	HO-NO ₂	30	85	104-106	113°
4	H ₃ C HO CH ₃	H ₃ C HO	20	87	170-172	-
5	ноос	HOOC	30	85	140-142	141°
6	но-Соон	0 ₂ N но—Соон	30	82	173-175	-
7	H ₃ C	H ₃ C-NO ₂	20	86	49-51	54 ^c
8	H ₃ COC	H ₃ COC	30	85	74-76	81°
9	Cl		30	83	85-87	83°

Table 1. Nitration of aromatic compounds^a

^a Reagents and condition: Aqueous SDS (0.05 M), Nitric acid (1.0 M);

^b Isolated yields; ^cRef. 22

During the isolation of the nitrated products by the usual techniques, certain level of SDS as impurity was always detected. Therefore, we employed a novel technique to isolate the nitrated products. After the reaction, the temperature of the reaction mixture was maintained below the Krafft temperature of SDS (15 °C

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for 0.05 M SDS),²³ which resulted in the precipitation of SDS. After removing the SDS precipitate by simple filtration, we could extract pure nitrated product from the filtrate with a suitable solvent followed by evaporation and crystallization.

There are reports wherein nitronium ion is considered as the active species even in dilute nitric acid, but in all such reactions the media used are not aqueous.^{16,24,25} Even in calcium nitrate tetrahydrate melt (a room-temperature molten salt known as hydrate melt) nitration of benzene was reported to take place and nitronium ion was shown to be the nitrating species.²⁶ Can nitronium ion be responsible for nitration in the present aqueous micellar medium which is not highly acidic? In an anionic micellar solution, polarity and acidity at the micelle - solution interface are entirely different from that in the bulk.²⁷⁻³¹ In aqueous solution containing SDS micelles, the pH is about 2 units less than that in the bulk²⁷⁻³¹ and the dielectric constant at the micellar interface is reported^{28,31} to be about 60 or even less. These characteristics of the micellar interface seem to indicate that in aqueous medium containing SDS micelles and dilute nitric acid the interfacial region around the micelles may be conducive to the formation of nitronium ions. This might be the reason why nitration takes place in the presence of micelles even if the concentration of nitric acid is low. Formation of nitronium ion through hydrolysis of the SDS monomers may be shown as

 $C_{12}H_{25}SO_{4}^{-} + H_{2}O \xrightarrow{H^{+}} C_{12}H_{25}OH + HSO_{4}^{-}$ $HSO_{4}^{-} \rightleftharpoons H^{+} + SO_{4}^{-}$ $HNO_{3} + H^{+} \rightleftharpoons NO_{2}^{+} + H_{2}O$

To confirm the generation of nitronium ion, we recorded the Raman spectra of aqueous 0.05 M SDS and 0.05 M SDS + 1.0 M HNO₃ solutions. The Raman spectrum of the latter after subtracting the contribution from the aqueous 0.05 M SDS solution is shown in Fig. 1A. The spectrum showed an intense peak at 1047 cm⁻¹, which can be attributed to nitrate and bisulfate (produced from the hydrolysis of SDS) ions as both these ions are reported³²⁻³⁶ to show Raman line in the range of 1040 – 1050 cm⁻¹. In view of the reported³²⁻³⁴ Raman line of nitronium ion at 1400 cm⁻¹, the Raman line at 1418 cm⁻¹ in Fig. 1B is indicative of the presence of nitronium ion in the solution.



Fig. 1. Raman spectra of (A) aqueous $0.05 \text{ M SDS} + 1.0 \text{ M HNO}_3$ solution after subtracting the contribution from aqueous 0.05 M SDS solution and (B) the enlarged view of the spectra in the range from 1175 to 1750 cm⁻¹.

An interesting aspect in the present nitrating medium is that the reaction appears to be one in which the rate is independent of the aromatic substrate. Therefore, the rate appears to be zero-order with respect to the aryl compound implying that the formation of nitronium ion is the rate-determining step.

Conclusions

In conclusion, a simple, mild and efficient synthesis of aromatic nitro- compounds has been reported in aqueous medium. A wide range of aromatic compounds was tested, bearing either electron-donating or electron-withdrawing substituents suggesting that this method can be used to synthesize a library of aromatic nitro compounds. The use of SDS (0.05 M) and dilute HNO₃ (1.0 M) as nitrating mixture in aqueous medium at room temperature makes this protocol environmental friendly. Moreover, high regioselectivity of the products with very easy separation technique renders this methodology very attractive. The method demonstrated for the removal of surfactant from the reaction medium can in general be applied in the cases of micellar catalyzed reactions and also in nanoparticle (synthesized in micellar medium) catalyzed organic reactions.

Experimental section

Materials

SDS (Fluka, \geq 99 % assay), HNO₃ (Merck, 69%), were used as received. All solutions were prepared in Millipore water. Stock solution of the acid (10.0 M) was prepared after standardization of HNO₃. The organic compounds were obtained either from Merck or from SD fine chemicals and were of AR grade.

The solvents used for extraction were obtained from Merck. All reactions were done at 25 °C.

Melting points were determined in open capillaries and are uncorrected. IR spectra of the samples in KBr disks were recorded in Perkin Elmer (Model Spectrum BXFT-IR) spectrometer. ¹H NMR (400 MHz and 300 MHz) spectra were recorded on Bruker Avance II-400 and 300 spectrometers in CDCl₃ and DMSO-d₆ (chemical shifts in δ with TMS as internal standard), respectively. Mass spectra were recorded on Waters ZQ-2695 and Bruker Daltonics (Esquire 3000) spectrometers. Liquid chromatography analyses were performed in Waters 2489 HPLC instrument with UV detector using C₁₈ column (particle size: 5µm, column size: 150×3.9 mm). Raman spectra were recorded in the range of 200 – 1800 cm⁻¹ using the 532 nm line from a solid state Nd:YAG laser (Cobolt AB, Sweden) and Synapse CCD detector based monochromator (Horiba Jobin Yvon, France). The laser power used was 30 mW. The sample solution was taken in a standard 1cm x 1cm cuvette Spectra were recorded at 25 °C.

Typical Procedure

A mixture of 1 mmol substituted aromatic compound **1a-i** and 25 ml of SDS (0.05 M) solution was taken in a round bottom flask. To this mixture HNO₃ was added such that the concentration of HNO₃ in the mixture was 1.0 M. The mixture was then stirred at 25 °C for the time mentioned in the Table 1 by using a magnetic stirrer. After completion (monitored by TLC), the reaction mixture was kept below the Krafft temperature of SDS (15 °C) till SDS precipitated. The mixture

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was then filtered and the filtrate was extracted with diethyl ether (3 x 10 mL) and dried over anhydrous sodium sulfate. After removing the solvent the product was recrystallized from acetone.

The HPLC traces of the crude product were taken. The recrystallized products were characterized by comparing their IR spectra, ¹H- NMR spectra, mass spectra and melting points (shown in Table 1) with those in the literature.

Acknowledgements

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Table of contents



Regioselective nitration of aromatic compounds is achieved in aqueous solution of sodium dodecylsulfate and dilute nitric acid at room temperature.

Supplementary Information

Regioselective nitration of aromatic compounds in an aqueous sodium dodecylsulfate and nitric acid medium

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1. ¹H-NMR Spectra:



Fig. S1: ¹H-NMR spectrum of 4-nitrophenol



Fig. S2: ¹H-NMR spectrum of 4-nitroaniline



Fig. S3: ¹H-NMR spectrum of 2,4-dinitrophenol



Fig. S4: ¹H-NMR spectrum of 2,5-dimethyl-4-nitrophenol



Fig. S5: ¹H-NMR spectrum of 3-nitrobenzoic acid



Fig. S6: ¹H-NMR spectrum of 4-hydroxy-3-nitrobenzoic acid



Fig. S7: ¹H-NMR spectrum of 4-nitrotoluene



Fig. S8: ¹H-NMR spectrum of 3-nitroacetophenone



Fig. S9: ¹H-NMR spectrum of 4-chloro-nitrobenzene



2. High Performance Liquid Chromatography (HPLC) Spectra:

Retention time (min)	Area	% Area	Height
23.761	175974010	100.00	3644882

Fig. S10. HPLC traces of 4-nitrotoluene



Retention time (min)	Area	% Area	Height
12.742	82809392	100.00	3898092

Fig. S11. HPLC traces of 3-nitroacetophenone



Retention time (min)	Area	% Area	Height
8.164	61597444	100.00	2297681

Fig. S12. HPLC traces of 4-nitrophenol



Scheme 1



Fig. 1. Raman spectra of (A) aqueous $0.05 \text{ M SDS} + 1.0 \text{ M HNO}_3$ solution after subtracting the contribution from aqueous 0.05 M SDS solution and (B) the enlarged view of the spectra in the range from 1175 to 1750 cm⁻¹.