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One Pot Amidation of Aromatic Aldehydes with Anilines Using Nano Gold as Critical Catalyst

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A B S T R A C T

The Aunps synthesized in this work exhibited spherical particles with mean size of 10 ±1nm. One pot batch reactor type reaction incorporated with Aunp and permonosulphate in the reaction between aniline and benzaldehyde resulted in the N-phenyl benzamides, which is the result of oxidative amidation reaction. The kinetics of the reaction was followed by time dependent UV absorbance values. The –I substituents in the aromatic ring of the benzaldehyde and +I effect substituents in the aromatic ring of the aniline, produce good kinetic rate constant and yield values. The two step processes of the oxidative amidation Schiff's base formation and subsequent oxidation to amide in the presence of Aunp becomes a multi component, cost effective and one pot reaction was made possible with appreciable rate constant and yield values.

Keywords: phenyl benzamides, amidation, benzaldehyde.

A R T I C L E I N F O

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1. Introduction

In synthetic organic chemistry the amide functional group is popular because it acts as a precursor for both acid or amine derivatisations [1]. Also,amides act as building blocks to construct complex pharmaceutical and amphiphilic (surfactant) type molecules. In the conventional method amides are synthesized from carboxylic acid derivatives

and as well as from amine derivatives [2,3]. When an aromatic amine and an aromatic aldehyde reacts Schiff's base is produced, which upon oxidation in acidic medium under drastic experimental condition leads to N-substituted amide such as N-phenyl benzamide. According to scheme-I given the reaction may be followed. In view of the eco-friendly in green chemistry methodology.

One pot multi component and batch type reactor condition can be adopted involving an active heterogeneous catalyst. With the emergence of metal nanoparticles which are prepared under mild experimental conditions exhibiting high stability, size control and significant catalytic activity, the use of such metal nano particles as catalyst, in the oxidative amidation reaction can be expected to be fruitful and stand well attempted. In the present work, gold nano particles (Aunp) are synthesized by using wet chemical method and sodium citrate as the stabilizing agent [4]. The Aunps are size characterized using UV-SPR and HRTEM measurements. Such Aunps are utilized as catalyst for the oxidative amidation reactions studied here. The progress of the reaction involving aromatic aldehyde(ring substituted benzaldehyde) with ring substituted aniline and potassium peroxomonosulphate serving as oxidant using Aunp as the catalyst, has been studied adopting time dependent UV spectra measurements.

The overall pseudo first order rate coefficient values and percentage yields are evaluated from the measurements. Optimizations of the reaction condition have been carried out based on the catalyst composition, reactant concentration, effect of ring substituents with +I or –I effects are also carried out. With aniline as reactant, aldehydes bearing p-ring substituent with electron withdrawing (-I) groups resulted in appreciable yields nearing 80%. After the end of the reaction, conversion of aldehydes to acids by the oxidant was observed to be negligible under adopted condition.Hence Aunp specifically catalyzed oxidative amidation of aromatic aldehydes with anilines in the presence of peroxomonosulphate oxidant in high yields [5, 6]. As compared with the traditional liquid phase reactions, where in citrate stabilized Aunps efficiently catalyzed the formation of anilides from the various ring substituted aromatic aldehydes and anilines [7].

2. Experimental

2.1 Chemicals:

Auric chloride($AuCl_3$) (hydrated), sodium citrate, aniline, ring substituted derivatives of aniline, benzaldehyde and ring substituted benzaldehydes as listed in Table-I were purchased as analytical grade reagents from Merck India Ltd., Potassium peroxomonosulphate was purchased from Loba chemie. India, as analytical reagent. The chemicals are used as such without further purification. Triple distilled water was used wherever necessary.

2.2 Synthesis of gold nanoparticles

Gold nanoparticles are synthesized using auric chloride as precursor and sodium citrate as stablising agent by reacting equal volumes of 1mM metal salt and 0.01M sodium citrate solutions. The solutions are mixed dropwise with constant stirring at 70^0C for 6 hours. The solution turns dark pink in colour after standing for 5 more hours. This indicates the formations of Aunps. The size of the nanoparticles in the form of aqueous suspensions are further characterized by using HRTEM and XRD measurements.

2.3 Particle size characterization

X-ray analysis was carried out using Bruker DS Advance model diffractometer, operating at 40KV and 30mA Cu Kα radiation with wavelength of $1.54A^0$and a step size of 0.02^0 in the 2θ range; $10\text{-}80^0$ was used. Figure I presents the XRD profiles of Aunps HRTEM measurement was made using SU6600, HITACHI model operating at an accelerating voltage of 100KV and the HRTEM photograph of the particles is shown in figure -2. The morphology and size of the nano crystallites are found to be spheroids with mean diameter of 10±1nm.

2.4 Procedure for Oxidative amidation

Batch reactor one pot type procedure was adopted and 2ml of Aunp aqueous suspension in as prepared condition was added to 10ml of 1mM aniline solution in dilute ethanol medium mixed with 10ml of 1mM freshly prepared peroxo monosulphate and stirred well at 25^0C.Then the reaction mixture was continuously stirred at 50^0C for 2hours[8,9]. At regular intervals of time, small aliquots are drawn out and UV spectra were recorded. The completion of the reaction was noted by the absorbance values at the characteristic wavelength of the reactant droping to zero. For product analysis, 20 times scale up reaction was carried out separately adopting similar procedure. The products are isolated by solvent extraction, evaporation and purification by recrystallization [10].

3. Results and Discussion

3.1 Size measurements of Aunps

In figure-1a XRD and figure-1b HRTEM measurements are shown for the Aunps. The XRD peak patterns are assigned as per JCPDS data file cards. Applying Scherrer formula to the maximum peak the mean size of the Aunp particles has been found to 10±1nm. The HRTEM photograph show the particles to be spherical, mono dispersed and the average particle size was found to be 10±1nm. The XRD and HRTEM values are match with each other within error limits.

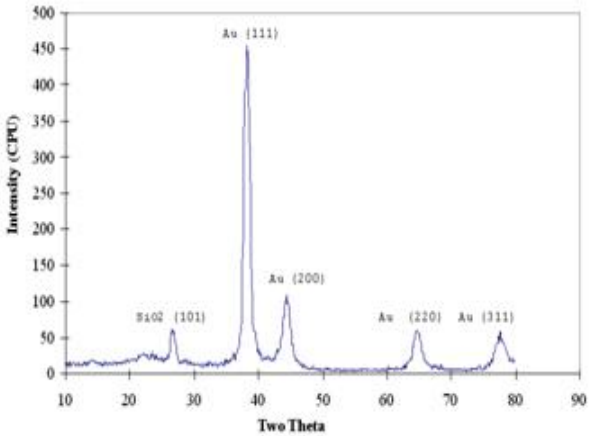

Figure 1: a. XRD pattern of gold nanoparticles

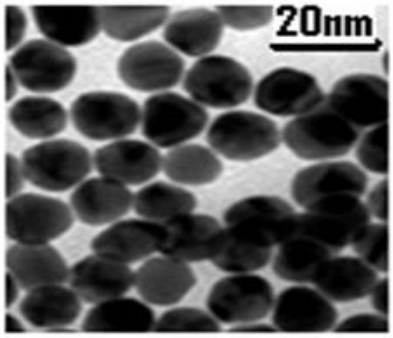

Figure 1b: HRTEM of gold nanoparticles

3.2 Catalytic oxidative amidation

In the absence of the addition of peroxomonosulphate formation of amide is not seen and also in the absence of Aunp, however in the presence of peroxo monosulphate aniline and benzaldehyde also no formation of amides was found. Upon mixing up the reactant mixture with Aunp at 50°C the absorbance values are seen to decrease smoothly with time, as and when the reaction progressed. In figure-2 the time dependent UV spectra of aromatic amines with various ring substituent during the progress of the reaction in the presence of Aunp, potassium monobisulphate are presented [11,12]. The absorbance decreases with time plots are shown in figure-3.The reaction conditions are maintained under pseudo first order condition and therefore when OD_o/OD_t versus time plots are made, best fit linear plots are obtained. Such kinetic plots are shown in figure-4. The slopes of the linear plots are used to determine the overall pseudo first order rate constant values.

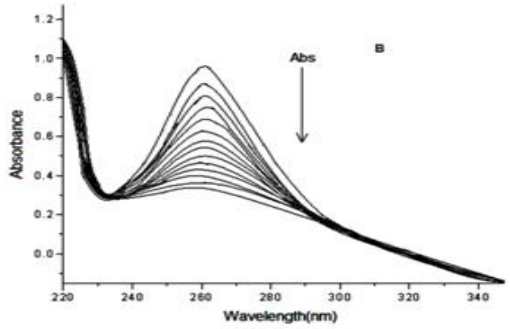

Figure 2: UV spectra of nitro aniline with time variation during the progress of the reaction with 4-Nitro Benzaldehyde catalyzed by gold nanoparticles at 25°C

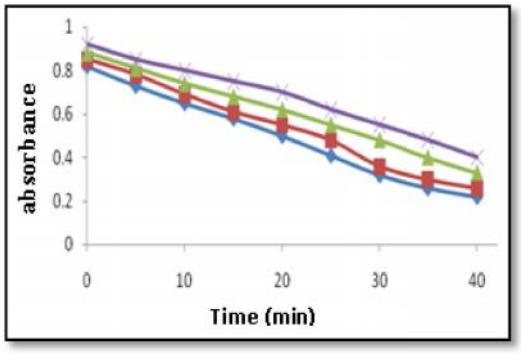

Figure 3a: Absorbance dependence with time plots of amidation reactions of nitro benzaldehyde with ring substituted anilines

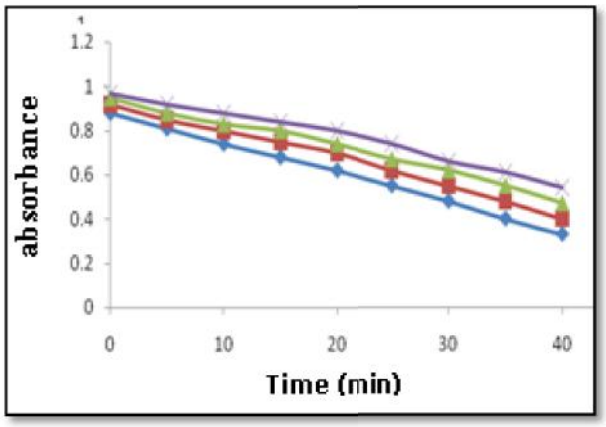

Figure 3b: Nitroanilines with ring substituted benzaldehydes catalyzed by gold nanoparticles at 25°C

The reaction procedure was adopted separately for each of the reactant with their aromatic ring being substituted +I and –I effect for both aniline and benzaldehyde. In table-1 the reaction parameters such as first order rate constant and percentage yield values for the anilines with benzaldehyde and the ring substituted derivatives are given[13,14]. In table-2 the reaction parameter of various aromatic amines with nitro benzaldehyde determined are given. The products such as N-substituted benzamides are ascertained from GC-MS recorded for the products resulted from scaled up reactions.

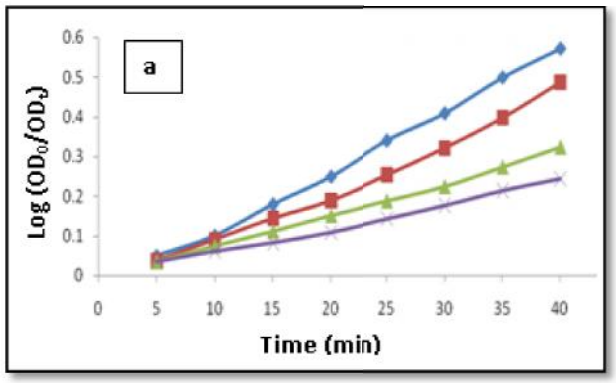

Figure 4a: The kinetic plots for the pseudo first order reactions of amidation reactions of nitro benzaldehyde with ring substituted anilines

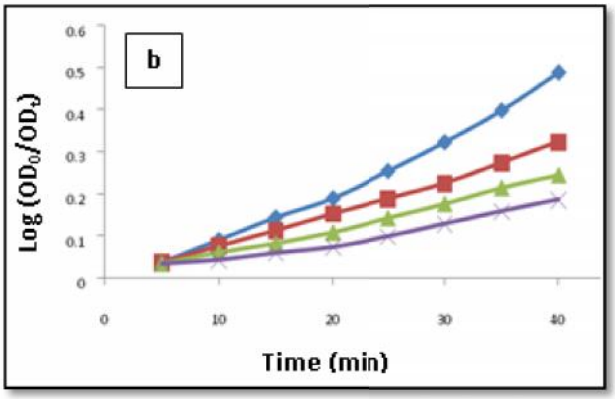

Figure 4b: Nitroanilines with ring substituted benzaldehydes catalysed by gold nanoparticles at 25°C

Table 1: The overall pseudo first order rate coefficient values of the amidation reactions with 4–nitro benzaldehyde and ring substituted anilines catalyzed by gold nanoparticles at 25°C

Reactant A	Reactant B	Rate Constant x 10^{-4} min^{-1}	% Yield	Half life Period X 10^{3} min
4-Methyl Aniline	4-Nitro Benzaldehyde	6.13	65	1.13
4-Bromo Aniline	4-Nitro Benzaldehyde	5.10	70	1.35
4-Chloro Aniline	4-Nitro Benzaldehyde	4.84	73	1.43
4-Amino Anisole	4-Nitro Benzaldehyde	3.83	75	1.8
4-Nitro Aniline	4-Nitro Benzaldehyde	2.57	95	1.69
3-Nitro Aniline	4-Nitro Benzaldehyde	1.50	90	4.59

Table 2: The overall pseudo first order rate coefficient values of amidation reactions with 3- nitro aniline and ring substituted benzaldehydes catalyzed by gold nanoparticles at 25°C

Reactant A	Reactant B	Rate Constant x 10^{-4} min^{-1}	% Yield	Half life Period X 10^{3} min
3-Nitro Aniline	Benzaldehyde	6.17	75	1.123
3-Nitro Aniline	3-Nitro Benzaldehyde	4.22	89	1.641
3-Nitro Aniline	4-Bromo Benzaldehyde	2.917	82	2.376
3-Nitro Aniline	4-Chloro Benzaldehyde	2.24	80	3.093
3-Nitro Aniline	4-Nitro Benzaldehyde	1.519	92	4.589
3-Nitro Aniline	3-Methyl Benzaldehyde	1.187	68	5.838
3-Nitro Aniline	4-Methyl Benzaldehyde	0.516	64	13.43

After the removal of the products through solvent extraction by evaporating away the excess ethanol solution the residue Aunp is recovered and was reused as catalyst for similar reaction. It was found that the rate parameter values are slightly decreased and the activity of the catalyst was reduced. This may be attributed to agglomeration of particles and chemical modification of the surface citrate stabiliser of the nano particles.

4. Conclusion

The Aunps synthesized in this work exhibited spherical particles with mean size of 10 ±1nm . One pot batch reactor type reaction incorporated with Aunp and permonosulphate in the reaction between aniline and benzaldehyde resulted in the N-phenyl benzamides, which is the result of oxidative amidation reaction. The kinetics of the reaction was followed by time dependent UV absorbance values. The –I substituents in the aromatic ring of the benzaldehyde and +I effect substituents in the aromatic ring of the aniline, produce good kinetic rate constant and yield values. The two step processes of the oxidative amidation Schiff's base formation and subsequent oxidation to amide in the presence of Aunp becomes a multi component, cost effective and one pot reaction was made possible with appreciable rate constant and yield values.

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