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Mini Review

A Review on Selective Synthesis and Yield Enhancement of *Ortho*-Nitrophenol in the Presence of Phase-Transfer Catalysts

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Abstract. Current studies were performed to review the synthesis and yield enhancement of *ortho*-nitrophenol in the presence of phase-transfer catalysts. Selective synthesis and yield enhancement of *ortho*-nitrophenol can be varied in the presence of phase-transfer catalysts under different synthetic mechanisms. The phenols and substituted phenols can be selectively nitrated at their *ortho/para* positions by direct or indirect nitration and by varying the reaction parameters such as dilution of acid, substrate and the strength of the catalyst. High selectivity can be achieved by indirect nitration with diluted nitric acid in the presence of tetra-butyl ammonium bromide (TBAB) and acetyl trimethylammonium bromide (CTAB). TBAB has been reported to be the most effective catalyst for the conversion of phenolic compounds into *o*-nitrophenol. However, this regio-selectivity will be reversed to *para*-position by using sodium bromide as a surfactant. The use of nitronium tetra fluoroborate suspended in acetonitrile process gives highest regio-selective nitration with a 95% yield of *ortho* product. Performing the nitration under sonication conditions lowers the reaction time and increases the *ortho/para* regio-selectivity. Under sonication conditions, maximum conversion into *ortho* derivative (95%) is achieved by using TBAB as catalyst in 20 min but maximum *para*-selectivity is achieved by using CTAB and NaBr catalysts. The use of $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$, H-beta zeolite, catalysts for selective nitration has also been reported. Greater than 85% yield of *o*-nitrophenol was observed by using microwaves system technology.

Keywords: TBAB, NaBr, regio-selectivity, *o*-nitrophenol, phase-transfer catalysts

Introduction

Nitrations of aromatic compounds are commonly studied reactions in agro industries (Olah *et al*., 2003) because nitro-products are important intermediates in pharmaceutical products. Due to excessive use of mix acids, the nitration process is not environmental friendly (Anuradha *et al*., 2006; Furniss, 1989). For synthesis of many phenolic derivatives, various nitrants such as concentration of nitric acid, aceticanhydride, sulfonic acid (Braddock, 2001) and oxides of nitrogen can be employed (Clark, 2012). Selectivity at *ortho* position can be achieved by catalytic nitration of aromatic hydrocarbons using by concentrated nitric acid (Laali and Gettwert, 2001). The phenolic compounds in nitration reactions are initially nitrated with sulfuric and nitric acid. The yield of end product during the nitration can be improved with different routes as investigated by numerous scientists. Many derivatives of phenolic compounds have been reported under different reaction conditions. Sodium salt of dioctyl sulfo-succinate is a commonly reported catalyst for conversion of phenol into *o*-nitro-phenol in micro emulsion solution (Häger *et al*., 2003). Selectivity and conversion into *ortho* derivative of phenols was greatly supported by micro-emulsion studies (Dey *et al*., 2013). The nitration of aromatic hydrocarbons with dilute nitric acid was also studied with advanced microwave technology (Vogel, 1970). However, the nitration of phenolic compounds generally leads to the formation of certain by products in the presence of concentrated

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nitric acid, because of the high rate of reaction (Holmberg, 2003). These side reactions can be overcome by performing the same reaction under mild conditions in the presence of suitable phase transfer catalysts e.g., tetrabutylammonium bromide (TBAB) (Geletii *et al*., 2001). The maximum selectivity at *ortho* position can be achieved with transition metal catalyzed chelation. The first palladium catalyzed *ortho* specific nitration was done in 2010. Since then, a strategy was investigated for targeted chelation Eat *ortho*-nitration of aryl sp^2 C-H bonds in the presence of copper/palladium catalysts and with different sources of nitro groups. This procedure supports the formation of *ortho*-derivative, as compared to traditional electrophilic nitration. In this protocol excellent regio-selectivity is obtained by the C-H cleavage and the sigma chelation. It offers excellent chemo selectivity for mono-nitrated products and practical applications for organic synthesis.

Current studies were used to review the literature on the selective synthesis and yield enhancement of *ortho*-nitrophenol in the presence of phase transfer catalysts.

Materials and Methods

It is a review article so relevant literature has been reviewed and cited.

Results and Discussions

Selective nitration process. The phenolic compounds can be mono-nitrated very easily (to *o/p* 2: 1) by using $NaNO_3$ and a two phase system at room temperature in presence of acidic media and catalytic amount of lithium (La) (Quertani *et al*., 1982). The claycop process (montmorillonite/ascorbic acid/CCU) supported with trihydrated copper(II) nitrate was reported by Lazslo, with the highest possible yield of 92% (Gigante *et al*., 1995). The use of nitronium tetra-fluoroborate suspended in acetonitrile process gives highest regio-selective nitration with a 95% yield of *ortho* product (Dadade *et al*., 2002; Gigante *et al*., 1995). There are reports of selectivity achievement to *ortho*-nitrophenol by using phase-transfer catalyst tetra-butylammonium bromide (TBAB) surfactant. The observed yield was calculated by gas chromatograph (GC) and reverse phase HPLC with primary standards. Following processes were carried out for *ortho* nitration:

- Nitration in the presence of micro emulsion medium
- Nitration reaction in the absence of surfactants
- Nitration through sono-chemical procedure

Selective nitration in the presence/absence of surfactants. It is observed that surfactants play a vital role for targeted *ortho* nitration. The surfactants reported for the nitration processes are comprised of two phases (aqueous and organic phases). The aqueous phase (100 mL) can be made by varying the equimolar concentration of various species such as HNO_3, acetic anhydride, catalyst (CTAB) and iso-octane (Table 1). The organic phase (25 mL) is phenol or a phenolic compound such as benzene, chlorobenzene, phenol-sulphonic acid (Table 1) (Yang *et al*., 2003). The nitration of phenols in the presence and absence of surfactant by using the aquous and organic phases are displayed in Tables 2 and 3, respectively.

All the above nitration (Tables 2 and 3) involve 100 mL aqueous phase along with 25 mL organic phase, also an agitation of 50 rpm is provided. The temperature of the reaction mixture is maintained with thermostatic bath at 30 °C during the process. To enhance optimum yield of *o*-nitrophenols, two sets of reactions were performed, one type reactions were performed in the

Table 1. Amounts of various components in 100 mL aqueous phase solution

Concentration of HNO_3 (mol/L)	CTAB (g)	*n*-butanol (ml)	Iso-octane (mL)
2.0	5.0	3.9	17.5
3.0	7.5	5.6	11.5
4.0	10	8.0	6.0
2.0	0.0	0.0	0.0
3.0	0.0	0.0	0.0

Table 2. Nitration of phenol (with surfactant or micro-emulsion media)

Concentration of HNO_3 (mol/L)	Phenol (g)	Ratio of *o/p*-nitrophenol
2.0	1.80	65/35
3.0	1.80	65/16
4.0	1.80	74/18

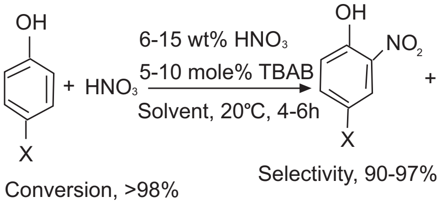
Table 3. Nitration of phenol (without surfactant)

Concentration of HNO_3 (mol/L)	Phenol (g)	Ratio of *o/p*-nitrophenol
2.0	1.80	55/41
3.0	1.80	35/45

presence of surfactant medium (Table 2), while second set of reactions was proceeded without surfactants (Table 3) (Cornelis *et al.*, 1988). Diethyl ether was used for de-mulsification and extraction and characterizations were performed by HPLC and GC-MS (Schofield, 1980). The micro emulsion media was used to convert the substrate phenol into *o*-nitrophenol (55%) and *p*-nitrophenol 41% (Cornelis *et al.*, 1988). Most importantly when reaction was conducted without using any surfactant media followed by NaOH hydrolysis at 130 °C (Braddock, 2001), then 35-55% yield of *o*-nitrophenol was observed (Mathew *et al.*, 2006). However, this conversion can be increased up to 80% by using some kinds of surfactants (e.g., CTAB or TBAB) with different concentrations. It enables nitronium ion to attack more easily on *ortho* position as compared to the *para* position of benzene ring.

Nitration of substituted phenols. The reported studies demonstrate that tetra-butylammonium bromide (TBAB) is an excellent regio-specific surfactant for yield enhancement of *o*-nitrophenol. It has been reported that with different concentrations of TBAB surfactants, highest yield of *o*-nitrophenol (90-97%) was observed (Table 4). It was also noticed that in the absence of TBAB surfactant, only traces of *o*-nitrophenol were formed (Zolfigol *et al.*, 2001). The whole reaction has been summarized as Scheme 1.

*Reaction conditions: (Substrates 10 mmole, TBAB, nitric acid solution 20 mmole, temperature of reaction at 20 °C.



(Equation 1)

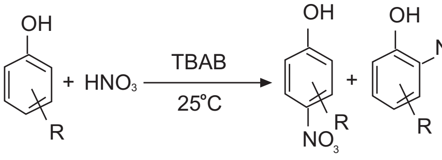
where:

X = H, F, CI, Br, CH_3 Ph and 2-phenylisopropyl.

Scheme 1. Nitration of phenol and substituted phenols.

Habibi *et al.* (2006) reported that complete conversion of phenol precursor can be achieved under specific reaction conditions by varying the amount of catalyst. It was observed that 5-10% concentration of TBAB is most effective for this purpose (equation 1 and Table 4). It was also observed that similar catalytic activity is achieved with tetra hexylammonium bromide for the conversion of substituted phenols into derivative products (Iranpoor *et al.*, 2005). The effect of temperature was also studied on different phases along with reaction time, it was found that 100% conversion takes place at 20 °C in 4 h reaction duration (Rajagopal and Srinivasan, 2003). Taking into time of exothermicity, ΔT was measured after every 5 min during the whole sequence of the reactions, with rise of temperature. It was concluded that formation of required isomer (90%) by maintaining the lower temperature is a safe way of conversion (Habibi *et al.*, 2006).

Nitration through sono-chemical process. Nowrouzi and Jonaghani (2011) proposed sono-chemical process for nitration of aromatic compounds. They performed effective nitration of phenol or substituted phenol in ultrasonic bath having a frequency of 33 kHz and electric power rating 100W (Nowrouzi and Jonaghani, 2011). For sono-chemical process, they investigated with different concentrations of organic phenol (10 mmol) and aqueous phase TBAB (5.0 mmol), nitric acid (6.0%) and I,2-dichloroethane (20 mL). The mixture was sonicated in water bath at 25 °C, the whole reaction was carried out in round bottom flask with mechanical stirrer or agitator in an ultrasonic water bath, the conversion of phenol into derivatives was monitored with GC-MS (Petrier *et al.*, 1998). The nitration of various phenolic compounds was performed in presence of TBAB phase transfer catalyst in ultrasonic bath. These results were also compared with those not involving ultrasonic conditions. The reaction can be best understood by following equation 2 (Kamal *et al.*, 2004).



(Equation 2)

Table 4. Nitration* of phenol (with surfactant TBAB)

Substituted phenol	TBAB (%)	Yield of *o*-nitrophenol (%)
Phenol	0	0.4
Phenol	5	90
4-chlorophenol	10	95
Benzoquinone	10	97

As shown in Table 5 that under silent conditions (stirring only), the nitration is achieved in 6 h with conversion of 59/41% into *ortho/para* forms. This low conversion can be increased by employing the same experiment in sonicated conditions with suitable amount of catalyst. In this way, 71-83/16% conversion into *ortho/para* forms is observed within 20 min. The results thus clarify that the regio-selectivity is enhanced under sonication conditions and reaction time is also lowered (Chen *et al*., 2014).

There are also reports regarding the effect of change of concentration of reagents and catalyst during the course of reaction (Table 6).

Table 5. Nitration of phenols and substituted phenols using dil. HNO_3 in the presence of TBAB

Entry	Substrate	Condition	Time	Conversion (%)	Selectivity		
					o-nitro	*p*-nitro	*o/p* ratio
1	Phenol	TBAB	20 min	95	83	16	5.18
2	Phenol	TBAB	40 min	95	74	24	2.96
3	Phenol	Silent	6 h	90	59	41	1.43

Table 6. Effects of various concentrations on nitration of phenol using ultrasonic conditions

Phenol (mmol)	HNO_3 (%)	TBAB (mmol)	Time	Conversion (%)	Selectivity		
					o-nitro	*p*-nitro	*o/p* ratio
Effect of TBAB concentration on *O/P* conversion in different time intervals							
10	6	2.5	4.0 h	30	72	27	2.66
10	6	5	40 min	95	74	25	2.96
10	6	10	20 min	95	83	16	5.18
Effect of substrate (phenol) concentration on *O/P* conversion in different time intervals							
5	6	5	20 min	95	75	24	3.12
10	6	5	40 min	95	74	25	2.96
20	6	5	45 min	50	70	29	2.41
Effect of nitric acid concentration on *O/P* conversion in under different time intervals							
10	3	5	4.0 h	20	67	32	2.09
10	6	5	40 min	95	74	25	2.96
10	12	5	5 min	95	71	28	2.53

Table 6 displays the effect of TBAB and various concentrations of substrates/nitric acid on the formation of *ortho* and *para* products and reaction time under ultrasonic conditions. The data clearly indicates that the sonicated conditions result in an increase of the selectivity as well as reduction of the reaction time (Tajik *et al*., 2009). Table 7 shows the nitration of phenol under sonication using different catalysts. The data (Table 7) demonstrates that maximum conversion into *ortho*-derivative (95%) is achieved by using TBAB as catalyst and a time duration of 20 min. However, maximum *para*-selectivity is occurred by using CTAB (90% conversion into *para*-isomer) and NaBr (72% conversion into *para*-isomer) catalysts (Habibi *et al*., 2006).

Table 7. *O/P* nitration of phenol under sonication conditions by using different catalysts/surfactants

Catalyst (5 mol)	Time (%)	Conversion (%)	Selectivity		
			o-nitro	*p*-nitro	*o/p* ratio
TBAB	20 min	95	83	16	5.18
CTAB	1 h	90	69	20	3.43
NaBr	1 h	72	26	73	0.35

Palladium catalyzed aromatic C-H bond nitration. Another nitration method was investigated by (Zhang *et al*., 2014) by using phenol and 2-bromopyridine and cross coupling of 2-phenoxypyridine. The efficient nitro source of $AgNO_3$ and $H_2S_2O_8$ mixture was used for palladium-catalyzed C-H bond nitration (Colby *et al*., 2009). It was reported that $PdCl_2$ and $Pd(PPh_3)_2Cl_2$ have low catalytic activity as compared to the $Pd(OCOCF_3)_2$ when screened in DCE which gave desired product of 76% yield. It was also investigated that more than 97% yield is obtained by using $Pd(OAc)_2$ for 48 h at 110 °C (Karimi Zarchi and Rahmani, 2011). It was found that in the absence of palladium catalyst these reactions could not yield the desired product. The potassium and sodium nitro sources with 1-4 dioxan and toluene solvents could be used for better yield in these reactions. It was noticed that yield is dramatically reduced when the catalyst load is dropped up to 5-10 mol. Thus, 58% and 87% yield was recorded in presence of $Pd(OAc)_2$ (catalyst) concentrations of 5 and 10 molar strengths, respectively (Zhang *et al*., 2014).

Nitration with H-beta catalyst. Another methodology for phenol nitration was reported with equivalent concentrations of nitric acid and phenol in presence of H-beta zeolite catalyst. The lanthanum nitrate on MoO_3/SiO_2 (MoO_3: 20 mol %) and $Fe_2O_3/MoO_3/SiO_2$ (Fe_2O_3=0.7; MoO_3=20 mol %) were used for the preparation of La H-beta catalyst. The reaction was performed in 3 mL of solvent between phenol (2.0 g) and H-beta (1.0 g) catalyst in the presence of 4 mL of dilute nitric acid (30%) under stirring conditions and varying the time period at room temperature. Diethyl ether was used for extraction of reaction product. The physical and chemical properties of H-beta catalyst were investigated by various techniques such as XRD and AAS before and after the reaction (Vogel, 2013). The 87% selectivity was recorded for *o*-nitrophenol conversion by this process, the highest conversion (96%) was recorded under experimental conditions involving the use of H-beta zeolite catalyst. However, the conversion was decreased to 60% if the acidity of the H-beta catalyst was dropped (Hancock and Clague, 1964).

Nitration through microwave (MW) system. Ergan *et al*. (2017) studied the synthesis of nitrophenols by microwaves system technology. The uncontrolled heat loss was prevented by equipping MW system with Pyrex tube covered with two collars (total volume of 10 mL), insulated fiberglass and Teflon film. They equipped MW system with infrared (IR) and fluoroptic temperature (FO) sensors. The reaction temperature was measured continuously with FO sensor that was submerged in the tube. The temperature was also controlled with another air inlet by simultaneous introduction of nitrogen gas. Continuous irradiation of MW was used for cooling purposes especially when concentrated materials were used. The temperature of outer surface of tube was maintained with an IR sensor (Ergan *et al*., 2017). Greater than 85% output of *o*-nitrophenol was calculated with RP-HPLC and GC-MS.

Conclusions

The use of nitronium tetra-fluoroborate suspended in acetonitrile process gives highest regio-selective nitration with a 95% yield of *ortho* product. The surfactants (e.g., CTAB or TBAB) reported for the nitration processes are comprised of two phases (aqueous and organic phases) and cause an increase of selectivity at ortho postion. A considerable selectivity of *o*-nitrophenol can be achieved with dilute nitric acid (6%) in presence of tetra-butylammonium bromide (TBAB) as catalyst. The micro-emulsion media was used to convert the substrate phenol into *o*-nitrophenol and *p*-nitrophenol. Complete conversion of phenol precursor can be achieved in 4 h at 20 °C by varying the amount of catalyst e.g., 5-10% TBAB or tetra-hexylammonium bromide, the use of lower temperature is a safe way of conversion. Performing the nitration under sonication conditions lowers the reaction time and increases the *ortho/para* regio-selectivity. Under sonication conditions, maximum conversion into *ortho*-derivative (95%) is achieved by using TBAB as catalyst in 20 min but maximum para-selectivity is achieved by using CTAB and NaBr catalysts. The use of $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$, H-beta zeolite, catalysts for selective nitration has also been reported. Greater than 85% yield of *o*-nitrophenol was observed by using microwaves system technology.

Conflict of Interest. The authors declare no conflict of interest.

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