

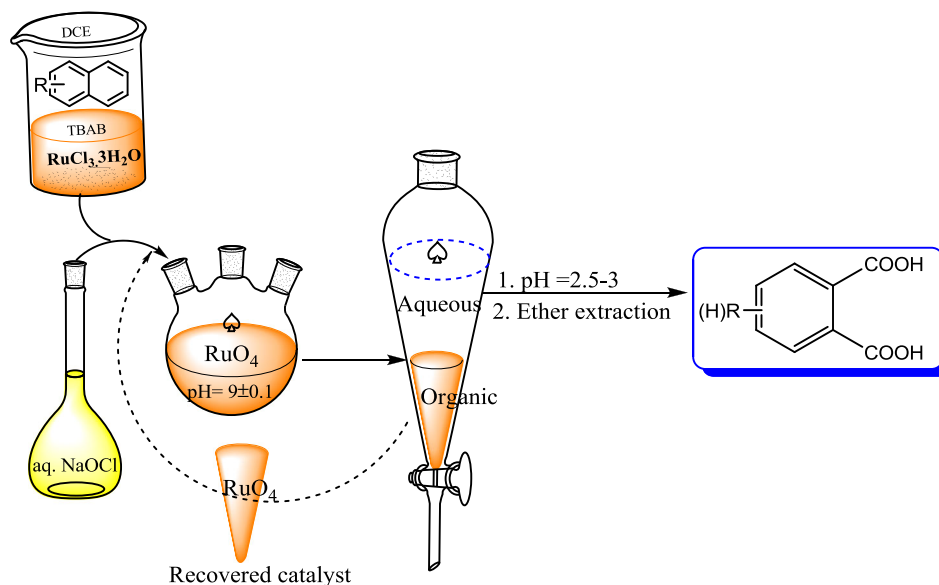
Naphthalenes Oxidation by Aqueous Sodium Hypochlorite Catalyzed by Ruthenium Salts Under Phase-Transfer Catalytic Conditions

Rajendra D. Patil¹ · Yoel Sasson¹

Received: 15 January 2016 / Accepted: 21 February 2016 / Published online: 1 March 2016
© Springer Science+Business Media New York 2016

Abstract Highly effective and fast oxidation of naphthalene(s) to phthalic acid(s) under biphasic conditions using nominal catalyst loading (0.5 mol%) of ruthenium chloride, 2.5 mol% tetrabutyl ammonium bromide as phase transfer catalyst and inexpensive aqueous sodium hypochlorite (NaOCl) as reagent has developed. Recovery, regeneration and reuse of the catalytic system add its merit to green chemistry.

Graphical Abstract A nominal loading (0.5 mol%) of ruthenium chloride as catalyst and inexpensive aqueous sodium hypochlorite (aq. NaOCl) as reagent are found to be highly effective reaction system for the partial oxidation of naphthalene(s) to phthalic acid(s) under phase transfer catalyst (PTC) conditions. Recovery, regeneration and reuse of the “ruthenium-PTC” catalytic system add its merit to green chemistry.



✉ Rajendra D. Patil
r_dpatil123@yahoo.co.in

Yoel Sasson
ysasson@huji.ac.il

¹ Casali Institute of Applied Chemistry, The Institute of Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Keywords Phase transfer catalysis · Naphthalene's · Phthalic acids · Ruthenium catalyst · Oxidation

1 Introduction

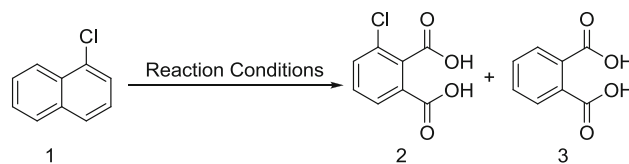
The partial oxidation of naphthalenes to the corresponding phthalic acids has been an effective and useful reaction for the production of aromatic dicarboxylic acids. The products phthalic acids have numerous practical applications in various industries such as polymers, adhesives and glues, electronics, synthetic perfumes etc. [1, 2]. Phthalic acids can be synthesized through the oxidation of their starting precursors such as naphthalenes, xylenes, benzaldehydes [3–5]. However the catalytic oxidation of naphthalene directly to phthalic anhydride and subsequent hydrolysis of anhydride into the phthalic acids has been remains the most common route for phthalic acid synthesis [3, 6]. There are several literature reports for the oxidation of naphthalenes using $\text{CeO}_2/\text{Al}_2\text{O}_3$, M (Ru, Pt, Pd, Co etc.)/ Al_2O_3 , V_2O_5 , $[\text{Ru}^{\text{IV}}(2,6\text{-Cl}_2\text{tpp})\text{Cl}_2]$ complex, RuO_4 etc. has reported [7–14]. Apart from this; metal salts (MOAc)/photoirradiation and superoxide (KO_2) were utilized for the naphthalenes oxidation [15–17].

An aqueous sodium hypochlorite (aq. NaOCl) is well known and useful oxidant in organic synthesis for an oxidation of various organic compounds [18]. An oxidation of naphthalenes carried out using aq. NaOCl at 60–70 °C during the period of 4–6 h [19, 20], however this method has limitations to oxidize strongly electron withdrawing substituted naphthalene's [19, 20]. The method utilizing aq. NaOCl in conjunction with ruthenium salt (RuO_2) has reported for oxidation of naphthalenes [21]. This RuO_2 -NaOCl system has advantages over utilizing only aq. NaOCl (without ruthenium salt) such as; reaction proceed at room temperature (instead at 60–70 °C) and efficient to oxidize various activated as well as non-activated naphthalenes [19–21]. However RuO_2 -NaOCl system has slow reaction rate towards strongly electron withdrawing substituted naphthalenes and took longer reaction time of some days in case of nitronaphthalenes (4–7 days) [21].

Our research group was introduced phase transfer catalysis in such related oxidation reactions [22, 23]. It has been found that when RuO_4 combined with suitable phase transfer catalyst, its activity (RuO_4) substantially changed [24, 25]. Therefore we hypothesize that reaction rate of naphthalenes (particularly non-activated naphthalenes) oxidation using RuO_2 -NaOCl [21] system could be substantially enhanced using phase transfer catalyst for both electron donating as well as electron withdrawing substituents.

An oxidation of ruthenium chloride by aq. NaOCl in situ generates ruthenium tetroxide (RuO_4) which has good solubility in DCE reaction solvent and act as true liquid phase oxidant during the present reactions [21–23]. To our delight; we found that using RuCl_3 -NaOCl system the reaction rate of various activated as well as non-activated naphthalenes oxidation has greatly improved under phase transfer catalytic conditions. To the best of our knowledge, RuCl_3 -NaOCl reaction system for the liquid phase partial oxidation of naphthalene to phthalic acid under phase transfer conditions has been not reported.

For the present study; we have chosen 1-chloronaphthalene as model substrate, ruthenium chloride ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) as catalyst, aq. NaOCl (house bleach) as reagent and experimental results obtained are presented in Table 1. Based on our earlier studies [22, 23]; we have selected 1,2-dichloroethane (DCE) is reaction solvent and ruthenium to PTC ratio was maintained at 1:5 mol% for the present study. Initially the reaction was performed using 1-chloronaphthalene, stoichiometric amount of aq. NaOCl (molar ratio of NaOCl/substrate = 8), 1 mol% $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 5 mol% TBAB at room temperature. After completion of the reaction at 1 h, 1-chloronaphthalene afforded 54 % isolated yield with 61 % selectivity for desired 3-chloro-phthalic acid **2** (Table 1, entry 1). The increase of molar ratio of NaOCl/substrate from 8 to 12 increases the reaction yield up to 75 % along with small increase in the selectivity for product **2** (Table 1, entry 2). A reduction of the ruthenium salt from 1 mol% to 0.5 mol% increases the reaction yield up to 84 % (Table 1, entry 3). Under similar reaction conditions; increase of NaOCl/substrate molar ratio from 12 to 16 decreases reaction yield (Table 1, entry 4) up to 62 %. An effort to decrease ruthenium salt from 0.5 to 0.2 mol%, causes decrease in the reaction yield (Table 1, entry 5). Next to optimize reaction temperature; reactions were carried out at variable temperatures (from 0 to 55 °C, Table 1, entries 6–8). As obtained results indicated that the best yield of product **2** could be obtained at room temperature (Table 1, entry 3). In the case of reaction carried out using didecyl dimethyl ammonium bromide (DDAB) instead of TBAB as PTC; relatively lower yield and selectivity of product **2** was observed (Table 1, entry 9). Reaction without PTC (TBAB) given only 68 % yield (Table 1, entry 10). Reaction did not proceed in absence of either ruthenium catalyst or aq. NaOCl (Table 1, entries 11–13). After details optimization study it was found that 0.5 mol% of ruthenium catalyst, 2.5 mol% PTC (TBAB), NaOCl/substrate in a molar ratio of 12, and reaction at room temperature were optimized parameters to achieve best yield and selectivity of product **2** under given conditions (Table 1, entry 3).

Table 1 Optimization of reaction conditions for oxidation of naphthalenes to phthalic acids

Entry	NaOCl (equiv.)	RuCl ₃ ·3H ₂ O (mol%)	PTC (mol%)	Temp (°C)	Time (h)	Yield 2 ^a	Product ratio (GC %) ^b	
							2	3
1	8	1	5	RT	1	54	61	39
2	12	1	5	RT	0.5	75	63	37
3	12	0.5	2.5	RT	0.5	84	65	35
4	16	0.5	2.5	RT	0.5	62	63	37
5	12	0.2	1	RT	1	60	63	37
6	12	0.5	2.5	0–5	1	NR	–	–
7	12	0.5	2.5	10–15	1	59	59	41
8	12	1	5	50–55	0.5	60	69	31
9	12	0.5	2.5 ^c	RT	0.5	58	67	33
10	12	0.5	–	RT	1	68	64	36
11	12	–	2.5	RT	1	NR	–	–
12	12	–	–	RT	1	NR	–	–
13	–	0.5	2.5	RT	1	NR	–	–

Reaction conditions: 1-chloronaphthalene 1 (5 mmol), catalyst (RuCl₃·3H₂O), PTC (TBAB), aq. NaOCl, DCE, open air atmosphere

^a Isolated yield calculated considering 3-chloro phthalic acid 2 as product

^b Selectivity based on GC area %

^c DDAB used as PTC. NR no reaction

Under the optimized reaction condition (Table 1, entry 3); we have subjected various naphthalenes derivatives and results are presented in Table 2. From Table 2 it is seen that various naphthalenes derivatives having electron donating as well as strongly electron withdrawing substituents were well tolerated and afforded good to better yields and better to excellent selectivity within shorter period of time (~0.5 h). From the Table 2 it is seen that substituent's exert a substantial directive effect on oxidation of substituted naphthalenes. Naphthalene with electron donating substituent (α -Naphthol) activates the substituted ring and increases the yield as well as selectivity towards phthalic acid (Table 2, entry 3). In contrast electron withdrawing substituent's protect the substituted ring and also decrease the overall reactions yields (Table 2, entries 1, 4–6). It has been observed in the literature reports that highly electron withdrawing derivatives (such as nitro derivatives) are difficult to oxidize as well as took longer reaction time and operate at higher temperature [7, 15–17, 19–21]. In addition oxidation of useful electron withdrawing derivative like 2-nitronaphthalene, 1-chloronaphthalene has been either not reported or rarely reported (Table 2, entries 1 and 4) [7, 15–17, 19–21]. For example

two literature methods developed for the oxidation of 1-nitro naphthalene involves liquid phase ruthenium catalyzed oxidation took place during period of 7 days while CeO₂/Al₂O₃ [7] system requires high temperature of reaction (363–373 K). However under present PTC conditions ruthenium catalyzed oxidation of 1-nitro naphthalene took place within period of 0.5 h and at room temperature (Table 2, entry 5). Further oxidation of 2-bromonaphthalene afforded corresponding 3-bromo phthalic acid with excellent selectivity (93 %) (Table 2, entry 6). In spite of alkaline environment of the reaction system; oxidation of 2-naphthoic acid with alkali sensitive carboxylic acid group has well tolerated (Table 2, entry 7).

Both the RuCl₃·3H₂O and aq. NaOCl found to be necessary components for the oxidation of naphthalene's. In absence of TBAB; reaction yield decreases. Therefore TBAB which is carrier for faster and continuous transport of catalyst and reagent from aqueous phase to organic phase has additive effect to the present catalytic system to get higher yield of oxidized products in relatively shorter time (~0.5 h). Prior to adding the substrate; the pH of aq. NaOCl solution brought to pH 9 by adding 20 % aq. sulfuric acid. Similarly during the course of the reactions; pH

dropped due to acidic nature of generated products (phthalic acid etc.) has maintained at $\text{pH } 9 \pm 0.1$ by manual addition of 20 % aq. NaOH. The reactions are markedly pH dependent and NaOCl solution must be maintained at pH 8.0–10.5. Above facts confirmed through control experiments; at initial high pH of aq. NaOCl (pH 12.7) reaction did not proceed while at lower pH reaction (below 8) did not lead to the desired products. In fact reaction solution has precisely maintained at $\text{pH } 9 \pm 0.1$ during all the reactions in the present work. Another important aspect to mention that reaction time requires for particular reaction has found no considerable dependence on the nature of substituents and almost all the reactions completed within reaction period of 30 min.

In complete reaction mechanism; TBAB as PTC play important role to carry proton and hypochlorite anions (OCl^-) from aqueous phase to organic phase (Scheme 1i) [22, 23]. The PTC (TBAB) may maintain in the organic solution the hypochlorite anion (ClO^-) [23] and possibly the reduction product(s) of RuO_4 during the catalysis helping ruthenium re-oxidation to RuO_4 therefore continuous and complete oxidation of naphthalene(s) substrates could possible. In naphthalene oxidation; formation of intermediate oxidized products such as α -Naphthol, 1,4 dihydroxy naphthalene, 1,4-naphthaquinone, phthalic anhydride are very much likely [7–14]. Literature reports confirm that; hydroxylation is the prerequisite for aromatic ring cleavage [26–28]. The functional group conversions such as α -Naphthol \rightarrow 1,4 dihydroxy naphthalene \rightarrow 1,4-naphthaquinone \rightarrow phthalic anhydride \rightarrow phthalic acid has been well known in the literature [7–14, 29]. Moreover RuO_4 and aq. NaOCl were capable of breaking aromatic ring [19, 20, 30, 31]. Therefore based on the literature we also assumed mechanistic pathways for present RuO_4 /PTC system as depicted in Scheme 1. To check our assumptions we have performed a controlled experiments with the assumed intermediates such as α -Naphthol, β -naphthol, 1,4-naphthaquinone, phthalic anhydride under optimized reaction condition of Table 1, entry 3. It is found that like naphthalenes; all these intermediates (except phthalic anhydride) almost showed similar reactivity and experimental observations. All the oxidation reactions of naphthalenes, α -naphthol, β -naphthol and 1,4-naphthaquinone were exothermic and showed almost similar increase of reaction internal temperature (23–52 °C) within period of 5–10 min. α -Naphthol, β -naphthol, 1,4-naphthaquinone afforded 83, 54, 66 % yields of phthalic acid respectively under optimized reaction conditions (Table 1, entry 3). Unlikely; reaction of phthalic anhydride was not substantially exothermic (temperature change = 23–33 °C) under present optimize conditions and did not proceed to phthalic acid product. However; when the reaction of phthalic anhydride carried out at 50–55 °C (instead at room

temperature) while other parameters of optimized reaction conditions (Table 1, entry 3) kept constant then it provided the good yield of phthalic acid (53 % yield). Above experimental observations are in well accordance with assumptions made for mechanistic pathways (Scheme 1) based on literature reports [7–14, 19–21, 26–31].

Upon attempts to recycle the present ruthenium-PTC catalytic system; we found good reactivity and recyclability of present catalytic system for four consecutive runs (84, 82, 68, 60 % respectively) using 1-chloronaphthalene as model substrate. The products were identified using GC, NMR, IR, and TLC, comparing them with authentic samples.

In summary; the present ruthenium-PTC catalytic system offers mild method for the oxidation of naphthalenes to phthalic acids at ambient conditions. Especially present method has better activity to oxidize highly withdrawing substrate under PTC conditions at room temperature and within shorter reaction period. Good chemo selectivity, regeneration-recovery and reuse of the ruthenium catalyst using inexpensive aqueous hypochlorite oxidant add its merit to green chemistry.

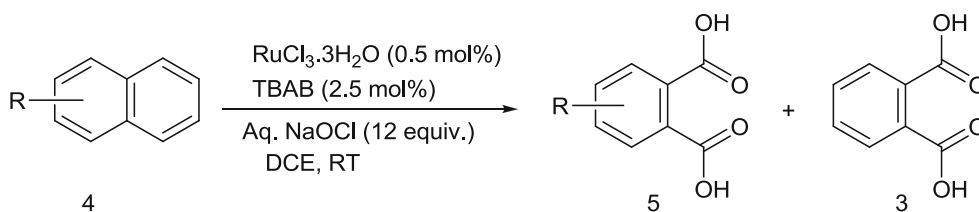
2 Experimental Section

2.1 General

Chemicals were purchased from commercial firms (Sigma Aldrich) and used without further purification. GC analyses were performed using Focus GC from Thermo Electron Corporation, equipped with low polarity ZB-5 column. ^1H -NMR spectra were recorded with Bruker DRX-400 instrument in DMSO. IR analysis was performed by FT-IR spectrometer; model Alpha from Bruker Optics.

2.2 General Procedure for Oxidation of Naphthalene

In a 250-mL three necked flask equipped with pH and temperature sensor were placed 40 mL of aq. NaOCl (10 % Assay) at room temperature. The pH at the aqueous phase was brought to $\text{pH } 9 \pm 0.1$ by addition of 20 % (v/v) H_2SO_4 . To this aqueous NaOCl solution; mixture of naphthalene (0.81 g, 5 mmol), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.0065 g, 0.5 mol%), tetrabutyl ammonium bromide (0.040 g, 2.5 mol%) and 10 mL of 1,2-dichloroethane were added. Stirring was commenced with a mechanical stirrer and reaction continued at room temperature (23 ± 2 °C) during the period of 10–30 min. The pH was controlled during the reaction by using manual addition of 20 % of NaOH to keep the pH at 9 ± 0.1 . After the hypochlorite solution was used up (reaction shows colour change from yellow to

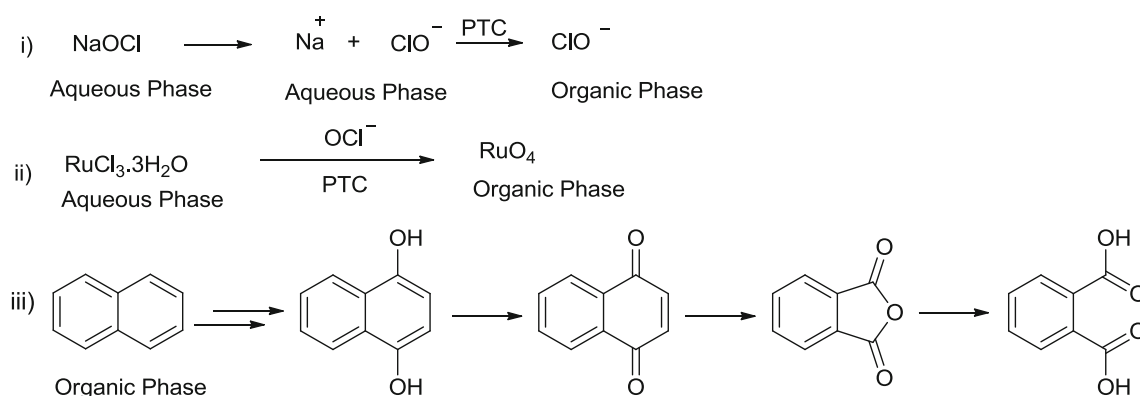
Table 2 Optimization of reaction conditions for oxidation of naphthalenes to phthalic acids

Entry	Substrate	Time (min)	Major product	Yield ^a (%)	Product ratio (%) ^b	
					5	3
1		30		84	65	35
2		30		58	–	–
3		30		83	99>	00
4		30		51	65	35
5		30		45	67	33
6		20		52	95	05
7		30		70	70	30

Reaction conditions: Naphthalene **4** (5 mmol), RuCl₃·3H₂O (0.5 mol%), TBAB (2.5 mol%), aq. NaOCl (12 Equiv.), DCE (10 mL), RT, open air atmosphere

^a Isolated yield calculated considering yield of major product. (mmol of major product/mmol of substrate × 100, where mmol of major product is wt of product/molecular weight of major product)

^b Selectivity based on GC area %



Scheme 1 Probable mechanism for oxidation of naphthalene to phthalic acid

white cloudy) a few drops of hypochlorite solution were added to reoxidize the ruthenium catalyst. The phases were separated and an aqueous phase is acidified with dilute 20 % aq. H_2SO_4 to brought pH at 2.5–3. The acidic solution containing organic products was extracted with diethyl ether ($30 \times 3 = 90$ mL); solvent evaporation resulted into crude 3-chlorophthalic acid (0.842 g, 4.2 mmol).

Derivatization of phthalic acids using *N, O*-bis(trimethylsilyl) trifluoroacetamide with 1 % trimethylchlorosilane (BSTFA) was performed for gc analysis.

2.3 Procedure for Silylation of Phthalic Acid

The 16 mg of 3-chlorophthalic acid (product) transferred into a clean and dry 2 mL glass vial. To this 160 μL BSTFA was added and mixture was heated at 60 °C for 30–40 min. From the resultant solution; two μL of each sample was injected into the gas chromatogram (GC).

2.4 Recovery and Reuse of Catalytic System ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/\text{TBAB}$)

After completion of the reaction the two phases of reaction mixture was allowed to separate. The desired product phthalic acid upon acidification was separated from aqueous layer while organic layer containing RuO_4 and TBAB in DCE recovered as such (please see: “General Procedure for Oxidation of Naphthalene” section).

2.5 Catalyst Reuse Experiment

The experimental procedure for reuse of catalytic system was similar as described above for general procedure for the oxidation of naphthalene. In a 250-mL three necked flask equipped with pH and temperature sensor were placed 40 mL of aq NaOCl (10 % Assay) at room temperature. The pH at the aqueous phase was brought to $\text{pH } 9 \pm 0.1$ by

addition of 20 % (v/v) H_2SO_4 . To this aqueous NaOCl solution; naphthalene (0.81 g, 5 mmol), recovered organic phase (containing 7 mL mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, TBAB and DCE) and 3 mL of DCE were added. Remaining experimental processes and separation of organic product was similar as described above for general procedure for oxidation of naphthalene.

Acknowledgments We are thankful to Elad Meller and Hani Gnyem of our lab for their help during the present research work.

References

- Lewis RJ (2001) Hawley's condensed chemical dictionary, 14th edn. Wiley, New York
- Encyclopedia Britannica Inc (2014) Carboxylic acid. Encyclopedia Britannica. Encyclopedia Britannica online (Web. 09 July 2014)
- Gupta M, Paul S, Gupta R, Loupy A (2005) Tetrahedron Lett 46:4957
- Dubreuil J, Garcia-Verdugo E, Hamley PA, Perez E, Pearson I, Thomas WB, Housley D, Parteinheimer W, Poliakov M (2009) Adv Synth Catal 351:1866
- Lim M, Yoon CM, An G, Rhee H (2007) Tetrahedron Lett 48:3835
- Lorz PM, Towae FK, Enke W, Jackh R, Bhargava N, Hilleshiem W (2007) Phthalic acid and derivatives. Ullman's encyclopedia of industrial chemistry. Wiley, Weinheim
- Rajiah T, Chary KVR, Rao KSR, Rao RN, Prasad R (2002) Green Chem 4:210 and references cited therein
- Zhang XW, Shen SC, Yu LE, Kawi S, Hidajat K, Simon Ng KY (2003) Appl Catal A 250:341
- Bruckner A, Baerns M (1997) Appl Catal A 157:311
- Zhang JL, Che CM (2005) Chem Eur J 11:3899
- Zhang XW, Shen SC, Hidajat K, Kawi S, Yu LE, Simon Ng KY (2004) Catal Lett 96:87
- Kulinich VP, Shaposhnikov GP, Gorelov VN, Chernyaeva EA (2006) Zh Obshch Khim 76:1387
- Nufiez MT, Martin VS (1990) J Org Chem 55:1928
- Radhika T (2006) Ph.D. thesis Chapter 7 titled “Vanadia supported on rice husk silica promoted rare earth oxides: characterization and catalytic application in oxidation reactions” <http://shodhganga.inflibnet.ac.in/handle/10603/8621>

15. Yamashita T, Tsurusako T, Yasuda M, Shima K (1991) *Chem Lett* 9:1487
16. Sotiriou C, Lee W, Giese RW (1900) *J Org Chem* 55:2159
17. Li W, Sotiriou C, Saha M, Fu PP, Giese RW (1993) *Synth Commun* 23:97
18. Chakrabartty SK, Kretschmer HO (1974) *J Chem Soc Perkin Trans* 1:222
19. Angert JL, Gatton SL, Reilly MT, Landolt RG (1977) *Fuel* 56:224
20. Landolt RG (1975) *Fuel* 54:299
21. Spitzer UA, Lee DG (1974) *J Org Chem* 39:2468 **and references cited therein**
22. Sasson Y, Zappi GD, Neumann R (1986) *J Org Chem* 51:2880
23. Sasson Y, Quntar AEA, Zoran A (1998) *Chem Commun* 73
24. Smith AB, Scarborough RM (1980) *Synth Commun* 10:205
25. Alper H (1987) Phase transfer catalysis, Chapter-II. In: Starks CM (ed) *New chemistry, catalyst, and applications.*, ACS Symposium Series ACS, Washington DC, pp 8–14
26. Pang X, Chang W, Chen C, Ji H, Ma W, Zhao J (2014) *J Am Chem Soc* 136:8714
27. Kluge M, Ullrich R, Dolge C, Scheibner K, Hofrichter M (2009) *Appl Microbiol Biotechnol* 81:1071
28. Huq FJ (2007) *Pharmacol Toxicol* 2:33
29. Sreekanth R, Prasanthkumar KP, Paul MMS, Aravind UK, Aravindakumar CT (2013) *J Phys Chem A* 117:11261
30. Lee DG, Engh M (1973) Chapter IV, Part B. In: Trahanovsky WS (ed) *Oxidation in organic chemistry.* Academic Press, New York
31. Berkowitz LM, Kylande PN (1958) *J Am Chem Soc* 80:6682