

Organocatalytic Aerobic Oxidation of Ethylbenzene Using 3, 4, 5, 6-Tetrachloro-*N*-hydroxyphthalimide and 1, 4-Diamino-2, 3-dichloro-anthraquinone

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Recently, *N*-hydroxyphthalimide (NHPI) attracted continuous attention due to its high catalytic efficiencies for aerobic oxidation of hydrocarbons, the important industrial processes, in combination with some metallic co-catalysts^[1]. We reported firstly an organocatalytic system encompassing anthraquinones and NHPI for efficient selective oxygenation of hydrocarbon^[2]. In its catalysis, 1,4-diamino-2,3-dichloro-anthraquinone (DACAQ) was found to be more effective than other used anthraquinones. Furthermore, NHPI analogues with electron-withdrawing substituents on aromatic ring show higher catalytic activities^[3]. Herein, 3,4,5,6-Tetrachloro-*N*-hydroxyphthalimide (TCNHPI) was synthesized and coupled with DACAQ to be an organocatalytic system. We wish to report its catalytic performance for oxidation of ethylbenzene by O₂.

TCNHPI was synthesized via the reaction of 3,4,5,6-tetrachlorophthalic anhydride and hydroxylamine hydrochloride in the presence of triethylamine, and was determined by NMR and IR. The catalytic oxidation was carried out in a 100 mL autoclave (Table 1). The conversions and product distributions were evaluated with GC by calibration curves with 1,2,4,5-tetramethylbenzene as an internal standard. PEHP was quanti-

fied by the literature method^[4].

Metal-promoted NHPI-catalyzed oxidation of hydrocarbons in literatures almost occurred in solution, where acetic acid was a popular solvent^[1]. In our test, ethylbenzene was oxidized directly without using any solvent. The coupled system of 0.33 mol% NHPI and 0.1 mol% DACAQ gave 21.9% ethylbenzene conversion (entry 6). In comparison, the conversion increased to 40.3% when TCNHPI was used at the same conditions (entry 3). Furthermore, the immediate decrease of pressure in TCNHPI-catalysis was observed, whereas the pressure change was observed after 1 h when NHPI was used. Unfortunately, the rate of TCNHPI catalysis reaction was so fast that over-oxidation took place and resulted in the formation of benzoic acid (BA). These results clearly exhibit that TCNHPI has the higher catalytic activity than NHPI, and TCNHPI/DACAQ can significantly promote aerobic oxidation of ethylbenzene.

Alkyl hydroperoxide is an initial product of autoxidation, which often exists with considerable quantities in the mixture. In accordance, 1-Phenylethyl hydroperoxide (PEHP) was a main product in the NHPI/DACAQ catalysis and the case of using 0.065%

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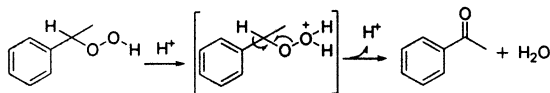
Biography: Yang Guan-yu, male, born in 1963.

Table 1 Aerobic oxidation of ethylbenzene catalyzed by TCNHPI/ DACAQ

Entry	Catalyst loading (%)		Conversion (%)	Products distribution (%)				
	DACAQ	TCNHPI		AcPO	PEA	PEHP	BA	Phenol
1	0.1	0.065	12.1	16.3	23.7	60.0	0	0
2	0.1	0.13	31.9	83.2	15.0	0	1.8	0
3	0.1	0.33	40.3	81.4	12.6	0	6.1	0
4	0.1	0.65	19.6	56.3	27.4	0	0	16.3
5	0.1	1.3	22.9	61.4	16.2	0	0	22.5
6	0.5	0.33	26.2	68.7	31.3	0	0	0
7	1.0	0.33	29.3	68.8	31.2	0	0	0
8	0.1	0.33 ^a	21.9	31.5	24.1	44.4	0	0

^aNHPI in stead of TCNHPI

TCNHPI and 0.1% DACAQ (entry 1). It was surprisingly found that any amount of PEHP was not determined when the loading amount of TCNHPI exceeded 0.13% . The reason was suggested to be the acid-catalyzed PEHP decomposition by TCNHPI (Scheme 1). ¹H NMR of TCNHPI and NHPI show the



Scheme 1 Acid-catalytic Decomposition of PEHP

hydrogen of their hydroxyl has 11.96 ppm and 10.85 ppm chemical shift values, respectively, implying the hydroxyl of TCNHPI possesses stronger acidity than NHPI. Such acidity also brought the formation of phenol (entry 4), whose route is just similar to the strong-acid-catalyzed decomposition of cumene hydroperoxide into phenol in Huck Process ^[5] . As a result, the

conversion decreased because of the radical-scavenging effect of phenol.

In conclusion, TCNHPI was synthesized. As an organocatalyst for aerobic oxidation of ethylbenzene in the absence of any solvent, this compound showed significant catalytic activity in combination with DACAQ.

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有机物 3, 4, 5, 6-四氯-*N*-羟基邻苯二甲酰亚胺和 1, 4-二氨基-2, 3-二氯蒽醌催化乙苯的分子氧氧化

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摘 要: 合成了 3, 4, 5, 6-四氯-*N*-羟基邻苯二甲酰亚胺并与 1, 4-二氨基-2, 3-二氯蒽醌组合成有机催化体系. 在无溶剂条件下, 该体系能够有效催化乙苯的分子氧氧化.

关键词: 有机催化; 乙苯; 氧化; 3, 4, 5, 6-四氯-*N*-羟基邻苯二甲酰亚胺; 1, 4-二氨基-2, 3-二氯蒽醌