Tetrahedron Letters 50 (2009) 1677–1680

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A free radical process for oxidation of hydrocarbons promoted by nonmetal xanthone and tetramethylammonium chloride under mild conditions

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ARTICLE INFO

Article history:
Received 10 November 2008
Revised 6 January 2009
Accepted 7 January 2009
Available online 19 January 2009

Keywords:
Aerobic oxidation
Hydrocarbons
Xanthone
Nitroxyl radical
Quaternary ammonium salts

ABSTRACT

A nonmetal catalytic system consisting of *N*-hydroxyphthalimide, xanthone, and tetramethylammonium chloride was developed. A wide range of hydrocarbons could be oxidized efficiently with dioxygen under mild conditions. In the presence of xanthone and tetramethylammonium chloride, catalytic activity of *N*-hydroxyphthalimide was greatly improved, and selectivity for alkyl hydroperoxide was remarkably decreased.

Liquid-phase oxidation of hydrocarbons is an important industrial process.[1,2] However, the reaction conditions are usually harsh industrially. For example, the Snia-viscosa process for oxidation of toluene operates at 165 °C.[2] The oxidation catalysts usually contain transition metals such as Co^{2+} and Mn^{2+}.[3] Though great advances have been made,[3] it is still a challenge to develop efficient oxidation catalytic systems from both an economic and environmental point of view. In the past several years, *N*-hydroxyphthalimide (NHPI) has attracted much attention for aerobic oxidation of hydrocarbons.[4–8] However, cocatalyst such as $Co(OAc)_2$ was required for the generation of the corresponding phthalimide *N*-oxyl radical (PINO) under mild conditions. Transition metals combined with NHPI have been intensely studied;[4–6] while the inherent advantages of a nonmetal catalytic system were often ignored. Some nonmetallic compounds such as aldehyde, AIBN, have been used as mediators combined with NHPI.[9] However, these compounds were often not recoverable. Our group has developed several organocatalytic systems such as NHPI/anthraquinones.[10–14] We are particularly interested in organocatalysis, and here we disclosed a novel nonmetal catalytic system for oxidation of hydrocarbons under mild conditions.

Free radical processes are usually involved in the liquid-phase aerobic oxidation of hydrocarbons. Oxygenated intermediates are usually more active than substrate itself. Some oxygenated compounds can play important roles during the oxidation process though their effects on the oxidation were often ignored.[15] Thus, it was possible for oxygenated compounds to perform as a catalyst if they could be recycled during the oxidation process. We noticed that xanthene could be facilely oxidized to xanthone nearly quantitatively through NHPI-catalyzed autoxidation process.[5] It was assumed that it could be used with NHPI to promote oxidation of other hydrocarbons. Primary investigations were carried out using ethylbenzene as a probe molecule (Table 1). To our delight, the combination of xanthone and NHPI could significantly promote the oxidation of ethylbenzene. The conversion of ethylbenzene increased to 40.8% compared with only about 10% conversion using NHPI alone. (Table 1, entry 4). The property of aromatic heterocyclic compounds is greatly affected by large conjugation system containing heteroatom in backbone. Then, other heterocyclic compounds were also studied besides xanthone (Table 1). However, 1-azaxanthone had no significant effect on both conversion and selectivity (Table 1, entry 3). Thioxanthone, acridone which contains S or N atom, decreased the catalytic activity (Table 1, entries 1 and 2). It was notable that the selectivity of 1-phenylethyl hydroperoxide (PEHP) was rather high (56–97%). Promoting the further conversion of PEHP was beneficial for favorable ketone/alcohol yield.

Recently, using quantum chemical calculations, Ive Hermans and co-workers believed that there was an established equilibrium $ROO^{\cdot} + NHPI \rightleftharpoons ROOH + PINO$ in NHPI-based oxidation process; the reverse reaction was very fast.[16] PINO is highly electrophilic and readily abstracts H-atoms from hydrocarbons much faster than $ROO^{\cdot}$.[17,18] In order to shift the equilibrium right to form more PINO, a third component could be introduced to reduce the concentration of ROOH.

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0040-4039/$ - see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2009.01.077

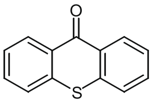
Table 1
Oxidation of ethylbenzene using NHPI and different aromatic heterocyclic compounds[a,b]

Entry	Aromatic heterocyclic compounds	Conv. (%)	Selectivity (%)		
			AcPO	PEA	PEHP
1	Thioxanthone	5.5	Trace	4.3	95.7
2	Acridone	7.2	1.2	1.6	97.2
3	1-Azaxanthone	10.3	Trace	7.7	92.2
4	Xanthone	40.8	34.0	9.7	56.3

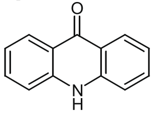
[a] Reaction conditions: 10 mmol ethylbenzene, 1 mmol NHPI, 1 mmol aromatic heterocyclic compound, 10 mL CH_3CN, 80 °C, 0.5 MPa O_2 ,4 h; AcPO: acetophenone, PEA: 1-phenylethanol, PEHP: 1-Phenylethyl hydroperoxide. Conversion and Selectivity of the products were determined by GC using an internal standard. Trace: it was detected, but it was too little to be accurately determined.

[b] The corresponding chemical structures of some compounds:

Thioxanthone:

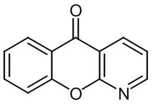


; Acridone:

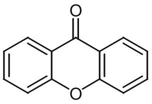


;

1-Azaxanthone:



; Xanthone:



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Quaternary ammonium salts have been reported for decomposition of alkyl hydroperoxide.[19] Then they were introduced to further optimize our nonmetal system (Table 2). Even when reaction temperature was decreased to 60 °C, NHPI/xanthone was still effective (Table 2, entry 5), but it was not efficient enough. With addition of 1 mol % tetramethylammonium chloride (TMAC) to NHPI/xanthone system, the conversion increased strikingly to 84.4% with 98.5% selectivity for acetophenone (AcPO), while the selectivity for PEHP remarkably decreased to less than 1% (Table 2, entry 7). It contrasted with the results obtained using NHPI/xanthone or NHPI/TMAC (Table 2, entries 4–7). NHPI alone was not efficient with high selectivity for PEHP (>98%) under 60 °C. TMAC and/or xanthone were inactive (Table 2, entries 2–4). Though NHPI/TMAC also showed some activities which were mentioned in the previous literatures,[20] the combination of xanthone and TMAC/NHPI resulted in much higher conversion and in quite different products distribution. Three components were indispensable to be efficient under mild conditions. Reaction in the beginning was severe in NHPI /xanthone/TMAC-mediated oxidation. The phenomenon was similar to oxidation using NHPI/$Co(OAc)_2$.

Table 2
Oxidation of ethylbenzene using different catalysts[a]

Entry	Catalysts	Conv. (%)	Selectivity (%)		
			AcPO	PEA	PEHP
1	None	0	–	–	–
2	Xanthone	0	–	–	–
3	TMAC	Trace	–	–	–
4	Xanthone/ TMAC	Trace	–	–	–
5	NHPI/xanthone	24.7	20.4	15.8	63.8
6	NHPI/ TMAC	33.4	26.7	12.3	61.0
7[b]	NHPI/xanthone/TMAC	84.4	98.5	0.3	0.2
8[c]	NHPI/xanthone/TMAC	86.4	91.3	0.7	0.7

[a] Reaction conditions: 10 mmol ethylbenzene, 1 mmol NHPI, 1 mmol xanthone,0.1 mmol TMAC,10 mL CH_3CN, 60 °C, 0.5 MPa O_2 , 6 h, Conversion and Selectivity of the products were determined by GC using an internal standard. TMAC: tetramethylammonium chloride.

[b] 1% benzoic acid.

[c] 80 °C, 0.05 mmol TMAC, 3 h, 7.2% benzoic acid was detected.

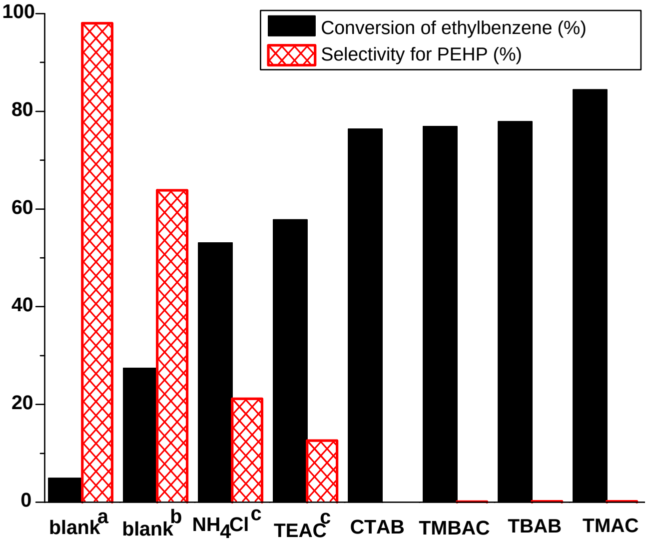


Figure 1. Oxidation of ethylbenzene using NHPI, xanthone and different quaternary ammonium salts. Reaction conditions: 10 mmol ethylbenzene, 1 mmol NHPI, 1 mmol xanthone, 0.1 mmol quaternary ammonium salts,10 mL CH_3CN, 60 °C, 0.5 MPa O_2, 6 h, TEAC: triethylamine hydrochloride; CTAB: Hexadecyltrimethyl ammonium bromide; TMBAC: benzyltrimethylammonium chloride; TBAB: tetrabutyl ammonium bromide; [a] NHPI alone; [b] NHPI and xanthone; [c] 0.2 mmol feed.

Some other quaternary ammonium salts were also studied (Fig. 1). Hexadecyltrimethyl ammonium bromide (CTAB), benzyltrimethyl ammonium chloride (TMBAC) and tetrabutyl ammonium bromide (TBAB), were also effective. The conversions were more than 75% with more than 98% selectivities for acetophenone and less than 1% selectivities for 1-phenylethyl hydroperoxide. But the TMAC seemed to be the best. Anion, either bromine ion or chloride ion, was nonessential in this system. Alkyl hydroperoxide is one of key intermediates during autoxidation of hydrocarbons. It cannot be determined directly by GC due to its thermolability. In some literatures, hydroperoxides were often ignored or directly measured as their decomposed products. However, selectivities for 1-phenylethyl hydroperoxide in the reaction mixture seemed to be adverse to the conversions of ethylbenzene (Fig. 1). With low conversion of ethylbenzene, the selectivity for 1-phenylethyl hydroperoxide was high. When the conversion increased, the selectivity for 1-phenylethyl hydroperoxide decreased. This observation was also in accordance with Ive Hermans's theoretical study.[16]

To further probe the potential of this nonmetal system, various hydrocarbons were successfully oxygenated by NHPI/xanthone/TMAC system under mild conditions (Table 3). Aromatic hydrocarbons with methylene such as diphenyl methane, tetralin, and fluorene could be oxidized smoothly with high conversions (65–94%) (Table 3, entries 1–3). The selectivity for corresponding ketone was also high and little hydroperoxide was detected (Table 3, entries 1 and 2). In contrast, the selectivity for 9-fluorenyl hydroperoxide was over 23% using NHPI/anthraquinone at 80 °C.[11] Toluene, *p*-xylene, and durene with methyl group could also be efficiently oxygenated with aromatic acid as main products (Table 3, entries 4–6). Cyclohexene was also oxygenated smoothly with cyclohex-2-enone as the main product (Table 3, entry 7). Cyclohexane was difficult to be oxidized under 60 °C, and few products were detected within 10 h, but when the reaction temperature was raised to 80 °C, good conversion of cyclohexane (33%) could also be obtained (Table 3, entry 9). Long induction period was observed during the oxidation of adamantane and toluene under 60 °C. For example, induction period was about 2 h during the oxidation of toluene, and it decreased to 20 min under 80 °C. This resulted in long reaction time under 60 °C (Table 3, entries 6 and 8).

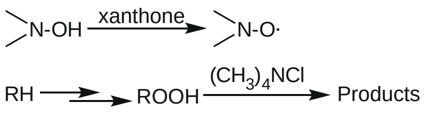
To explain these findings, several experiments were carried out. Firstly, addition of 5 mol % hydroquinone to the system completely

Table 3
Oxidation of various substrates by NHPI/xanthone/TMAC system[a]

Entry	Substrate	Time (h)	Conv. (%)	Main products select (%)	
1	Diphenyl methane	4	65	Benzophenone (98)	Benzhydrol (2)
2	Fluorene	4	91	9-Fluorenone (96)	9-Fluorenol (4)
3	Tetralin	4	94	1-Tetralone (92)	1-Tetralol (4)
4	Durene	3	94	2,4,5-Trimethyl benzaldehyde (23)	2,4,5-Trimethyl benzoic acid (59)
5	*p*-Xylene	3	69	*p*-Tolualdehyde (23)	4-Toluic acid (76)
6	Toluene	8	35	Benzaldehyde (16)	Benzoic acid (82)
7	Cyclohexene	4	77	Cyclohex-2-enone (61)	Cyclohex-2-enol (7)
8	Adamantane	8	92	2-Adamantanol (52)	1,3-Damantanediol (34)
9[b]	Cyclohexane	4	33	Cyclohexanone (50)	Acid (34)

[a] Reaction conditions: 10 mmol liquid substrates or 5 mmol solid substrates, 10 mol % NHPI, 10 mol % xanthone, 0.5 mol % TMAC,10 mL CH_3CN, 60 °C, 0.5 MPa O_2. Conversion and selectivity were determined by GC.

[b] Reaction was carried out at 80 °C. Acid was determined by titration.



Scheme 1. Proposed catalytic mechanism.

stopped the reaction. This indicated that a radical pathway was involved in the main reaction course. When oxidation of 1-phenylethanol was carried out using NHPI/xanthone/TMAC system under 60 °C, only 36% conversion of 1-phenylethanol was obtained. Without additive, alkyl peroxide was believed to decompose to ketone and alcohol through Russell pathway.[6] Quaternary ammonium salts were reported for homolytic cleavage of alkyl hydroperoxide.[19] TMAC was proposed to be responsible for high selectivity of AcPO. In the presence of TMAC, AcPO was possibly directly produced from decomposition of 1-phenylethyl hydroperoxide rather than from further oxidation of 1-phenylethanol. Such catalytic decomposition might also account for excessive oxidation of ethylbenzene to benzoic acid (Table 2, entries 7 and 8). More than 7% benzoic acid was detected within 3 h if the reaction was performed at 80 °C (Table 2, entry 8). This observation was quite different from our previous reports of heterogeneous catalytic decomposition using HY.[10] In that case, nonradical cleavage route was proposed, and few excessive oxidation products were detected.

Based on the experiments described above, a hypothetical mechanism of NHPI/xanthone/TMAC system was suggested (Scheme 1). In our previous reports, it was confirmed that the one-electron-transfer interaction of anthraquinones and NHPI resulted in the formation of PINO.[10,11] Aromatic heterocyclic compounds bearing a carbonyl group have structure similar to that of anthraquinone. In this system, xanthone possibly facilitated the formation of PINO via a one-electron transfer through a pathway similar to anthraquinone. The H-atoms of hydrocarbon were abstracted by PINO to produce alkyl radical, which further led to formation of alkyl hydroperoxide. Then alkyl hydroperoxide was directly decomposed to corresponding oxygenated products catalyzed by TMAC. Compared with NHPI/ anthraquinone system,[11] higher conversion was obtained in lower temperature while selectivity of alkyl peroxide was remarkably reduced in the presence of xanthone and TMAC. In the NHPI-transition metal system, transition metal such as $Co(OAc)_2$ was believed to have two functions: (1) assisting the generation of PINO; and (2) catalyzing the decomposition of alkyl hydroperoxide into products.[4–8] Here two nonmetal molecules attained similar purposes. The synergistic effect of three components greatly improved both the activities and selectivities for more favorable ketone/alcohol.

In summary, a novel efficient nonmetal system consisting of NHPI, xanthone, and TMAC was developed for oxidation of hydrocarbons. A wide range of hydrocarbons could be efficiently oxygenated with molecular oxygen under mild conditions. Impressive performance for aerobic oxidation of hydrocarbons catalyzed by nonmetal molecules was demonstrated. This report may be helpful for further development of nonmetal catalysis for oxidation.

Acknowledgments

We gratefully acknowledge the financial support from the Natural Science Foundation of China (20672111 and 20736010) and the Knowledge Innovation Program of the Chinese Academy of Sciences (DICP K2007D6).

Supplementary data

General procedure for the oxidation, hydroperoxide analysis and detailed GC measurement methods are available. Qualitative analysis of products by GC–MS. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.01.077.

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