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Unexpected Catalytic Activity of N-Hydroxyphthalimide Combined with Some Co-catalyst in Oxidation of Organic Substrates by Dioxygen

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The combination of N-hydroxyphthalimide and various co-catalyst affords an efficient catalytic system for the aerobic oxidation of organic substrates. Thus, acids, tertiary and quaternary ammonium salts and typical Lewis acids (*e.g.* BF_3) are effective co-catalysts. Their role is concerned to weakness the O–H bond in NHPI *via* hydrogen bond formation or as the result of the donor-acceptor interaction.

Key words: aerobic oxidation, N-hydroxyphthalimide, dioxygen, catalysis, kinetics

Selective catalytic oxidation using dioxygen is one of the most attractive transformations in organic synthesis [1] and very important in response to environmental policies [2]. In 1995, Ishii reported a novel catalysis of N-hydroxyphthalimide (**NHPI**) in the oxidation of organic compounds by molecular oxygen [3]. His papers showed that NHPI combined with some transition metals complexes is an efficient catalyst system for the aerobic oxidation of various organic substrates under mild conditions [4]. Other effective additive in the oxidation reactions catalyzed by NHPI is acetaldehyde [5]. Recently, Ishii reported a catalytic activity of NHPI combined with quaternary ammonium salts in oxidation of alcohols with dioxygen without any reducing agents [6].

Our studies on catalytic activity of NHPI and additives as co-catalyst in oxidation reaction of organic substrates with dioxygen [7,8] showed that results were dependent on MeCN sources. We observed a high catalytic activity of NHPI in the systems, where MeCN from Apolda was used. For example, the aerobic oxidation of cyclohexanol (**1**) catalyzed by NHPI showed 2.23 and 0.50 mmol O_2 uptake and conversion of **1** 45.4 and 15.4% for Apolda's MeCN (only dried over MS 4A) and dried and distilled acetonitrile, respectively. Analytical studies of Apolda's MeCN showed a trace of pyridine (GC-MS) and pyridinium hydrochloride (ESI-MS). This prompts us to study of tertiary and quaternary ammonium salts influence on the catalytic activity of NHPI in oxidation of several organic substrates by dioxygen [8].

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EXPERIMENTAL

All reagents used were of analytical grade. The subject of our studies were the multicomponent systems containing organic substrate, dioxygen, catalyst (NHPI), co-catalyst (acids, tertiary and quaternary ammonium salts, Lewis acid) and solvent. The standard conditions for oxidation reactions of organic substrates were: substrate 5 mM, NHPI 0.5 mM (0.0816 g), co-catalyst 0.025 mM, and acetonitrile (MeCN was dried over MS 4 Å and distilled under nitrogen atmosphere) into full volume 10 cm^3 at atmospheric pressure of O_2, T = 75°C, time = 20 h (according to Ishii *et al.* [3]). The reactions were carried out at constant volume in a thermostated glass-reactor equipped with a magnetic stirring bar and connected to an automatic gas absorption measuring apparatus controlled by a computer. Substrate, acetonitrile and NHPI were added to the reactor at oxygen atmosphere. Next, fixed amount of co-catalyst was introduced in one portion, immediately after which stirring was started and progress of the absorbed dioxygen was measured. The mmole of oxygen that reacted was calculated from the volume, pressure and temperature data using the ideal gas equation. The reaction products were detected on a capillary column HP-5 (25×0.2×0.33 mm) using a Hewlett-Packard HP 5890 II series gas chromatograph coupled with Hewlett Packard Model mass selective detector HP 5971 for the GC-MS analyses or FID detector for quantitative analyses.

RESULTS AND DISCUSSION

The oxidation of cyclohexanol in acetonitrile was chosen as a model for study of co-catalyst influence on NHPI activity (Table 1). The aerobic oxidation of **1** in the presence of a catalytic amount of NHPI (10 mol%) produced cyclohexanone (**2**) with selectivity 73.8% but the conversion was much lower (15.4%, entry 1) than reported by Ishii [3]. However, when the reaction was carried out in the presence of pyridinium hydrochloride (entry 2) or other ammonium salts, the conversion of **1** markedly increased to 43.1% and up to 72.8%, respectively. Simultaneously increased selectivity to **2**. On the basis of these results, tetrabutylammonium chloride (**TBAC**) was chosen for optimalization of the new catalytic system NHPI–$[Bu_4N]Cl$. We found that 5 mol% of NHPI and 1.5 mol% of TBAC lets to be very effective catalyst. Activity of this system was studied in the oxidation of various organic substrates with O_2 (Table 2). Primary alcohol (1-hexanol, entry 1) was oxidized to acid *via* aldehyde with a high conversion and selectivity. On the other hand, 2-pentanol was moderate converted, but selectively to ketone. The oxidation of alkyl benzenes proceeds with conversions *ca.* 47÷64%, except *p*-xylene (82.2%), forming the corresponding aldehydes and acids, although the oxidation of ethylbenzene gave acetophenone in high selectivity. In the absence of TBAC, the conversions of these organic substrates were very low (less than 23%). These results showed that the effectivity of ammonium salts as co-catalysts is connected with the weakness of O–H bond in NHPI molecule, that lets to formation of nitroxyl radical. In our opinion, in this catalytic system the formation of hydrogen bonding O–H····Cl is possible. In fact, we observed this interaction in IR spectra when $[Bu_4N]Cl$ was added to the solution of NHPI in acetonitrile. The loss of a very strong absorption band of ν(OH) at *ca.* 3200 cm^{-1} (from NHPI) and the appearance of a wide band at *ca.* 2600 cm^{-1} prove the existence of strong hydrogen bonding O–H·····Cl. This prompt us to use acids as co-catalysts for the oxidation of **1** with O_2

catalyzed by NHPI. Figure 1 presents the dependence of dioxygen absorption on activity of NHPI combined with those acids. These results clearly demonstrate that the activity of these co-catalysts is proportional to their strength. It is interesting to note that in the case of organic acids we observed a high consumption of dioxygen and a higher conversion of **1** (72.2% with CF_3COOH). However, the selectivity to **2** was lower (from 55.3% for HOAc to 68.5% for CF_3COOH) and GC-MS showed macrocyclic by-products, cyclopentadecane and oxacycloheptadecan-2-one. In the case of mineral acids, the reactions were very fast and main by-products were dicyclohexyl ester of hexanedioic acid and traces of 2-chloro- and 2-hydroxy-cyclohexanone, respectively for H_2SO_4 and HCl. We studied also the influence of Lewis acid (BF_3) on the catalytic activity of NHPI in the aerobic oxidation of **1**. Reaction was fast ($V = 6.4\times10^{-3}$ mmol of O_2/min.) and dioxygen uptake was as high as in the case of CF_3COOH. Conversion of **1** was 78.7% and products were **2** and 2-oxepanone obtained with selectivity 36.4 and 11.0%, respectively (other by-products were acids and their esters). In the same conditions, LiCl was used as an additive and showed exactly the same activity as observed for catalytic system NHPI–$[Bu_4N]Cl$. However, the effect of lithium salts: $LiClO_4$, LiOAc and Liacac was inert.

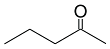
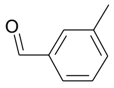
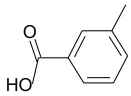
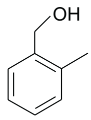
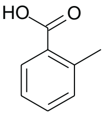
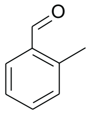
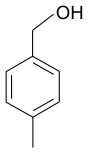
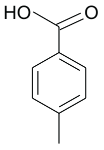
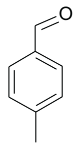
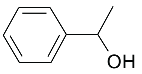
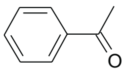
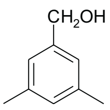
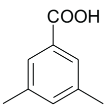
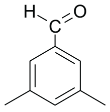
Table 1. Aerobic oxidation of cyclohexanol catalyzed by NHPI and additive[a].

Entry	Additive	O_2 uptake [mmol]	Conv.[b] [%]	$V\times10^{-3}$ [c] [mmol O_2/min]	Selectivity[b] [%]
1	None	0.50	15.4	0.7	73.8
2	[PyH]Cl	1.31	43.1	4.0	81.0
3	$[Et_3NH]Cl$	2.35	72.8	3.7	73.5
4	$[(EtO)_3NH]Cl$	2.26	70.5	3.5	74.6
5	$[Me_4N]Cl$	1.43	49.0	3.2	85.7
6	$[Et_4N]Cl$	1.09	36.7	5.4	83.8
7	$[Bu_4N]Cl$	1.50	49.6	3.2	81.6
8	$[Bu_4N]Br$	1.05	36.1	3.1	86.2
9	$[Bu_4N]I$	0.15	6.3	0.2	~100

[a] Cyclohexanol (5 mmol) was allowed to react under dioxygen atmosphere (1 atm.) in the presence of NHPI (10 mol%) and co-catalyst (0.7 mol%) at 75°C for 20 h.
[b] Conversion of **1** and selectivity to **2** were calculated based on HPLC analysis.
[c] Maximum speed of oxygen absorption.

In summary, we conclude that additives, which weaker the O–H bond in NHPI molecule, and which can be realized by formation of hydrogen bonding O–H·····X, where X = electronegative atom or ion with a lone electron pair (halogen ion in ammonium salts, Brønsted acids), or by donor-acceptor interaction (Lewis acid), will be an effective co-catalyst for the oxidation of organic substrates with dioxygen catalyzed by NHPI.

Table 2. Oxidation of several organic compounds using NHPI–[Bu_4N]Cl catalytic system[a].

Entry	Substrate	O_2 uptake [mmol]	Conv.[b] [%]	Products; selectivity, [%][c]
1	1-hexanol	4.41 (3.56)	88.0 (68.0)	  (7.1) ~99[d] (92.9)
2	2-pentanol	1.04 (0.29)	41.6 (11.6)	 ~100 (~100)
3	m-xylene	2.84 (0.48)	47.2 (10.2)	  59.6 (87.7) 40.4 (0)[e]
4	o-xylene	4.01 (0.45)	59.1 (9.8)	   5.1 (17.2) 76.6 (0) 18.3 (12.8)
5	p-xylene	4.67 (0.90)	82.2 (19.3)	   2.7 (13.8) 29.9 (0) 67.4 (86.2)
6	ethylbenzene	3.40 (1.02)	63.8 (23.2)	  (20.2) 93.8[f] (59.0)[g]
7	mesitilene	2.53 (0.64)	63.8 (12.8)	   3.2 (0) 16.3 (0) 80.5 (~100)

[a] Substrate (5 mmol) was allowed to react under dioxygen atmosphere (1 atm) in the presence of NHPI (5 mol%) and Bu_4NCl (1.5 mol%) at 75°C for 20 h.

[b] Conversion of the substrate; in parenthesis in the absence of TBAC.

[c] Selectivity of the products was determined by GC analysis using internal standards.

[d] GC-MS analysis showed a trace of n-hexanal.

[e] In the absence of TBAC 3-methylbenzylalcohol was formed with selectivity 12.3%.

[f] GC-MS analysis showed traces of benzenemethanol, benzaldehyde and benzoic acid.

[g] Other products were benzaldehyde and ethylbenzene hydroperoxide.

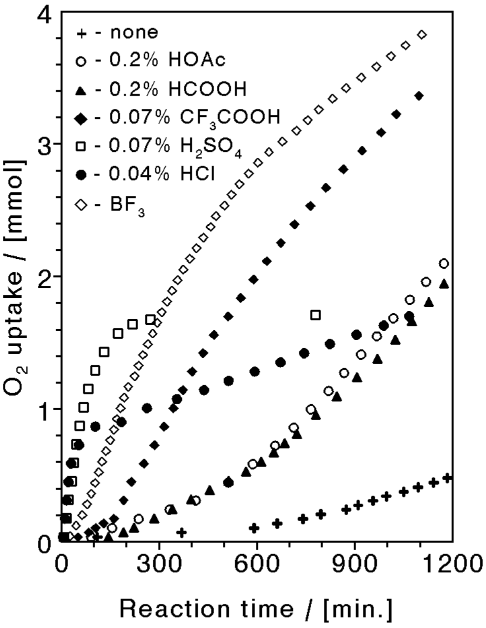


Figure 1. Acids as co-catalysts in the aerobic oxidation of cyclohexanol catalyzed by NHPI.

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REFERENCES

1. Sheldon R.A., *J. Mol. Catal.*, **20**, 1 (1983) and *Catal. Today*, **1**, 351 (1987); Strukul G., *Angew. Chem. Int. Ed.*, **37**, 1199 (1998); Sheldon R.A., Arends I.W.C.E. and Dijksman A., *Catal. Today*, **57**, 157 (2000); Hartmann M. and Ernst S., *Angew. Chem. Int. Ed.*, **39**, 888 (2000).
2. Clark J.H. and Macquarrie D.J., *Chem. Soc. Rev.*, **25**, 303 (1996); Choudary B.M., Kantam M.L. and Santhi P.L., *Catal. Today*, **57**, 17 (2000); Tenbrink G.J., Arends I.W.C.E. and Sheldon R.A., *Science*, **287**, 1636 (2000); Anastas P.T., Bartlett L.B., Kirchhoff M.M. and Williamson T.C., *Catal. Today*, **55**, 11 (2000).
3. Ishii Y., Nakayama K., Takeno M., Sakaguchi S., Iwahama T. and Nishiyama Y., *J. Org. Chem.*, **60**, 3934 (1995).
4. Iwahama T., Sakaguchi S., Nishiyama Y. and Ishii Y., *Tetrahedron Lett.*, **36**, 6923 (1995); Ishii Y., Iwahama T., Sakaguchi S., Nakayama K. and Nishiyama Y., *J. Org. Chem.*, **61**, 4520 (1996); Ishii Y., Kato S., Iwahama T. and Sakaguchi S., *Tetrahedron Lett.*, **37**, 4993 (1996); Ishii Y., *J. Mol. Catal. (A)*, **117**, 123 (1997); Yoshino Y., Hayashi Y., Iwahama T., Sakaguchi S. and Ishii Y., *J. Org. Chem.*, **62**, 6810 (1997); Sakaguchi S., Takase T., Iwahama T. and Ishii Y., *Chem. Commun.*, 2037 (1998).
5. Einhorn C., Einhorn J., Marcadal C. and Pierre J.L., *Chem. Commun.*, 447 (1997).
6. Matsunaka K., Iwahama T., Sakaguchi S. and Ishii Y., *Tetrahedron Lett.*, **40**, 2165 (1999).
7. Kwaskowska-Chęć E., Sobczak J.M. and Ziółkowski J.J., XIII International Summer School on Coordination Chemistry, Polanica, Poland, 2–8. June, 1996, Abstracts, p.108.
8. Sobczak J.M. and Ziółkowski J.J., IV Conference on Non-waste Technology and Utilisation of Waste in Chemical Industry and Agriculture, Łukęcin, Poland, 18–21 May, 1998, pp. 335–338.